Determination of Transient Plate Efficiencies from Operational Data

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Methods are presented for the determination of the transient values of the vaporization efficiencies from the knowledge of various combinations of the transient values of operating variables. For the case where the temperature and the composition of the liquid phase for each plate are known, a direct solution for the vaporization efficiencies is presented. Also, a method is presented for the determination of the mixing parameters of a generalized plate model on the basis of known transient values of certain operating variables.

The objective of the work described herein was the development of suitable methods for the determination of transient plate efficiencies from the knowledge of various sets of results from field tests. In the achievement of this objective, it was possible to take advantage of the work that had been done on steady state distillation problems by Davis et al. (*1*) and Taylor et al. (*6*) and on unsteady state distillation by Waggoner et al. (*10*) and Tetlow et al. (*8*). For certain sets of data from field tests for columns at steady state operation, methods for the determination of plate efficiencies were available from the work of Davis et al. and Taylor et al. For solving problems involving columns at unsteady state operation, numerical methods had been developed by Waggoner et al. and by Tetlow et al. In these numerical methods it was supposed that the efficiencies were known and that it was required to find the transient solution of the problem under consideration.

It appeared that a suitable method for the determination of the transient plate efficiencies could be developed by replacing the steady state equations in the methods developed by Davis et al. and Taylor et al. by corresponding equations for the unsteady state models proposed by Waggoner et al. This approach, a logical extension of previous work, was successful, and the resulting methods are described in the first two sections that follow.

A third procedure was developed for the determination of the transient plate efficiencies for the case where the compositions and plate temperatures are known functions of time. The equations needed in the application of this method are presented in a subsequent section.

Also, a method was developed for separating the mixing effects of the liquid on each plate and in its downcomer which was not involved in mass transfer from the plate efficiencies of the liquid on each plate that was involved in mass transfer. This method was developed by replacing the steady state equations in the methods of Taylor et al. and Davis et al. by the unsteady state equations for the model described by Tetlow et al. (*8*). An example of this method is presented in which the plate efficiencies and mixing effects are determined simultaneously.

In the method described in the next section, it is supposed that the product distributions (b_i/d_i) and the temperatures (T_j) are known as functions of time from the results of field tests. In addition to the knowledge of the values of these variables, it is supposed that the usual specifications such as the distillate rate, reflux rate, column pressure, type of condenser, number of plates, location of the feed plate, the complete definition of the feed, and the holdups are known. Information over and above this, such as any combination of product distributions (b_i/d_i) and temperatures (T_j), is hereafter referred to as *additional specifications.*

ADDITIONAL SPECIFICATIONS: ALL PRODUCT DISTRIBUTIONS (b_i/d_i) AND TEMPERATURES (T_j) AS FUNCTIONS OF TIME

On the basis of these known values of the operating variables, the procedure that follows determines a set of plate efficiencies required to obtain agreement between results calculated by Waggoner's model (*10*) and the results of field tests.

In the method developed, the transient operation period is subdivided into time increments. At the beginning of each time period (time t_n), it is supposed that the values of all variables are known. On the basis of these values and the known b_i/d_i's and T_j's at the end of each time period (time $t_n + \Delta t$), the efficiencies at the end of a given time period required to give a set of calculated values for the b_i/d_i's and T_j's that are in agreement with the known values of these variables are determined. The equations to be solved at the end of each time period follow.

The transient vaporization efficiency is defined by

$$y_{ji} = E_{ji}\, K_{ji}\, x_{ji} \tag{1}$$

At any time t, the actual mole fraction of component i in the liquid leaving plate j is denoted by x_{ji}, the mean mole fraction of component i in the vapor entering plate $j - 1$ by y_{ji}, and the K values of component i (evaluated at the temperature and pressure at which the liquid leaves plate j) by K_{ji}. When the activity γ_{ji} is included as a multiplier for K_{ji}, it is also evaluated on the basis of the temperature, pressure, and composition of the liquid leaving plate j.

