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Unsteady State Behavior of Multicomponent Distillation Columns:

Part I: Simulation

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A very general form of the basic column equations is presented which allows a wide choice in the form of the specifications of variables required to define the column operation. Variable plate holdups, variable plate efficiencies, heat losses from the column, and finite time liquid flow dynamics are some of the specifications considered. The values of the implicit column variables during the unsteady state period are found by a method which is independent of the numerical procedure chosen to solve the differential equations. Computer runs with the Kutta-Merson method used to solve the differential equations were made for a column approaching steady state at total reflux. The effect of different variable specifications on this computer column are discussed.

The unsteady state behavior of distillation columns has been the subject of much study in the past decade. Complete literature reviews have been made by Archer and Rothfus (*1*), Williams (*23*), and Renfroe (*17*), among others. There is undoubtedly a great deal of industrial work which has not been published. The most complete studies in connection with binary distillation have been carried out by Huckaba and his co-workers (*10, 4*), who obtained good agreement between experimental work and digital computer simulation, and by Gerster and his coworkers (*2, 11*), who obtained good agreement between analogue simulation and experimental work. In both cases the computer work was tailored very closely to the specific system under consideration and involved many simplifying assumptions.

Work in multicomponent systems has been much less detailed and has not been subjected to experimental verification. Rosenbrock (*18, 19*) presented a general model of a distillation column and a numerical method of solving the differential equations. The computer solution was restricted by the assumption of constant molal overflows and holdups. Comparison of computed and experimental results for a complicated transient showed that plate temperature profiles had essentially the same shape. Mah, Michaelson, and Sargent (*12*) proposed a numerical solution method based on finding an exact solution of a linear approximation of the basic column differential equations. Meadows (*13*) simulated a multicomponent batch distillation on a digital computer. His program allowed him to test the effect of various assumptions by providing for the inclusion or exclusion of heat balances on each tray and a choice of constant volume or constant molal holdup on each tray. Peiser and Grover (*16*) reported the use of a very complete column model which included the effects of tray hydraulics and condenser and reboiler heat exchange dynamics. The model was applied to an actual column which was experiencing operating difficulty. The controlled response of the column to a step change in feed concentration of the light key component was computed. The various aspects of this response were used to design a control system for the column. The physical dimensions of the model were varied so as to give the desired controlled response. These changes were then made on the actual column in the field, and they corrected the operating difficulty. No overall picture of the column behavior was given, and there was also no indication of the numerical method used to solve the general differential equations of the model. Moczek, Otto, and Williams (*15*) simulated the response of a large distillation column using the methods of Rosenbrock, but with fewer restrictive assumptions. The change in light component concentration in the distillate, bottoms, and side streams were plotted for a large number of step change upsets. These plots were used to develop approximate transfer functions which could be used to represent the system for control purposes. Cadman, Rothfus, and Kermode (*3*) have used a linearized column model to design and evaluate feed forward control systems.

The most extensive experimental work has been done by Renfroe (*17*). He distilled a mixture of benzene, toluene, xylene, and *n*-heptane in a semicommercial scale column. He performed two experiments in which the column was operated with feed, distillate, and bottom product streams. The column was allowed to come to steady state and was then disturbed by a step change in benzene concentration in the feed and by a pulse of benzene in the feed. Hand samples were taken of vapor and liquid at several locations. These results and extensive data on heat and material balances are reported. The data for the step disturbance were used to determine time constants and lag times for transfer functions representing the benzene concentration transient. The pulse data were converted to frequency response plots for several three-plate sections in the column. Transfer functions which would give equivalent responses were also reported. Simulation on a small computer showed the same trends as the actual test but could not duplicate the concentration values observed in the column.

Holland and his co-workers (*7, 20, 22*) have done the most work on computer simulation. They have adapted the theta convergence procedure used in steady state calculations to unsteady state problems. All of their work is based upon the use of the iterative, implicit method (called the *Crank-Nicholson method* by Rosenbrock) as the basic numerical procedure. In the initial work, provision was made for enthalpy balances and for the assumptions of either constant molal, constant mass, or constant volume holdup in a single mixed pool plate. The latest work has presented a model which can account for the effect of channeling, transfer lag, mixing, and mass transfer on each plate by considering separate holdups to account for each of these functions. Distefano (*5*) studied many numerical methods for use in simulating multicomponent batch distillations. He concluded that a modified predictor-corrector method (the Adams-Moulton-Shell procedure) was the one best suited for the solution of his distillation model.

