$\xi(\lambda)$ = average age of the molecules having a life expectation, t
μ_{max} = maximum specific growth rate, t
$\tau = \mu_{max}\bar{t}$ = mean holding time in the overall system, dimensionless

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The Calculation of Unsteady State Multicomponent Distillation Using Partial Differential Equations

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A method is presented for calculating unsteady state multicomponent distillation using partial differential equations. The equations are solved by treating them as continuous in theoretical stage direction and stepped in time. Although some restrictions were placed on the problems actually solved, the method itself is not restricted by number of trays, number of components, number, type or combination of upsets, or by the thermodynamics of the system, and the method readily lends itself to hybrid computer solution.

There are two parts to the development of a mathematical simulation of unsteady state multicomponent distillation. First it is necessary to consider the physical and chemical properties of the system, by which to formulate its mathematical model. Second we must find a way of solving the equations of the mathematical formulation.

Marshall and Pigford (*8*) first published the differential equations describing the transient behavior of one distillation plate. Their work, and other early work was confined to binary systems, or to systems in which an additional nonvolatile component was present. A number of assumptions were made by Marshall and Pigford (*8*), and became standard in later work:

1. The equations were considered continuous in time, and differenced in theoretical stage. This would appear logical.
2. Linear equilibrium relationships between vapor and liquid compositions were assumed, of the form

$$y = mx + b \qquad (1)$$

3. Constant molal overflow was assumed. Later workers assumed that liquid flow rate was a linear function of temperature profile.
4. Ideal trays were assumed.

Authors who followed Marshall and Pigford include Lapidus and Amundson (*6*), Acrivos and Amundson (*1*), Mickley, Sherwood, and Reed (*9*), Rose and coworkers (*11* to *15*), Rosenbrock (*16*), Huckaba and Tour (*5*), Davidson (*2*), Wilkinson and Armstrong (*20*), Waggoner (*19*), and Holland (*4*).

The limiting assumptions of Marshall and Pigford (*8*) were relaxed as solution techniques for the derived mathematical models improved. The linear equilibrium relationships were replaced by an endless variety of equations, while for liquid flow rate, simplified enthalpy relationships were considered. Tetlow, Groves, and Holland (*18*) took into account tower hydraulics, and in addition to considering component enthalpies individually, used vapor-liquid equilibrium relationships of third order with respect to temperature.

In their earliest work, Marshall and Pigford (*8*) Laplace transformed their equations with respect to time, and thus obtained a set of linear algebraic equations, differenced in theoretical stage. Laplace transforming worked only on very simple mathematical models, so in general numerical solutions had to be obtained. Rose (*13* to *15*) used the Euler predictor for the time differential, and since his equations were written for each theoretical stage, he in effect differenced his equations in the theoretical stage direction using the obvious step size of one theoretical stage. He thus solved the problem using the method of lines. The very serious drawback of this system was that numerical stability could never be guaranteed, and, in fact, was only possible using very small step sizes. Later workers concentrated on alleviating the numerical stability problem by going to steadily more complex numerical solution techniques.

In this work it was concluded early that the real cause of the numerical instability problems that beset mathematical solutions was in the theoretical stage direction differencing. Numerical solutions had been obtained using very small time steps, but with the very large theoretical stage step size of one theoretical stage. This restriction was removed by approximating the theoretical stage direction with differential equations, and solving the equations numerically using a theoretical stage step size of less than one. The instability problems then completely vanished.

THEORY

Consider heat and mass balances over one theoretical stage in the rectifying section of a tower. Finite-difference subscript notation is used as in Figure 1*a*, and differential subscript notation is used as in Figure 1*b*. From Figure 1*a* we obtain the well-known equations for total mass balance over one theoretical stage:

$$V_{n+1} - V_n + L_{n-1} - L_n = \frac{d}{dt}(\Lambda_n - \lambda_n) \tag{2}$$

If we neglect vapor holdup λ_n in comparison to liquid holdup Λ_n, we obtain Equation (3) for one component:

$$V_{n+1}\, y_{n+1,i} - V_n y_{n,i} + L_{n-1}\, x_{n-1,i} - L_n x_{n,i} = \frac{d}{dt}(\Lambda_n x_{n,i}) \tag{3}$$

By enthalpy balance over one theoretical stage, we obtain Equation (4):

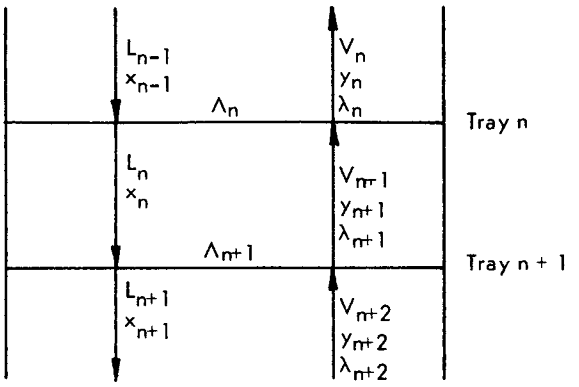
$$V_{n+1}\, h_{n+1} - V_n h_n + L_{n-1}\, H_{n-1} - L_n H_n = \frac{d}{dt}(\Lambda_n H_n) \tag{4}$$

By overall mass balance, we obtain Equation (5):

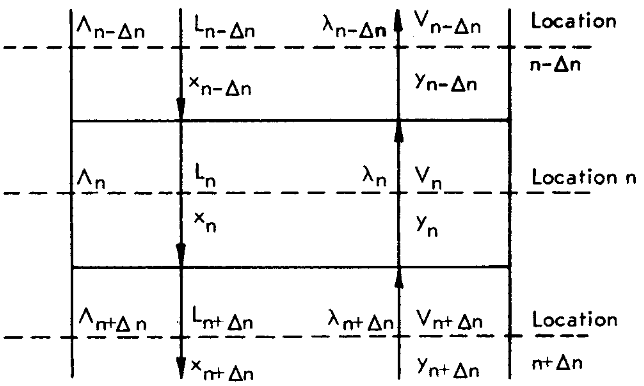
$$V_n = L_{n-1} + D + \overline{\Lambda} \tag{5}$$

From Equations (3) and (5) we obtain Equation (6):

$$y_{n,i} = \frac{L_{n-1}}{L_{n-1} + D + \overline{\Lambda}}\, x_{n-1,i} + \frac{D}{L_{n-1} + D + \overline{\Lambda}}\, x_{D,i} + \frac{(\overline{\Lambda x_i})}{L_{n-1} + D + \overline{\Lambda}} \tag{6}$$



(a) Subscripts Denote Equilibrium Stage Origin



(b) Subscripts Denote Tower Location

Fig. 1. Illustration of part of the rectifying section of a tower.

