SIMULATION OF THREE-PHASE DISTILLATION COLUMN USING BUBBLE POINT AND Φ-Φ APPROACH

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ABSTRACT

Most of organic compounds are partially miscible in water and due to their solubility criteria split into two liquid phases. So design of equipments that separate two liquid phase systems differ from one liquid phase system equipments.

A mathematical model and a computer program have been developed to simulate three-phase distillation columns. The proposed procedure is based on linearization of equations and solving them by Newton-Raphson method. Average liquid compositions are chosen as independent variables and temperature, vapor compositions and two liquid phase compositions are obtained by three-phase bubble point calculations on each tray. For predicting thermodynamic properties, equation of state is used.

NOMENCLATURE

A_j	:	Submatrix of j-th stage in Jacobian matrix
B_j	:	Diagonal submatrix of j-th stage in Jacobian matrix
C_j^p	:	Submatrix of j-th stage and p-th column in Jacobian matrix
E_j	:	Murphree efficiency on tray j
f	:	Residual function
$\mathbf{f}$	:	Vector of residual function
F	:	Feed flow rate, K-mole/hr
h_j	:	Liquid enthalpy on tray j, KJ/K-mole
$\overline{h}_j$	:	Average liquid enthalpy on tray j, KJ/K-mole
H_{f_j}	:	Feed enthalpy on tray j, KJ/K-mole
H_j	:	Vapor enthalpy on tray j, KJ/K-mole
J	:	Jacobian matrix

K_i	:	K-value of component i, y_i / x_i
$\overline{K}_i$	:	Mixed K-value of component i, $y_i / \overline{x}_i$
L_j	:	Liquid flow rate on tray j, Kg-mole / hr..
N	:	Number of stages in distillation column
nc	:	Number of components
P	:	Pressure, Bar
Q_j	:	Heat Load on tray j, KJ/hr
S_x, S_y	:	summation equations of liquid and vapor phases
T	:	Temperature, K
U_j	:	Liquid sidestream flow rate on tray j, Kg-mole/hr
V_j	:	vapor flow rate on tray j, Kg-mole/hr
W_j	:	Vapor sidestream flow on tray j, Kg-mole/hr
x_i	:	Liquid composition of component i
$\overline{x}_i$	:	Average liquid composition of component i
X	:	Vector of average liquid composition
y_i	:	Vapor composition of component i
z_i	:	Feed composition of component i
α	:	The step width
ε	:	Stopping criteria
ϕ_i	:	Fugacity coefficient of component i
γ	:	Activity coefficient
Ψ	:	Liquid fraction (L/F)
Ω	:	Residual function

Subscripts

i	:	Component number i
j	:	Stage number j
k	:	Stage number k
m	:	Component number m
nc	:	Final component number
p	:	Stage number p

Superscripts

L	:	Liquid phase
r	:	Iteration number r
V	:	vapor phase

I	:	Liquid phase I
II	:	Liquid phase II
*	:	In equilibrium with bulk liquid

Abbreviation description

EOS	:	Equation of state
LLE	:	Liquid-liquid equilibria
MUNIFAC	:	Modified UNIFAC
NGL	:	Natural gasoline liquid
PSRK	:	Pridictive SRK
SRK	:	Soave-Redlich-Kwong
UNIFAC	:	UNIQUAC Functional Group Activity Coefficients
UNIQUAC	:	UNIversal QUAsi Chemical

INTRODUCTION

One of the common vapor-liquid separation processes is distillation. Where one or more trays in distillation column contain two liquid phases and one vapor phase, this column is known as three-phase distillation column. This type of distillation occurs when at least one component in liquid mixture is semi-miscibble or immiscibble in others. For example, since solubility of water in hydrocarbon mixtures is finite, if enough water is added to a hydrocarbon mixture, two liquid phases will be produced, one aqueous phase and one hydrocarbon phase. Another example for three-phase distillation is extractive distillation where a substance which is relatively nonvolatile in comparison to other components of mixture, is added to mixture and two liquid phases will be produced.

Distillation is normally the least expensive of possible methods for separating a given mixture and in many cases it is the only feasible method, but in some cases where large flow rates, high number of trays, high energy investment, or expensive special materials to prevent corrosion are required, distillation is an expensive method and other alternatives must be checked. Distillation has the disadvantage of required energy in the form of heat to produce the necessary vaporization.

Although batch distillation was known from hundred years ago, the theory of distillation was not studied and formulated with mathematical relations until the work of Sorel in 1893 [1]. The equations, which describe a countercurrent, multistage separation process operating at steady state, while appearing to be quite simple, are in fact highly nonlinear and interdependent. Hence, the calculations that

are necessary to solve them are intrinsically iterative, complex and large in number. If equation of state is applied for phase equilibria, this nonlinearity increases.

