Development and Application of a Simulation Model for Three-Phase Distillation

The model of the multicomponent, multistage distillation column has been extended to three coexisting phases. The new model contains the well-known modeling equations of the two-phase distillation column as a special case. The versatility of the new simulation model is demonstrated with practical distillation problems.

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SCOPE

The models of multicomponent, multistage countercurrent unit operations, such as distillation and liquid-liquid extraction, are usually restricted to two countercurrent phases. A significant number of chemical engineering processes, however, have two partly miscible liquid phases and a vapor phase. This type of system cannot be simulated adequately by assuming only two phases. Therefore, a model of the distillation column with three-phase stages has been derived.

The more recent approaches to solving the modeling equations of two-phase multistage countercurrent operations use the Newton-Raphson technique within iterative solution procedures. The calculation method for the three-phase distillation problem presented here requires the conversion of the modeling equations into forms similar to those of the two-phase distillation problem. These equations are then solved by a Newton-Raphson iterative procedure for correction of the liquid compositions.

The simulation model presented can be used not only for the simulation of three-phase distillation columns, but also for columns with any combination of two- and three-phase stages. This is believed to be an essential feature of the method, because in a distillation process involving components which may form regions of immiscibility the phase type of a column is usually not known until the computation is completed.

CONCLUSIONS AND SIGNIFICANCE

A new model has been employed to simulate the steady state distillation column. It takes into account three phases, a vapor phase and two partly miscible liquid phases. Thus, the model also includes the simulation of a liquid-liquid phase separator within the distillation column.

To describe analytically the phase separation of the liquid at a stage, the phase splitting parameter η is introduced. A three-phase stage is defined by $0 < \eta < 1$, a two-phase stage by $\eta = 1$. If $\eta = 1$ for all stages, the new modeling equations reduce to the well-known equations of the two-phase distillation. Therefore, with the presented set of modeling equations, all types of stages can be adequately simulated.

A computational scheme for the three-phase distillation problem is presented. It is based on an iterative solution method which uses a Newton-Raphson technique and consists of linearizing the component mass balances with the liquid compositions as the independent variables. The method can be regarded as a modified bubble point procedure which has a block tridiagonal form rather than the usual tridiagonal structure. This was found to be a very efficient solution algorithm because of the highly composition dependent equilibrium ratios encountered in three-phase distillation.

It is known that industrial distillations frequently have three phases. These distillation columns can be simulated with the new model. The selected examples cover the simulation of stripping columns with a top phase separator, the very common case where low boiling components are removed by distillation from a mixture which is only partly miscible, and a particular distillation operation, by which an additional separation effect is gained by a side stream phase separator.

Considerable progress has been made in recent years in correlating and predicting thermodynamic properties. This resulted in an increasing use of more complex correlations within the simulation of countercurrent flow columns. So far, only distillation column models have been used which take into account two countercurrent phases. A significant number of chemical engineering processes, however, have three phases, two partly miscible liquid phases and a vapor phase. This type of system cannot be simulated adequately by assuming only two phases. In fact, this two-phase assumption will give larger errors when a process is simulated in which water and organic components become only partly miscible within a distillation column. Therefore, the model of the steady state distillation column is extended to three coexisting phases.

MODELING OF THE THREE-PHASE DISTILLATION COLUMN

The model of the steady state three-phase distillation column consists of a number of interconnected theoretical stages as shown in Figure 1. Feed streams can be introduced to each stage, and side streams can be taken from each stage. Heat can also be added or withdrawn at each stage. The assumption of phase equilibrium at each stage is made. The modeling equations of stage n are derived from the mass balance of each component, the enthalpy balance, the stoichiometric conditions for all phases, and the phase equilibrium conditions. The following equations also apply to stage 1 with $G_0 = 0$ and to stage N with $L'_{N+1} = L''_{N+1} = 0$ (see Figure 1):

Component i mass balance equation:

$$G_{n-1}y_{i,n-1} + L'_{n+1}x'_{i,n+1} + L''_{n+1}x''_{i,n+1} + F_n z_{i,n} - (G_n + S_n{}^G)y_{i,n} - (L'_n + S'_n)x'_{i,n} - (L''_n + S''_n)x''_{i,n} = 0, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \quad (1)$$

Enthalpy balance equation:

$$G_{n-1}h^G{}_{n-1} + L'_{n+1}h'_{n+1} + L''_{n+1}h''_{n+1} + F_n h^F{}_n + Q_n - (G_n + S^G{}_n)h^G{}_n - (L'_n + S'_n)h'_n - (L''_n + S''_n)h''_n = 0, \quad \text{for} \quad 1 \leq n \leq N \quad (2)$$

Stoichiometric equations:

$$\sum_{i=1}^{M} y_{i,n} = 1, \quad \text{for} \quad 1 \leq n \leq N \quad (3)$$

$$\sum_{i=1}^{M} x'_{i,n} = 1, \quad \text{for} \quad 1 \leq n \leq N \quad (4)$$

$$\sum_{i=1}^{M} x''_{i,n} = 1, \quad \text{for} \quad 1 \leq n \leq N \quad (5)$$

Phase equilibrium equations:

$$y_{i,n} = K'_{i,n}x'_{i,n}, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \quad (6)$$

$$y_{i,n} = K''_{i,n}x''_{i,n}, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \quad (7)$$

$$x''_{i,n} = K^*_{i,n}x'_{i,n}, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \quad (8)$$

