* = characteristic property
$\bar{\ }$ = partial molar property

Subscripts

1 = solute
2 = solvent or pure component
c = critical property

LITERATURE CITED

Amagat, E. H., "Internal Pressure of Fluids," *Annals de chem. phys.*, **28**, 5 (1913).

Chueh, P. L., and J. M. Prausnitz, "A Generalized Correlation for the Compressibilities of Normal Liquids," *AIChE J.*, **16**, 471 (1969).

Gubbins, K. E., and J. P. O'Connell, "Liquid Compressibilities and Angle Dependent Correlation Functions," in preparation.

Lyckman, E. C., C. A. Eckert and J. M. Prausnitz, "Generalized Reference Fugacities for Phase Equilibrium Thermodynamics," *Chem. Eng. Sci.*, **20**, 685, 703 (1965).

O'Connell, J. P., "Thermodynamic Properties of Solutions from Correlation Functions," *Mol. Phys.*, **20**, 27 (1971a).

———., "Molecular Thermodynamics of Gases in Mixed Solvents," *AIChE J.*, **17**, 653 (1971b).

Orentlicher, M., and J. M. Prausnitz, "Thermodynamics of Hydrogen Solubility in Cryogenic Solvents at High Pressures," *Chem. Eng. Sci.*, **19**, 775 (1964).

Prausnitz, J. M., "Thermodynamic Representation of High Pressure Vapor-Liquid Equilibria," *ibid.*, **18**, 613 (1963).

———., and P. L. Chueh, *Computer Calculations for High Pressure Vapor-Liquid Equilibria*, p. 27, Prentice-Hall, Englewood Cliffs, N. J. (1968).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, pp. 6-42, 571-636, McGraw Hill, New York (1966).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, pp. 26-36, 249-307, Plenum Press, New York (1969).

Spencer, C. F., and R. P. Danner, "Improved Equation for Prediction of Saturated Liquid Density," *J. Chem. Eng. Data*, **17**, 236 (1972).

Manuscript received March 28, 1972; revision received May 26, 1972; paper accepted July 20, 1972.

Calculation Method for the Response Time to Step Inputs for Approximate Dynamic Models of Distillation Columns

A calculation method to determine the response time to be used for approximate mathematical models is developed for the dynamic behavior of distillation columns. Previous work has shown that the concept of *Inventory time* can be successfully used to approximate the response time, that is, the 60% point of the step response, of distillation columns operating at a high degree of separation. A modified version of the inventory time method, based on the minimum change of storage, has been developed to predict the response time for other ranges of separation within reasonable bounds of error, ± 10%. Only steady state and design data were used. A rigorous nonlinear simulation generates the steady state and transient data upon which the approximate models are based.

While the modified inventory time method developed cannot handle every possible operating condition with the desired degree of accuracy, it has been shown to apply over a much wider range of operating conditions than the original inventory time method.

W. A. WEIGAND
A. K. JHAWAR and
T. J. WILLIAMS

School of Chemical Engineering
Purdue University
Lafayette, Indiana 47907

SCOPE

Distillation, the most widely used separation technique in the processes industries, is a nonlinear dynamic process. The extent of the nonlinear behavior is highly dependent on the range of operation of the column. In addition, disturbances in column operation can cause product quality to be upset for considerable periods of time. Since many columns operate at very high rates of production, a decrease in the product which is off specification could potentially lead to great economic savings. A means of substantially reducing this period is to use a combination

of both feedback and feedforward control. Feedforward control, in turn, requires an accurate model of the process which is simple in form since it must be used on line. Furthermore, in order to account for model dependence on operating condition, an approximate model which adapts to the existing condition is desirable. Also, approximate dynamic models which are determined from steady state design data and calculations alone, in this sense similar to the models developed by Thal-Larson (1960) for a class of heat exchangers, would be very desirable since they would avoid the need to introduce experimental disturbances for model determination whenever the level of operating conditions change. The desirability for an adaptive model dependent on steady state design data which can then be precalculated and tabulated or, if calculation time permits, continuously update the variable parameter values is pointed out by Williams (1972) with reference to the future use of process control computers. With this is mind the present study was undertaken with the objective of producing improved models which could eventually be used as described above.

