# Mathematical Modeling and Numerical Integration of Multicomponent Batch Distillation Equations

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**A mathematical model for multicomponent batch distillation was derived, and a FORTRAN IV program was written for solution on a digital computer. The program has been used in the simulation of several commercial batch distillation columns.**

**A calculation procedure for the numerical solution of batch distillation equations starting from total reflux steady state conditions was developed, and the step-by-step procedure is presented here. Also included is a discussion of the stability and relative computational effectiveness of various numerical integration techniques when applied to transient distillation calculations. The discussion applies equally well to both batch distillation and unsteady state continuous distillation.**

Most of the published work on transient distillation calculations has been primarily concerned with continuous distillation rather than with batch distillation, which is inherently an unsteady state process. The reason for this is twofold. First, there is wider industrial interest in continuous distillation, and second, unsteady state continuous distillation models are more easily derived and the related computational problems are less severe than those of batch distillation. For example, transients in continuous distillation are usually in the form of relatively small upsets from steady state operation, whereas in batch distillation individual components can completely disappear from the column, first from the reboiler and then from the entire column.

Continuous distillation models have been solved with the use of linear perturbation methods on an analog computer (*1* to *3*) and by employing numerical integration techniques in the solution of nonlinear models on a digital computer (*4* to *6*). In general, most dynamic distillation models have been developed and solved for binary systems. There are, however, several publications pertaining to the solution of unsteady state multicomponent distillation models (*7*, *8*).

Primarily, batch distillation models have been methods of the so-called "short-cut" type, for example, minimum reflux ratio, minimum number of theoretical trays, etc. (*9* to *12*). Interest in computer solution of batch distillation equations was initiated by the work of Rose, Johnson, and Williams (*13* to *15*) who used an IBM computer in their early work. The main assumptions of their model were: binary system, constant relative volatility, equal molal overflow, theoretical trays, and constant molal hold-up.

Although the authors presented both calculated and experimental results for comparison, the simplicity of the model and calculational procedure, and the slowness of the early digital device, made the study one of academic interest only.

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Huckaba and Danly (*16*) presented the first really significant simulation of a batch distillation column. The main assumptions made in the formulation of the mathematical model included binary system, constant weight holdups, linear enthalpy relationships, and adiabatic operation.

The common assumption of constant molal overflow was not made and therefore heat balances were included in the distillation model. In addition, the model was programmed to handle nonlinear equilibrium relationships and plate efficiency correlations. All calculations were performed on an IBM-650 digital computer using the modified Euler numerical integration technique. Experimental data were provided to test the validity of the model. Although highly successful from a simulation standpoint, the usefulness of the model is limited by the fact that it is applicable to binary systems only.

Meadows (*17*) presented the first (and to date, the only) multicomponent batch distillation model in the published literature. The model is as rigorous as is practical from a computational standpoint, the main assumptions being perfect mixing on all trays, negligible vapor holdup, adiabatic operation, theoretical trays, and constant volume plate holdup.

A complete derivation of the model was included for heat, material, and volume balances around various sections of the column; however, no satisfactory method of solution was presented.

## MATHEMATICAL MODEL

Unlike unsteady state continuous distillation, in which the transient response results from upsets in the operating conditions of a column at steady state, batch distillation is inherently an unsteady state process. The initial conditions for continuous distillation are the steady state conditions from which the transient begins. In batch distillation, one has two alternate procedures from which to choose.

In one case, one can consider the initial time as that in which heat is initially applied to the reboiler. In this case, the model must account for the thermal dynamics of the column itself, the filling of the trays with liquid, etc. A more practical approach is to assume that the product drawoff is to commence from a batch column operating at total reflux steady state.

The latter approach was adopted as the procedure to follow in this work. Therefore the initial conditions for the unsteady state model were the results of a total reflux steady state calculation. Since total reflux steady state modeling is common knowledge, the steady state equations will not be presented here.

The unsteady state model results from heat and material balances around the various parts of the column shown in Figure 1. The mathematical model was formulated on the following assumptions: adiabatic operation, constant volume of liquid holdup, negligible vapor holdup, negligible fluid dynamic lags, and theoretical trays.

It was felt that the common assumption of constant molal overflow would be a serious limitation to the usefulness of the model and therefore this assumption was not made in this work. However, in the absence of enthalpy data, the algorithm presented can be used as a constant molal overflow model by using arbitrary constants for the liquid and vapor enthalpies for each component.

In addition, due to the severe changes in compositions on each plate, the assumption of constant plate holdup (either in molar or weight units) is invalid in batch distillation calculations. Therefore the assumption of constant volume holdup was employed, and variations in the molal (or weight) plate holdup were accounted for by variations in the liquid density as a function of composition. The model was programmed, however, so that calculations could be performed for constant plate holdup by using the same (arbitrary) value of density for each component in the system, in which case molal (or weight) plate holdup was used in lieu of volume holdup.

### Heat and Material Balance Equations

The derivation of the basic mathematical model consists essentially of heat and material balances around the three sections of the column shown in Figure 1, namely, the condenser-accumulator, an arbitrary plate, and the reboiler, together with the equilibrium relationships and other equations of state.

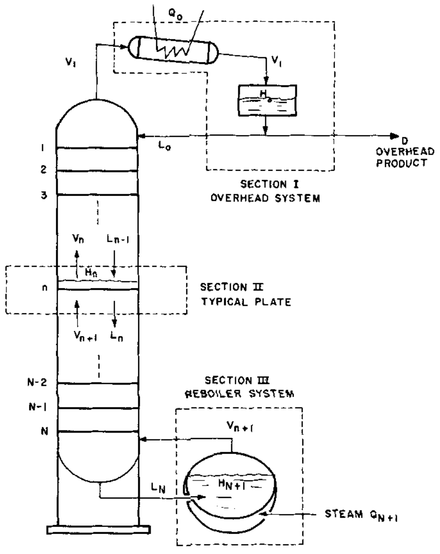

Fig. 1. Schematic of a batch distillation column.