The three-phase equilibrium of the vapor phase and the two liquid phases $'$ and $''$ is represented by Equations (6) to (8). The $K'_{i,n}$ and $K''_{i,n}$ are the vapor-liquid equilibrium ratios of component i at stage n with reference to the liquid phases $'$ and $''$, respectively. The liquid-liquid equilibrium ratio is $K^*_{i,n}$. A comparison of Equations (6), (7), and (8) shows that only two of these equations are independent; therefore, the equilibrium ratios are interrelated by

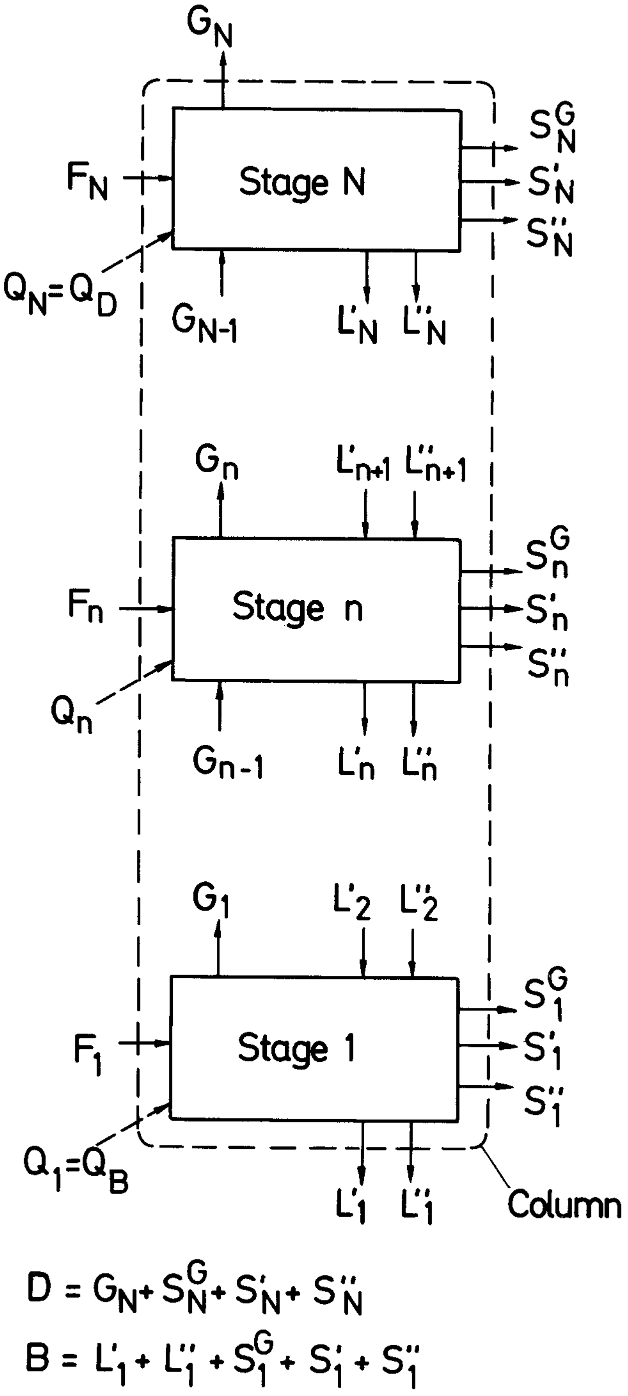

Fig. 1. Schematic diagram of model column.

$$K^*_{i,n} = K'_{i,n}/K''_{i,n}, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \quad (9)$$

For the solution of Equations (1) to (8), the following functions are assumed. The stage index n is dropped for convenience in the following section.

Enthalpy function of the gas phase:

$$h^G = h^G(y_i, y_j, \ldots p, T) \quad (10)$$

Enthalpy functions of the liquid phases:

$$h' = h'(x'_i, x'_j, \ldots T) \quad (11)$$

TABLE 1. COMPARISON OF THREE- AND TWO-PHASE DISTILLATION FOR UNKNOWNS AND EQUATIONS. QUANTITIES GIVEN ARE FOR THIS EXAMPLE: FEED STREAMS, RATE OF SIDE STREAMS, HEAT ADDED TO OR REMOVED FROM EACH STAGE

Equations:	Three phase	Two phase
Component mass balance equations	$M \cdot N$	$M \cdot N$
Enthalpy balance equations	N	N
Stoichiometric equations	$3 \cdot N$	$2 \cdot N$
Phase equilibrium equations	$2M \cdot N$	$M \cdot N$
I	$N(3M + 4)$	$N(2M + 3)$
Unknowns:		
Vapor and liquid internal flow rates	$3N$	$2N$
Vapor and liquid mole fractions	$3M \cdot N$	$2M \cdot N$
Stage temperatures	N	N
I	$N(3M + 4)$	$N(2M + 3)$

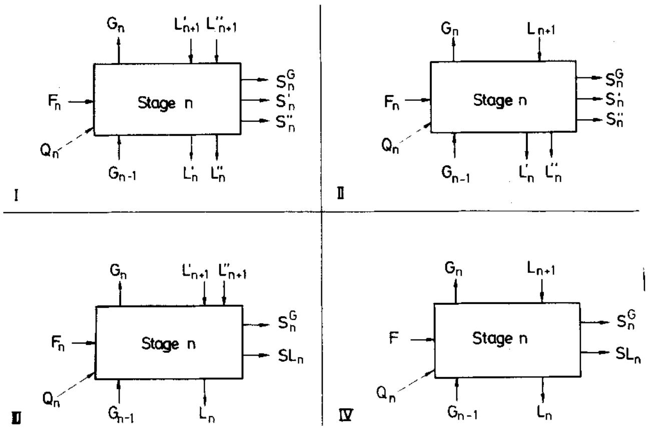

Fig. 2. Models of stage n for three- and two-phase distillation.