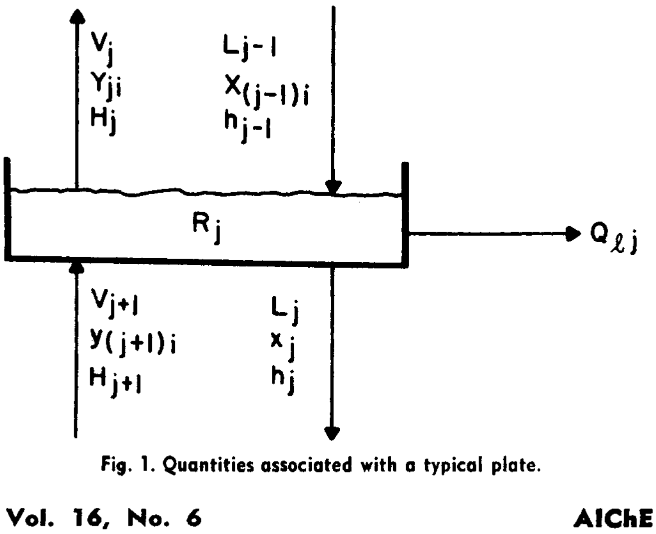

Fig. 1. Quantities associated with a typical plate.

These references show the present state of the study of multicomponent distillation dynamics. There is agreement on the general type of model which should be used but very little knowledge of the effects of the simplifying assumptions made in attempting to solve the equations. There is disagreement about the mathematical procedure which should be used to obtain this solution. In all the methods which have been used, the solution of the energy balance and the total material balance depend on the mathematical method chosen. Finally there is virtually no experimental work available to permit the results of computer simulations to be compared with the operation of a real column.

The goals of this work were to develop a general modeling procedure to determine how difficult it is to simulate the behavior of an operating distillation column and to determine which parameters have the most significance in the accuracy of the simulation. The general procedure would allow a wide choice of simplifying assumptions about the column and permit any appropriate numerical procedure to be used. Because simulations are undertaken for many different purposes, this flexibility is essential to permit solutions to be obtained with the degree of accuracy that is desirable or economically feasible. This paper considers the various equations and relationships which may be used and prèsents a general technique of solving the system of nonlinear differential equations which forms the mathematical model of a distillation column. The use of the technique is demonstrated for a column approaching steady state at total reflux.

GENERAL DESCRIPTIVE EQUATIONS

Williams (*23*) has discussed the specific equations which must be written to describe a distillation column and the assumptions that may be made in writing and solving them. In the general equations and methods presented in this work, three assumptions are made. Vapor holdup is considered negligible on and between the plates. All the liquid on and leaving each plate is considered well mixed and has a concentration equal to that of the liquid leaving the plate. Finally, there is a definite relationship between the concentration of a component in the vapor and liquid leaving each plate, and this relationship is established instantaneously. These assumptions have been made by virtually everyone who has studied distillation column dynamics. The assumptions made about the condenser and reboiler systems depend much more on the specific systems being studied. In this work they also are considered to be well-mixed pools. The procedures to be followed for a more complicated model of the plate would be essentially the same, with allowances made for the additional sections of each plate.

The quantities associated with a typical plate are shown in Figure 1. The following mass and energy balances are obtained by applying the basic conservation equations to the plate. A material balance may be written for each component in the system:

$$d(R_j x_{ji})/dt = V_{j+1} y_{(j+1)i} + L_{j-1} x_{(j-1)i} - V_j y_{ji} - L_j x_{ji} \tag{1}$$

A total material balance is also frequently useful and is simply the sum of the component balances:

$$d(R_j)/dt = V_{j+1} + L_{j-1} - V_j - L_j \tag{2}$$

The final equation is the general energy balance in which the kinetic and potential energy terms have been neglected:

$$d(R_jh_j)/dt = V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j - Q_{lj} \quad (3)$$

The treatment of the material and energy balances depend heavily on the technique chosen to solve them, as well as on the simplifying assumptions. The usual form of the component balance has been based on the assumption of constant molal holdup on each plate. This leads to Equation (1) written in the form

$$dx_{ji}/dt = (V_{j+1}y_{(j+1)i} + L_{j-1}x_{(j-1)i} - V_jy_{ji} - L_jx_{ji})/R_j \quad (4)$$

A more general approach to the solution may be made by avoiding this assumption at the start. By using the total material balance equation for dR_j/dt, Equation (2) may be substituted in Equation (1) and rearranged to give a component balance which is independent of the assumptions made about the holdups:

$$R_jdx_{ji}/dt = V_{j+1}(y_{(j+1)i} - x_{ji}) + L_{j-1}(x_{(j-1)i} - x_{ji}) - V_j(y_{ji} - x_{ji}) \quad (5)$$

The independent variable in these equations is time, and the dependent variable is liquid concentration. In order for these equations to be completely determined, a number of other variables or relationships among variables must be specified. The operation of the distillation column can then be characterized by the solution of the complete set of plate equations.