The first successful application of three-phase distillation was discovered by Young [2] who prepared absolute alcohol from a binary mixture of ethanol and water and used benzene as the entrainer with a batch distillation process. Since alcohols are a valuable raw material for many industries such as polymer material production, from Young's work until now, other entrainers suggested to produce absolute alcohol from ethanol and water mixture, for example : carbontetrachloride, trichloroethylene, ethyl ether, butanol, cyclohexane, ethyl acetate, iso-octane, pentane, etc..

Extension of existing mathematical models describing standard two phase distillation to cover three phase distillation is relatively straightforward. Difficulties arise, however, when attempting to find a solution to the equation set. Cairus and Furzer [3] give a good overview on existing simulation methods.

The method used in this work is classified in bubble point methods. In general, the bubble point method uses the summation and equilibrium equations to determine the stage temperature from a standard bubble point calculation. The previous work on this method for three-phase distillation was done by Block and Hegner [4] and Kinoshita et al. [5]. In the previous three-phase distillation simulation procedures, γ-ϕ approach for phase equilibria was used but in this work ϕ-ϕ approach using proper equation of state is proposed.

PROPOSED METHOD FOR THREE-PHASE DISTILLATION

Algorithm used in this work is based on the recent work of Shimizu et al. [6] extended to three phase systems. Original work of Shimizu et al. is a bubble point approach that has been applied for two phase systems and with 100% column efficiency. Shimizu et al. assumed that vapor phase is ideal and they used Margules and Wilson correlations for liquid phase. An improvement to Shimizu et al. work is a new form of residual relations that are implicit functions. In the extension of this method to three phase distillation, mixed K-values and average liquid compositions that are introduced by Niedzwiecki et al. [7], with ϕ-ϕ and γ-ϕ approaches in phase equilibria are used.

GOVERNING EQUATIONS

Figure 1 is a sketch of the assumed general j-th stage of a multistage distillation column. Each stage has a feed flow, vapor and liquid side stream flows, and heat input or heat removal. Each stage is in a state of equilibrium. The overall mass balance, the component mass balances and equilibrium relationships of the components, the composition summation equations, and the heat balance are as follows :

Overall mass balance in the j-th stage :

$$L_{j-1} - (L_j + U_j) - (V_j + W_j) + V_{j+1} + F_j = 0 \qquad (j = 1, 2, ..., N) \qquad (1)$$

Mass balance of the i-th component in the j-th stage :

$$L_{j-1}\bar{x}_{i,j-1} - \left(L_j + U_j\right)\bar{x}_{i,j} - \left(V_j + W_j\right) y_{i,j} + V_{j+1}y_{i,j+1} + F_j z_{i,j} = 0$$

$$(i = 1, 2, ..., nc ; j = 1, 2, ..., N) \qquad (2)$$

where

$$\bar{x}_{i,j} = \frac{\Psi_{1,j}\, x^{I}_{i,j} + \Psi_{2,j}\, x^{II}_{i,j}}{\Psi_{1,j} + \Psi_{2,j}} \qquad (i = 1, 2, ..., nc ; j = 1, 2, ..., N) \qquad (3)$$

Equilibrium relationship of the i-th component in the j-th stage :

$$y_{i,j} - y_{i,j+1} - E_j \left(\bar{K}_{i,j}\, \bar{x}_{i,j} - y_{i,j+1} \right) = 0$$

$$(i = 1, 2, ..., nc ; j = 1, 2, ..., N) \qquad (4)$$

where E_j is Murphree efficiency as defined by Treybal [8].
Summation equations of the liquid and vapor in the j-th stage :

$$S_{xj} = \sum_{i=1}^{nc} \bar{x}_{i,j} - 1 = 0 \qquad\qquad (j = 1, 2, ..., N) \qquad (5)$$

$$S_{yj} = \sum_{i=1}^{nc} y_{i,j} - 1 = 0 \qquad\qquad (j = 1, 2, ..., N) \qquad (6)$$

Energy balance in the j-th stage :

$$L_{j-1} \bar{h}_{j-1} - \left(L_j + U_j\right) \bar{h}_j - \left(V_j + W_j\right) H_j$$
$$+ V_{j+1} H_{j+1} + F_j H_{f_j} - Q_j = 0$$

$$(j = 1, 2, ..., N) \qquad (7)$$

where

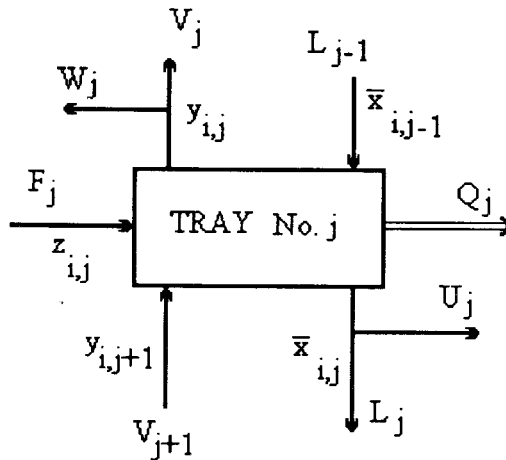$$\bar{h}_k = \frac{\Psi_{1,k} h_k^{I} + \Psi_{2,k} h_k^{II}}{\Psi_{1,k} + \Psi_{2,k}} \qquad (8)$$

Fig. 1: The j-th stage in the column

The number of plates starts from the condenser (zero tray), and continues to the reboiler where it is the final number of plates.