For the condenser-accumulator system, the total mass balance and the component balance are

$$L_o = RD \tag{1}$$

$$\frac{dH_o}{dt} = V_1 - L_o - D = V_1 - D(R+1) \tag{2}$$

and

$$\frac{d(H_o\vec{x}_o)}{dt} = V_1\vec{y}_1 - L_o\vec{x}_o - D\vec{x}_o \tag{3}$$

Use of Equation (2) in Equation (3) results in

$$\frac{d\vec{x}_o}{dt} = \frac{V_1}{H_o}(\vec{y}_1 - \vec{x}_o) \tag{4}$$

Solving Equation (2) for $V_1$ and using a numerical approximation to the derivative of $dH_o/dt$ (which will be denoted by $\delta_t\, H_o$ and will be explained later), results in

$$V_1 = D(R+1) + \delta_t H_o \qquad (5)$$

The overall enthalpy balance around the overhead system yields

$$\frac{d(H_o I_o)}{dt} = V_1 J_1 - (L_o + D)\, I_o - Q_o \qquad (6)$$

Using Equation (2) in Equation (6) and solving for $Q_o$ results in

$$Q_o = V_1\,(J_1 - I_o) - H_o\,(\delta_t I_o) \qquad (7)$$

For an arbitrary plate $n$ $(1 \leqq n \leqq N)$ in the column (section II in Figure 1) the total mass balance, the component balance, and the enthalpy balance yield, respectively

$$\frac{dH_n}{dt} = V_{n+1} + L_{n-1} - V_n - L_n \qquad (8)$$

$$\frac{d(H_n \vec{x}_n)}{dt} = V_{n+1}\,\vec{y}_{n+1} + L_{n-1}\,\vec{x}_{n-1} - V_n \vec{y}_n - L_n \vec{x}_n \qquad (9)$$

$$\frac{d(H_n I_n)}{dt} = V_{n+1}\,J_{n+1} + L_{n-1}\,I_{n-1} - V_n J_n - L_n I_n \qquad (10)$$

Using Equation (8) in Equations (9) and (10) results in the following equations:

$$\frac{d\vec{x}_n}{dt} = \frac{1}{H_n}\,[V_{n+1}\,(\vec{y}_{n+1} - \vec{x}_n) + L_{n-1}\,(\vec{x}_{n-1} - \vec{x}_n) - V_n\,(\vec{y}_n - \vec{x}_n)] \qquad (11)$$

and

$$V_{n+1} = \frac{1}{J_{n+1} - I_n}\,[V_n\,(J_n - I_n) - L_{n-1}\,(I_{n-1} - I_n) + H_n \cdot \delta_t I_n] \qquad (12)$$

where the derivative $dI_n/dt$ has been replaced by a numerical approximation $\delta_t I_n$. Solving Equation (8) for $L_n$ yields

$$L_n = V_{n+1} + L_{n-1} - V_n - \delta_t H_n \qquad (13)$$

An analogous procedure for the reboiler results in the reboiler equations:

$$\frac{d\vec{x}_{N+1}}{dt} = \frac{1}{H_{N+1}}\,[-V_{N+1}\,(\vec{y}_{N+1} - \vec{x}_{N+1}) + L_N\,(\vec{x}_N - \vec{x}_{N+1})] \qquad (14)$$

and

$$Q_{N+1} = V_{N+1}\,(J_{N+1} - I_{N+1}) - L_N\,(I_N - I_{N+1}) + H_{N+1}\,(\delta_t I_{N+1}) \qquad (15)$$

In summary, then, the equations describing the rate of change of composition with time are given by Equations (4), (11), and (14), and those describing liquid and vapor flow rates by Equations (1), (5), (12), and (13). The heat duty relationships are given by Equations (7) and (15).

In the flow rate equations the rate of change of holdup and enthalpy with time was approximated by a numerical differentiation procedure of low order. Since the flow rates are very large compared with the rate of change of holdup and enthalpy over a single integration interval, it is believed that this approximation (which greatly simplifies the computational procedure) is justified.

### Holdups

The assumption of constant volume holdup on the plates was made. Therefore, the molal holdup is given by

$$H_n = G_n \rho_n \qquad (16)$$

where $G_n$ = volume of liquid holdup on plate $n$, and $\rho_n$ = the density of the liquid on plate $n$.

To complete the molal holdup calculation, an expression for liquid density as a function of temperature, pressure and composition is needed:

$$\rho_n = f(\vec{x}_n\ T_n,\ P_n) \qquad (17)$$

The reboiler holdup at any time is calculated from an algebraic combination of the initial charge, the material in the column, and the total material removed from the column, as

$$H_{N+1} = H^{0}_{N+1} - \sum_{n=0}^{N} H_n - \Delta D_{\text{total}} \qquad (18)$$

### Equilibrium Relationship

The ultimate success of any distillation model depends upon the accuracy of the vapor-liquid equilibrium relationship employed. The most commonly used form of this relationship for multicomponent mixtures is

$$y_{i,n} = K_{i,n} x_{i,n} \qquad (19)$$

where $K_{i,n}$ is used most frequently as a function of liquid composition, temperature, and pressure, that is

$$K_{i,n} = f_i\,(\vec{x}_n,\ T_n,\ P_n) \qquad (20)$$

The computational problem here is to find each $K_{i,n}$ such that

$$\sum_{i=1}^{C} y_{i,n} = 1.0 \qquad (21)$$

which is commonly referred to as a *bubble-point* calculation. The most commonly used forms for $K_i$ (called $K$ values) in order of increasing complexity are Raoult's law, the Antione equation, or some complex equation of state.

### Enthalpy Equations

Since the mathematical model involves heat balances, it requires values of the liquid and vapor enthalpies throughout the column and throughout the transient. Therefore the following types of enthalpy relationships must be provided:

$$I_n = f(\vec{x}_n,\ T_n) \qquad (22)$$

and

$$J_n = f(\vec{y}_n,\ T_n) \qquad (23)$$

It should be recognized that Equations (22) and (23) include the pure component enthalpies as a function of temperature plus some reliable mixing rule.