In difference subscript notation, we obtain from Equations (2), (3), and (4), Equations (7), (8), and (9):

$$V_n - V_{n-\Delta n} + L_{n-\Delta n} - L_n = \frac{d}{dt}(\Lambda_n + \lambda_n) \tag{7}$$

$$V_n y_{n,i} = V_{n-\Delta n}\, y_{n-\Delta n,i} + L_{n-\Delta n}\, x_{n-\Delta n,i} - L_n x_{n,i} = \frac{d}{dt}(\Lambda_n x_{n,i}) \tag{8}$$

$$V_n h_n - V_n h_{n-\Delta n} + L_{n-\Delta n} H_{n-\Delta n} - L_n H_n = \frac{d}{dt}(\Lambda_n H_n) \tag{9}$$

We note that in Equations (7), (8), and (9), Δn has been taken equal to one theoretical stage. Approximating differences by differentials, we obtain Equations (10), (11), and (12) from Equations (7), (8), and (9).

$$\frac{\partial V}{\partial n} = \frac{\partial L}{\partial n} + \frac{\partial \Lambda}{\partial t} \tag{10}$$

$$V\frac{\partial y_i}{\partial n} + y_i\frac{\partial V}{\partial n} = L\frac{\partial x_i}{\partial n} + x_i\frac{\partial L}{\partial n} + \Lambda\frac{\partial x_i}{\partial t} + x_i\frac{\partial \Lambda}{\partial t} \tag{11}$$

$$V\frac{\partial h}{\partial n} + h\frac{\partial V}{\partial n} = L\frac{\partial H}{\partial n} + H\frac{\partial L}{\partial n} + \Lambda\frac{\partial H}{\partial t} + H\frac{\partial \Lambda}{\partial t} \tag{12}$$

In difference subscript notation, Equations (13) and (14) are obtained from Equations (5) and (6). (See Figure 1 for clarification.)

$$V_n = L_n + D + \overline{\Lambda} \tag{13}$$

$$y_{n,i} = \frac{L}{L + D + \overline{\Lambda}}\, x_{n,i} + \frac{D}{L + D + \overline{\Lambda}}\, x_{D,i} + \frac{(\overline{\Lambda x_i})}{L + D + \overline{\Lambda}} \tag{14}$$

We will now attempt to condense Equations (10) to (14) into a more manageable system of equations by eliminating terms in V and y, but first it is necessary to find a substitute for the partial differential $\partial y_i/\partial n$. For $\Delta n = 1$, we have the equilibrium relationship

$$y_{n,i} = K_{n+\Delta n,i} x_{n+\Delta n,i} \tag{15}$$

from which it is both possible and generally accepted to derive Equation (16), which is rigorous.

$$\frac{\partial y_i}{\partial n} = \frac{\partial^2 (K_i x_i)}{\partial n^2} + \frac{\partial (K_i x_i)}{\partial n} \tag{16}$$

Since Equation (16) contains a second-order term, we start instead with Equation (17).

$$\frac{\partial y_i}{\partial n} = \frac{K_{n+\Delta n,i} x_{n+\Delta n,i} - K_{n,i} x_{n,i}}{\Delta n} \tag{17}$$

Keeping Δn equal to 1.0, we obtain Equation (18) from Equation (17).

$$\frac{\partial y_i}{\partial n} = y_{n,i} - K_{n,i} x_{n,i} \tag{18}$$

Equation (16) is accurate for all Δn, but Equation (18) is only accurate for $\Delta n = 1.0$. When Δn is allowed to take values less than 1.0, in order that Equation (18) remain valid, we must assume that the vapor composition profile between theoretical stages is represented by a Taylor series truncated after the second term.

$$y_{n,i} = y_{n-\Delta n,i} + \left(\frac{\partial y_i}{\partial n}\right) \delta n \Bigg|_{\delta n \le 1} \tag{19}$$

The approximation represented by Equation (19) was found to be unsatisfactory for trace components, as is discussed later.

From Equations (10) to (15) and (18) we are able to represent the system more conveniently by Equations (20) to (23) (see Appendix A).

$$\frac{\partial L}{\partial n} + \frac{\partial \Lambda}{\partial t} = \varphi (L + D + \overline{\Lambda}) \tag{20}$$

$$\frac{\partial x_i}{\partial n} + \frac{\Lambda}{L} \frac{\partial x_i}{\partial t} = \left[\frac{(L + D + \overline{\Lambda})(1 - K_i)}{L} - (1 + \varphi) \frac{D}{L} \right] x_i + \frac{D}{L} (1 + \varphi) x_{Di} + \frac{1 + \varphi}{L} \xi_i \tag{21}$$

where

$$\varphi = \left[\frac{1}{h - H} \left(\frac{L}{L + D + \overline{\Lambda}} \frac{\partial H}{\partial n} + \frac{\Lambda}{L + D + \overline{\Lambda}} \frac{\partial H}{\partial t} - \frac{\partial h}{\partial n} \right) \right] \tag{22}$$

and

$$\xi_i = \overline{\Lambda} x_i - (\overline{\Lambda x_i}) \tag{23}$$

A further equation was developed for temperature as a function of theoretical stage, starting with Equations (24) and (25).

$$\sum \frac{\partial x_i}{\partial n} = 0.0 \tag{24}$$

$$\sum K_i x_i = 1 \tag{25}$$

In this work mixing effects on vapor-liquid equilibrium were neglected, and for K_i Equation (26) was used.

$$K_i = \frac{C_i}{\Pi} e^{C_i'/T} \tag{26}$$

This simplification was merely a convenience, and it would have been just as easy, from the standpoint of the theory, although perhaps not from the standpoint of computation, to have included mixing effects.