Howard (7) has described a method for determining exactly how many variable specifications are required. For a conventional column with a total condenser, reflux splitter, N plates above and M plates below the feed, and a reboiler, the number of variables to be specified is $3\,N + 3\,M + C + 16$. The variables which conveniently fix the column model are as follows:

Pressures, on all plates, condenser, reboiler, and reflux splitter	$N + M + 4$
Holdups, on all plates, condenser and reboiler	$N + M + 3$
Heat leaks, on all plates and splitter	$N + M + 2$
Feed stream, composition, flow rate, temperature, and pressure	$C + 2$
Reflux temperature	1
Reflux ratio	1
Distillate rate	1
Number of plates, N and M	2

In addition, the vapor liquid distribution relationships must be specified. The form of the individual plate specifications (pressures, holdups, and heat leaks) depends upon the assumptions which are made about the column operation. They are actually complicated functions of the vapor and liquid flow rates and the plate geometry but have been considered constant in most of the previously reported work. The exterior column specifications may be made by choosing numerical values.

The distribution relationships are defined in relation to true thermodynamic equilibrium and fix the plate temperature as well as the vapor composition. They assume that the rate of the mass transfer process is effectively infinite compared with other column processes. At equilibrium the concentration of a component in the vapor phase is related to that in the liquid by

$$Y_{ji}^* = K_i(T, P)\,x_{ji} \quad (6)$$

in which $K_i(T, P)$ is called the *equilibrium constant* or *distribution coefficient*. The equilibrium constant is actually a function of the vapor and liquid composition as well as the temperature and pressure. When we consider the overall accuracy required of many unsteady state calculations, the additional computing effort required to include the explicit effect of composition is unnecessary. Throughout this work it is assumed that K values as a function of T and P are available in the concentration ranges of interest. A composition dependent K could be used with only minor changes in the equations which are developed. Equation (6) is subject to the condition that the sum of all the component concentrations be equal to unity:

$$\sum_{i=1}^{NC} Y^*_{ji} = 1$$

These equations are used to define an ideal plate. A real plate will have a lower concentration of the more volatile components in the vapor for a given liquid concentration. This departure from the equilibrium values is accounted for by using a plate efficiency. There are two expressions for efficiency in common use. The vaporization efficiency is defined as a fractional approach to the equilibrium value:

$$E^0_{ji} = Y_{ji}/Y^*_{ji} \quad (7)$$

The Murphree efficiency represents a fractional enrichment from plate to plate:

$$E^M_{ji} = Y_{ji} - Y_{(j-1)i}/Y^*_{ji} - Y_{(j-1)i} \quad (8)$$

Both these relationships are subject to the condition

$$\sum_{i=1}^{NC} Y_{ji} = 1$$

The efficiencies depend on the vapor and liquid flow rates, the concentrations, and the column geometry. Much of the previous work has assumed that the plates were ideal.

In addition to these equations, the complete physical and thermodynamic properties of the materials must be known, and a set of initial concentrations must be specified to provide the arbitrary constants which complete the solutions of the differential equations.

DETERMINATION OF THE IMPLICIT VARIABLES

Consider that at some time t all the values of the concentrations, vapor and liquid flow rates, and holdups are known throughout the column. By some numerical procedure it is possible to predict the compositions at some future time $t + \Delta t$. That is

$$x_{t+\Delta t} = x_t + \Delta t f(dx/dt|_t)$$

Some numerical methods also require dx/dt evaluated at $t + \Delta t$. In this case, the values of flow rates, holdups, and equilibrium constants at $t + \Delta t$ must be estimated by some means and then corrected by iteration. Regardless of the procedure used, the set of compositions at the new time is known and completely determines all other parameters in the column. The next step in the solution represents the heart of the problem. These new values of the parameters must be found from the new compositions by using the several implicit relationships which define them.

The first variable which must be found is the plate pressure. This can probably be considered constant during a time increment with very little error. If there is significant variation in the pressure owing to changes in the flow rates and holdups, then the following process must be iterated from the starting point of an assumed pressure change.

The temperature and vapor compositions are calculated by using the bubble point and tray efficiency relationships. These values and the thermodynamic properties of the materials are used to calculate vapor and liquid stream enthalpies.

The three remaining parameters, the holdups, and the vapor and liquid flow rates are found from the simultaneous solution of the remaining equations. These are the energy balance, the total balance, the relationship defining the plate holdup, and the relationship defining the heat losses.

The energy balance must be rearranged to eliminate the derivative terms. The enthalpies of the streams may be represented in terms of the enthalpies of the pure components, which are functions of temperature only, and a heat of mixing, which is a function of composition. This is the usual calculation procedure, even though it neglects the effect of temperature on the heat of mixing. The equation for the enthalpy of the liquid on a plate will be given by

$$h_j = \sum_{i=1}^{NC} x_{ji} f_i(T_j) + \phi_M(x_{ji} \ldots x_{jNC}) \tag{9}$$

This relationship may be used to determine dh/dt in terms of dx/dt and so convert Equation (3) into an algebraic equation. An expression for dh_j/dt is

$$dh_j/dt = \sum_{i=1}^{NC} x_{ji} d\{f_i(T_j)\}/dt + \sum_{i=1}^{NC} f_i(T_j)\, dx_{ji}/dt + \sum_{i=1}^{NC} (\partial\phi_M/\partial x_{ji})(dx_{ji}/dt) \tag{10}$$

and

$$\begin{aligned} d\{f_i(T_j)\}/dt &= (d\{f_i(T_j)\}/dT_j)(dT_j/dt) \\ &= d\{f_i(T_j)\}/dT_j \sum_{i=1}^{NC} (\partial T_j/\partial x_{ji})(dx_{ji}/dt) \end{aligned} \tag{11}$$

$\partial T_j/\partial x_i$ will be considered in detail later.