FORMULATION OF THE PROBLEM

In order to solve this problem, average liquid compositions are chosen as the independent variable and component mass balances and average liquid composition

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summation for all trays are solved simultaneously by Newton-Raphson method. Residual functions, which are observed, have an implicit form as :

$$f_{i,j} = \frac{L_{j-1}\,\overline{x}_{i,j-1} - \left(L_j + U_j\right)\overline{x}_{i,j} - \left(V_j + W_j\right)y_{i,j} + V_{j+1}\,y_{i,j+1} + F_j\,z_{i,j}}{L_{j-1} + V_{j+1} + F_j}$$

$$(i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad (9)$$

$$f_{nc,j} = S_{xj} = \sum_{i=1}^{nc} \overline{x}_{i,j} - 1 \qquad\qquad (j = 1, 2, ..., N) \qquad (10)$$

Since the value of the flow rate depends on the particular problem, to minimize its effect, equation (2) is taken as the numerator, and the total inputs of the flow rates as the denominator. The objective function that must be minimized to obtain the final result must be independent of number of trays (N) and number of components (nc), then, becomes :

$$\Omega = \frac{\displaystyle\sum_{i=1}^{nc}\sum_{j=1}^{N}\left(f_{i,j}\right)^2}{nc \times N} < \varepsilon \qquad (11)$$

With Newton-Raphson method, the correction $dX^{(r)}$ is found where r is the number of iteration. Therefore, a new value of X for substitution in the next iteration is given by :

$$X^{(r+1)} = X^{(r)} + \alpha\, dX^{(r)} \qquad (12)$$

where α is the step width and X is the vector of the average liquid composition. Other variables, which are assumed to be dependent variable, are vapor composition, temperature, liquid and vapor flow rates in each tray. Temperature can be found with three-phase bubble point calculation. Since equilibrium equations are solved in bubble point calculations, thus, mixed K-values are calculated. So vapor compositions in this tray may be calculated by equation (4) as :

$$y_{i,j} = y_{i,j+1} + E_j \left(\overline{K}_{i,j}\, \overline{x}_{i,j} - y_{i,j+1} \right)$$

$$(i = 1, 2, ..., nc\; ; j = 1, 2, ..., N) \tag{13}$$

In the calculation of the heat balance, successive corrections are made to the liquid and vapor flow rates so as to satisfy both the mass balance equation and the heat balance equation. From equation (1), the liquid flow rate is :

$$L_j = L_{j-1} - U_j - (V_j + W_j) + V_{j+1} + F_j \qquad (j = 1, 2, ..., N) \tag{14}$$

From equations (6) and (7), the vapor flow rate is :

$$V_{j+1} = \frac{-L_{j-1}\left(\overline{h}_{j-1}-\overline{h}_j\right)+\left(V_j+W_j\right)\left(H_j-\overline{h}_j\right)- V_{j+1}\left(H_{j+1}-\overline{h}_j\right)-F_j\left(H_{f_j}-\overline{h}_j\right)+Q_j}{\left(H_{j+1}-\overline{h}_j\right)}$$

$$(j = 1, 2, ..., N) \tag{15}$$

SOLUTION PROCEDURE

The calculations used in this study are described by the following stepwise outline :

1. Select the liquid feed composition as starting point in all trays.
2. With flash calculation in each tray, independent variables are corrected.
3. Calculate the mixed K-values and temperature in each stage from the three-phase boiling point calculation. Since, phase stability tests are checked in this step, thus, one or two stable liquid phase(s) can be identified.
4. Calculate the vapor compositions in each stage from equation (13).
5. Correct the liquid and vapor flow rates by using equations (14) and (15).
6. If this is first iteration, continue the procedure, else, calculate the objective function from equation (11). If the criterion for convergence is satisfied, stop calculations and print results. If not, go on to the next step.
7. Calculate the correction dX with the Newton-Raphson method, and set the step width α in maximum available value where independent variables of next step are between, or equal to, zero and unity.

8. Using the corrected liquid composition, correct the other dependent variables in steps 3 through 5. Evaluate the objective function, and, if this function is lower than the previous value, go back to step 6. If this function is not lower than the previous value, go on to the next step ignoring the changes in dependent variables.