Since the sum of the y_{ji}'s at the end of the time period ($t_n + \Delta t$) under consideration has the value of unity, it follows that

$$f_j = \sum_{i=1}^{c} E_{ji}\, K_{ji}\, x_{ji} - 1 \tag{2}$$

In addition, the E_{ji}'s must also satisfy the set of component material balances, the total material balances, and an en-

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thalpy balance for each plate j at time $t_n + \Delta t$, the end of the time period under consideration. For a typical plate j ($j \neq 0, f-1, f, N+1$), the component material balance is given by

$$\int_{t_n}^{t_n+\Delta t} [v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji}]\, dt = u_{ji}|_{t_n+\Delta t} - u_{ji}|_{t_n} \quad (3)$$

the total material balance by

$$\int_{t_n}^{t_n+\Delta t} [V_{j+1} + L_{j-1} - V_j - L_j]\, dt = U_j|_{t_n+\Delta t} - U_j|_{t_n} \quad (4)$$

and the enthalpy balance by

$$\int_{t_n}^{t_n+\Delta t} [V_{j+1} H_{j+1} + L_{j-1} h_{j-1} - V_j H_j - L_j h_j]\, dt = U_j h_j|_{t_n+\Delta t} - U_j h_j|_{t_n} \quad (5)$$

These integral difference equations were converted to algebraic form by use of the implicit method as described by Waggoner et al. (*10*). For example, when the integral on the left-hand side of Equation (3) is approximated by the implicit method, the following result is obtained:

$$[\mu(v_{j+1,i} + l_{j-1,i} - v_{ji} - l_{ji}) + (1-\mu)(\overset{o}{v}_{j+1,i} + \overset{o}{l}_{j-1,i} - \overset{o}{v}_{ji} - \overset{o}{l}_{ji})]\,\Delta t = u_{ji} - \overset{o}{u}_{ji}, \ (0 \leqq \mu \leqq 1) \quad (6)$$

The superscript *o* is used to denote the values of the variables at the beginning of the time period (time t_n) and the absence of a superscript their values at the end of the time period (time $t_n + \Delta t$) under consideration. As shown by Waggoner (9), the inherited error remains bounded for all values of μ in the interval $0.5 < \mu \leqq 1$.

The set of unsteady state algebraic equations obtained from Equations (3), (4), and (5) was solved for the E_{ji}'s by use of the same general procedure described by Davis et al. and Taylor et al. for the steady state equations. This is a trial process in which a set of E_{ji}'s is assumed and the algebraic forms of Equations (3), (4), and (5) are solved for the product distributions (b_i/d_i). Let the calculated set of product distributions so obtained be denoted by the subscript *ca* and the specified set by the subscript *co*. Then the objective of the trial process is to find a set of E_{ji}'s such that $\theta_i = 1$ for all i, where

$$\theta_i = \frac{(b_i/d_i)_{co}}{(b_i/d_i)_{ca}} \quad (7)$$

Now for the set of specifications under consideration, $j + i$ (or $N + 2 + c$) quantities are specified; namely, $N + 2$ values of T_j and c values of b_i/d_i. Since there exist jxi [or $c(N + 2)$] values of E_{ji} to be determined, the relationship

$$E_{ji} = \bar{E}_i \beta_j \quad (8)$$

introduced in reference 3, was used to generate jxi [or $c(N + 2)$] values of E_{ji} from j values of the plate factors β_j and i (or c) values of the component efficiencies $\bar{E}_i$. The set of $\bar{E}_i$'s and β_j's required to satisfy the totality of specifications and all of the unsteady state equations for the column at time $t_n + \Delta t$ was found by use of the same general procedure developed by Taylor et al. for columns at steady state operation. After the desired set of E_{ji}'s had been found, they were taken as the initial values of the variables for the next time period, and the calculational procedure was repeated.

ADDITIONAL SPECIFICATIONS: SOME BUT NOT ALL PRODUCT DISTRIBUTIONS (b_i/d_i) AND SOME BUT NOT ALL TEMPERATURES (T_j AS FUNCTIONS OF TIME

For the case where these additional specifications are known for a column at steady state operation, a method for determination of the corresponding plate efficiencies was available (*1*, *6*). For columns at unsteady state operation, a suitable method for determination of the plate efficiencies was again obtained in the same manner as described for the first set of additional specifications.