## CALCULATION PROCEDURES

As mentioned previously, the initial conditions for the unsteady state calculations were the results of total reflux steady state conditions. Therefore, a steady state calculation procedure, which is unavoidably one of trial and error, was necessary. The procedure used in this work was an iterative, plate-to-plate technique using direct substitution with adaptive acceleration and damping. The initial estimate of the steady state reboiler composition was that of each component in the initial charge to the column. Plate-to-plate calculations were then performed up the column to the overhead condenser. Special provisions were included to prevent the composition of a component on any plate from exceeding that allowed by the amount of the component in the initial charge. After each complete calculation up the entire column, the total amount of each component in the reboiler, on each plate, and in the condenser was calculated, and this was compared with the amount in the original charge. A success was registered when the calculated amount in the entire system equaled that in the initial charge. When the test succeeded for each component, convergence was assumed.

The unsteady state solution technique was one of numerical integration of a system of differential equations starting from total reflux steady state with a finite amount of product drawoff. This procedure was followed because of the availability of the digital computer, and because the resulting differential equations were highly nonlinear. Analog computers have proven adequate for the solution of systems of linear differential equations (*1, 2*). For very large systems of equations, or for nonlinear differential equations, digital computers have been shown to be more practical (*4, 6* to *8*.) The use of large-scale analog/digital/hybrid computers, which make optimum use of the speed of the analog and the accuracy, storage, and nonlinear function generation of the digital, should be investigated further for the simulation of large multicomponent commercial distillation columns (*18* to *20*).

### Step-by-Step Calculational Procedure

From a total reflux steady state condition, transient operation begins with the first drop of product drawoff. Computationally, this means that the product rate jumps discretely from a value of zero to some finite value, say $D$. For a particular reflux ratio $R$ this value of $D$ would be

$$D = \frac{\overset{o}{L_o}}{R + 1} \tag{24}$$

(For purpose of discussion, let the superscript $o$ denote steady state total reflux, and the superscript $^+$ denote the instant that product drawoff is begun.) With product drawoff the reflux rate immediately drops to

$$\overset{+}{L_o} = \overset{o}{L_o} - D \tag{25}$$

It can be easily shown that with the assumption of negligible fluid dynamic lags, the flow rates up and down the column $(1 < n < N)$ become

$$\overset{+}{V_n} = \overset{o}{V_n} \tag{26}$$

and

$$\overset{+}{L_n} = \overset{o}{L_n} - D \tag{27}$$

(It should be stated here that although the assumption of negligible fluid dynamic lags does not seriously affect the composition profiles, it does result in errors in the calculated flow rates, especially in the first portion of the transient response.)

These values of flow rates are used in Equations (4), (11), and (14) to produce finite composition derivatives and the solution carried one time step from time $t = 0$ to $t = \Delta t$.

Thereafter, the following computational procedure is followed for each increment. With the composition derivatives at the beginning of an increment, the compositions are carried via the numerical integration procedure to the end of the increment. Here liquid densities, plate holdups, and liquid and vapor enthalpies are calculated. From these values of plate holdups and liquid enthalpy and from past stored values, one obtains approximations to $dH_n/dt$ and $dI_n/dt$ as $\delta_t H_n$ and $\delta_t I_n$ using some low-order numerical differentiation formula. Equations (1), (5), (12), and (13) are then used to obtain updated value of flow rates. The reboiler holdup is calculated from Equation (18). With the values of composition, holdup, and enthalpy calculated at the end of the increment as the values at the beginning of the next, new composition derivatives are calculated and the calculation cycle is repeated.

When using numerical integration techniques to solve multicomponent distillation equations, the following question always arises: Does one work with only $C - 1$ components and obtain the other by difference, or does one work with all $C$ components and normalize the sum of the compositions to equal one? The latter was adopted in this work for two reasons: first, because it is difficult, in a general program, to pick which $C - 1$ components to use (or which component should be obtained by difference); and second, because it is believed that the normalization of the sum of the components to equal one acts as a damping device on small numerical errors. In addition, the compositions were normalized after both the predictor and corrector calculations in the numerical technique.

It should be mentioned at this point that in this work all calculations were performed by picking an arbitrary value of product drawoff:

$$D = \frac{\alpha H^o{}_{N+1}}{R^o + 1} \quad (\alpha = \text{constant, hr.}^{-1}) \tag{28}$$

and integrating in the time domain $t$. Although this is entirely equivalent to picking an arbitrary $\Delta D$ over each increment (instead of $\Delta t$), the time domain was used throughout the program to provide for future expansion of the program to handle more sophisticated operational schemes. At present, the program integrates in the time increments $\Delta t$, which when multiplied by the constant overhead product drawoff rate $D$, gives the fractional product drawoff in the increment, that is

$$\Delta D = D \cdot \Delta t \tag{29}$$

Also, with constant product drawoff, the total distilled at the end of the $m^{\text{th}}$ time increment is given by

$$\Delta D_{\text{total}} = \sum_{j=1}^{m} \Delta D_j = D \sum_{j=1}^{m} \Delta t_j = D \cdot t_m \tag{30}$$

Output of the program, then, is meaningful only for compositions as a function of fraction vaporized.

For other operational schemes (such as constant reboiler heat duty input in lieu of constant product drawoff rate), the model will require a relationship between product rate and reboiler heat duty. This can be obtained by using the total column enthalpy balance

$$Q_{N+1} - Q_o - DI_o = \sum_{n=0}^{N+1} \frac{d(H_n I_n)}{dt} \tag{31}$$

in conjunction with Equations (5) and (7).