The component balance, Equation (5), gives dx_{ji}/dt, and $R_j dh_j/dt$ may be written

$$\begin{aligned} & V_{j+1}\Bigg(\sum_{i=1}^{NC} (f_i(T_j) + \partial\phi_M/\partial x_{ji})(y_{(j+1)i} - x_{ji}) \\ & \quad + \sum_{i=1}^{NC} x_{ji} df_i(T_j)/dT \sum_{i=1}^{NC} \partial T_j/\partial x_{ji}(y_{(j+1)i} - x_{ji}) \Bigg) \\ & \quad + L_{j-1}\Bigg(\sum_{i=1}^{NC} (f_i(T_j) + \partial\phi_M/\partial x_{ji})(x_{(j-1)i} - x_{ji}) \\ & + \sum_{i=1}^{NC} x_{ji} df_i(T_j)/dT \sum_{i=1}^{NC} \partial T_j/\partial x_{ji}(x_{(j-1)i} - x_{ji}) \Bigg) \qquad (12) \\ & \quad - V_j \Bigg[\sum_{i=1}^{NC} (f_i(T_j) + \partial\phi_M/\partial x_{ji})(y_{ji} - x_{ji}) \\ & \quad \pm \sum_{i=1}^{NC} x_{ji} df_i(T_j)/dT \sum_{i=1}^{NC} \partial T_j/\partial x_{ji}(y_{ji} - x_{ji}) \Bigg] \end{aligned}$$

The equivalent of $h_j dR_j/dt$ may be subtracted from the right side of Equation (3) to give

$$V_{j+1}(H_{j+1} - h_j) + L_{j-1}(h_{j-1} - h_j) - V_j(H_j - h_j) - Q_{lj} \tag{13}$$

Statements (12) and (13) are equal and may be rearranged in a combined form to give the final equation for the energy balance:

$$0 = V_{j+1}[(H_{j+1} - h_j) - A_j] + L_{j-1}[(h_{j-1} - h_j) - B_j] - V_j[(H_j - h_j) - C_j] - Q_{lj} \tag{14}$$

in which A_j, B_j, and C_j are the coefficients of V_{j+1}, L_{j-1}, and V_j in (12). All terms except the flow rates are known functions of x_{ji}.

In any series of calculations the values of V_j and L_{j-1} will be known from the previous plate calculation and Q_l is specified; thus, V_{j+1} may be calculated. The total material balance and the holdup specification are used to find L_j, and the calculation is then carried to the next plate. In this way all values of the flow rates and holdups at $t + \Delta t$ may be found and used in evaluating dx/dt at $t + \Delta t$. This value of the derivative is then used in the numerical procedure to find the next set of compositions.

The nature of the term $\partial T/\partial x_i$ requires additional consideration. T is an implicit function of x defined by the bubble point calculation

$$\sum_{i=1}^{NC} K_i(T) x_i = \sum Y_i^* = 1 \tag{15}$$

where the distribution coefficient $K_i(T)$ is some known function of T at the specified pressure. Various partial derivatives of one variable with respect to another which are defined by such an implicit function may be determined by following the chain rule method illustrated by Mickley, Sherwood, and Reed (*14*). Write the left side of (15) as a general function Z of all the variables. The desired partial derivative will be given by

$$\partial T/\partial x_i = -(\partial Z/\partial x_i)/(\partial Z/\partial T) \tag{16}$$

This expression can be evaluated from the bubble point relationship.

Note that because the sum of the mole fractions must equal unity, only $C - 1$ of the compositions are independent. The bubble point relationship should be written

$$\sum_{i=1}^{NC-1} K_i(T) x_i + K_c(T)\left(1 - \sum_{i=1}^{NC-1} x_i\right) = 1 \tag{17}$$

and

$$Z(T, x_i) = \sum_{i=1}^{NC-1} [K_i(T) - K_c(T)] x_i + K_c(T) \tag{18}$$

The partial derivatives are thus

$$\partial Z/\partial x_i = \Delta K_i(T) \tag{19}$$

$$\partial Z/\partial T = \sum_{i=1}^{NC-1} \Delta K_i'(T) x_i + K_c'(T) \tag{20}$$

Finally, the working expression for $\partial T/\partial x_i$ is given by

$$\partial T/\partial x_i = -\Delta K_i(T) \Bigg/ \sum_{i=1}^{NC-1} \Delta K_i'(T) x_i + K_c'(T) \tag{21}$$

This expression should be used in the summation terms of the energy balance. A composition dependent K would require only the modification of Equation (19). The summations must be considered over the $C - 1$ independent components rather than over all C of them in the terms which are used in representing dT/dt.