$$h'' = h''(x''_i, x''_j, \dots T) \tag{12}$$

Vapor-liquid equilibrium ratios:

$$K'_i = K'_i(x'_i, x'_j, \dots y_i, y_j, \dots p, T) \tag{13}$$

$$K''_i = K''_i(x''_i, x''_j, \dots y_i, y_j, \dots p, T) \tag{14}$$

Liquid-liquid equilibrium ratio:

$$K^*_i = K^*_i(x'_i, x'_j, \dots x''_i, x''_j, \dots T) \tag{15}$$

NUMBER OF UNSPECIFIED VARIABLES AND EQUATIONS

There are for the three-phase distillation the $N(3M + 4)$ independent Equations (1) to (6) and (8). The $N(3M + 4)$ unspecified variables are $3NM$ vapor, liquid′, and liquid″ mole fractions; $3N$ vapor, liquid′, and liquid″ internal flow rates; and the N stage temperatures. If the feed streams are given, the remaining variables, which must be specified, are number of stages, pressure of stages, rate and location of side streams, and rate and location of heat sources and sinks. For many practical problems it is convenient to exchange unspecified variables with an equal number of specified ones. The number of equations and unknowns, that is, unspecified variables, for the three- and two-phase distillation are compared in Table 1.

The distillation of a mixture, the components of which may form miscibility gaps, can lead to a distillation column with any combination of two- and three-phase stages as shown in Figure 2. In this case, there is also an equal number of equations as there are unknowns I. The value of I depends on the number N^P of stages with phase splitting of the liquid:

$$I = N(2M + 3) + N^P(M + 1) \tag{16}$$

DERIVATION OF THE WORKING EQUATIONS

Four new variables, $\overline{L}_n$, $\overline{x}_{i,n}$, η_n, and $\overline{h}_n$, are introduced to give forms of Equations (1) and (2) which are better fitted to the following solution procedure. The sum of the flow rates of the liquid streams leaving stage n is given by

$$\overline{L}_n = L'_n + S'_n + L''_n + S''_n, \quad \text{for} \quad 1 \leq n \leq N \tag{17}$$

Similarly, the overall mole fraction of component i in the liquid streams leaving stage n is

$$\overline{x}_{i,n} = ((L'_n + S'_n)x'_{i,n} + (L''_n + S''_n)x''_{i,n})/\overline{L}_n, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \tag{18}$$

In the general case of three-phase distillation, each stage has to be examined to determine whether the liquid forms one or two phases. Therefore, the phase splitting parameter η_n is introduced:

$$\overline{x}_{i,n} = \eta_n x'_{i,n} + (1 - \eta_n)x''_{i,n}, \text{ for } 1 \leq i \leq M, \ 1 \leq n \leq N \tag{19}$$

With η_n, a three-phase stage is defined by $0 < \eta_n < 1$; for a stage with only one liquid phase, η_n is set to $\eta_n = 1$. If $\eta_n = 1$ for all stages, the new modeling equations reduce to the well-known equations for the two-phase distillation.

From Equations (17), (18), and (19) we obtain

$$L'_n + S'_n = \eta_n \overline{L}_n, \quad \text{for} \quad 1 \leq n \leq N \tag{20}$$

and

$$L''_n + S''_n = (1 - \eta_n)\overline{L}_n, \quad \text{for} \quad 1 \leq n \leq N \tag{21}$$

Combining Equations (4) and (5) with (19), we get

$$\sum_{i=1}^{M} \overline{x}_{i,n} = 1, \quad \text{for} \quad 1 \leq n \leq N \tag{22}$$

By using these definitions, the mass and enthalpy balances, Equations (1) and (2), can be converted into forms which are similar to those of the two-phase distillation.

Component i mass balance equation:

$$G_{n-1}y_{i,n-1} + L'_{n+1}x'_{i,n+1} + L''_{n+1}x''_{i,n+1} + F_n z_{i,n} - (G_n + S^G_n)y_{i,n} - \overline{L}_n \overline{x}_{i,n} = 0, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \tag{23}$$

Enthalpy balance equation:

$$G_{n-1}h^G_{n-1} + L'_{n+1}h'_{n+1} + L''_{n+1}h''_{n+1} + F_n h^F_n + Q_n - (G_n + S^G_n)h^G_n - \overline{L}_n \overline{h}_n = 0, \quad \text{for} \quad 1 \leq n \leq N \tag{24}$$

The $\overline{h}_n$ is given by

$$\overline{h}_n = \eta_n h'_n + (1 - \eta_n)h''_n, \quad \text{for} \quad 1 \leq n \leq N \tag{25}$$

LIQUID SIDE STREAM AND PHASE SEPARATOR

A liquid side stream at stage n is specified by its flow rate SL_n and by the liquid phases which are withdrawn. Two distinct cases for defining a liquid side stream will be considered. In the first case, the side stream is assigned to have a composition equal to the overall composition of all liquid streams leaving stage n:

$$x^{SL}{}_{i,n} = \bar{x}_{i,n}, \quad \text{for} \quad 1 \leq i \leq M \tag{26}$$

The flow rates of the phases $'$ and $''$ are then related to the flow rate of the liquid side stream by

$$S'_n = \eta_n SL_n \tag{27}$$

and

$$S''_n = (1 - \eta_n) SL_n \tag{28}$$

In the second case, a single-phase side stream of phase $'$ is withdrawn. This is equivalent to the simulation of a liquid-liquid phase separator. The composition of the liquid side stream is

$$x^{SL}{}_{i,n} = x'_{i,n}, \quad \text{for} \quad 1 \leq i \leq M \tag{29}$$

The flow rates of the phases $'$ and $''$ become

$$S'_n = SL_n \tag{30}$$

and

$$S''_n = 0 \tag{31}$$

For the simulation of a phase separator, the conditions

$$0 < \eta_n < 1 \tag{32}$$

for phase splitting and

$$\bar{L}_n \eta_n \geq SL_n \tag{33}$$

for the internal flow rate of phase $'$ at stage n must be fulfilled. Equations similar to (29) through (33) can be derived if phase $''$ is to be withdrawn.