Using Equation (5) in (7) to eliminate $V_1$ results in the equation

$$Q_o = [D(R + 1) + \delta_t H_o] \, (J_1 - I_o) - H_o \, (\delta_t I_o) \tag{32}$$

One can then eliminate $Q_o$ from Equation (31) using Equation (32). Solving the resulting equation for the overhead product rate results in

$$D = \frac{Q_{N+1} - J_1 \delta_t H_o - \sum_{n=1}^{N+1} \delta_t \, (H_n I_n)}{(R + 1) \, J_1 - RI_o} \tag{33}$$

where again all derivatives $d/dt$ have been replaced by a numerical approximation $\delta_t$.

## NUMERICAL METHODS

The main criterion to use in the selection of a suitable numerical integration procedure for transient distillation calculations is the stability characteristics of the procedure. For example, given the choice between two methods, it is usually advantageous to use the one with the greater stability range, even at the expense of a large increase in the truncation error. The reason for this is that in problems of this nature the maximum step size for numerical integration is nearly always limited by the absolute stability of the method. Therefore the step size required is usually so small that the truncation error is small independent of the order of the method.

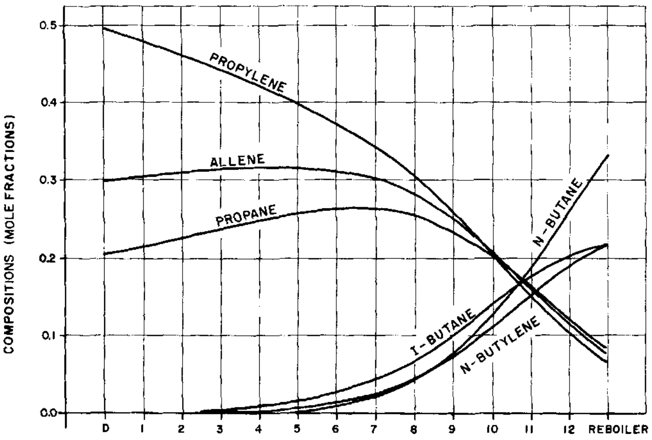

Fig. 2. Steady state composition profile, run 1.

Stability problems are apparent when the maximum allowable step size is very small compared with the time constant of the system, that is, when the maximum step size is so small that very little change takes place in the actual system over one integration step. Mah et al. (*7*) discussed the instabilities of numerical integration techniques when applied to continuous distillation calculations. It should be mentioned that these problems are compounded in batch distillation because the time constant of the reboiler is very large compared with the time constant of a plate. The fast response on a plate limits the integration interval to a small step, whereas large damping in the reboiler results in slow response of the total system.

The stability limits of approximately ten of the best known and proven techniques (and a few newer ones) for numerical solution of differential equations were compared —some theoretically, some empirically, and some both ways.

The theoretical approach was to investigate the roots of the characteristic equation of the method. If the method possesses consistency (all of the methods tried do†; one root will approximate the true solution of the nonlinear differential equation:

$$\frac{dx}{dt} = f(x, t) \tag{34}$$

which has been linearized, e.g.,

$$\frac{dx}{dt} = \left(\frac{\partial f}{\partial x}\right)_{(x_o,\, t_o)} x \quad + F\,(x_o, t_o, t) \tag{35}$$

The other roots (there will be $n$ roots if one uses an $n^{\text{th}}$ order numerical integration scheme) will be extraneous roots, which bare no resemblance to the true solution. When the absolute value of an extraneous root is larger than that of the true root, the method is said to be relatively unstable, that is, the extraneous root will dominate the solution as the number of integration steps becomes large. If, in the above-mentioned case, the true root has an absolute value less than one (the true solution is decaying), and an extraneous root has an absolute value greater than one (the computer solution is increasing without bounds), the method is said to be absolutely unstable.

In the empirical approach, the following procedure was followed. A complete solution was obtained with an extremely small step size in order to establish an accurate solution. The increment size was then increased systematically in a series of runs until the solution blew up, that is, until ridiculous results were obtained.

The following numerical integration techniques were investigated: (a) forward, backward, and modified Euler (*21*), (b) Runge-Kutta—second, third, and fourth order (*21*), (c) third-order Adams-Moulton-Shell (*22*, *23*), (d) fourth-order Adams-Moulton (*24*), (e) fourth-order Milne (*21*, *25*), (f) fourth-order Hamming (*21*, *25*), (g) fourth-order Fehlberg (*26*), (h) Butcher's method (*27*), (i) Setter's method (*28*).

Before discussing any specific technique, it is necessary to discuss the manner in which one applies a predictor-corrector method. In essence one uses the open-end predictor equation to extrapolate from time ($t$) to time ($t + \Delta t$), or from the point $x_t$ to the point $x_{t+1}$. Using the predicted $x_{t+1}$ one then applies a closed-end corrector equation to interpolate for an improved value of $x_{t+1}$. One can then follow a rigorous truncation error analysis to modify the corrected value or both the predicted and corrected values. Predictor-corrector methods applied in this manner require but two functional (derivative) evaluations per increment independent of the order of the method. One can also apply predictor-corrector methods with several repeated corrector applications at the end of the interval, in which case the number of functional evaluations per increment is directly proportional to the number of such corrector iterations.

With $P$ representing a predicted value, $C$ a corrected value, $M_p$ modified predicted value, and $M_c$ a modified corrected value, some typical predictor-corrector schemes might be: (a) $P$-$C$, (b) $P$-$C$-$M_c$, (c) $P$-$M_p$-$C$-$M_c$, (d) $P$-$C$-$C$ (denoted $P$-$2C$), (e) $P$-$C$-$M_c$-$C$-$M_c$, (f) $P$-$M_p$-$C$-$M_c$-$C$-$M_c$, (g) $P$-$nC$.*

To illustrate, the fourth-order Adams-Moulton equations applied in the manner of scheme (c) is shown below:

Predict:

$$\overset{(P)}{x_{t+1}} = x_t + \frac{h}{24}\,(55x'_{t+1} - 59x'_t + 37x'_{t-1} - 9x'_{t-2}) \tag{36}$$

Modify:

$$\overset{(M_p)}{x_{t+1}} = \overset{(P)}{x_{t+1}} + \frac{251}{270}\left(\overset{(C)}{x_t} - \overset{(P)}{x_t}\right) \tag{37}$$

Correct:

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* Where $P$-$nC$ denotes one predictor application followed by "$n$" corrector applications or iterations.