9. Reduce the step width in α $1/\sqrt{2}$, and go back to step 8.

In step 7 of the above procedure, Newton-Raphson method is used to update the values of independent variables with

$$X(r+1) = X(r) + \alpha\, dX(r)$$
$$dX = -J^{-1}\, f$$

where α is optimized in steps 8 and 9, f is vector of residual function, and $J = (\partial f / \partial X)$ is the Jacobian matrix. The Jacobian matrix is an $(nc \times N) \times (nc \times N)$ dimensional matrix, which has the following structure:

$$
J =
\begin{bmatrix}
B_1 & C_1^2 & C_1^3 & C_1^4 & & \cdots & & C_1^N \\
A_2 & B_2 & C_2^3 & C_2^4 & & \cdots & & C_2^N \\
0 & A_2 & B_3 & C_3^4 & & \cdots & & C_3^N \\
\vdots & & & \ddots & & & & \\
0 & & 0 & A_2 & B_j & C_j^{j+1} & \cdots & C_j^N \\
\vdots & & & & & \ddots & & \\
0 & & \cdots & & 0 & A_2 & B_{N-1} & C_{N-1}^N \\
0 & & \cdots & & 0 & 0 & A_2 & B_N
\end{bmatrix}
\qquad (16)
$$

A_j, B_j, and C_j^P are $(nc \times nc)$ dimensional submatrices, and 0 is zero submatrix. Each term in equation (16) can be expressed in the forms described as follows :

$$A_j = \left[\frac{\partial f_{i,j}}{\partial x_{m,j-1}} \right] \qquad (i = 1, ..., nc\; ; m = 1, ..., nc;\ j = 1, ..., N) \quad (17)$$

$$B_j = \left[\frac{\partial f_{i,j}}{\partial \overline{x}_{m,j}} \right] \qquad (i = 1, ..., nc \; ; \; m = 1, ..., nc; \; j = 1, ..., N) \quad (18)$$

$$C_j^p = \left[\frac{\partial f_{i,j}}{\partial \overline{x}_{m,p}} \right] \quad (i = 1, ..., nc \; ; \; m = 1, .., nc; \; j = 1, .., N; \; p = j+1,...,N) \quad (19)$$

where

$$\frac{\partial f_{i,j}}{\partial \overline{x}_{m,j-1}} = \begin{cases} \dfrac{L_{j-1}}{L_{j-1} + V_{j+1} + F_j} & (i = m; \; i < nc) \\ 0 & (i \neq m) \\ 0 & (i = nc) \end{cases}$$

$$\frac{\partial f_{i,j}}{\partial \overline{x}_{m,j-1}} = \begin{cases} \dfrac{1}{L_{j-1} + V_{j+1} + F_j} \left[V_{j+1} - \left(E_j - 1 \right) \left(V_j + W_j \right) \right] \dfrac{\partial y_{i,j}}{\partial \overline{x}_{m,p}} & (p = j+1) \\ \dfrac{\left(E_j - 1 \right)^{(p-j-1)}}{L_{j-1} + V_{j+1} + F_j} \left[V_{j+1} - \left(E_j - 1 \right) \left(V_j + W_j \right) \right] \dfrac{\partial y_{i,j}}{\partial \overline{x}_{m,p}} & (p = j+2,...,N) \end{cases}$$

In the above relations :

$$\frac{\partial y_{i,j}}{\partial \overline{x}_{m,j}} = E_j \frac{\partial \left(\overline{K}_{i,j} \overline{x}_{i,j} \right)}{\partial \overline{x}_{m,j}} \tag{20}$$

where these derivatives are determined with numerical method.

PHASE EQUILIBRIA

Mixed K-value for three-phase systems is determined by average liquid-phase composition, $\overline{x}_i$.

$$\overline{K}_i = \frac{y_i^*}{\overline{x}_i} = \frac{K_i^I x_i^I \left(\Psi_1 + \Psi_2 \right)}{\Psi_1 x_i^I + \Psi_2 x_i^{II}} = \frac{K_i^{II} x_i^{II} \left(\Psi_1 + \Psi_2 \right)}{\Psi_1 x_i^I + \Psi_2 x_i^{II}} \tag{21}$$

where

$$\overline{x}_i = \frac{\Psi_1 x_i^I + \Psi_2 x_i^{II}}{\Psi_1 + \Psi_2} \tag{22}$$

K_i^I and K_i^{II} are calculated from fugacity coefficients of phases.

$$K_i^I = \frac{y_i^*}{x_i^I} = \frac{\phi_i^{L^I}}{\phi_i^V}$$

$$\tag{23}$$

$$K_i^{II} = \frac{y_i^*}{x_i^{II}} = \frac{\phi_i^{L^{II}}}{\phi_i^V}$$

where fugacity coefficients are calculated from equations of state.

The equation of state proposed for predicting nonideal mixture properties is PSRK EOS [9], but for hydrocarbon mixtures SRK EOS may be used with acceptable accuracy. If hydrocarbon mixture contains enough water, one aqueous-phase and one hydrocarbon-phase form. In this system, if SRK EOS was used, the improvements, reported by Erbar et al. [10] for aqueous phase interaction parameters, are used. Erbar et al. [10] introduced new interaction parameter for aqueous phase as linear function of temperature where hydrocarbon phase interaction parameters were assumed to be a constant value.