If phase splitting does not occur at stage n, that is, $\eta_n = 1$, the compositions of the liquid side stream become $\bar{x}_{i,n}$, for $1 \leq i \leq M$. If Equation (32) is satisfied, but Equation (33) is not, the result of the computation will have negative flow rates. Similar effects are well known from two-phase distillation if the internal flow rate is smaller than the corresponding flow rate of a specified side stream.

METHOD OF SOLUTION OF EQUATIONS

Most of the model equations which describe multicomponent, multistage countercurrent flow columns are nonlinear. Therefore, in the usual approach to solving these equations, successive iteration procedures are employed. The generalized linear methods (Ortega and Rheinboldt, 1970) treat all equations as linear. The well-known bubble point and sum rate methods of Friday and Smith (1964) are examples of this class. This concept was improved by Wang and Henke (1966) by developing a tridiagonal matrix method. The more recent methods of Thomich (1970), Goldstein and Stanfield (1970), Naphtali and Sandholm (1971), Gelbe and Nomine (1971), and Ishii and Otto (1973) account for the high nonlinearity of some of the equations by solving these with Newton-Raphson methods.

In principle, the system of equations describing the three-phase distillation column can be solved by any of the commonly used procedures for the two-phase distillation problem. In the following, we will focus our attention on correction methods which use the Newton-Raphson technique. There is an advantage to solution procedures which use the liquid compositions (Ishii and Otto, 1973) or, equivalently, the component flow rates (Naphtali and Sandholm, 1971) as independent variables, obtaining the improved liquid compositions by linearization rather than by making use of the tridiagonal matrix algorithm of Wang and Henke (1966). The reason is that the assumption of nearly composition independent vapor-liquid equilibrium ratios, inherent in the tridiagonal matrix algorithm, is not fulfilled within the model of three-phase distillation. Therefore, in the solution algorithm proposed here, the component mass balance equations are linearized and the liquid compositions are treated as the independent variables. The method can be regarded as a modified bubble point procedure which has a block tridiagonal form rather than the usual tridiagonal structure. The procedure may be summarized as follows:

1. Some initial set of $\bar{x}_{i,n}$ is assumed.
2. Phase splitting of the liquid is computed by an iterative procedure for all stages with Equations (4), (5), (8), and (19), whereby the $x'_{i,n}$, $x''_{i,n}$, and the η_n are obtained. Stage n with one liquid phase gives $\eta_n = 1$.
3. The $y_{i,n}$ and T_n are computed by a bubble point iterative procedure with Equations (3) and (6).
4. The G_n, L'_n, L''_n and $\bar{L}_n$ are calculated with Equations (20), (21), and (24) and from an overall material balance which is obtained by the summation of Equation (23) with Equations (3), (4), (5), and (22):

$$G_{n-1} + L'_{n+1} + L''_{n+1} + F_n - G_n - S^G{}_n - \bar{L}_n = 0, \qquad \text{for} \quad 1 \leq n \leq N \tag{34}$$

5. These results are substituted into Equation (23) in order to obtain the residuals of the component mass balances for the iteration step ν, the $r^\nu{}_{i,n}$. With the Newton-Raphson procedure, the $\bar{x}_{i,n}$ are improved at the next iteration level. The $r_{i,n}$ are therefore expanded as functions of the $\bar{x}_{k,m}$ by using Taylor's approximation truncated after the first term:

$$r^{\nu+1}_{i,n} = r^\nu{}_{i,n} + \sum_{m=n-1}^{n+1} \sum_{k=1}^{M} \frac{\partial r_{i,n}}{\partial \bar{x}_{k,m}} \Delta\bar{x}_{k,m} = 0, \qquad \text{for} \quad 1 \leq i \leq M-1, \quad 1 \leq n \leq N \tag{35}$$

The final solution requires the $r_{i,n}$ to be zero; hence, the $r^{\nu+1}_{i,n}$ are set equal to zero. The variation of the stage index m of Equation (35) follows from Equation (23) because the residuals $r_{i,n}$ of stage n are only functions of the variables of stages $n-1$, n and $n+1$. Since the scaling restriction, Equation (22), has to hold, the $\Delta\bar{x}_{k,m}$ are correlated by

$$\sum_{k=1}^{M} \Delta\bar{x}_{k,m} = 0, \quad \text{for} \quad 1 \leq m \leq N \tag{36}$$

$$\Delta\bar{x}_{M,m} = - \sum_{k=1}^{M-1} \Delta\bar{x}_{k,m}, \quad \text{for} \quad 1 \leq m \leq N \tag{37}$$