By differentiating Equations (25) and (26), we may derive Equation (27).

$$\frac{\partial T}{\partial n} = \frac{T^2 \sum_i \left(K_i \frac{\partial x_i}{\partial n} \right)}{\sum_i (K_i C_i' x_i)} \tag{27}$$

For the stripping section of the tower, we may similarly derive the following equations:

$$\frac{\partial x_i}{\partial m} - \frac{\Lambda}{L} \frac{\partial x_i}{\partial t} = \left[\frac{(L - B - \overline{\Lambda})(K_i - 1)}{L} - \frac{B}{L} (1 - \varphi) \right] x_i + \frac{B}{L} (1 - \varphi) x_{Bi} + \frac{1 - \varphi}{L} \xi_i \tag{28}$$

$$\frac{\partial L}{\partial m} = \varphi (L - B - \overline{\Lambda}) \tag{29}$$

$$\varphi = \frac{1}{h - H} \left[\frac{L}{L - B - \overline{\Lambda}} \frac{\partial H}{\partial m} - \frac{\Lambda}{L - B - \overline{\Lambda}} \frac{\partial H}{\partial t} - \frac{\partial h}{\partial m} \right] \tag{30}$$

Equation (27) remains unaltered in the stripping section.

Finally we write the overall heat balance equations. For the rectifying section we obtain Equation (31).

$$(L + D + \overline{\Lambda}) h + R H_R = L H + (R + D) h_R + (\overline{\Lambda H}) \tag{31}$$

For the stripping section we obtain Equation (32).

$$L H + H_{\text{reb}} = (L + D + \overline{\Lambda}) h + B H_B + (\overline{\Lambda H}) \tag{32}$$

In place of Equations (21) and (28), Equations (33) and (34) were employed for trace components. Trace components are defined as components whose distillate or bottoms compositions, in the rectifying or stripping sections, respectively, are less than 1% of their feed composition.

$$\frac{\partial x_i}{\partial n} + \frac{\Lambda}{L} \frac{\partial x_i}{\partial t} = \left[\ln \left(\frac{L}{K_i (L + D + \overline{\Lambda})} \right) \right] x_i + \frac{(1 + \varphi)}{L} \xi_i \tag{33}$$

$$\frac{\partial x_i}{\partial m} - \frac{\Lambda}{L} \frac{\partial x_i}{\partial t} = \left[\ln \left(\frac{K_i (L - B - \overline{\Lambda})}{L} \right) \right] x_i + \frac{(1 - \varphi)}{L} \xi_i \tag{34}$$

It is possible to derive Equations (33) and (34) from Equations (21) and (28) by making the usual assumptions for trace components, and by eliminating the assumption of Equation (19), which is invalid for trace components. The derivations are given in Appendix A.

STEADY STATE AND INITIALIZATION

The system of equations developed was first considered for the steady state, by neglecting all time-dependent terms. This was done for two reasons; to check the agreement of the steady state results with the results of other, well-tested methods; and to develop the initialization routine for the unsteady state calculation. Comparisons were made for a six-hydrocarbon feed, 50-theoretical stage tower, using the results given by a well-tried multicomponent matrix solution program (*10*). The lower limits of accuracy for integration were checked by comparing results for a five-hydrocarbon system with the results obtained using the program of Hansen et al. (*3*) for six-, ten-, and fourteen-theoretical stage towers, using a very high reflux ratio of 2.5 (*10*). Agreement was found to be excellent in all cases, but began to deteriorate where there were three or less theoretical stages between the overhead or bottom and the feed (*10*).

INITIAL ESTIMATION OF TRACE COMPOSITIONS

An interesting aspect of the steady state equations was that they allowed the development of further equations to make initial estimates of overhead and bottoms traces compositions. In Equation (33) time-dependent terms are ignored, and liquid and temperature profiles are assumed to be constant; then by integrating Equation (33) we obtain Equation (35).

$$x_{Di} = K_{1,i}x_{f,i}\left[\frac{L}{K_i(L + D)}\right]^{1-N_{F,D}} \tag{35}$$

Similarly, from Equation (34) we derive Equation (36).

$$x_{Bi} = x_{f,i}\left[\frac{K_i(L - B)}{L}\right]^{1-N_{F,B}} \tag{36}$$

In Equation (35) liquid flow rate was taken equal to the reflux rate, while in Equation (36) it was taken equal to the sum of bottoms product and reboil rates. The temperature was taken equal to the overhead or bottoms temperature, plus 80% of the difference to the feed temperature.

STEADY STATE REESTIMATION OF DISTILLATE AND BOTTOMS COMPOSITIONS

Distillate and bottoms compositions were reestimated on the basis of the differences in compositions at the feed tray, as calculated from the two ends of the column. The reiteration procedure used was the well-known method based on stripping factors (*17*). Equation (37), derived from Equation (35), and Equation (38), derived from Equation (36), were found to be more accurate for reestimating trace component compositions for the first two iterations.

$$(x_{Di})_{\text{co}} = K_{1,i}(x_{f,i})_{\text{co}}\left(\frac{K_{1,i}(x_{f,i})_{\text{ca}}}{x_{D,i}}\right)^{+\frac{(N_{f,d})_{\text{co}} - 1}{(N_{f,d})_{\text{ca}} - 1}} \tag{37}$$

$$(x_{B,i})_{\text{co}} = (x_{f,i})_{\text{co}}\left(\frac{(x_{f,i})_{\text{ca}}}{x_{B,i}}\right)^{-\frac{(N_{f,b})_{\text{co}} - 1}{(N_{f,b})_{\text{ca}} - 1}} \tag{38}$$

THE INTEGRATION PROCEDURE

Integration was carried out using Runga-Kutta-Gill numerical integration in the theoretical stage direction, with step sizes of between 0.5 and 0.1 theoretical stage. 0.5 was the step size employed for steady stage integration and 0.2 was the usual step size for unsteady state integration. There was no appreciable increase in accuracy when smaller step sizes were taken. In unsteady state calculations time steps of between 0.05 and 0.2 hr. were used.