ADDITIONAL SPECIFICATIONS: x_{ji} ($0 \leqq j \leqq N+1$), AND $1 \leqq i \leqq c$); X_{Di} ($1 \leqq i \leqq c$); AND T_j ($0 \leqq j \leqq N+1$)

It is understood, of course, that the reflux rate, distillate rate, holdups, number of plates, the complete definition of the feed, the type of condenser, and the column pressure are also fixed. Although this particular set of specifications is seldom known in practice, it is of interest because it leads to a unique set of E_{ji}'s, which may be computed directly without resorting to the use of trial and error procedures.

As shown by Waggoner et al. (*10*), the L_j's may be determined by enthalpy balances that require only the knowledge of the T_j's and x_{ji}'s at the end of the time period under consideration. After the L_j's have been determined, the corresponding V_j's may be obtained from the total material balances. On the basis of this set of total flow rates and the known values of x_{ji} and T_j, the component material balances may be solved for the E_{ji}'s in the following manner. First, Equation (6) is solved for the unknown flow rates $v_{j+1,i}$ and v_{ji} in terms of the known holdups and flow rates as follows:

$$v_{j+1,i} - v_{ji} = \frac{u_{ji} - \overset{o}{u}_{ji}}{\mu\Delta t} - \sigma[\overset{o}{v}_{j+1,i} + \overset{o}{l}_{j-1,i} - \overset{o}{v}_{ji} - l_{ji}] - [l_{j-1,i} - l_{ji}] \quad (9)$$

The unknown flow rates may be stated in terms of the unknown efficiencies, namely

$$v_{ji} = V_j y_{ji} = V_j E_{ji} K_{ji} x_{ji} = a_{ji} E_{ji} \quad (10)$$

where

$$a_{ji} = V_j K_{ji} x_{ji}$$

For a conventional column with a partial condenser, the component material balances for any component i are represented by the following matrix equation.

$$\begin{bmatrix} -a_{0i} & -a_{1i} & 0 & 0 & 0 & \ldots & 0 \\ 0 & -a_{1i} & a_{2i} & 0 & 0 & \ldots & 0 \\ 0 & 0 & -a_{2i} & -a_{3i} & 0 & \ldots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & \cdots & 0 & -a_{Ni} & & -a_{N+1,i} \\ 0 & \cdots & \cdots & 0 & 0 & & -a_{N+1,i} \end{bmatrix} \begin{bmatrix} E_{0i} \\ E_{1i} \\ E_{2i} \\ \cdots \\ E_{Ni} \\ E_{N+1,i} \end{bmatrix} = \begin{bmatrix} P_{0i} \\ P_{1i} \\ P_{2i} \\ \cdots \\ P_{Ni} \\ P_{N+1,i} \end{bmatrix} \quad (11)$$

where

$$P_{0i} = \frac{u_{0i} - \overset{o}{u}_{0i}}{\mu\Delta t} - \sigma[\overset{o}{v}_{1i} - \overset{o}{l}_{0i} - \overset{o}{d}_i] + l_{0i}$$

$$P_{ji} = \frac{u_{ji} - \overset{o}{u}_{ji}}{\mu\Delta t} - \sigma[\overset{o}{z}_{ji} + \overset{o}{v}_{j+1,i} + \overset{o}{l}_{j-1,i} - \overset{o}{v}_{ji} - \overset{o}{l}_{ji}] - [l_{j-1,i} - l_{ji}] - z_{ji}, \ (1 \leqq j \leqq N)$$

$$z_{ji} = 0(j \neq f-1, f);\ z_{f-1,i} = v_{Fi};\ z_{fi} = l_{Fi}$$

$$P_{N+1,i} = \frac{u_{N+1,i} - \overset{o}{u}_{N+1,i}}{\mu\Delta t} - \sigma\,[\overset{o}{l}_{Ni} - \overset{o}{v}_{N+1,i} - \overset{o}{b}_i] - [l_{Ni} - b_i]$$

The following expression for E_{ji} is obtained by application of the matrix multiplication rule to Equation (11), followed by successive substitution of the expression for $E_{j+1,i}$ into the one for E_{ji}.