If Equations (35) and (37) are combined, we get

$$r^{\nu+1}_{i,n} = r^\nu{}_{i,n} + \sum_{m=n-1}^{n+1} \sum_{k=1}^{M-1} \left(\frac{\partial r_{i,n}}{\partial \bar{x}_{k,m}} - \frac{\partial r_{i,n}}{\partial \bar{x}_{M,m}} \right) \Delta\bar{x}_{k,m} = 0, \qquad \text{for} \quad 1 \leq i \leq M-1, \quad 1 \leq n \leq N \tag{38}$$

The partial derivatives of Equation (38) together with Equation (23) become

$$r^{\nu+1}_{i,n} = r^\nu{}_{i,n} + G_{n-1} \sum_{k=1}^{M-1} \left(\frac{\partial y_{i,n-1}}{\partial \bar{x}_{k,n-1}} - \frac{\partial y_{i,n-1}}{\partial \bar{x}_{M,n-1}} \right) \Delta\bar{x}_{k,n-1}$$

TABLE 2. NRTL PARAMETERS

Components ij	τ_{ij}	τ_{ji}	α_{ij}
Butyl alcohol (1)—Water (2)	0.90047	3.51307	0.48
Water (2)—Butyl acetate (3)	5.04652	1.75717	0.34
Butyl acetate (3)—Butyl alcohol (1)	−0.30827	1.15161	0.30
Butyl alcohol (1)—Water (2)	0.90047	3.51307	0.48
Water (2)—Propyl alcohol (3)	2.7425	−0.07149	0.30
Propyl alcohol (3)—Butyl alcohol (1)	−0.61259	0.71640	0.30

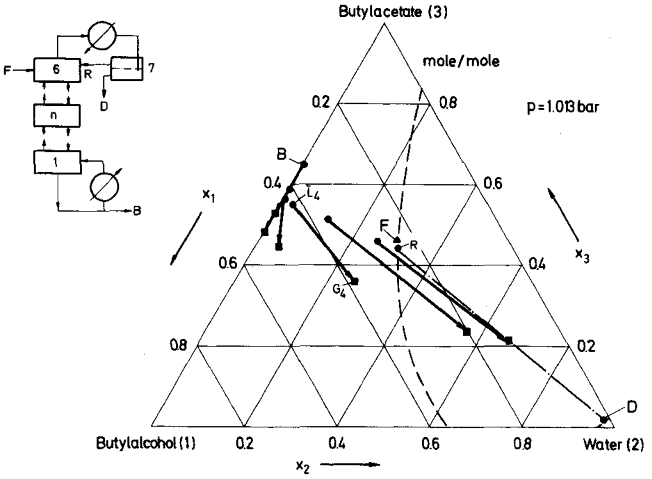

Fig. 3. Stage compositions of a stripping column with top phase separator (Example 1).

Flow rates:

$F = 50$ mole/h, $B = 34.84$ mole/h, $D = 15.16$ mole/h, $R = 13.8$ mole/h.

● **liquid compositions**
■ **vapor compositions**
——→ **liquid-vapor tie line**
· — · — **liquid-liquid tie line**
— — — **binodal curve**

$$+\left[L'_{n+1} \sum_{k=1}^{M-1} \left(\frac{\partial x'_{i,n+1}}{\partial x_{k,n+1}} - \frac{\partial x'_{i,n+1}}{\partial x_{M,n+1}} \right) \right.$$

$$\left. + L''_{n+1} \sum_{k=1}^{M-1} \left(\frac{\partial x''_{i,n+1}}{\partial x_{k,n+1}} - \frac{\partial x''_{i,n+1}}{\partial x_{M,n+1}} \right) \right] \Delta\bar{x}_{k,n+1}$$

$$- (G_n + S^G_n) \sum_{k=1}^{M-1} \left(\frac{\partial y_{i,n}}{\partial x_{k,n}} - \frac{\partial y_{i,n}}{\partial x_{M,n}} \right) \Delta\bar{x}_{k,n}$$

$$- \bar{L}_n \Delta\bar{x}_{i,n} = 0, \quad \text{for} \quad 1 \leq i \leq M-1, \quad 1 \leq n \leq N \tag{39}$$

In Equation (38) or (39), the partial derivatives of the vapor compositions are treated as a function of the liquid compositions $\bar{x}_k$ and of the temperature T. Thus we have to write, omitting the stage index

$$\frac{\partial y_i}{\partial \bar{x}_k} = \left(\frac{\partial y_i}{\partial \bar{x}_k} \right)_{T, \bar{x}_l \neq k} + \left(\frac{\partial y_i}{\partial T} \right)_{\bar{x}_l} \left(\frac{\partial T}{\partial \bar{x}_k} \right)_{\bar{x}_l \neq k} \tag{40}$$

Since the temperature T is used as a dependent variable, the system will remain near the bubble point condition.

Equation (38) may also be expressed in vector notation as follows:

$$\mathbf{R}\Delta\mathbf{x} = -\mathbf{r} \tag{41}$$

The $\mathbf{r}$ is the vector of the residuals of the component mass balances; the $\Delta\mathbf{x}$ is the vector of the corrections of the actual $\bar{x}_{k,n}$. The Jakobian matrix $\mathbf{R}$, the matrix of the partial derivatives, has a block tridiagonal form. Thus, Equation (41) may be written as

$$\begin{bmatrix} a_{1,1} & a_{1,2} & & \\ a_{2,1} & a_{2,2} & a_{2,3} & \\ & a_{n,n-1} & a_{n,n} & a_{n,n+1} \\ & & a_{N,N-1} & a_{N,N} \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_n \\ b_N \end{bmatrix} = - \begin{bmatrix} c_1 \\ c_2 \\ c_n \\ c_N \end{bmatrix} \tag{42}$$