In addition to Equation (26) for vapor-liquid equilibrium, Equation (39) was used to calculate enthalpies.

$$H = H_a + H_b T + H_c T^2 \tag{39}$$

With each step in the theoretical stage direction, the calculated temperature and flow rates were corrected to ensure heat and material balance. The temperature correction was found to be 0.01°F. or less for most of the tower, rising to as much as 1°F. adjacent to the feed, overhead, or bottoms. Flow rate corrections were generally negligible, and very rarely more than 1% of the previous flow rate.

CONVERGENCE

At the start of each new step in time, estimates were made for the distillate and bottoms compositions using equations which are given and derived elsewhere (*10*). The estimated distillate and bottoms compositions were reestimated after each pair of integrations (from the tower ends to the feed tray). The reestimation method used was analogous to the steady state reestimation procedure outlined above, and is available elsewhere (*10*).

The unsteady state convergence procedures were not reliable, and it is probable that a number of arbitrary constants would have to be altered by trial and error to obtain convergence for each new system calculated.

RESULTS

In Figures 2, 3, 4, and 5 results are reported for a 10% increase in the reflux ratio to a 50-theoretical stage tower, with a feed of six hydrocarbons. Tower conditions are listed in Table 1. In Figure 2 an interesting oscillation will be noted for the distillate concentration of hexane. This result is in agreement with the work of Levey (*7*). Constant total molal holdup was assumed for all the calculations presented in these results, and liquid mixing effects were ignored. The number of iterations required for closure are listed in Table 2.

In Figure 6 results are compared with some reported by Tetlow, Groves, and Holland (*18*) for a 24-theoretical stage tower, with a five-hydrocarbon feed, subject to a step change of 10% in the feed rate. Direct comparisons could not be made, since there were a number of differences in the problems solved:

1. Tetlow et al. considered varying molal holdup, which was not considered by the computer program of this method, as written.

2. It was not clear what transient reboiler and condenser duties were used by Tetlow et al. They would appear to have been calculated on the basis of constant steam and cooling water rates, together with fixed overall heat transfer coefficients for each heat exchanger.

3. Tetlow et al.'s equations for component enthalpy and vapor-liquid equilibrium neglected mixing effects, but were otherwise entirely different from Equation (39).

Fortunately the effects of these differences were not overwhelming. The variation in molal holdup on trays was small, as was the variation in condenser and reboiler duties, and although the forms of the component enthalpy and vapor-liquid equilibrium constants were different, suitable adjustments of the empirical constants in Equations (26) and (39) enabled the calculated values to be in close agreement. Tetlow et al.'s case III was, however, the closest parallel, and is the one reported for comparison. Details of the towers solved are given in Table 3, and the number of iterations required are given in Table 2. The results will be seen to be a good agreement.

TABLE 1. SPECIFICATIONS FOR THE SIX-COMPONENT FIFTY-THEORETICAL STAGE PROBLEM SOLVED AS IN FIGURES 2 TO 5

Number of trays	50 (Reboiler counts as 1)
Feed tray	25
Feed rate	50 moles/hr.
Distillate rate	20 moles/hr.
Bottoms rate	30 moles/hr.
Initial reflux rate	20 moles/hr.
Upset reflux rate	22 moles/hr.
Condenser holdup	5 moles
Reboiler holdup	5 moles
Tray holdup	1 mole per tray
Tower pressure	300 lb./sq. in. abs.
Pressure drop per tray	0 lb./sq. in. per tray
Feed Composition:	
Ethane	0.05 mole fraction
Propane	0.30 mole fraction
Butane	0.40 mole fraction
Pentane	0.10 mole fraction
Hexane	0.10 mole fraction
Feed condition	Saturated liquid
Reflux condition	Subcooled to 100°F.

TABLE 2. THE NUMBER OF ITERATIONS REQUIRED FOR CLOSURE AS A FUNCTION OF TIME

Step No.	Time, hr.	Iterations A	Iterations B	Iterations C
1a	0.05		17	
1	0.1	13	18	9
2	0.2	16	25	4
3	0.3	10	19	4
4	0.4	17	26	6
5	0.5	9	20	10
6	0.6	3	19	9
7	0.7	5	8	
8	0.8	7	12	
9	0.9	4	10	
10	1.0	10	7	
11	1.1	5	6	
12	1.2	12	6	
13	1.3	5		
14	1.4	10		
15	1.5	4		
16	1.6	2		

A, see Table 1; B, see Table 3; C, see Table 4.

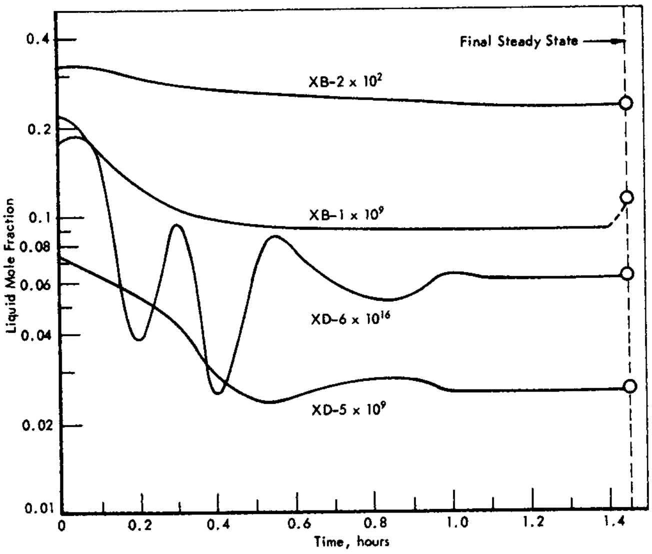


Fig. 2. Six-component 50-tray tower response to a 10% increase in reflux rate. Ethane and propylene compositions in the bottoms and pentane and hexane composition in the overhead.