The physical and thermodynamic properties of some systems of materials are such that the properties of solutions are essentially constant when computed on a unit mass basis but quite variable when computed on a unit mole basis. For systems of this type it may be more convenient to work with mass fraction concentration units and mass flow rates. The general material and energy balance, Equations (1), (2), and (3), are correct if written in this system of units. All the other equations and expressions could be used in these units also except the terms $\partial T/\partial x_i$. The bubble point expression is valid only in mole units. A relationship for $\partial T/\partial \bar{x}_i$, where the $\bar{x}_i$ denotes mass friction, must be found from the molal unit terms through use of the chain rules. This is complicated by the fact that the mole fraction of one component depends upon the weight fraction of all the others. The additional complexity of this calculation would indicate that the overall procedure should be carried out in both systems of units, with the concentrations being converted from one to the other as required.

The equations which have been derived for a normal plate may be extended to apply to a feed plate or a side stream plate by the addition of a term which represents the flow of that stream. For a feed plate, for example, the conservation equations become

$$R_j dx_{ji}/dt = V_{j+1}(y_{(j+1)i} - x_{ji}) + L_{j-1}(x_{(j-1)i} - x_{ji}) + F(x_{Fi} - x_{ji}) - V_j(y_{ji} - x_{ji}) \tag{22}$$

$$dR_j/dt = V_{j+1} + L_{j-1} + F - V_j - L_j \tag{23}$$

$$d(R_j h_j)/dt = V_{j+1}H_{j+1} + L_{j-1}h_{j-1} + Fh_F - V_jH_j - L_jh_j + Q_{lj} \tag{24}$$

Equation (14) would then simply include an additional term

$$+ F[(h_F - h_j) - D_j] \tag{25}$$

This represents no additional difficulties in solving the equations, since the flow rate of the additional stream would be specified.

The exact procedure to be followed in determining the flow rates will depend upon the relationships chosen to specify the holdups. The procedure for a few of the most common holdup assumptions is illustrated in the next section.

SPECIFIC EXAMPLES FOR COMMON HOLDUP SPECIFICATIONS

Calculations start around the condenser with the determination of the vapor rate from the top plate and the condenser heat duty. The calculation around the top plate will then illustrate how to find V_2 and L_1 and so proceed down the column. The reason for starting at the top in this way is that the specified variables make it easier to do so. In all cases the reflux temperature, reflux ratio, and distillate rate are specified. The condenser-accumulator system is considered to be perfectly mixed.

Constant molal holdup has been by far the most common specification. Under this assumption the total material balance is equal to zero. The condenser balance contains only three terms, and, since L_c and D are specified, V_1 is found directly. The energy balance for the condenser is given by

$$0 = V_1[(H_1 - h_c) - A_0] - Q_c$$

The specification of the reflux temperature fixes h_c and permits the condenser heat load to be found. The energy balance for the first plate is Equation (14), and only V_2 is unknown in this equation. The total balance for plate one will give L_1. The procedure may be continued down the column with the flow rates of the two streams passing above a plate always known.

Constant volume holdup is probably the constant holdup specification which is closest to the real behavior of a plate. If the volume of a plate $^{-}V^{-}$ is constant, then the molal holdup can be expressed as the product of the plate volume and the molal volume:

$$R_j = {}^{-}V^{-}\; v(x_i, T_j) \tag{26}$$

Assume that the specific volume of the mixture can be expressed as the weighted sum of the volumes of the components:

$$v(x_i T_j) = \sum_{i=1}^{NC} x_i v_i(T_j) \tag{27}$$

The total balance then becomes

$${}^{-}V^{-}\, d\left(\sum_{i=1}^{NC} x_i v_i(T_j)\right) \Big/ dt = V_{j+1} + L_{j-1} - V_j - L_j \tag{28}$$

The left side of this equation may be expanded and manipulated in exactly the same way as the energy balance was treated to give the final form of the total balance as

$$0 = V_{j+1}(1 - F_j) + L_{j-1}(1 - G_j) - V_j(1 - K_j) - L_j \tag{29}$$

in which the coefficients F, G, K have the form

$$F_j = v(x_i, T_j)\left[\sum_{i=1}^{NC} x_{ji} d(v_i(T_j)) \Big/ dT_j \sum_{i=1}^{NC} \partial T_j/\partial x_{ji} \, [y_{(j+1)i} - x_{ji}] + \sum_{i=1}^{NC} v_i(T_j)[y_{(j+1)i} - x_{ji}]\right] \tag{30}$$

This equation may be combined with the energy balance in exactly the same way as was done for the constant molal case to give the flow rates.