The elements of the matrix in Equation (42) are quadratic submatrices, the elements of which are

$$a_{n,m} = \begin{bmatrix} d_{1,1} & d_{1,2} & d_{1,k} & d_{1,M-1} \\ d_{2,1} & d_{2,2} & d_{2,k} & d_{2,M-1} \\ d_{i,1} & d_{i,2} & d_{i,k} & d_{i,M-1} \\ d_{M-1,1} & d_{M-1,2} & d_{M-1,k} & d_{M-1,M-1} \end{bmatrix} \tag{43}$$

where

$$d_{i,k} = \frac{\partial r_{i,n}}{\partial \bar{x}_{k,m}} - \frac{\partial r_{i,n}}{\partial \bar{x}_{M,m}} \tag{44}$$

and

$$b_n = \begin{bmatrix} \Delta x_{1,n} \\ \Delta x_{2,n} \\ \Delta x_{k,n} \\ \Delta x_{M-1,n} \end{bmatrix} \tag{45}$$

$$c_n = \begin{bmatrix} r_{1,n} \\ r_{2,n} \\ r_{k,n} \\ r_{M-1,n} \end{bmatrix} \tag{46}$$

It is obvious from a comparison of Equations (38) and (39) how the partial derivatives in Equation (44) are obtained. The block tridiagonal matrix system, Equation (42), is solved and yields the $\Delta\bar{x}_{i,n}$ for $1 \leq i \leq M-1$, $1 \leq n \leq N$.

6. The $\Delta\bar{x}_{M,n}$ for $1 \leq n \leq N$ are computed by Equation (37).

7. The new $\bar{x}_{i,n}$ are computed from the following equation:

$$\bar{x}^{\nu+1}_{i,n} = \bar{x}^{\nu}_{i,n} + \lambda\Delta\bar{x}_{i,n}, \quad \text{for} \quad 1 \leq i \leq M, \quad 1 \leq n \leq N \tag{47}$$

λ is a damping factor. It may be computed with a method outlined by Thomich (1970).

Steps 2 through 7 are repeated, using the new sets of $\bar{x}^{\nu+1}_{i,n}$, until two independent convergence criteria for each of the $r_{i,n}$ and $\Delta\bar{x}_{i,n}$ are satisfied.

CONVERGENCE CHARACTERISTICS

The convergence characteristics of solution procedures which use the Newton-Raphson technique are known to depend on the initial estimates of the independent variables. This experience was also made with the presented solution algorithm. In practice, however, the designer of a distillation column first inspects the phase equilibria, thus getting a rough idea what the initial estimates should therefore be. Under such conditions the convergence stability of the proposed procedure is very satisfying.

The presented solution algorithm for three-phase distillation can be extended by increasing the number of the independent variables; for example, the G_n, $\bar{L}_n$, and T_n can be employed in addition to $\bar{x}_{i,n}$. In this case we

TABLE 3. PRINT-OUT OF THE SIMULATION OF A DISTILLATION COLUMN WITH THREE- AND TWO-PHASE STAGES (EXAMPLE 2)

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 N    T      G                            Y1       Y2       Y3
             L̄      L'      L''           X̄1       X̄2       X̄3         X1'      X2'      X3'        X1''     X2''     X3''
12  88.4   0.00                       0.014694 0.601846 0.383460
12       116.00                       0.030840 0.619607 0.349552
11  88.9 116.00                       0.030840 0.619607 0.349552
11        87.10                       0.057763 0.647114 0.295123
10  89.5 116.10                       0.051038 0.640244 0.308718
10        87.22                       0.084724 0.672762 0.242514
 9  90.1 116.22                       0.071278 0.659498 0.269224
 9        87.31                       0.107482 0.690801 0.201717
 8  90.5 116.31                       0.088372 0.673049 0.238578
 8       137.43                       0.130386 0.689119 0.180495
 7  90.9 116.43                       0.105757 0.688604 0.205639
 7       137.56                       0.145868 0.702242 0.151890
 6  91.3 116.56                       0.124055 0.704093 0.171852
 6       137.66                       0.161569 0.712946 0.125485
 5  91.7 116.66                       0.142601 0.716722 0.140677
 5       137.73 128.49    9.25        0.176541 0.721817 0.101642 0.187443 0.705573 0.106984 0.025094 0.947484 0.027422
 4  92.0 116.73                       0.160279 0.727187 0.112534
 4       137.79 118.88   18.91        0.190069 0.729288 0.080643 0.216519 0.693227 0.090254 0.023784 0.955993 0.020223
 3  92.2 116.79                       0.176248 0.735998 0.087754
 3       137.84 111.69   26.15        0.201919 0.735426 0.062655 0.243862 0.682274 0.073864 0.022770 0.962448 0.014782
 2  92.4 116.84                       0.190233 0.743236 0.066531
 2       137.88 106.19   31.68        0.212108 0.740407 0.047485 0.268828 0.672697 0.058475 0.021992 0.967358 0.010650
 1  92.6 116.88                       0.202257 0.749110 0.048634
 1        21.00  19.11    1.89        0.266935 0.691971 0.041094 0.291195 0.664390 0.044416 0.021393 0.971128 0.007478

NF   TF     F                            Z1       Z2       Z3
 8  90.2  50.00L                      0.130000 0.650000 0.220000

NSL  TS     SL     S'      S''          XSL1     XSL2     XSL3        X1'      X2'      X3'        X1''     X2''     X3''
12  88.4  29.00                       0.030840 0.619607 0.349552