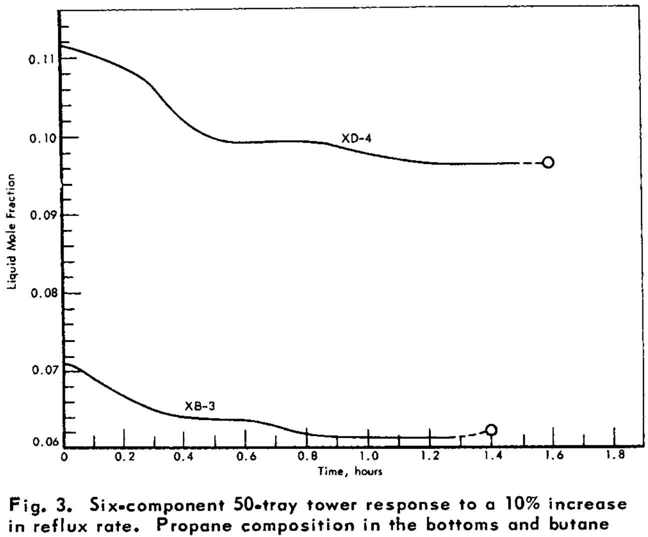


Fig. 3. Six-component 50-tray tower response to a 10% increase in reflux rate. Propane composition in the bottoms and butane composition in the distillate.

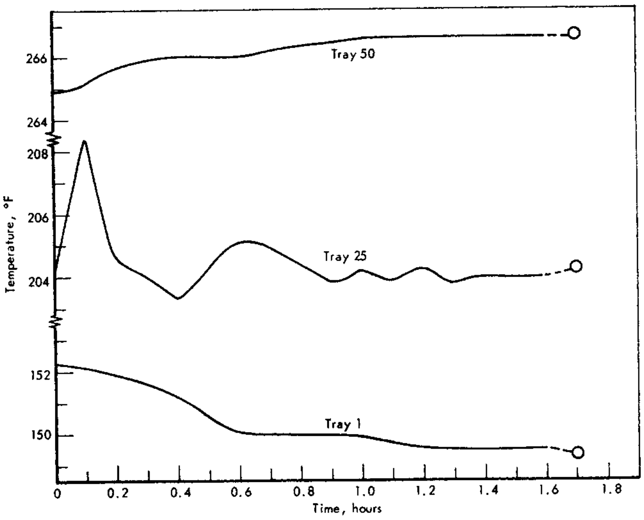


Fig. 4. Six-component 50-tray tower response to a 10% increase in reflux rate. Temperature profiles on trays 1, 25, and 50.

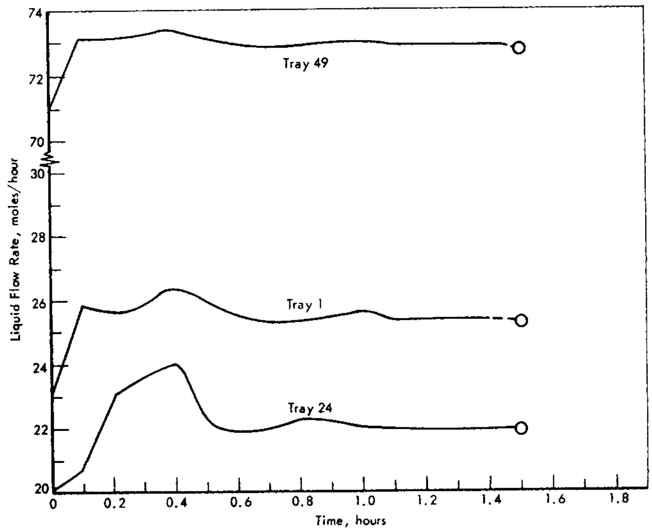


Fig. 5. Six-component 50-tray tower response to a 10% increase in reflux rate. Liquid flow rate profiles on trays 1, 24, and 49.

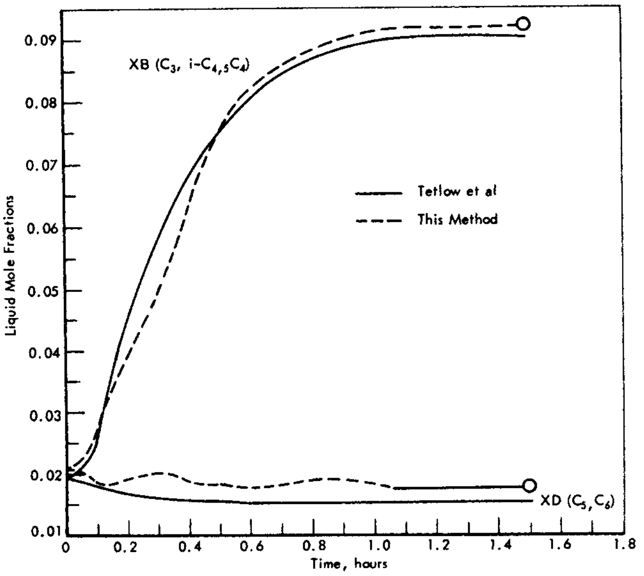


Fig. 6. Five-component 24-tray tower comparison with the results of Tetlow et al.'s Case III.

In Figures 7, 8, and 9 results are presented for the tower described in Table 3, subject to a series of six multiple upsets, as in Table 4. The number of iterations per step in time are given in Table 2. It will be seen that the handling of large numbers of multiple upsets presents no difficulty.