Variable holdups can cause a great deal of additional difficulty. The procedures which must be followed depend upon the assumptions made about the fluid flow dynamics of the column. If it is assumed that flow disturbances are transmitted through the column much more quickly than concentration disturbances, the holdups may be considered constant within any time increment. Equations (14) and (2) could then be used to find the instantaneous flow rates, and the flow depth relationship would give the new value of the holdup.

If the actual time lag for a flow disturbance must be considered, the liquid flow rate must be made a function of time. This can be done by using the flow-depth-holdup relationships to change variables in the total balance. Numerical integration of the resulting equation is necessary to determine the liquid flow rates. The vapor flow rates can still be found from the energy balance.

In this section the general principles which must be applied to solve the unsteady state equations describing a multicomponent distillation column have been presented. Their application has been illustrated for the more common types of holdup specifications in problems which have the reflux temperature, reflux ratio, and distillate rate also specified. The application of the methods for other speci-

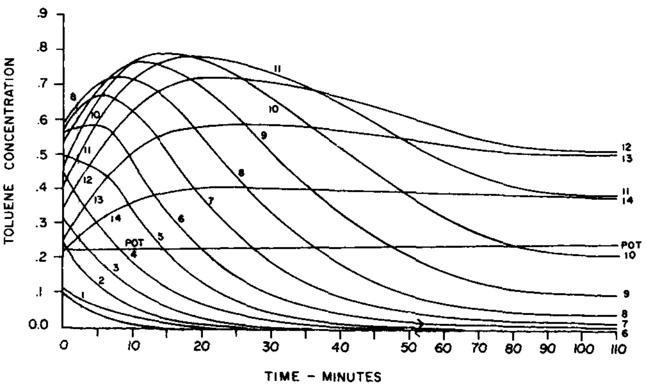

Fig. 2. Toluene concentration profile for a column with vaporization efficiencies equal to 1.0, constant mass holdups, and constant vapor and liquid flow rates.

fications such as vapor rate or reboiler heat duty is straightforward.

COMPUTER IMPLEMENTATION AND RESULTS

In order to test the computation procedures described in the preceding section, computer programs were written to simulate the approach to the initial steady state of a distillation column at total reflux. An IBM-7040 computer was used. The column consisted of a total condenser, fourteen plates, and a reboiler, all of which were considered perfectly mixed. The mixture being distilled was considered to be benzene, toluene, and ethylbenzene. The column operation is described by an appropriate form of Equation (2), Equation (5), Equation (14), and the vapor-liquid equilibrium efficiency relationship for the sixteen regions in the column.

The number of variables which had to be specified to insure a unique set of operating characteristics for the column was determined by the degrees of freedom method discussed earlier. For this column, operating at total reflux the number of variables which must be specified is $3NP + 5$, where NP is the number of plates. Thus forty-seven variables and the initial concentrations must be specified. These variable specifications may be made either as constants or in the form of equations which vary with time or various system parameters. The variables which were selected to define the computer column are the pressures at all locations, the holdups in the condenser and on the plates, the plate heat leaks, the reflux temperature, and the reflux flow rate.

Plate temperatures were taken to be the bubble point temperatures of the liquid leaving the plates. This bubble point calculation also determined the composition of the equilibrium vapor. The actual composition of the vapor stream leaving the plate was determined by using efficiency relationships as described earlier. The holdups may be calculated to fit any desired specifications. In this work they were considered to be either constant or to vary exponentially with time and could be calculated either in mass or mole units. They were, however, considered constant in each time increment. Vapor and liquid flow rates were calculated by the rigorous method. Provision was also made for simply considering the flow rate constant at any location in the column. The numerical method used was the Kutta-Merson version [Fox (6)] of the well known Runge-Kutta process. It has the advantage of providing an indication of the size of the truncation error made in each time step. The magnitude of the truncation error is of the order of Δt^5. The complete programs and additional discussion about them have been presented earlier (9).

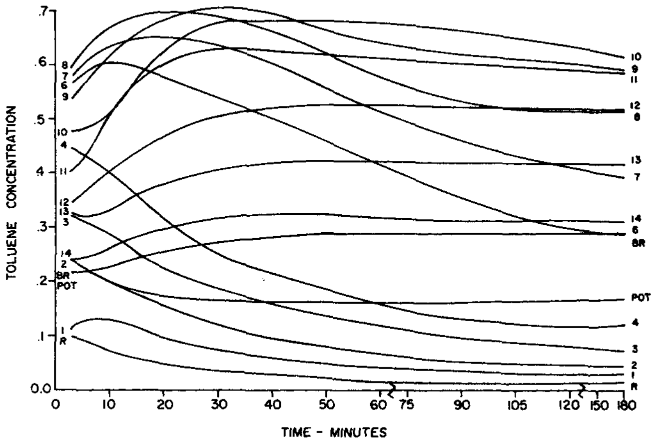

Fig. 3. Toluene concentration profile for a column with measured vaporization efficiencies, variable mass holdups, and variable vapor and liquid flows.