TABLE 1. STABILITY LIMITS FOR VARIOUS NUMERICAL INTEGRATION TECHNIQUES

| Numerical routine | Limiting increment size $(\overline{\Delta t})_{(\max)}$ (dimensionless)<br>Theoretical | Empirical |
|---|---|---|
| 1. Forward Euler (*21*) | 2.0 | — |
| 2. Modified Euler (*21*) | | |
| a. *P-C* | 2.0 | 1.1 |
| b. *P-3C* | 2.0 | 1.3 |
| c. *P-6C* | 2.0 | 1.5 |
| d. *P-10C* | 2.0 | 1.6 |
| e. $P$-$\infty C$* | 2.0 | — |
| f. *C*† | Unlimited | — |
| 3. Backward Euler (*21*) | | |
| a. *P-C* | 1.0 | 0.7 |
| b. *P-2C* | 1.4 | 0.8 |
| c. *P-3C* | 1.0 | 0.7 |
| d. *P-4C* | 1.2 | — |
| e. $P$-$\infty C$* | 1.0 | — |
| f. *C*† | Unlimited | — |
| 4. Runge-Kutta (*21*) | | |
| a. Second order | 2.0 | 1.1 |
| b. Third order | 2.5 | 2.0 Unstable‡ |
| c. Fourth order | 2.7 | 2.0 |
| 5. Third-order Adams-Moulton-Shell (*22,23*) | | |
| a. *P-C* | 1.8 | 1.5 |
| b. $P$-$C$-$M_c$ | 2.0 | 1.5 |
| c. $P$-$M_p$-$C$-$M_c$ | 1.6 | 1.1 |
| d. *P-2C* | 1.2 | 1.0 |
| e. *P-3C* | — | 1.3 |
| f. *P-6C* | — | 1.4 |
| g. *P-10C* | — | 1.6 |
| h. $P$-$\infty C$* | 2.4 | — |
| i. *C*† | 6.0 | — |
| 6. Fourth-order Adams-Moulton (*24*) | | |
| a. *P-C* | 1.3 | — |
| b. $P$-$M_p$-$C$-$M_c$-$C$-$M_c$ | 0.6 | — |
| c. $P$-$C$-$M_c$-$C$-$M_c$ | 1.0 | — |
| d. *P-2C* | 0.9 | — |
| e. *C*† | 2.9 | — |
| 7. Fourth-order Milne (*21,25*) | | |
| a. *P-C* | 0.8 | — |
| b. $P$-$M_p$-$C$-$M_c$ | 0.5 | — |
| c. *P-2C* | Unstable | — |
| d. *P-3C* | Unstable | — |
| e. *C*† | Unstable | — |
| 8. Fourth-order Hamming (*21,25*) | | |
| a. *P-C* | 0.5 | — |
| b. $P$-$M_p$-$C$-$M_c$ | 0.8 | — |
| c. *P-2C* | 0.9 | — |
| d. *C*† | 2.7 | — |
| 9. Fourth-order Fehlberg (*26*) | | |
| a. Adams predict-1 Fehlberg correction | — | 1.5 Unstable‡ |
| b. Adams predict-10 Fehlberg corrections | — | 1.5 Unstable‡ |
| c. Milne predict-1 Fehlberg correction | 1.0 | — |
| d. Milne predict-2 Fehlberg corrections | 0.7 | — |
| e. Fehlberg corrector | 1.3 | — |
| 10. Butcher (*27*) | | |
| a. Two-point Butcher predictor-corrector (*P-P-C*) | 2.5 | 2.0 Unstable‡ |
| 11. Stetter (*28*) | | |
| a. Two-point Stetter predictor-corrector (*P-C*) | 1.0 | 0.5 Unstable‡ |

* $P - \infty C$ means that the corrector is iterated until it converges.
† *C* denotes the stability limit of the closed-end corrector equation alone (implicit solution).
‡ Only one value was tried and at this value the method was unstable. No attempt was made to find the correct limiting increment size.

$$\overset{(C)}{x}_{t+1} = x_t + \frac{h}{24}\left(9\overset{(M_p)}{x'}_{t+1} + 19x'_t - 5x'_{t-1} + x'_{t-2}\right) \tag{38}$$

Modify:

$$\overset{(M_c)}{x}_{t+1} = \overset{(C)}{x}_{t+1} - \frac{19}{270}\left(\overset{(C)}{x}_{t+1} - \overset{(P)}{x}_{t+1}\right) \tag{39}$$

In a rigorous sense, Equation (37) should contain the difference between the corrected and predicted value at the $(t + 1)$ step, as in Equation (38). Since the corrected value of the dependent variable $x^{(C)}_{t+1}$ will not be available at this stage, it is recommended that one use the difference between the corrected and predicted value at the previous increment. Applied thusly, an iterative procedure is avoided.

The results of the numerical study are shown in Table 1, which gives the maximum dimensionless increment size $(\overline{\Delta t})_{\max}$ tolerable from a stability standpoint for the various numerical integration schemes tried. A dimensionless increment size was used to provide for a common base to compare the above integration techniques for various distillation columns using different chemical systems. The dimensionless time increment used in this work is given by

$$\overline{\Delta t} = \left(-\frac{df}{dx}\right)\Delta t \tag{40}$$

where $(\partial f/\partial x)$ is defined by Equation (35) [see also Equations (41) and (42)].

From Table 1, it can be seen that the third-order Adams-Moulton-Shell method (hereinafter denoted SHELL) has better stability characteristics than any of the other techniques tried, that is, for an equivalent number of derivative evaluations the SHELL method allowed the largest maximum dimensionless time increment $(\Delta t)_{\max}$ at stability limits.

