Simple Model for Dynamic Simulation of Stage Separation Processes with Very Volatile Components

Masahiro Kinoshita
Tritium Engineering Laboratory
Department of Thermonuclear Fusion Research
Japan Atomic Energy Research Institute
Tokai-mura, Ibaraki-ken 319-11, Japan

Dynamic simulation of stage separation processes is a significant field in chemical engineering. Among those processes, a distillation column has long been a major process. The emphasis of earlier work was on formulations of mathematical equations using various assumptions (Peiser and Grover, 1962; Holland and co-workers, 1965, 1966, 1967; Howard, 1970). In the last ten years, however, development of stable and efficient algorithms for integrating the basic equations has attracted much more attention, and some powerful integration techniques have been developed (Ballard and Brosilow, 1978; Gallun and Holland, 1982; Prokopakis and Seider, 1983). The present note examines the earlier work.

The simplest model uses the assumption of constant molal overflows and liquid holdups, but in the models developed by Holland and his co-workers (1965, 1966), provision is made for incorporating heat balances and for choosing either constant molal or volume holdup specifications. Howard (1970) presented a general modeling procedure that allows a wide choice of simplifying assumptions. Peiser and Grover (1962) included the effects of tray hydraulics and condenser and reboiler heat exchange dynamics. Although most of these works are based on the assumption of perfect mixing of liquid on and leaving each tray, the later models by Holland et al. (1967) accounted for the effect of channeling, transfer lag, and mixing. Those studies are all highly significant regardless of the assumptions made, because the dynamic simulation is performed by choosing a model best suited to the case considered. The simulation is undertaken for many different purposes, and we choose a model that is expected to give adequate reliability with minimum computational effort. Although a number of models are thus available, the assumption of negligible vapor holdups was used by everyone. The author is concerned with this assumption, and the significance of vapor holdups in some situations is originally pointed out from a unique viewpoint.

For simplicity, the following assumptions are made: there is perfect mixing between the liquid and vapor phases and within each phase; hydraulic effects are negligible; and molal holdups of liquid and vapor can be considered constant. Then, the variation rate of the amount of a component on a tray is given by

$$D_{i,j} = H_{Lj}(dx_{i,j}/dt) + H_{Vj}(dy_{i,j}/dt). \tag{1}$$

The first assumption means that there is no interphase mass transfer resistance and the vapor and liquid leave the tray at equilibrium. Assuming that the volatility $\alpha_{i,j}$ $(=y_{i,j}/\ x_{i,j})$ is constant, Eq. 1 is reduced to

$$D_{i,j} = (H_{Lj} + \alpha_{i,j}H_{Vj})(dx_{i,j}/dt). \tag{2}$$

Hence, the degree of the contribution of H_{Vj} should be estimated by comparing H_{Lj} with $\alpha_{i,j}H_{Vj}$. The degree can be significantly large in cases where (1) extremely volatile components are present; (2) the column is operated at cryogenic temperature; or (3) a partial condenser is used and its volume is very large. Case 1 is found in distillation of heavy hydrocarbon mixtures where hydrogen, nitrogen, and methane are present, and in separation of wide boiling mixtures by absorbers and strippers. The most significant example where all three cases mentioned above are found is hydrogen isotope distillation with the presence of helium. Such processes are becoming increasingly more important in the fusion fuel cycle (Steiner and Flanagan, 1983). A typical feed comprises helium, protium, deuterium, and tritium, from which packed columns arranged in a cascade remove helium and protium and produce pure streams of deuterium and

tritium. The order of the volatility of helium is in the range from 10^2 to 10^3, and varies greatly depending on liquid composition and temperature (Kinoshita, 1983). In addition, H_{Vj}/H_{Lj} is roughly 10^{-1} per theoretical stage owing to the cryogenic temperature and low liquid density. In such circumstances, the vapor holdup terms are much more important than the mass transfer resistance, hydraulic effects, and heat balances. The present note derives working equations for dynamic simulation of stage separation processes by incorporating vapor holdups. The above-mentioned assumptions are used with the exception that the term, $dy_{i,j}/dt$ is treated in a rigorous manner. Heat balances are also excluded in the model.