P = 1.013 BAR  ,  DP = 0.000 BAR  ,  QB =1392. WATT  ,  QD =1393. WATT

T IN DEG.C,  G,L̄,L',L'',F,SL,S',S'',SG IN MOLE/H,  Y,X̄,XSL,X',X'',Z IN MOLE/MOLE

COMPONENTS: 1=BUTYLALCOHOL, 2=WATER, 3=PROPYLALCOHOL
```

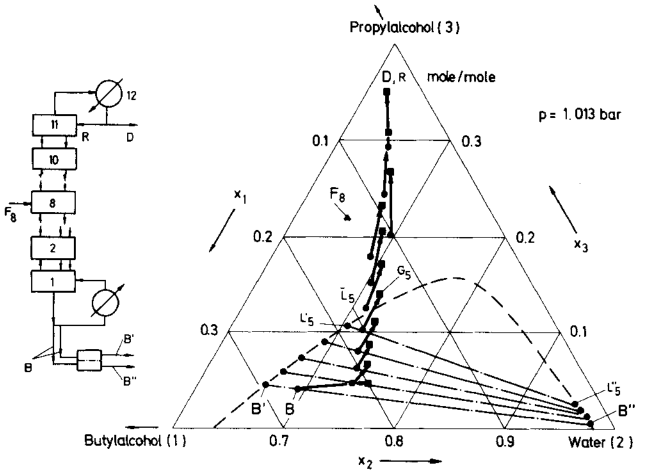

Fig. 4. Stage compositions of a distillation column with three- and two-phase stages (Example 2).

Flow rates:

$F = 50$ mole/h, $B = 21$ mole/h, $D = 29$ mole/h, $R = 87$ mole/h.

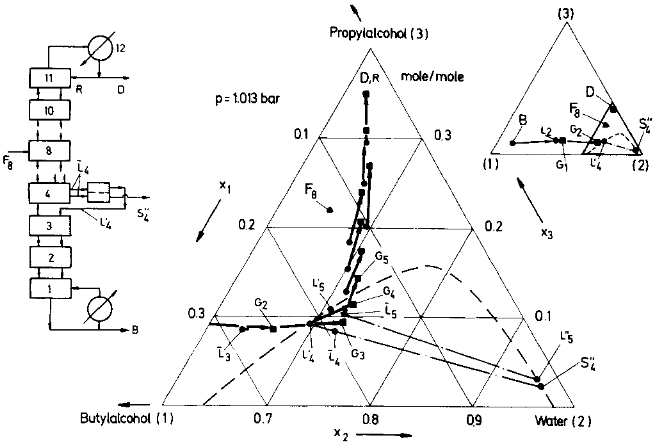

Fig. 5. Stage compositions of a distillation column with a side stream phase separator (Example 3). The complete ternary diagram is shown in the upper right; the miscibility gap is shown enlarged in the center.

Flow rates:

$F = 50$ mole/h, $B = 6.53$ mole/h, $D = 29$ mole/h, $S_4 = 14.47$ mole/h, $R = 87$ mole/h.

found that for three-phase distillation columns the convergence stability improves only slightly, whereas the computational effort increases considerably. The reason for this convergence characteristic is that the three-phase distillation columns usually are of the distillation type as defined by Friday and Smith (1964). Of course, if a three-phase column is more of the absorption type, other pertinent variables in addition to $\overline{x}_{i,n}$ should also be treated as independent variables.

EXAMPLE PROBLEMS

Three example problems, which are typical to those encountered in the chemical industry, were selected to illustrate the simulation of three-phase distillation columns. For demonstration purposes, the number of components has been limited to three. The calculation of the phase equilibria for the examples is outlined in the Appendix. The NRTL equation was used for the computation of the activity coefficients. The NRTL parameters are listed in Table 2. The vapor pressures were computed with the Antoine equation.

The simulation of a stripping column with a top phase separator is demonstrated with the first example. This kind of operation is used for removing small amounts of water from organic components or vice versa. In Figure 3, the column of the example is shown. The feed is a mixture of butyl alcohol and butyl acetate, saturated with water. The simulation is done with seven stages. The feed is introduced at stage 6, and stage 7 simulates the condenser and the phase separator. The organic phase is refluxed to the column, and the water phase is withdrawn. The bottom product of butyl alcohol and butyl acetate contains 50(mole) p.p.m. water. The result of the computation is depicted in Figure 3. If the liquid is subcooled for the phase separation, the phase separator and the column have different bubble pressures. In this case, one has to introduce temperature dependence of the NRTL parameters.

An industrial distillation operation, which is frequently used, is illustrated in the second example: Low boiling components are separated by distillation from a mixture which is only partly miscible. More generally, this operation includes the removal of low boiling organic compounds of one type (alcohols, amines, etc.) from mixtures of water and higher boiling components of the same type. In the example, a feed of butyl alcohol, water, and propyl alcohol is to be separated into a propyl alcohol rich top product and a butyl alcohol rich bottom product. The distillation problem and its solution are outlined in Figure 4 and Table 3. The column is simulated by twelve stages, and the feed is introduced at stage 8. At stages 1 to 5, two liquid phases are formed, and the bottom product is separated into an organic and a water phase. The slope of distillation, as shown in Figure 4, is characteristic for the existence of a ternary dividing distillation line which extends from the binary azeotrope water, butyl alcohol with 76 mole % water, to the binary azeotrope propyl alcohol, water with 43 mole % propyl alcohol. This ternary dividing distillation line is closely followed by the vapor compositions within the column.

The third example, depicted in Figure 5, illustrates a particular distillation operation with a side stream phase separator. The distillation conditions (feed rate and composition, heat duty of the reboiler, etc.) are the same as in the second example, with the exception that the phase separator is moved from the bottom to stage 4. From the side stream phase separator the water phase is withdrawn, and the organic phase is given back to the column. A comparison of the calculated stage compositions, Figure 5, with those of the second example, Figure 4, shows no remarkable changes in the rectifying section of the column. The composition of the water stream leaving the column also changes only very slightly. However, the butanol product is now obtained with a considerably lowered water content. This additional separation effect is gained by no more than moving the phase separator from the bottom into the side stream position.