TABLE 3. SPECIFICATIONS OF THE PROBLEMS SOLVED BY TETLOW ET AL. AND BY THIS PAPER, AND IN FIGURE 6

	This method		Tetlow et al. Case III	
Number of trays	24		24	
Feed tray	5		5	
Initial feed rate	600 moles/hr.		600 moles/hr.	
Upset feed rate	660 moles/hr.		660 moles/hr.	
Initial distillate rate	300 moles/hr.		300 moles/hr.	
Initial reflux rate	600 moles/hr.		600 moles/hr.	
Condenser holdup	60 moles		120 cu. ft.	
Reboiler holdup	70 moles		210 cu. ft.	
Tray holdup	1 mole		varying	
Tower pressure	300 lb./sq. in. abs.		300 lb./sq. in. abs.	
Pressure drop per tray	0 lb./sq. in. abs.		0 lb./sq. in. abs.	
Feed composition:	Initial		Upset	
	Liquid	Vapor	Liquid	Vapor
Propane	0.163	0.3895	0.1559	0.3835
i-Butane	0.1407	0.1978	0.1296	0.1890
Butane	0.1463	0.1690	0.1333	0.1603
Pentane	0.3230	0.1819	0.3241	0.1922
Hexane	0.2270	0.0618	0.2571	0.0750
Feed rates, moles/hr.	502.02	97.98	584.76	75.24

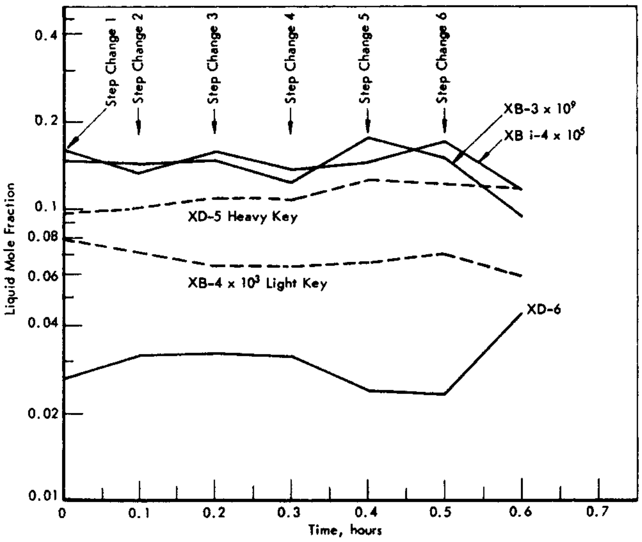


Fig. 7. Five-component 24-tray tower subject to six sequential multiple step changes. Composition profiles.

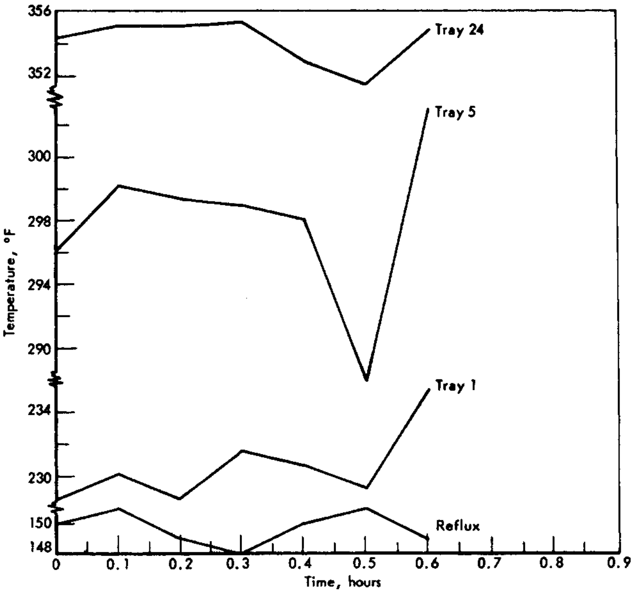


Fig. 8. Five-component 24-tray tower subject to six sequential multiple step changes. Temperature profiles.

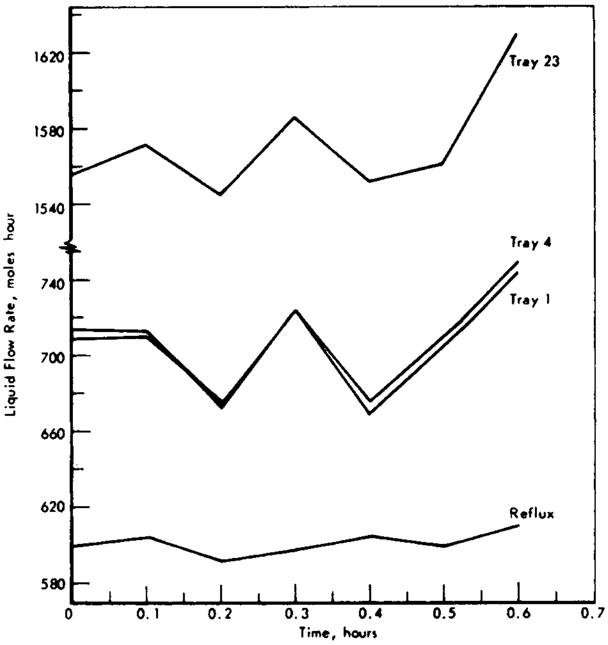


Fig. 9. Five-component 24-tray tower subject to six sequential multiple step changes. Liquid flow rate profiles.

TABLE 4. SPECIFICATIONS FOR THE SIX-UPSET PROBLEM SOLVED AS IN FIGURES 7 TO 9

	Step change number						
Feed	Initial	1	2	3	4	5	6
Propane	0.16	0.16	0.16	0.157	0.169	0.168	0.154
i-Butane	0.15	0.147	0.15	0.151	0.15	0.15	0.145
Butane	0.14	0.138	0.131	0.14	0.142	0.147	0.146
Pentane	0.33	0.33	0.33	0.325	0.333	0.335	0.329
Hexane	0.22	0.225	0.229	0.227	0.206	0.20	0.226
T_{ref}, °F.	150.0	151.0	149.0	148.0	150.0	151.0	149.0
Feed, moles/hr.	600.0	601.0	603.0	598.0	600.0	599.0	602.0
Ref, moles/hr.	600.0	604.0	592.0	598.0	605.0	600.0	610.0
Dist., moles/hr.	300.0	302.0	297.0	300.0	302.0	298.0	302.0

CONCLUSIONS

A method has been developed which allows the transient response of a multicomponent distillation tower to be calculated for a wide range of multiple upsets to the tower operating conditions. The results appear to be accurate. The main disadvantages of the method are:

1. The convergence procedure is dependent upon a number of empirical constants.
2. Due to the high cost of computer time, only a limited number of problems were solved, thus a claim that the method is general cannot be substantiated.
3. All the problems solved assumed no liquid mixing nonidealities, and constant total molal holdup on the trays. (Note that componential holdups may vary.) To remove these assumptions would not affect the integration in the tray direction, but it would represent an added strain on an already unreliable convergence procedure.