Phase equilibria method used in this work was the one reported by Nelson [11] and test criteria on number of existing phases was the one suggested by Bünz et al. [12]. The combination of these procedures help to reduce CPU time. These methods with the use of equation of state formed the basis of the phase equilibria calculation and were applied in this work. The main advantage of this method as Nelson [11] cited is removal of trivial solution from solution results of phase equilibria. Besides, since the solution procedure is simple, in cases where equation of state dictates the number of existing phases, the criteria of equation of state is usable.

RESULTS

Two examples of distillation are considered. The first is a two-phase system and the results are compared with the result obtained by Moshfeghian [13]. The second is a three phase system.

Example 1. The deethanizer column of Mahshahr NGL plant is studied. This example has been simulated by Moshfeghian previously [13]. The column specification is given in Tables 1 and 2. The calculated temperature profile of column is shown in Figure 2 and the result of H_2S composition on each tray is shown in Figure 3. In Table 3 the calculated results of this work are compared with the design values and simulation results obtained by Moshfeghian [13].

Table 1. The Deethanizer Column Specifications.

Feed pressure , Bar	25.97	No. of trays (without cond. & reboiler)	39
Condenser press., Bar	24.94	Feed tray	13
Reboiler pressure, Bar	25.83	Reflux ratio (L_0/F)	0.4438
Condenser type	Partial	Bottoms ratio (B/F)	0.7749

Table 2: Feed Stream Specification for Deethanizer Column

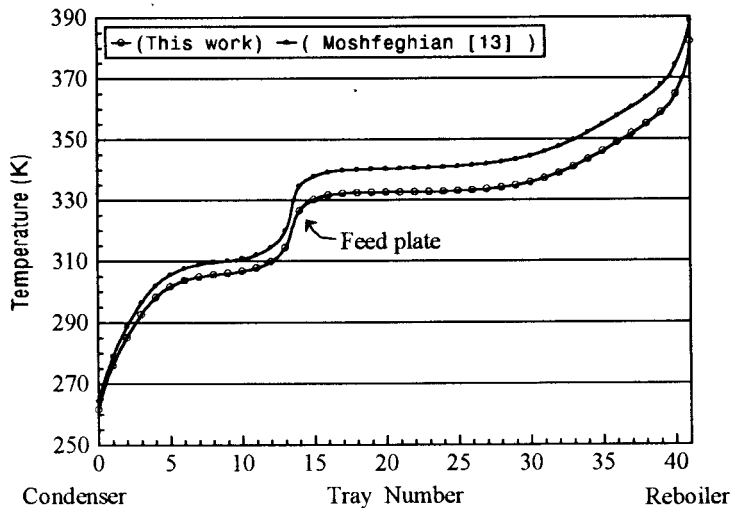| Component Name	Flow Rate (Moles/Hr)
Methane	484.76
Carbon dioxide	100.56
Hydrogen sulfide	27.97
Ethane	1355.20
Propane	2429.60
I-Butane	579.53
N-Butane	1535.10
I-Pentane	500.90
N-Pentane	590.05
N-Hexane	516.96
Heptane plus (N-Decane)	497.93
Total	8618.55
Temperature, K	330.56
Pressure, Bar	25.96

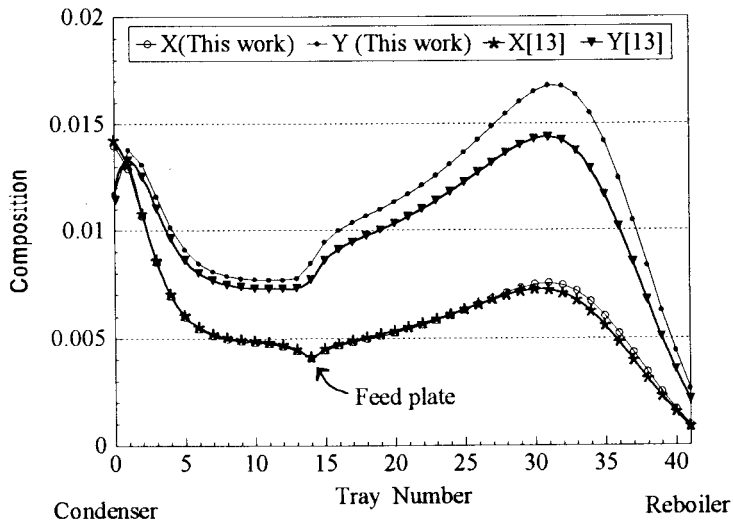**Fig. 2: Temperature profile for deethanizer column**

Fig. 3: H₂S composition profile (deethanizer)

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Table 3. Vapor flow rates (Moles/Hr.) from Condenser and Liquid Flow Rates (Moles/Hr.) from Reboiler of Deethanizer Column