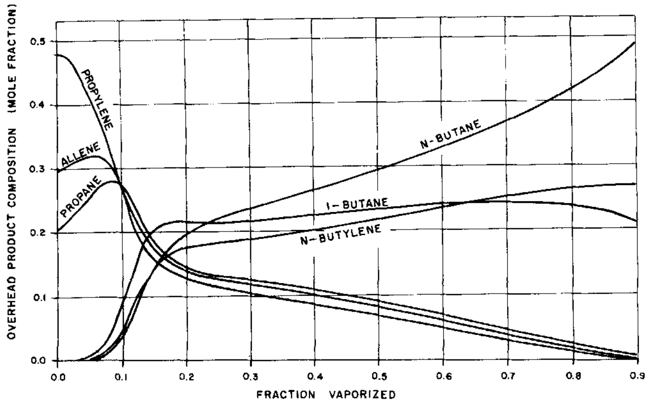

Fig. 3. Transient response—overhead product, run 1.

The SHELL equations were derived from the so-called Newton divided-difference interpolation formula. The method is capable of using history points which are not equally spaced. Therefore this unique feature of the method obviates the need to call a time-consuming self-starting routine after each change in increment size. Since the SHELL equations reduce to the Adams-Moulton equations for equally spaced history points, it was assumed that the SHELL equations possessed stability characteristics similar to those of the Adams-Moulton equations of the same order. Brown and co-workers (*24*) showed that the stability range of the Adams-Moulton equations is inversely proportional to the order of the method, the maximum tolerable integration step size of the third-order method, for example, being twice that of the fifth-order method.

It was therefore decided that (of the methods tried) the third-order SHELL equations were best suited for the numerical solution of the distillation model. The numerical study also showed that the most ideal application of the SHELL equations were in a predictor-corrector fashion, with a modification of the corrector value by conventional means (*23*). This modification, of course, makes the method one of the fourth-order accuracy.

## PROGRAM PERFORMANCE

Table 1 gives the maximum dimensionless step size $(\overline{\Delta t})_{\max}$ for the various numerical techniques tested in this work. From this table, one can obtain an approximate limiting step size $(\Delta t)_{\max}$ in hours using the dynamic distillation equations together with Equation (40). With a rearrangement of Equation (40), the integration step size in hours is limited by

$$(\Delta t)_{\max} \leq (\overline{\Delta t})_{\max} \Big/ \left(-\frac{\partial f}{\partial x}\right)_{\max} \tag{41}$$

For a system of linear differential equations, the quantity that plays a role similar to that of $(-\partial f/\partial x)_{\max}$ in the case of a single differential equation is the absolute value of the largest negative eigenvalue of the Jacobian matrix. If one considers the tridiagonal matrix system of distillation equations to be in the linear form given by Equation (35) [where $(\partial f/\partial x)$ in this case denotes the Jacobian matrix], the maximum increment size tolerable from a stability standpoint is approximately limited by

$$(\Delta t)_{\max} \leq (\overline{\Delta t})_{\max}/|\lambda|_{\max} \tag{42}$$

where $|\lambda|_{\max}$ is the absolute value of the largest negative eigenvalue of the Jacobian matrix. The greatest upper bound on $|\lambda|_{\max}$, which can be obtained from the Gerschgorin theorem (*29*) on the linearized tridiagonal set of differential equations representing dynamic distillation, is given approximately by the maximum of

$$|\lambda|_{\max} \leq 2\left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \tag{43}$$

for each component on each tray. It can be shown by induction that the least upper bound on the absolute value of the largest negative eigenvalue is given approximately by

$$|\lambda|_{\max} \geq \left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \tag{44}$$

for each component on each tray. That is, the absolute value of at least one eigenvalue of the tridiagonal matrix will always be greater than or equal to the absolute value of the largest diagonal element. Therefore, the range of $|\lambda|_{\max}$ as given by Equations (43) and (44) is

$$\left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \leq |\lambda|_{\max} \leq 2\left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \tag{45}$$

From Equations (42) and (45) one has that the maximum increment size tolerable from a stability standpoint is approximately bounded in the range

$$\frac{(\overline{\Delta t})_{\max}}{2} \Big/ \left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \leq (\Delta t)_{\max} \leq (\overline{\Delta t})_{\max} \Big/ \left(\frac{L_n + K_{i,n} V_n}{H_n}\right)_{\max} \tag{46}$$

For example, Equation (46) states that $(\Delta t)_{max}$ can never exceed $(\overline{\Delta t})_{max}/(L + KV/H)$ and may be as small as $(\overline{\Delta t})_{max}/[2(L + KV/H)]$.

Typically, the quantity $(L_n + K_{i,n} V_n)/H_n$—hereafter referred to as the $(L + KV/H)$ factor—varies between 50 to 1,000 hr.$^{-1}$ for standard distillation applications. In general, the $(L + KV)/H$ factor is influenced by physical parameters in the following ways:

1. A small concentration of a highly volatile component produces a high $K$ value which results in a high $(L + KV)/H$ factor.
2. A high reflux ratio results in high liquid rates down the column which tends to increase the $(L + KV)/H$ factor.
3. A high boilup rate produces a high vapor rate up the column, thus a high $(L + KV)/H$ factor.
4. Low plate holdups yield high $(L+ KV)/H$ factors.