The main advantage of the method presented here over previous work is that by allowing a step size in the theoretical stage direction of less than one, the time step size may be taken as large as 6 min., even immediately following a large step change, without any numerical instability. The equations derived for composition and liquid profile changes were found to be highly stable, even in the presence of a certain amount of random noise. Instabilities, when they occurred, were always caused by very poor initial estimates of distillate and bottoms compositions, arising from the closure routine.

It was not possible to make direct comparisons with other computer programs for solution times. However, in this case, times of between 30 and 100% of the real problem time were found necessary. It should be noted, however, that between 90 and 95% of computer time was taken up with numerical integration. Since this method is abundantly suited to hybrid solution, computer times of 5% of real time would be realistic on a hybrid computer.

NOTATION

A_i = multiplier of x_i in partial differential equation for component i in the rectifying section
B = bottoms product rate, moles/hr.
b_i = bottoms product rate for component i
B_i = multiplier of x_{di} in partial differential equation for component i in the rectifying section; see Equation (43)
C_i = first constant in the equation for K_i
C_i' = second constant in the equation for K_i
D = distillate rate, moles/hr.
d_i = distillate rate for component i, moles/hr.
F = feed rate, moles/hr.
F_i = feed rate of component i, moles/hr.
H = liquid enthalpy, B.t.u./mole
h = vapor enthalpy, B.t.u./mole
H_a, H_b, H_c = constants of the equation for component liquid enthalpy
h_a, h_b, h_c = constants of the equation for component vapor enthalpy
K_i = vapor-liquid equilibrium constant for component i
L = liquid flow rate, moles/hr.
N_m = total number of trays
N_f = feed tray number
$N_{f,d}$ = number of trays in the rectifying section
$N_{f,b}$ = number of trays in the stripping section
P = pressure, lb./sq. in. abs.
R = reflux rate, moles/hr.
R_v = reboiler holdup, moles
T = temperature
t = time
V = vapor flow rate, moles/hr.
v_i = vapor flow rate of component i, moles/hr.
W = reflux flow rate , moles/hr.
x_i = liquid mole fraction of component i
$(x_{f,i})_d$ = feed tray composition of component i as calculated from the top tray
$(x_{f,i})_b$ = feed tray composition of component i as calculated from the bottom tray
Y_i = vapor composition of component i

Greek Letters

Λ = liquid holdup, moles (for the interval Δn of the column if difference notation, as in Figure 1*b*, but for one theoretical stage in equilibrium stage notation, as in Figure 1*a*

$$\overline{\Lambda} = \sum_{n}^{1} \frac{d}{dt}(\Lambda_n)$$

$$\overline{\Lambda x_i} = \sum_{n}^{1} \frac{d}{dt}(\Lambda_n x_{i,n})$$

$$\overline{\Lambda H} = \sum_{n}^{1} \frac{d}{dt}(\Lambda_n H_n)$$

λ = vapor holdup, moles
ξ_i = $\pm\{\overline{\Lambda} x_i - (\overline{\Lambda x_i})\}$ (+ in the rectifying section; – in the stripping section)
φ = enthalpy term in liquid flow rate differential equation

Subscripts

B = bottoms product
co = corrected
ca = calculated
D = distillate
F = feed tray
f = feed stream
i = component number
j = tray number
m = stripping section tray number
n = rectifying section tray number
R = reflux
reb = reboiler
t = time
$t + \Delta t$ = time $t + \Delta t$
w = bottom tray

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APPENDIX A

The Derivation of Equations (20) and (21)

In the following derivations, the location subscript n of the difference system as per Figure 1*b* is dropped. We start with Equation (11)

$$V\frac{\partial y_i}{\partial n}+y_i\frac{\partial V}{\partial n}=L\frac{\partial x_i}{\partial n}+x_i\frac{\partial L}{\partial n}+\Lambda\frac{\partial x_i}{\partial t}+x_i\frac{\partial \Lambda}{\partial t} \tag{11}$$

For V we substitute into Equation (11) with the version of Equation (13) below

$$V=L+D+\overline{\Lambda} \tag{1A}$$

written in differential form, $\overline{\Lambda}$ is given by Equation (2*A*).

$$\overline{\Lambda}=\int_1^n\left(\frac{\partial\Lambda}{\partial t}\right)dn \tag{2A}$$

Thus, by differentiating Equation (1*A*) with respect to n, we obtain the substitution for $\partial V/\partial n$:

$$\frac{\partial V}{\partial n}=\frac{\partial L}{\partial n}+\frac{\partial \Lambda}{\partial t} \tag{3A}$$

For y_i, we substitute into Equation (11) with Equation (4*A*), obtained from Equation (14)

$$y_i=\frac{L}{L+D+\overline{\Lambda}}x_i+\frac{D}{L+D+\overline{\Lambda}}x_{D,i}+\frac{(\overline{\Lambda x_i})}{L+D+\overline{\Lambda}} \tag{4A}$$

For $\partial y_i/\partial n$ we substitute into Equation (11) with Equation (5*A*), obtained from Equation (19).

$$\frac{\partial y_i}{\partial n}=y_i-k_i x_i \tag{5A}$$

By substituting Equations (1*A*) to (5*A*) into Equation (11), we obtain Equation (6*A*).