Component	Simulation (This work)		Simulation [13] (Moshfeghian)		Design
name	Cond.	Reboiler	Cond.	Reboiler	Cond.
Methane	484.76	0	484.76	0	484.76
CO_2	100.56	0	100.56	0	100.56
H_2S	22.09	5.88	21.67	6.3	22.99
Ethane	1266.92	88.28	1267.89	87.31	1283.56
Propane	66.13	2363.47	65.11	2364.49	48.59
I-Butane	0	579.53	0	579.53	0
N-Butane	0	1535.10	0	1535.10	0
I-Pentane	0	500.90	0	500.90	0
N-Pentane	0	590.05	0	590.05	0
N-Hexane	0	516.96	0	516.96	0
C_7^+	0	497.93	0	497.93	0
Total (Moles/Hr.)	1940.46	6678.09	1940.00	6678.55	1940.46
Temperature (K)	261.74	382.16	264.29	388.84	266.67

Example 2. A mixture of butanol, water and propanol is fed to a column at boiling point condition. A description of problem is indicated in Table 4 and feed condition is described in Table 5. This column contains 10 trays in addition to reboiler and condenser. Column operates at constant atmospheric pressure.

This problem is solved and the results are indicated in Figures 4 to 7. In Figure 4, temperature profile is shown and in figures 5 to 7 the compositions of components on each tray are plotted. As can be seen in these figures, in the lower trays there are two liquid phases but in other trays there is only one liquid phase; therefore, an interruption in liquid phase composition curves can be seen. One of liquid phases is water rich phase and the other liquid phase contains small amount of water with respect to the aqueous phase.

Table 4: Three-Phase Column Specifications.

Column pressure	1.01325 Bar
No. of trays (without total condenser and reboiler)	10
Distillate flow rate	29 Moles/Hr.
Bottom flow rate	21 Moles/Hr.
Reflux ratio (L_0/D)	3

Table 5: Feed Stream Specifications for Three-Phase Column.

Component Name	Mole Fraction
Butanol (1)	0.13
Water (2)	0.65
Propanol (3)	0.22
Feed flow rate	50 Moles/Hr.
Feed Temperature	351.5 K
Feed pressure	1.01325 Bar
Feed tray	4
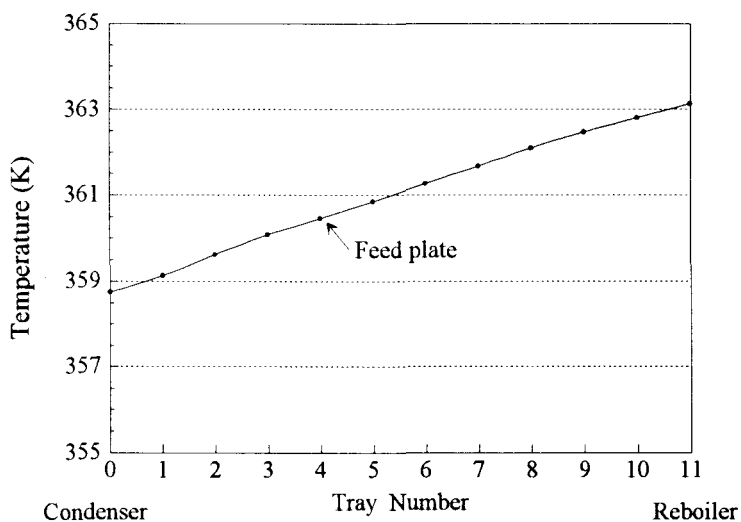
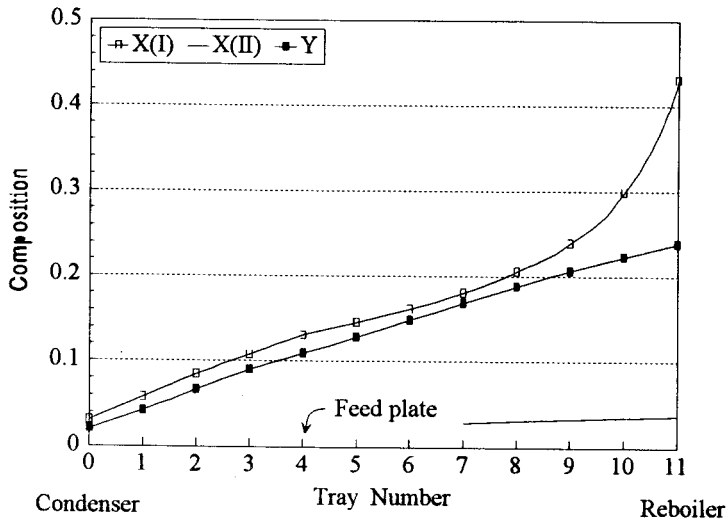**Fig. 4: Temperature profile for three-phase column example**