$$E_{ji} = -\frac{1}{a_{ji}} \sum_{k=j}^{N+1} P_{ki} \qquad (12)$$

It remains to be shown that the E_{ji}'s given by Equation (12) satisfy the temperature functions given by Equation (2). Consider, first, the reboiler ($j = N + 1$), for which Equation (12) gives

$$E_{N+1,i} = -\frac{P_{N+1,i}}{V_{N+1} K_{N+1,i}\, x_{N+1,i}}$$

Substitution of this expression for $E_{N+1,i}$ into Equation (2) yields

$$f_{N+1} = \frac{-\sum_{i=1}^{c} P_{N+1,i}}{V_{N+1}} - 1$$

or

$$V_{N+1} f_{N+1} = \left\{ -\left[\frac{U_{N+1} - \overset{o}{U}_{N+1}}{\mu\Delta t}\right] + \sigma\,[\overset{o}{L}_N - \overset{o}{V}_{N+1} - \overset{o}{B}] + [L_N - B] \right\} - V_{N+1} \qquad (13)$$

When the integral difference equation representing the total material balance enclosing the reboiler is reduced to algebraic form by the implicit method, and the resulting expression is solved for V_{N+1}, the following result is obtained

$$V_{N+1} = -\left[\frac{U_{N+1} - \overset{o}{U}_{N+1}}{\mu\Delta t}\right] + \sigma\,[\overset{o}{L}_N - \overset{o}{V}_{N+1} - \overset{o}{B}] + [L_N - B] \qquad (14)$$

Thus, for $j = N + 1$, Equation (2) reduces to

$$V_{N+1} f_{N+1} = V_{N+1} - V_{N+1} = 0$$

or

$$f_{N+1} = 0$$

Similarly, it is shown that the E_{ji}'s given by Equation (12) make $f_j = 0$ for all j.

The procedure described above is obviously applicable for columns at steady state operation. For this case, the definition of the a_{ji}'s remains the same as that given after Equation (10), and the definitions of the P_{ji}'s become

$P_{0i} = l_{0i}$
$P_{ji} = l_{ji} - l_{j-1,i} - z_{ji};\ z_{ji} = 0\,(j \neq f - 1, f);\ z_{f-1,i} = v_{Fi};$ and $z_{fi} = l_{Fi},$
$P_{N+1,i} = b_i - l_{Ni}$

DETERMINATION OF THE TRANSIENT EFFICIENCIES FOR THE GENERALIZED MODEL OF A PLATE

Although the details of this model together with the complete set of equations are presented by Tetlow et al. (8), a brief description of this model follows. A graph of the generalized model of a plate is presented in Figure 1 of Tetlow et al. (8). As indicated there, the holdup of the plate and downcomer is divided into three parts. The holdup U_j is for mass transfer, the holdup U_{Dj} is for plug flow without mass transfer, and the holdup U_{Mj} is for perfect mixing without mass transfer. The flow rate L_j leaving the mass transfer section of plate j is divided into three fractions:

$$\lambda_{Cj}\, L_j,\ \lambda_{Dj}\, L_j,\ \lambda_{Mj}\, L_j$$

where

$$\lambda_{Cj} + \lambda_{Dj} + \lambda_{Mj} = 1 \qquad (16)$$

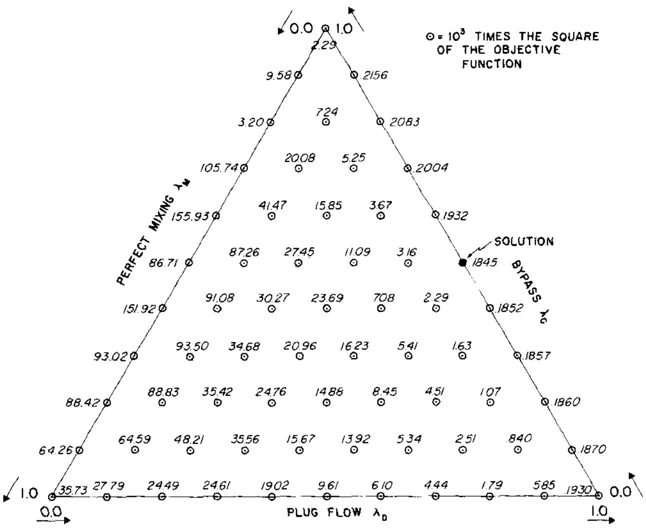

Fig. 1. Contour of the objective function in the λ domain for example 1.