Effect of the Size of the Time Increment

The Kutta-Merson integration method can be unstable if the size of the time increment is chosen too large. In runs with the initial conditions of run 30, the system was found to be unstable for a Δt equal to 0.5 and stable for a Δt equal at 0.2. Under these conditions the plate time constants (the ratio of the mole holdup to the mole liquid flow rate) were in the range 0.3 to 0.5 min. The truncation error was of more importance than the stability in this work. With a Δt of 0.2 the column seemed to operate in a normal manner. The average truncation error, however, after 5 min. of column operation was 2.6×10^{-2}. A reduction in the step size to 0.1 produced a disproportionate reduction in the truncation error to only 3×10^{-7} after 5 min. of computer operation. The concentration profiles obtained with this step size were identical to those obtained with a step size of 0.05. One other experiment was conducted in which the column was operated with a Δt of 0.1 for 15 min., at which time the truncation error was 2.5×10^{-7}, and then the step size was increased to 0.2. At the end of an additional 5 min. of operation, the truncation error was 6.9×10^{-2}. In view of this last experiment it is felt that great care must be exercised in increasing the step length despite a very small truncation error.

No general rules with regard to choosing the size of the time increment were formulated. It was felt that a truncation error of the order of 10^{-7} was completely satisfactory, and the size of the time step was adjusted by trial until this accuracy was achieved. In practice, a Δt of 0.1 was always satisfactory.

Concentration Profiles

When a proper time step was chosen, the column seemed to operate in a perfectly satisfactory manner as indicated by the composition profiles. This was true regardless of the assumptions made about the holdups, the vapor and the liquid flow rates, and the plate efficiencies. The composition profiles were not the same, of course, under different assumptions, but they did behave in essentially the same manner. This may be seen by comparing the composition profiles shown in Figures 2 and 3. Figure 2 shows the toluene concentration variation for a system in which the holdup is constant, the vapor and liquid flow rates are constant at steady state values, and the plate efficiencies are all equal to 1.0. Figure 3 shows the toluene concentration profile for a system in which holdups vary according to an exponential relationship, vapor and liquid flow rates are calculated by the rigorous method, and the efficiencies approximate predicted real steady state values. The nature of the movement of the toluene through the column is seen to be the same. This comparison is typical of that which could be obtained for any component under any of the sets of assumptions which were used in various experiments.

The composition profiles themselves gave no indication whether or not the computation was proceeding correctly. The truncation error was also of no help, since it had been made the correct order of magnitude and always decreases as the calculation proceeded. The overall material balance did provide a very good indication of the correctness of the column operation. On all runs operating under unrealistic assumptions or in which the truncation error was large, the number of moles in the column decreased continuously with time. Material had to disappear from the system in order for the various specifications to be satisfied. In the runs made by using the rigorous assumptions, the total amount of material in the column remained constant.

Flow Rates

The computer column can provide information about the variation in vapor and liquid flow rates which cannot be obtained from a real column. Table 1 shows the flow rates and the unsteady state coefficients in the energy balance at various times during several computer runs. In all cases the volume of the reflux flow was constant during the course of the run. The passing vapor and liquid flows are very nearly equal during the unsteady state period. The largest difference is only 5%. The change in flow rate during the course of the distillation is less than 10% on even the most active plate. The unsteady state coefficients are relatively unimportant in determining the flow rates compared with the concentration-temperature caused changes in enthalpy values. This is seen by comparing their values to the vapor enthalpies which are in the range 17,000 to 24,000 B.t.u./lb. mole and to the liquid enthalpies which are in the range 3,600 to 8,000 B.t.u./lb. mole. The largest unsteady state terms are less than 10% of the enthalpy values which are associated with them. Their actual effect is less than 1%, since they cancel each other out in the calculation.

The behavior of the correction terms is an indication of the validity of the calculation procedure. The A_j coefficients tend to zero at steady state, which is expected since they involve the term $(y_{(j+1)i} - x_{ji})$ which becomes zero. The B_j and C_j coefficients tend to become equal. This is also the expected behavior, since V_j and L_{j-1} should become equal and $(V_jC_j - L_{j-1}B_j)$ should go to zero. The difference in the magnitudes of these coefficients is a result of the increase in the heat capacity as the temperature increases down the column.

The Effect of Column Specifications on the Approach to Steady State

The obvious factors such as holdups and flow rates have the expected effects. The smaller the holdup the faster the concentration on a plate can change. Thus, the computer column with variable holdup approaches steady state more rapidly than the one with the holdups constant at the larger steady state value. The larger the flow rates the greater the transport of material to and from the plates. Thus, the larger the reflux flow specification the faster the column will approach steady state. The plate efficiencies have an effect similar to that of the flow rates in that a high plate efficiency for the most volatile component indicates greater flow of the component through the column. A more important effect of the efficiencies is that they completely determine the final steady state concentration profile.