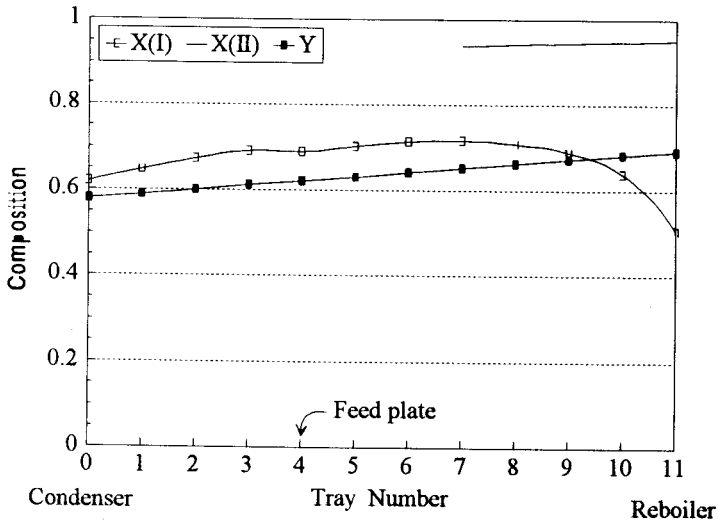**Fig. 5: N-Butanol distribution profile**
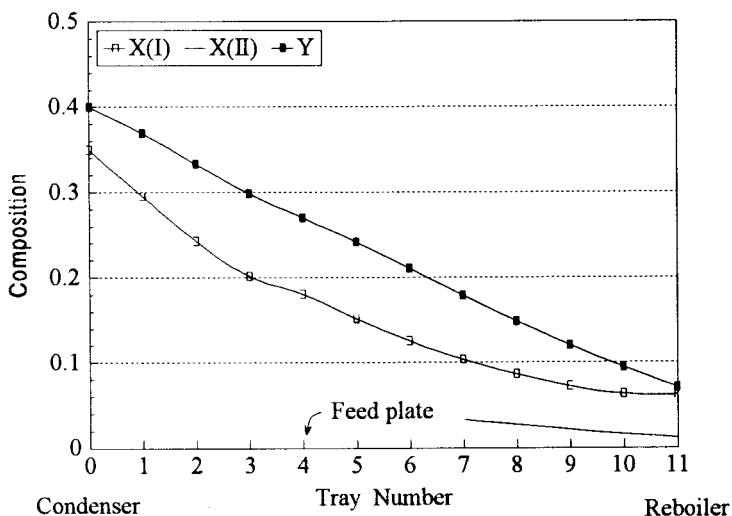

Fig. 6: Water distribution profile

Fig. 7: N-Propanol distribution profile

CONCLUSIONS

In this work, we have extended the Shimizu et al. [6] algorithm of two-phase distillation to three-phase distillation column. A major difference, in addition to number of phases, is the use of equation of state instead of activity coefficient relations in phase equilibria calculations. Since equation of state is used, the procedure can be applied to high pressure systems. Also the property such as enthalpy departure can be obtained directly from equation of state and therefore additional relations are not required.

Based on our evaluation, we conclude that the original cubic equations of state can not give good agreement with the polar mixture experimental data, and therefore improved equations based on group contribution are better to be applied in simulation. Another improvement in the SRK EOS for three-phase systems containing water is done by Erbar et al. [10] that introduced two different interaction parameter for hydrocarbon phase and aqueous phase where aqueous phase interaction parameter is linear function of temperature. For hydrocarbon mixture containing water, this improved SRK EOS may be used in three-phase systems.

The recommended equation of state is PSRK EOS which can be applied for polar mixture with good accuracy. Since MUNIFAC [14] coefficients are available for a large number of components, they have been used in the mixing rule relations.

With these equations of state, simulation procedure can be improved. The simulation method that is used was bubble point method. In the bubble point method, liquids and vapor, which are in equilibrium in all iterations and stage temperatures, have been found by bubble point calculations.

To improve the convergence of bubble point method, a test of convergence was performed in each iteration before changing the independent variables. Another improvement is generation of initial values with a few successive flash iterations. Since vapor and liquid flow rates are dependent variables and these variables are nearly constant values, therefore, in the first few iterations they can be assumed to be constant without any problem. This assumption speeds up convergence.

The method used in this work is a bubble point three-phase procedure that is similar to the work of Block and Hegner [4] and Kinoshita et al. [5]. The differences and improvements of this method with respect to their method are discussed in the following section.

In Block and Hegner method, LLE and bubble point algorithm are performed independently and LLE is performed without previous stability tests. Also they assumed that vapor phase is an ideal gas. Kinoshita et al. used their proposed algorithm for three-phase equilibria. They noted that trivial solution is a major problem in their work. Also equation of state is not used in the simulation of three-phase distillation columns by Kinoshita et al.