Liquid at the rate $\lambda_{Cj}\, L_j$ bypasses or proceeds by channeling to the mass transfer section of plate $j + 1$. Liquid at the rate $\lambda_{Dj}\, L_j$ enters and passes through the plug flow holdup U_{Dj} before entering the mass transfer section of plate $j + 1$. Liquid at the rate $\lambda_{Mj}\, L_j$ passes through the perfect mixer with the holdup U_{Mj} before entering the mass transfer section of plate $j + 1$.

The holdups $\mathcal{M}_{Dj}$ and M_{Dj} in mass (or volumetric) units were computed on the basis of the mass (or volume) of liquid in the downcomer as follows

$$\mathcal{M}_{Dj} = \frac{\lambda_{Dj}}{\lambda_{Dj} + \lambda_{Mj}} \begin{bmatrix} \text{mass (or volume) of} \\ \text{liquid in the down-} \\ \text{comer of plate } j \end{bmatrix} \qquad (16)$$

$$\mathcal{M}_{Mj} = \frac{\lambda_{Mj}}{\lambda_{Dj}} \mathcal{M}_{Dj} \qquad (17)$$

Actually, a part of the liquid in the holdup $\mathcal{M}_j$ on plate j may be included in the holdups $\mathcal{M}_{Dj}$ or $\mathcal{M}_{Mj}$ if such representation best describes the behavior of plate j.

The holdups in mass (or volumetric) units were considered fixed over each time period. At the end of each time period, a new set of holdups was determined by use of the customary fluid dynamic relationships for columns at steady state operation. These relationships were used to determine the total liquid holdup on the plate and in the downcomer for each plate.

The generalized model for a plate may be used in the procedures described above by replacing the equations for the model of Waggoner et al. (10) by those of Tetlow et al. (8). For any choice of the fractions λ_{Cj}, λ_{Dj}, and λ_{Mj}, satisfying Equation (16), the plate efficiencies are determined in a manner analogous to that described above.

For poor choices of the λ's, the remaining effects of channeling, plug flow, and mixing are absorbed in the plate efficiencies, E_{ji}'s, and primarily in the β_j's. A more precise method for choosing the λ's consists of finding that set of λ's (λ_C, λ_D, λ_M) for all j such that the deviation of each β_j from unity is minimized. For the case where one set of λ's is chosen for all j, the corresponding problem in optimization may be stated in terms of an objective function as follows:

$$O(\lambda_C, \lambda_D) = \sqrt{\frac{\sum_{j=0}^{N+1} (\beta_j - 1)^2}{N+2}} \qquad (18)$$

Only two of the three λ's are independent. Since their sum is unity, $\lambda_M = 1 - \lambda_C - \lambda_D$ for any choice of λ_C and λ_D. Actually, instead of only one set of independent variables, λ_C and λ_D, as many as $N + 1$ sets could be determined, one set for each independent β. [There are a total of $N + 2$ values of β, but only $N + 1$ are independent, since the normalization procedure described by Davis et al. (*1*) requires that the product of β's have the value of unity.]

Although the objective function may be stated in various forms such as the sum of the β_j's, the particular form selected has the geometrical significance that

$$\sqrt{\sum_{j=0}^{N+1} (\beta_j - 1)^2}$$

represents the length of the vector from the origin in a $(\beta_j - 1)$ dimensional space to the point $[(\beta_0 - 1), (\beta_1 - 1), \ldots, (\beta_N - 1), (\beta_{N+1} - 1)]$. The term $N + 2$ is used to obtain an average of the deviations. The set of values of λ_C, λ_D, and λ_M that minimizes the objective function may be found by any one of several search techniques (*11*). For each choice of values for λ_C and λ_D, the corresponding β_j's were determined as described above.