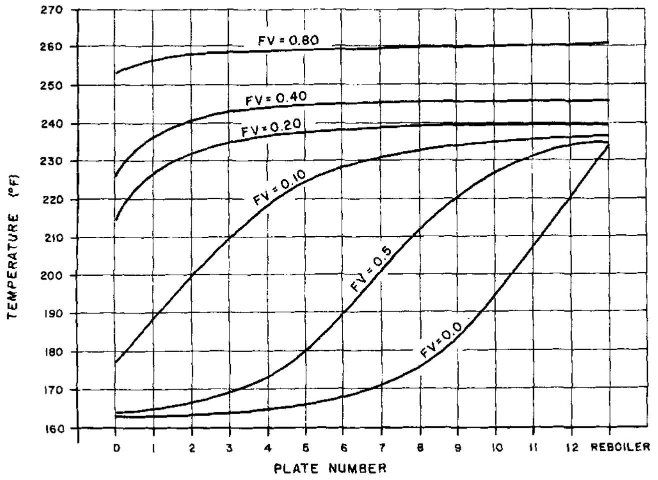

*Fig. 4. Unsteady state temperature profiles, run 1.*

For batch distillation the $(L + KV)/H$ factor will usually be a maximum on a plate rather than at the reboiler, because plate holdups are generally much smaller than the reboiler holdup. This means that the fast response of the plate limits the integration step size to a small value, while the slow response of the reboiler controls the overall dynamic response. Therefore, with batch distillation, one must consider not only the maximum allowable step size, but also the total time to empty the reboiler, which is directly proportional to the initial reboiler holdup. The net result, of course, is that one must consider both the $(L + KV)/H$ factor and the initial reboiler charge to get an estimate of total computer time. It should be noted that the same is not necessarily true for unsteady state continuous distillation, where the ratio of reboiler to plate holdup is not nearly as great as that in batch distillation.

For batch distillation, both of the above effects can be incorporated into a single term in which the maximum step size is given as a fraction of the product removal from the column on each integration step. Upon simplification, Equation (46) takes the form below for batch distillation calculations (as a delta fraction vaporized over one integration step):

$$\frac{(\overline{\Delta t})_{max}}{2}\,\frac{H_n}{H^o_{N+1}}\left(\frac{1}{R + (R + 1)K_{i,n}}\right)_{max} \tag{47}$$

$$\leq (\Delta \text{F.V.})_{calc} \leq (\overline{\Delta t})_{max}\,\frac{H_n}{H^o_{N+1}}\left(\frac{1}{R + (R + 1)K_{i,n}}\right)_{max}$$

where

$$\Delta\text{F.V.} = \frac{\Delta D}{H^o_{N+1}} \tag{48}$$

For a typical pilot-plant type of batch distillation tower a test problem was simulated using a six-component hydrocarbon system. Sample data for the system and operating conditions for run 1 are given in Table 2. For run 1, the calculated steady state profile is shown in Figure 2, and the dynamic response is shown in Figure 3. From the response given in Figure 3, the severe composition transients that occur in batch distillation can be seen, where plate compositions change drastically and some components essentially disappear from the system. The computational difficulties with this type of operation are much more complex than with continuous distillation, where transient operation results from upsets which cause rela-

Table 2. Data for Sample Problem

(Run 1)

I. Column
Number of plates, $N$ = 12
Diameter = 12 in.
Plate holdup, $H_n$ = 0.04 moles
Accumulator holdup, $H_0$ = 0.04 moles
II. Initial charge $(H^o_{N+1})$ = 5 moles

| Component | Mole % |
|---|---|
| Allene | 0.10 |
| Propylene | 0.10 |
| Propane | 0.10 |
| $N$-Butylene | 0.20 |
| $I$-Butane | 0.20 |
| $N$-Butane | 0.30 |

III. Reflux ratio $R/D$ = 1.0
IV. Column Pressure = 440 lb./sq.in. (for all plates)
V. Equilibium data
$\ln(K_{i,n} \cdot P_n) = A_i - B_i/(C_i + T_n)$
$A_i, B_i, C_i$ = Antione coefficients
VI. Enthalpy data
a. Liquid

$$I_n = \sum_{i=1}^{C} x_{i,n}(D_i + E_i T_n)$$

$D_i, E_i$ — pure component liquid enthalpy constants
b. Vapor

$$J_n = \sum_{i=1}^{C} y_{i,n}(F_i + G_i T_n)$$

$F_i, G_i$ — pure component vapor enthalpy constants
VII. Density data

$$\rho n = \sum_{i=1}^{C} x_{i,n}(M_i + N_i T_n)$$

$M_i, N_i$ — pure component density constants tively small variations in plate compositions. Figure 4 shows the temperature profile for run 1 as a function of the fraction vaporized. From this one can follow the trend of the dynamic response for the entire column throughout the transient period.

Typical computation time (in minutes) for the particular column are given in Table 3. All calculations were performed on an IBM-7044 digital computer using the third-order Adams-Moulton-Shell predictor-corrector integration scheme. From Table 3 one can see the strong dependence of computer times on the $H_n/H^o_{N+1}$ ratio and reflux ratio ($R$). [Meadows (*17*) reported computer times in hours using an IBM-7070 digital computer for batch distillation calculations on a five-plate column with a somewhat similar chemical system.] Also shown in Table 3 is a comparison between the average delta fraction vaporized used by the computer program, $(\Delta \mathrm{F.V.})_{\mathrm{ave}}$, and the maximum allowable delta fraction vaporized calculated from Equation (47), $(\Delta \mathrm{F.V.})_{\mathrm{calc}}$. Since the third-order Adams-Moulton-Shell equations were used in the computer program, the value of $(\overline{\Delta t})_{\max}$ of 1.5 from Table 1 was used in Equation (47). From Table 3 one can see the remarkable agreement between the actual average delta fraction vaporized used by the computer program, which seeks the largest allowable step size automatically based on a truncation error estimate (see reference *23*), and the value estimated from the simple relationship given by Equation (47).

TABLE 3. COMPUTER TIMES FOR SAMPLE PROBLEM

| Run No. | $H^o_{N+1}$ | $H_n$ | $R$ | Fraction vaporized | 7044 time,* min. | $(\Delta \mathrm{F.V.})_{\mathrm{ave}}$† | $(\Delta \mathrm{F.V.})_{\mathrm{calc}}$‡ |
|---|---|---|---|---|---|---|---|
| 1 | 5 | 0.04 | 1.0 | 0.98 | 5 | 0.00168 | 0.00150 to 0.00300 |
| 2 | 5 | 0.04 | 3.0 | 0.34 | 5 | 0.00077 | 0.00066 to 0.00132 |
| 3 | 10 | 0.04 | 0.5 | 0.20 | 1 | 0.00142 | 0.00106 to 0.00212 |
| 4 | 10 | 0.04 | 5.0 | 0.18 | 6 | 0.00024 | 0.00021 to 0.00042 |
| 5 | 30 | 0.04 | 0.5 | 0.20 | 3 | 0.00043 | 0.00036 to 0.00072 |
| 6 | 30 | 0.04 | 5.0 | 0.06 | 6 | 0.00009 | 0.00007 to 0.00014 |

* Computer time per integration step was approximately constant at 0.4 to 0.6 sec./step for all runs.
† $(\Delta \mathrm{F.V.})_{\mathrm{ave}}$ is the average delta fraction vaporized per integration step used by the computer program.
‡ $(\Delta \mathrm{F.V.})_{\mathrm{calc}}$ is the limiting delta fraction vaporized per integration step calculated from Equation (47).