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APPENDIX

The following relations are obtained for i-th component of j-th tray as shown in Figure 1 where it contains two liquids and one vapor phase by written mass, efficiency, equilibrium, and energy equations respectively.

$$L_{j-1}^{I} x_{i,j-1}^{I} + L_{j-1}^{II} x_{i,j-1}^{II} - \left(L_j^I + U_j^I\right) x_{i,j}^I - \left(L_j^{II} + U_j^{II}\right) x_{i,j}^{II} -$$

$$\left(V_j + W_j\right) y_{i,j} + V_{j+1} y_{i,j+1} + F_j z_{i,j} = 0$$

$$(i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad (A1)$$

$$y_{i,j} - y_{i,j+1} - E_j \left(y_{i,j}^* - y_{i,j+1}\right) = 0$$

$$(i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad (A2)$$

$$y_{i,j}^* = K_{i,j}^I x_{i,j}^I = K_{i,j}^{II} x_{i,j}^{II} \quad (i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad (A3)$$

$$L_{j-1}^I h_{j-1}^I + L_{j-1}^{II} h_{j-1}^{II} - \left(L_j^I + U_j^I\right) h_j^I - \left(L_j^{II} + U_j^{II}\right) h_j^{II} -$$

$$\left(V_j + W_j\right) H_j + V_{j+1} H_{j+1} + F_j H_{f_j} - Q_j = 0$$

$$(j = 1, 2, ..., N) \qquad (A4)$$

If we want to solve these relations for a distillation column which in some trays, there are three phases and in some others two phases, it is necessary to know the number of phases in each step of solution. If the three-phase region is not specified, the Jacobian matrix may be singular. In some solution methods, where all of the equations were solved simultaneously, the three-phase region must be specified in the beginning of the solution. Niedzwiecki et al. [7] proposed the method by using pseudo-K-value concept that does not need the prior knowledge of the number of existing phases in each stage. This method allows the LLE calculation to be performed outside the main Newton-Raphson procedure and the average or pseudo values are used instead of actual values in equations written to

Jacobian matrix. The average values of $x_{i,j}$, $K_{i,j}$ and $h_{i,j}$ are obtained from main equations as follows :

$$L_j^I \, x_{i,j}^I + L_j^{II} \, x_{i,j}^{II} = \left(L_j^I + L_j^{II} \right) \, \overline{x}_{i,j}$$

$$(i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad \text{(A5)}$$

Then by dividing both sides by $(L_j^I + L_j^{II})$ and noting the definitions of $\Psi_{1,j}$ and $\Psi_{2,j}$:

$$\Psi_{1,j} = \frac{L_j^I}{L_j^I + L_j^{II} + V_j} \qquad (j = 1, 2, ..., N) \qquad \text{(A6)}$$

$$\Psi_{2,j} = \frac{L_j^{II}}{L_j^I + L_j^{II} + V_j} \qquad (j = 1, 2, ..., N) \qquad \text{(A7)}$$

average liquid composition will be defined as :

$$\overline{x}_{i,j} = \frac{\Psi_{1,j} x_{i,j}^I + \Psi_{2,j} x_{i,j}^{II}}{\Psi_{1,j} + \Psi_{2,j}} \qquad (i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \quad \text{(A8)}$$

By the following definition

$$\overline{K}_{i,j} = \left. y_{i,j}^* \middle/ \overline{x}_{i,j} \right. \qquad (i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \qquad \text{(A9)}$$

and by using the $\overline{x}_{i,j}$ in the above relation, $\overline{K}_{i,j}$ is expressed as :

$$\overline{K}_{i,j} = \frac{K_{i,j}^I \, K_{i,j}^{II} \left(\Psi_{1,j} + \Psi_{2,j} \right)}{\Psi_{1,j} K_{i,j}^{II} + \Psi_{2,j} K_{i,j}^I} \qquad (i = 1, 2, ..., nc \; ; j = 1, 2, ..., N) \quad \text{(A10)}$$

The equation (4) will be obtained by using $\overline{K}_{i,j}\ \overline{x}_{i,j}$ instead of $y_{i,j}^{\bullet}$ in the equation (A2).

To produce energy equation based on average liquid enthalpy ($\overline{h}_j$), terms of liquid energy from equation (A4) are extracted and are equal to average liquid phase energy.

$$L_j^I h_j^I + L_j^{II} h_j^{II} = \left(L_j^I + L_j^{II} \right) \overline{h}_j \qquad (j = 1, 2, ..., N) \qquad (A11)$$

By dividing both sides by $(L_j^I + L_j^{II})$:

$$\overline{h}_j = \frac{\Psi_{1,j} h_j^I + \Psi_{2,j} h_j^{II}}{\Psi_{1,j} + \Psi_{2,j}} \qquad (j = 1, 2, ..., N) \qquad (A12)$$

Therefore, in this work, the result matrix is obtained by average values and any simplification assumption is not used. Also, the singular matrix does not appear and the knowledge of three-phase region is not necessary before starting the solution; and the stability of phases are distinguished in equilibrium calculation outside the Newton-Raphson solution.