ILLUSTRATIVE EXAMPLE

Fortunately, the component parts of the first two procedures proposed had been checked by use of field tests, because no one complete set of unsteady state data was reported in the literature. The basic procedures of Taylor et al. and Davis et al. had been thoroughly tested by determining the efficiencies for about 75 columns. Similarly, the unsteady state equations of Waggoner (*9, 10*) had been compared with the results of several field tests.

The proposed methods were subjected, however, to severe tests by use of a wide variety of numerical examples, the results of which are available (*2*). In these examples, the results of field tests were simulated by solv-

TABLE 1. STATEMENT OF EXAMPLE 1

Initial conditions—steady state operation

Specifications

Comp. No.	Component	$F^\circ X^\circ$, moles/min.
1	C_3H_8	6
2	n-C_4H_{10}	2
3	n-C_5H_{12}	2

Other conditions

$B = 5.0$, Reflux ratio $= 2.0$ boiling point liquid feed, total condenser, column pressure $= 300$ lb./sq. in. abs., plate distribution as shown under steady state solution, tray floor area $= 15.2$ sq. ft., downcomer cross-sectional area $= 2.2$ sq. ft., length of overflow weir $= 3.75$ ft., height of overflow weir $= 0.25$ ft., condenser volume $= 2$ cu. ft., reboiler volume $= 50$ cu. ft., reflux drum volume $= 100$ cu. ft., column base $= 30$ cu. ft. The efficiencies are given by setting $t = 0$ in the formulas that follow for the upset for example 1. The curve fits for the K values and enthalpies were taken from Tables A-4 and A-8 of reference 3.

Steady state solution

Plate No.	Temp., °F.	Vapor rate, moles/min.
0 (Condenser)	132.22	5.00
1	135.91	15.00
2	140.18	14.64
3	152.44	14.11
4 (Feed)	174.01	13.07
5	194.90	13.01
6 (Reboiler)	244.01	10.63

Component	d_i	b_i
C_3H_8	4.8626	1.13735
n-C_4H_{10}	0.13732	1.86264
n-C_5H_{12}	0.00003	1.99997

Upset for example 1

Specifications for $t = 0^+$

Comp. No.	Component	$F X$, moles/min.
1	C_3H_8	1
2	n-C_4H_{10}	4
3	n-C_5H_{12}	5

Other conditions for $t = 0^+$

In addition to the conditions stated for the steady state solution, the following conditions are applicable at unsteady state for the generation of the results of field tests: $\lambda_{Dj} = 1$ $(0 \leqq j \leqq N)$, $\lambda_{C,N+1} = 1$, and the hydraulic relationships stated by Tetlow et al. (*8*). The physical properties needed in these relationships were taken from "Engineering Data Book," 7 ed., Natl. Gasoline Assoc., Tulsa, Okla., 1957. The following component efficiencies and plate factors were employed.

Plate factors, β_j*

$\beta_0 = 1.0$

$\beta_1 = 1.1 - (0.01)/(0.1 + 0.1t)$

$\beta_2 = 1.1 - 0.1\, e^{-0.01t^2}$

$\beta_3 = 1.0 - (0.01t)/(0.1 + 0.1t^3)$

$\beta_4 = 0.95 + 0.05\, e^{-0.01t^2}$

$\beta_5 = 1.0 + (0.01t)/(0.2 + 0.1t)$

$\beta_6 = 1 \Big/ \prod_{j=1}^{5} \beta_j$

Component factors, $\overline{E}_i$*

$\overline{E}_1 = 1.05 - (0.01t)/(0.2 + 0.1t)$

$\overline{E}_2 = 1.02 + (0.02t)/(0.2 + 0.1t)$

$\overline{E}_3 = 0.9 + 0.15\, e^{-0.01t^2}$

where t is in minutes in the formulas for β_j and $\overline{E}_i$.