$$\frac{1}{D(x_i-x_{Di})+\Lambda x_i-(\overline{\Lambda x_i})}\frac{\partial x_i}{\partial n}+\frac{(\Lambda/L)}{D(x_i-x_{Di})+\Lambda x_i-(\overline{\Lambda x_i})}\frac{\partial x_i}{\partial t}$$
$$+\frac{1}{L(L+D+\overline{\Lambda})}\left(\frac{\partial L}{\partial n}+\frac{\partial\Lambda}{\partial t}\right)=\frac{(L+D+\overline{\Lambda})(1-K_i)x_i}{L(D(x_i-x_{Di})+\overline{\Lambda x_i}-(\overline{\Lambda x_i}))}-\frac{1}{L} \tag{6A}$$

We note again the use of the general notation:

$$\overline{f}=\int_0^n\left(\frac{\partial f}{\partial t}\right)dn \tag{7A}$$

By the same substitutions [Equations (1*A*) to (5*A*)] into Equation (12), we obtain Equation (8*A*).

$$\frac{\partial L}{\partial n}=\frac{L}{h-H}\frac{\partial H}{\partial n}-\frac{(L+D+\overline{\Lambda})}{h-H}\frac{\partial h}{\partial n}-\frac{\partial\Lambda}{\Lambda t}-\frac{\Lambda}{h-H}\frac{\partial H}{\partial t} \tag{8A}$$

φ is defined by Equation (22).

$$\varphi=\left[\frac{1}{h-H}\left(\frac{L}{L+D+\overline{\Lambda}}\frac{\partial H}{\partial n}+\frac{\Lambda}{L+D+\overline{\Lambda}}\frac{\partial H}{\partial t}-\frac{\partial h}{\partial n}\right)\right] \tag{22}$$

Substituting φ into Equation (8*A*), we obtain Equation (21).

$$\left(\frac{\partial L}{\partial n}+\frac{\partial\Lambda}{\partial t}\right)=\varphi(L+D+\overline{\Lambda}) \tag{21}$$

We now substitute Equation (21) into Equation (6*A*), and obtain Equation (9*A*).

$$\frac{\partial x_i}{\partial n}+\frac{\Lambda}{L}\frac{\partial x_i}{\partial t}=\left[\frac{(L+D+\overline{\Lambda})}{L}(1-K_i)-(1+\varphi)\frac{D}{L}\right]x_i$$
$$+\frac{D}{L}(1+\varphi)x_{Di}+\frac{1+\varphi}{L}[\overline{\Lambda}x_i-(\overline{\Lambda x_i})] \tag{9A}$$

But from Equation (23)

$$\xi_i=\overline{\Lambda}x_i-(\overline{\Lambda x_i}) \tag{23}$$

Substitution of Equation (24) into Equation (9*A*) yields Equation (22) directly.

The Derivation of Equations (33) and (34)

Consider Equation (24). For the case of constant holdup

$$\xi_i=\Lambda\frac{\partial x_i}{\partial t} \tag{10A}$$

Even for the case of nonconstant holdup, Equation (10*A*) is a good approximation of Equation (24), since $\partial\Lambda/\partial t$ is usually much smaller than $\partial x_i/\partial t$. Furthermore φ, from Equation (23), is also usually very small, of the order of 0.01. Thus Equation (10*A*) yields the approximation of Equation (11*A*).

$$\frac{\Lambda}{L}\frac{\partial x_i}{\partial t}\simeq\frac{1+\varphi}{L}\xi_i \tag{11A}$$

Substituting Equation (11*A*) into Equation (22), we obtain Equation (12*A*). We note that x_{Di} has been neglected for a trace component.

$$\frac{\partial x_i}{\partial n}=\left[\frac{(L+D+\overline{\Lambda})(1-K_i)}{L}-(1+\varphi)\frac{D}{L}\right]x_i \tag{12A}$$

Let us now replace Equation (19) for $\partial y_i/\partial n$ by Equation (13*A*). We recall that Equation (19) became an approximation when tray direction step sizes less than 1.0 were taken. Equation (13*A*) is

$$\frac{\partial y_i}{\partial n}=y_i-f_i x_i \tag{13A}$$

where f_i is an as yet undetermined function. We may then reduce Equation (12*A*) to Equation (14*A*):

$$\frac{\partial x_i}{\partial n}=g_i x_i \tag{14A}$$

where g_i is a function of f_i.

If we integrate Equation (14*A*), assuming g_i to be constant over a small interval, we obtain Equation (15*A*).

$$x_{n,i}=x_{n-\Delta n,i}\,e^{gi(\Delta n)} \tag{15A}$$

However, neglecting $x_{D,i}$, we obtain Equation (16*A*) from Equation (14).

$$x_{n,i}=\frac{1}{K_{n,i}}\left[\frac{L}{L+D+\overline{\Lambda}}x_{n,i}+\frac{(\overline{\Lambda x_i})_n}{L+D+\overline{\Lambda}}\right] \tag{16A}$$

The second term inside the brackets in Equation (16*A*) represents the integral of the component holdup change with time up to point n. For a trace component this is negligibly small, since $x_{n,i}$ is such a rapidly increasing function. Therefore as Δn in Equation (15*A*) tends to zero

$$e^{gi(\Delta n)}=\frac{L}{K_{n,i}(L+D+\overline{\Lambda})} \tag{17A}$$

and

$$\frac{\partial x_{n,i}}{\partial n}=\left[\ln\left(\frac{L}{K_i(L+D)}\right)\right]x_{n,i} \tag{18A}$$

It is of interest to note that the multiplier of $x_{n,i}$ in Equation (22) may be rewritten as

$$1-K_i\left(\frac{L+D}{D}\right)-\frac{D\varphi}{L}$$

the first two terms of which are the first two terms of the expansion of the multiplier of $x_{n,i}$ in Equation (18*A*).

Combining Equations (11*A*) and (18*A*), we obtain Equation (33).

$$\frac{\partial x_i}{\partial n}+\frac{\Lambda}{L}\frac{\partial x_i}{\partial t}=\left[\ln\left(\frac{L}{K_i(L+D+\overline{\Lambda})}\right)\right]x_i+\frac{(1+\varphi)}{L}\xi_i \tag{33}$$

The derivation of Equation (34) is identical to the derivation of Equation (33), and is therefore not repeated.

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