Derivation of Working Equations

The model column is illustrated in Figure 1. The component material balances are expressed by

$$H_{Lj}(dx_{i,j}/dt) + H_{Vj}(dy_{i,j}/dt) = F_j z_{i,j} + L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} - (L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j}, \quad i = 1, \ldots, m; \quad j = 1, \ldots, N, \tag{3}$$

$$L_0 = V_{N+1} = W_1 = U_N = 0. \tag{4}$$

The vapor mole fractions are calculated by solving

$$Z_j = \sum_{i-1}^{m} K_{i,j}x_{i,j} = 1 \tag{5}$$

for T_j and then from the vapor-liquid equilibrium relationship:

$$y_{i,j} = K_{i,j}x_{i,j}. \tag{6}$$

Mathematical complexity is caused by $dy_{i,j}/dt$, which has never appeared in the previously reported models. By using Eq. 6, we obtain

$$dy_{i,j}/dt = K_{i,j}(dx_{i,j}/dt) + (dK_{i,j}/dt)x_{i,j}. \tag{7}$$

Since $K_{i,j}$ can be considered a function of $x_{1,j}, \ldots, x_{m-1,j}$, and T_j, $dK_{i,j}/dt$ is given by

$$dK_{i,j}/dt = \sum_{k-1}^{m-1} (\partial K_{i,j}/\partial x_{k,j})(dx_{k,j}/dt) + (\partial K_{i,j}/\partial T_j)(dT_j/dt). \tag{8}$$

Since T_j is a function of $x_{1,j}, \ldots, x_{m-1,j}$, we obtain

$$dT_j/dt = \sum_{k-1}^{m-1} (\partial T_j/\partial x_{k,j})(dx_{k,j}/dt). \tag{9}$$

Substituting Eq. 9 in Eq. 8 yields

$$dK_{i,j}/dt = \sum_{k-1}^{m-1} [\partial K_{i,j}/\partial x_{k,j} + (\partial K_{i,j}/\partial T_j)(\partial T_j/\partial x_{k,j})] \cdot (dx_{k,j}/dt). \tag{10}$$

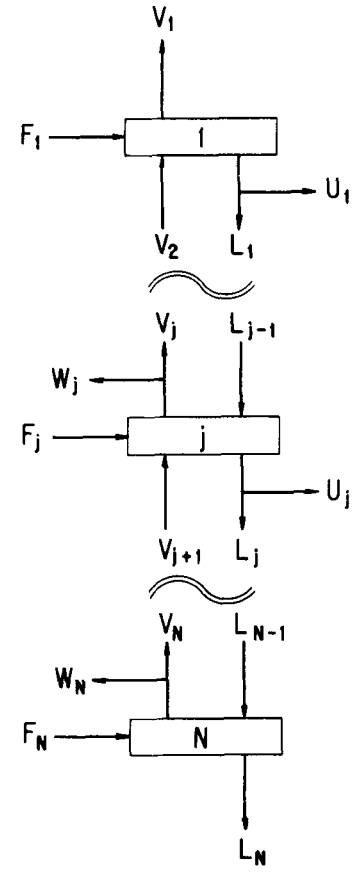

Figure 1. Model column for mathematical simulation.

From Eqs. 7 and 10, we obtain

$$dy_{i,j}/dt = K_{i,j}(dx_{i,j}/dt) + x_{i,j}\sum_{k-1}^{m-1} \eta_{i,k,j}(dx_{k,j}/dt), \tag{11}$$

where

$$\eta_{i,k,j} = \partial K_{i,j}/\partial x_{k,j} + (\partial K_{i,j}/\partial T_j)(\partial T_j/\partial x_{k,j}). \tag{12}$$

Substituting Eq. 11 in Eq. 3 and rearranging the resultant equations yields the following matrix equations:

$$d\vec{x}_j/dt = \bar{\bar{A}}_j^{-1}\vec{D}_j, \quad j = 1, \ldots, N$$

$$d\vec{x}_j/dt = \begin{bmatrix} dx_{1,j}/dt \\ \vdots \\ dx_{m,j}/dt \end{bmatrix}, \quad \vec{D}_j = \begin{bmatrix} D_{1,j} \\ \vdots \\ D_{m,j} \end{bmatrix}$$

$$\bar{\bar{A}}_j = \begin{bmatrix} A_{11,j} & \cdots & A_{1m,j} \\ \vdots & \ddots & \vdots \\ A_{m1,j} & \cdots & A_{mm,j} \end{bmatrix} \tag{13}$$

where

$$A_{kk,j} = H_{Lj} + K_{k,j}H_{Vj} + x_{k,j}H_{Vj}\eta_{k,k,j},$$
$$k = 1, \ldots, m-1$$
$$A_{kn,j} = x_{k,j}H_{Vj}\eta_{k,n,j},$$
$$n = 1, \ldots, m-1;\ k = 1, \ldots, m-1;\ k \neq n$$
$$A_{km,j} = 0,\ k = 1, \ldots, m-1$$
$$A_{mk,j} = x_{m,j}H_{Vj}\eta_{m,k,j},\ k = 1, \ldots, m-1$$
$$A_{mm,j} = H_{Lj} + K_{m,j}H_{Vj} \tag{14}$$

The term $D_{i,j}$ denotes the righthand side of Eq. 3.