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* The formulas were modified after those given in Section 20 of "Chemical Business Handbook," J. H. Perry, ed., McGraw-Hill, New York, 1954.

ing selected unsteady state problems on the basis of selected sets of component efficiencies $\overline{E}_i$ and plate factors β_j. The temperatures (T_j) and product distributions (b_i/d_i) so obtained were taken as the results of field tests. On the basis of these T_j's and b_i/d_i's, the corresponding plate efficiencies were determined by the first two methods proposed. The $\overline{E}_i$'s and β_j's so determined agreed to within four significant figures of the values used to generate the *field test results*. All types of variations for the $\overline{E}_i$'s and β's were employed. Some of the functions employed for the component efficiencies and plate factors increased with time, some decreased with time, some went through a maximum, some through a minimum, and some remained very nearly constant with respect to time. Also, examples were solved in which the transient values of the $\overline{E}_i$'s and β_j's were selected by use of a random number generator.

The method described for the third set of additional specifications was tested by use of the x_{ji}'s and T_j's of the generated field tests, and again good agreement between the calculated E_{ji}'s and the values used to generate the field tests were obtained. This particular method was developed in an attempt to make use of the experimental results of Luyben et al. (*5*) and others. Unfortunately, it was impossible to use any of the experimental data in the literature, because the workers who determined compositions did not determine the corresponding temperatures as functions of time.

To illustrate the procedure for the simultaneous determination of the plate efficiencies and the set of λ's that minimizes the objective function, Equation (18), a set of operating data was generated on the basis of the $\overline{E}_i$'s, β_j's, and λ_j's given for example 1 in Table 1. On this basis, the corresponding sets of transient values of the product distributions and temperatures were obtained, and these results were taken as the additional specifications. It was further supposed that the accumulator-condenser and plate N were in plug flow, the bottoms were withdrawn directly from the reboiler $(\lambda_{C,N+1} = 1)$, and that the λ's for the remaining plates were the same; that is

$$\lambda_C = \lambda_{Cj};\ \lambda_D = \lambda_{Dj};\ \lambda_M = \lambda_{Mj}\ (1 \leqq j \leqq N-1)$$

To determine the efficiencies and the corresponding λ's needed to minimize the objective function, the pattern search of Hooke and Jeeves (*4*) was used. In the application of this search technique, a set of λ's was selected and then the $\overline{E}_i$'s and β_j's needed to satisfy the additional specifications were determined. The β_j's so obtained were used to evaluate the objective function. For each choice of λ's, this procedure was repeated. A graph of the search for the first time period after the upset is given by Groves (*2*). To verify the minimum found by the pattern search for the first time period, the objective function was evaluated at each of the points shown in Figure 1. The solution set of λ's gave a set of $\overline{E}_i$'s whose members agreed to within three significant figures of those given in Table 1 at time $t = 0.1$ min. The accuracy with which the $\overline{E}_i$'s could be computed was not appreciably better than the agreement between the aforementioned $\overline{E}_i$'s. The close agreement of the $\overline{E}_i$'s at the solution set of λ's is a characteristic of this particular example and not a general result. However, as might be expected, example 1 does demonstrate that the general result that the β_j's corresponding to the solution set of λ's are generally closer to unity than those used to generate the temperatures and product distributions as shown in Figure 1.

In summary, suitable methods for the determination of transient plate efficiencies from the results of field tests have been developed. For all problems considered, convergence to the correct solutions was achieved by use of these methods. Because of the relatively small amount of data required for the first two and the last method described (the methods that involve some combination of the product distributions and temperatures), these methods are best suited for the analysis of the results of field tests of commercial columns, where it is difficult to obtain extensive sets of data. However, where it is possible to obtain extensive data such as compositions and temperatures throughout the column, the second method should prove particularly useful.

ACKNOWLEDGMENT

This work was supported in part by Humble Oil and Refining Company, Monsanto Company, the National Science Foundation, and the Texas Engineering Experiment Station. This support is gratefully acknowledged.