This simple test problem is a good example of the effect of instability of the numerical integration technique on total computer time. The computation time per integration step for this problem was approximately the same for all runs given in Table 3 (roughly 0.4 to 0.6 sec./integration step). However, increases in the reflux ratio ($R$) and decreases in the $H_n/H^o_{N+1}$ ratio tend to increase the $(L + KV)/H$ factor, which results in smaller allowable integration step sizes ($\Delta t$), as can be seen from Equation (46). This means, of course, that many more such integration steps are required to generate a complete solution, thus resulting in an increase in total computer time. The approximate value of $(L + KV)/H$ for this relatively small pilot-plant column for run 4 was approximately 250 $\mathrm{hr.}^{-1}$, a value which produced a rather stringent test of the stability of the numerical technique. With such a high $(L + KV)/H$ factor, the numerical technique is restricted to very small integration step sizes [see Equation (46)]. For larger commercial size batch columns which possessed smaller $(L + KV)/H$ factors, complete solutions were obtained in less than 4 min. of computer time, even though the computation time per increment was much longer than that of the pilot-plant column.

## CONCLUSIONS AND RECOMMENDATIONS

A mathematical model of multicomponent batch distillation was derived and a step-by-step calculation procedure outlined. The stability of several of the most widely used numerical integration routines (and a few newer ones) was investigated either theoretically or empirically using the simulation model. It was concluded that of the methods tried, the Adams-Moulton-Shell predictor-corrector method possessed the most favorable stability characteristics for numerical solution of transient distillation models.

It was also concluded, however, that even the most stable numerical integration techniques are not entirely satisfactory for the solution of transient distillation equations and other so-called "stiff" differential equations. The forms of these differential equations are such that a small error in the calculated compositions will produce large errors in the derivatives, which tend to propagate as the calculations progress.

It has been shown that Table 1 together with Equations (46) and (47) can be used to give a reliable estimate of the maximum allowable integration step size for transient distillation calculations. Use of this information with an estimate of computation time per integration step should provide one with an approximate value for overall computer time for any particular application.

Because of the extreme sensitivity of transient distillation equations to the stability of numerical integration techniques, the following areas are recommended for future research:

1. For pure digital simulation, the following classes of techniques are worthy of further investigation:
    a. Methods which transform the dependent variable in such a manner that the resulting systems of equations will not be stiff in the neighborhood of the value of the independent variable at which the transformation is made (*7*, *30*).
    b. Methods which do not depend upon polynomial fits to past history points, such as those using exponential differences and sums (*31* to *33*).
    c. Methods which were developed for systems which possess characteristics similar to those of a distillation column, that is, highly damped systems (*34*, *35*), coupled systems with greatly different time constants (*36*), etc.

2. Because of the tremendous speed advantage that the analog computer has over the digital computer in solving differential equations, the hybrid computer—which makes optimum use of the best features of both machines—should be investigated further as a practical means for performing dynamic distillation calculations (*19, 20*).

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## NOTATION

$C$ = number of components; also a value from corrector equation (use is always clear from context)
$D$ = overhead product rate
$f$ = arbitrary functional relationship
F.V. = fraction vaporized, that is, $\Delta D_{\text{total}}/H^o_{N+1}$
$H_n$ = liquid holdup on plate $n$
$I_n$ = liquid enthalpy on plate $n$
$J_n$ = vapor enthalpy on plate $n$
$K_{i,n}$ = equilibrium constant of component $i$ on plate $n$
$L_n$ = liquid flow from plate $n$
$M_C$ = modified corrector value
$M_P$ = modified predictor value
$N$ = total number of plates
$N + 1$ = reboiler
$P$ = value from the predictor equation
$P_n$ = pressure on plate $n$
$Q_o$ = heat removed at the overhead condenser
$Q_{N+1}$ = heat supplied to the reboiler
$R$ = reflux ratio
$t$ = independent variable, time
$T_n$ = temperature on plate $n$
$V_n$ = vapor flow from plate $n$
$x_{i,n}$ = liquid composition of component $i$ on plate $n$
$\vec{x}_n$ = liquid composition vector on plate $n$
$y_{i,n}$ = vapor composition of component $i$ in equilibrium with the liquid on plate $n$
$\vec{y}_n$ = vapor composition vector on plate $n$

### Greek Letters

$\Delta D$ = integration step size in terms of overhead product rate
$\Delta D_{\text{total}}$ = total product removed from column, Equation (30)
$\Delta$F.V. = integration step size in terms of fraction vaporized
$\Delta t$ = integration step size, hr.
$\overline{\Delta t}$ = normalized time increment, defined by Equation (40), dimensionless
$\delta_t$ = numerical approximation to the derivative $d/dt$
$|\lambda|_{\max}$ = absolute value of the largest negative eigenvalue of the Jacobian matrix
$\rho_n$ = density of the liquid on plate $n$

### Superscripts

$o$ = total reflux steady state value
$+$ = first instant after steady state
$'$ = first derivative with respect to time

### Subscripts

$C$ = value from the corrector equation
$i$ = component $i$
$n$ = arbitrary plate in the column
$N$ = bottom plate
$N + 1$ = reboiler
$o$ = overhead accumulator
$P$ = value from the predictor equation
$t$ = independent variable, time

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