By solving Eq. 13, $dx_{i,j}/dt$ can be calculated; it can be expressed

$$dx_{i,j}/dt = f_{i,j}(x_{1,j}, \ldots, x_{m,j}),$$
$$i = 1, \ldots, m;\ j = 1, \ldots, N. \tag{15}$$

Hence, a numerical technique can be applied to the integration of Eq. 15. The partial derivative $\partial T_j/\partial x_{i,j}$ is calculated from the requirement that the sum of all the vapor mole fractions be equal to unity (Howard, 1970). This calculation is made by assuming that pressure is independent of time. Extending the expression derived by Howard to cases of nonideal solutions, we obtain

$$\partial T_j/\partial x_{i,j} = -(\partial Z_j/\partial x_{i,j})/(\partial Z_j/\partial T_j), \tag{16}$$

$$\partial Z_j/\partial x_{i,j} = K_{i,j} - K_{m,j} + \sum_{k=1}^{m-1} x_{k,j}(\partial K_{k,j}/\partial x_{i,j} - \partial K_{m,j}/\partial x_{i,j}) + \partial K_{m,j}/\partial x_{i,j},\ i = 1, \ldots, m-1, \tag{17}$$

$$\partial Z_j/\partial T_j = \sum_{k=1}^{m-1} x_{k,j}(\partial K_{k,j}/\partial T_j - \partial K_{m,j}/\partial T_j) + \partial K_{m,j}/\partial T_j. \tag{18}$$

Conclusion

If H_{Vj} is neglected, $dx_{i,j}/dt$ is greatly overestimated for components having very large volatility. For these components even a small change of $x_{i,j}$ results in a considerable change of $y_{i,j}$. As a consequence, $x_{i,j}$ and $y_{i,j}$ change far more rapidly than the correct values. The calculation results for the other components are also subject to this miscalculation and quite erroneous. Thus, the present model avoids such errors in cases where very volatile components are present within the column.

It is a highly interesting task for the future to develop a more rigorous model by accounting for the mass transfer resistance, hydraulic effects, and heat balances. Information on some experimental results will also be valuable.

Acknowledgment

The author wishes to express his sincere thanks to T. Takamatsu, Kyoto University, for useful comments.

Notation

F_j = flow rate of feed supplied to stage j, mol/h
H_{Lj} = liquid holdup on stage j, mol
H_{Vj} = vapor holdup on stage j, mol
$K_{i,j}$ = vapor-liquid equilibrium ratio for component i on stage j
L_j = flow rate of liquid stream leaving stage j, mol/h
m = total number of components
N = number of total stages
t = time, h
T_j = temperature on stage j, K
U_j = flow rate of liquid sidestream from stage j, mol/h
V_j = flow rate of vapor stream leaving stage j, mol/h
W_j = flow rate of vapor sidestream from stage j, mol/h
$x_{i,j}$ = mole fraction of component i in liquid stream leaving stage j
$y_{i,j}$ = mole fraction of component i in vapor stream leaving stage j
$z_{i,j}$ = mole fraction of component i in feed supplied to stage j

Subscripts

i = component index
j = stage index

Literature Cited

Ballard, D. M., and C. B. Brosilow, "Dynamic Simulation of Multicomponent Distillation Columns," AIChE Ann. Meet., Miami, Paper No. 42a (Nov., 1978).

Gallun, S. E., and C. D. Holland, "Gear's Procedure for the Simultaneous Solution of Differential and Algebraic Equations with Application to Unsteady State Distillation Problems," *Computers and Chem. Eng.*, **6**, 231 (1982).

Holland, C. D, *Unsteady State Processes with Applications in Multicomponent Distillation*, Prentice-Hall, Englewood Cliffs, NJ (1966).

Howard, G. M., "Unsteady State Behavior of Multicomponent Distillation Columns," *AIChE J.*, **16**, 1,022 (1970).

Kinoshita, M., "Studies on Simulation Procedures for Stage Processes in Fusion Fuel Cycle and Distillation Systems," Doctoral Diss., Kyoto University (1983).

Peiser, A. M., and S. S. Grover, "Dynamic Simulation of a Distillation Tower," *Chem. Eng. Prog.*, **58**, 65 (1962).

Prokopakis, G. J., and W. D. Seider, "Dynamic Simulation of Azeotropic Distillation Towers," *AIChE J.*, **29**, 1,017 (1983).

Steiner, D., and C. A. Flanagan, "Design Description of the Fusion Engineering Device," *Nucl. Technol/Fusion*, **3**, 6 (1983).

Tetlow, N. J., D. M. Groves, and C. D. Holland, "A Generalized Model for the Dynamic Behavior of a Distillation Column," *AIChE J.*, **13**, 476 (1967).

Waggoner, R. C., and C. D. Holland, "Solution of Problems Involving Conventional and Complex Distillation Columns at Unsteady State Operation," *AIChE J.*, **11**, 112 (1965).

Manuscript received June 20, 1984, and revision received Jan. 28, 1985.