The initial values of the holdups also affect the steady state concentrations. The reason for this is that they determine the total amount of material available for distribution around the column. A column which has holdups which vary from 1.0 to 1.42 lb. will have a much lower level of benzene concentrations throughout the column at steady state than one with the same initial conditions but

TABLE 1. TYPICAL FLOW RATES AND PARAMETERS IN THE UNSTEADY STATE ENERGY BALANCE EQUATIONS

Time, min.	Plate	Liquid flow from plate, lb. mole/min.	Vapor flow to plate, lb. mole/min.	C_j	B_j, B.t.u./ lb. mole	A_j
			Run 30			
8	2	0.02305	0.02317	−76.9	−69.9	−11.3
	8	0.02697	0.02795	−409.3	−233.4	−214.2
	15	0.03122	0.03299	−1031.0	−401.1	−642.1
68	2	0.02339	0.02343	−2.9	−2.8	−0.17
	8	0.02933	0.02961	−68.1	−65.7	−3.7
	15	0.03197	0.03250	−807.0	−710.6	−105.1
133	2	0.02342	0.02343	−2.2	−2.2	−0.0034
	8	0.02956	0.02966	−59.9	−59.8	−0.20
	15	0.03229	0.03248	−743.0	−720.0	−26.3
			Run 16			
8	2	0.04727	0.04741	−57.4	−52.1	−7.9
	8	0.04950	0.05036	−258.8	−194.0	−75.2
	15	0.05318	0.05466	−269.4	−120.4	−150.9
133	2	0.04780	0.04782	−7.08	−7.08	−0.0044
	8	0.05165	0.05175	−129.8	−129.7	−0.37
	15	0.05401	0.05421	−226.2	−219.8	−6.9
			Run 31			
Steady state	2	0.02337	0.02337	−16.6	−16.6	−0.012
	8	0.02816	0.02817	−290.5	−290.2	−0.35
	15	0.03254	0.03255	−428.8	−426.6	−2.29

a constant holdup of 1.42 lb. In the variable holdup case much of the benzene placed in the system initially must be used to fill the holdup requirements of the upper plates at steady state. The concentration base from which enrichment is begun on the lower plates is thus much smaller than it is when the plates have already been filled.

CONCLUSIONS

The computer model and calculation procedure presented in this paper are capable of representing a real distillation column with any desired degree of rigor. The form in which the equations are written provides the model with great flexibility. It is capable of using any form of the variable specifications which define the column operation. Thus the holdups, for example, may be considered variable during the course of an unsteady state period or they may be considered constant in any system of units. Approximate models indicate essentially the same behavior as those which are more exact, but the actual values of the column variables will not be correct.

The novel method of finding vapor and liquid flow rates in the unsteady state based upon their unique dependence on composition permits the flow rates to be determined exactly rather than by the numerical solution of a differential equation. The energy balance which is used to determine the vapor flow rates provides a measure of the effect of the unsteady state terms. They were found to be negligible in this work, and the steady state energy balance could have been used to determine the vapor flow rates at any time during the unsteady state period.

The explicit type of numerical integration methods, such as the Kutta-Merson method, can be used for the simulation of unsteady state column behavior despite their conditional stability.

The overall behavior of the model column is essentially the same as the behavior one would expect of a real distillation column. It can be relied upon to give a true picture of the general nature of the behavior of distillation columns in unsteady state operation. The real utility of the model column, however, is its ability to represent a specific real column. This problem is treated in Part II.

NOTATION

A_j = coefficient in the unsteady state energy balance associated with V_{j+1}
B_j = coefficient in the unsteady state energy balance associated with L_{j-1}
C = number of components in the system, used interchangeably with NC
C_j = coefficient in the unsteady state balance associated with V_j
D_j = coefficient in the unsteady state energy balance associated with a feed stream
$E^M{}_{ji}$ = Murphree plate efficiency for a component
$E^0{}_{ji}$ = vaporization plate efficiency for a component
f = general functional relationship
F = feed flow rate
F_j = coefficient in the total balance with a constant volume holdup specification
G_j = coefficient in the total balance with a constant volume holdup specification
h = liquid enthalpy
H = vapor enthalpy
$K(T, P)$ = vapor-liquid equilibrium constant
K_j = coefficient in the total balance with a constant volume holdup specification
L = liquid flow rate
M = number of plates below the feed plate
N = number of plates above the feed plate
NC = number of components in the system, used interchangeably with C
P = total pressure
Q_l = heat loss
R = holdup on a plate
t = time
Δt = time increment
T = temperature
v = general function for molal volume
V = vapor flow rate
$^-V^-$ = holdup volume on a plate
x = liquid concentration, mole fraction
$\bar{x}$ = liquid concentration, mass fraction
y = actual vapor concentration, mole fraction
Y^* = equilibrium vapor concentration, mole fraction
Z = general bubble point function
ϕ_M = heat of mixing function

Subscripts

i = individual component
j = location in the column

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