NOTATION

a_{ji} = appears in the coefficient matrix of the component material balances given by Equation (11); defined after Equation (10)
b_i = molal flow rate of component i in the bottoms; B = total flow rate
c = total number of components
d_i = molal flow rate of component i in the distillate; D = total flow rate
E_{ji} = vaporization efficiency for plate j and component i
$\overline{E}_i$ = component efficiency for component i for all j
f_j = temperature function for plate j
K_{ji} = equilibrium constant for plate j and component i; evaluated at the temperature and pressure of the liquid leaving the mass transfer section of plate j
l_{ji} = molal flow rate of component i in the liquid leaving the mass transfer section of plate j
L_j = total molal flow rate of liquid leaving the mass transfer section of plate j
$\mathcal{M}_j$ = mass transfer holdup in mass (or volumetric) units for plate j
$\mathcal{M}_{Dj}$ = plug flow holdup in mass (or volumetric) units for plate j
$\mathcal{M}_{Mj}$ = perfect mixer holdup in mass (or volumetric) units for plate j
N = total number of actual plates; the plates are numbered from the top down, the condenser is assigned the number 0, and the reboiler the number $N + 1$
O = objective function; defined by Equation (18)
P_{ji} = constants in the component material balances; definition follows Equation (11)
x_{ji} = mole fraction of component i in the liquid leaving the mass transfer part of plate j
y_{ji} = mole fraction of component i in the vapor entering plate $j - 1$

Greek Letters

β_j = plate factor of the vaporization efficiency; defined by Equation (8)
$\lambda_{Cj},\lambda_{Dj},\lambda_{Mj}$ = fractions of the liquid stream L_j that bypass through the plug flow holdup, and the perfect mixer, respectively
μ = weighting factor
θ_i = θ function for component i; defined by Equation (7)

Subscripts

ca = calculated value
co = specified value
i = component number
j = plate number

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Manuscript received March 3, 1966; revision received August 11, 1966; paper accepted September 30, 1966. Paper presented at A.I.Ch.E. Dallas meeting.

Heterogeneous and Homogeneous Reactions in a Tubular Reactor

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Irreversible, first-order, simultaneous heterogeneous and homogeneous reactions in an isothermal tubular reactor under laminar flow conditions are studied. Accurate values of the eigenvalues, eigenfunctions, and radial concentration profiles are found for the dilute system. Criteria are given as to when the homogeneous reaction may be neglected with respect to the heterogeneous reaction and vice versa. It is found that for a certain range of the rate parameters well-known limiting solutions apply. Outside this range, the new solutions must be used.

The interaction of simultaneous, first-order homogeneous and heterogeneous chemical reactions in an isothermal tubular reactor under fully developed laminar flow conditions is studied. The irreversible reaction

$$A \rightarrow \text{products} \tag{1}$$

is considered at steady state conditions.

A limiting case of this problem, namely, no homogeneous reaction and infinite heterogeneous reaction rate, is the classical Graetz problem for which accurate values of the eigenvalues and vectors were obtained numerically by Brown (*1*) and asymptotically by Sellars et al. (*2*).

Lauwerier (*3*) considered a finite, first-order homogeneous reaction, but no heterogeneous reaction. An asymptotic solution for the large eigenvalues which was independent of the reaction rate constant was deduced. Recently, Hsu (*4*) solved the same problem by numerical integration for one value of the homogeneous rate constant. Cleland and Wilhelm (*5*) also considered the case of no heterogeneous reaction with a finite-difference method and supported their theoretical profiles with experimental data. Katz (*6*) considered heterogeneous reaction alone from an integral equation viewpoint.

Work on combined first-order heterogeneous and homogeneous reactions has been reported by Walker (*7*), who considered both radial and axial diffusion but reported only the first eigenvalue and considered the concentration profiles from an asymptotic viewpoint. Deviations from the one-dimensional case were of prime consideration. Krongelb and Strandberg (*8*) used finite-difference methods to investigate a second-order homogeneous reaction with first-order heterogeneous kinetics.

It is desired to obtain radial concentration profiles and to deduce under what conditions the homogeneous reaction may be neglected in favor of the heterogeneous reaction and vice versa. In this way combined reaction phenomena may be described in terms of one controlling rate parameter.

ANALYSIS

The dimensionless form of the continuity equation for a dilute component is

$$(1-y^2)\frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial y^2} + \frac{1}{y}\frac{\partial c}{\partial y} - Kc \tag{2}$$

with boundary conditions

$$\frac{\partial c}{\partial y} = 0 \qquad y = 0 \tag{3a}$$