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NOTATION

a, b, c, d = elements of matrix or vector
B = bottom product molar flow rate
D = top product molar flow rate
F = feed stream molar flow rate
f = fugacity

G = vapor stream molar flow rate
h = specific enthalpy
I = number of equations for a distillation column
K = equilibrium ratio
L = liquid stream molar flow rate
M = total number of components
N = total number of stages, including reboiler and condenser
p = pressure
Q = rate of heat input to a stage
R = reflux stream molar flow rate
$\mathbf{R}$ = Jacobian matrix
r = residual of the component material balance
$\mathbf{r}$ = column vector of r
S = side stream molar flow rate
SL = externally specified liquid side stream molar flow rate
T = temperature
x = composition of liquid, mole fraction
$\mathbf{x}$ = column vector of x
y = composition of vapor, mole fraction
z = composition of feed, mole fraction

Greek Letters

η = phase splitting parameter defined by Equation (19)
α = coordination parameter of the NRTL equation
γ = activity coefficient
λ = damping factor
ν = iteration number
τ = interaction energy parameter of the NRTL equation

Superscripts

F = feed
G = vapor phase
P = indicating phase splitting
SL = liquid side stream
ν = iteration number
$-$ = overall quantity of two- or single-phase liquid stream
$'$, $''$ = liquid phase $'$ and $''$, respectively
$*$ = liquid-liquid equilibrium
o = pure component

Subscripts

i, j, k, l = component index
M = index of last component
m, n = stage index
N = top stage

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APPENDIX A: CALCULATION METHOD FOR EQUILIBRIUM RATIOS

The condition of the three-phase equilibrium for given pressure ($p^G = p' = p''$) and temperature ($T^G = T' = T''$) is

$$f_i^G = f_i' = f_i'' \tag{A1}$$

These fugacity relations of component i can be expressed by (Prausnitz, 1969)

$$y_i p = x_i' \gamma_i'(x_i', x_j', \ldots T) p_i^o(T) \tag{A2}$$

$$y_i p = x_i'' \gamma_i''(x_i'', x_j'', \ldots T) p_i^o(T) \tag{A3}$$

$$x_i' \gamma_i'(x_i', x_j', \ldots T) p_i^o(T) = x_i'' \gamma_i''(x_i'', x_j'', \ldots T) p_i^o(T) \tag{A4}$$

The Poynting correction and the vapor phase fugacity coefficients were neglected because $p_i^o \approx p \approx 1$ bar for the systems under consideration. The vapor-liquid equilibrium ratios follow from Equations (A2) and (A3):

$$K_i' = y_i/x_i' = \gamma_i'(x_i', x_j', \ldots T) p_i^o(T)/p \tag{A5}$$

$$K_i'' = y_i/x_i'' = \gamma_i''(x_i'', x_j'', \ldots T) p_i^o(T)/p \tag{A6}$$

The liquid-liquid equilibrium ratio is obtained from Equation (A4):

$$K_i^* = x_i''/x_i' = K_i'/K_i'' = \gamma_i'(x_i', x_j', \ldots T)/\gamma_i''(x_i'', x_j'', \ldots T) \tag{A7}$$

For comparison, the two-phase vapor-liquid equilibrium ratio is given by

$$K_i = y_i/x_i = \gamma_i(x_i, x_j, \ldots T) p_i^o(T)/p \tag{A8}$$

This is Equation (A5) for $x_i' = x_i$.

In principle, any of the equations for the dependence of the activity coefficient on composition can be used for the computation of the three-phase equilibrium, for example, the van Laar and Margules equations, the NRTL equation of Renon and Prausnitz (1968), and the recently developed UNIQUAC equation of Abrams and Prausnitz (1974). However, the Wilson equation is not applicable because it cannot describe three-phase equilibria. For the examples of this paper, the NRTL equation is employed. It has three parameters, α_{ij}, τ_{ij}, τ_{ji}, for each binary system

$$\gamma_i = \gamma_i(x_i, x_j, \ldots \tau_{ij}, \tau_{ji}, \alpha_{ij}, \ldots \tau_{ik}, \ldots) \tag{A9}$$

and for the phases $'$ and $''$

$$\gamma_i' = \gamma_i'(x_i', x_j', \ldots \tau_{ij}, \tau_{ji}, \alpha_{ij}, \ldots \tau_{ik}, \ldots) \tag{A10}$$

$$\gamma_i'' = \gamma_i''(x_i'', x_j'', \ldots \tau_{ij}, \tau_{ji}, \alpha_{ij}, \ldots \tau_{ik}, \ldots) \tag{A11}$$

The α_{ij}, τ_{ij}, and τ_{ji} are fitted to binary equilibrium data. Since the binary system ij has three parameters, it is often necessary, as shown for instance by Hegner et al. (1973) and by Bender and Block (1975), to select the best set of parameters by adjusting to binary three-phase equilibria or to ternary liquid-liquid equilibrium data.

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