Distefano, May, and Huckaba (1967) considered the problem of a model for feedforward control of a distillation tower subject to a sequence of upsets. Avoiding the assumptions of constant molal overflow and linear equilibrium relationships, a digital computer was used to precompute a feedforward control scheme from their mathematical model for a prescribed sequence of upsets to the distillation column. Their results were then verified experimentally. The drawback of their technique was that their complex mathematical model needed an average of 12 minutes of computing time on the IBM 7094 for a single transient run, therefore, it could not be used on-line. Yet significantly these authors recognized that the inherent nonlinearity of the system for high separations could not be ignored. DeLorenzo et al. (1970) and Bernardi et al. (1971) have studied the transient behavior of distillate composition in distillation columns. The authors, dealing with the inherent nonlinear behavior, define an asymmetry function to account for the fact that, for step changes of either vapor or reflux, the leaving and returning transients have different response times. The fact that linear models, developed by Lamb et al. (1961), are adequate for certain operating conditions has been shown by Luyben et al. (1963). Other studies which deal with the development of approximate linear models in terms of transfer function relationships have been performed by Gilliland and Mohr (1961), Mohr (1965), and Whal and Harriott (1970).

An attempt to approximate column dynamics in a more general way was made by Rosenbrock (1960) when he introduced the concept of a *disturbance function.* With a similar objective in mind the concept of *inventory time* was introduced by Moczek et al. (1965) for a three-component mixture. Working with very fine separations, the inventory time was shown to be equal to the 60% response point for step inputs. It was also shown to be equal to the sum of time constants and the dead time for second-order dead time models. It is to be noted that although the inventory time was used to determine a linear approximate model, it is reflective of the nonlinear behavior since it indicates changes in response with operating level in the column and also the dependence of the response on the magnitude of the input. A further study of inventory time was made by Bhat and Williams (1969, 1970). The present work is a continuation of the utility of inventory time and its application to the problem mentioned previously. The approach used employs the examination of some of the concepts of approximate modeling. The method developed in this study is based on the nonlinear behavior produced by a rigorous nonlinear simulation of distillation columns with 10, 25, and 40 plates.

CONCLUSIONS AND SIGNIFICANCE

A method to predict the 60% response point for step inputs of feed composition and reflux rate for distillation columns operating under a wide range of conditions has been developed. The desired accuracy was set at ± 10%, but, when our method applies, the error is usually much less. The method, based on the minimum change of storage of the lighter component of a binary, requires only steady state data and design variables. The data used to develop the method was generated by the rigorous simulation of six columns ranging from 10 to 40 plates. The columns investigated possess a wide range of holdups and liquid and vapor rates. Rigorous simulation, rather than experimentation with actual columns, was chosen for two reasons. First, the cost of experimentation in terms of equipment and time is prohibitive for the size and range of conditions for the columns used in this study. Secondly and more importantly, it has been well established that rigorous simulation, usually after some adjustment of some parameters in the program, can produce actual column behavior. Two particular examples of this are to be found in the work Distefano, May, and Huckaba (1967) for columns exhibiting strong nonlinear behavior and the work of Luyben et al. (1963) for columns with linear behavior.

Analysis of the data led to the conclusion that there exist various regions of steady state operation which possess distinct dynamic behavior, each of which requires a particular analysis. These are:

1. A region of very fine (overhead mole fraction > 0.99 and bottoms < 0.01) separation at both ends of the column which exhibits very strong nonlinear behavior. Equations (16) and (17) predict the 60% response point for this region, the average error being 5.7%.
2. A region where the separations is not as fine as the first region but is still a good separation (overhead mole fraction > 0.97 and bottoms < 0.03). The dynamic behavior is still strongly nonlinear and Equations (16) and (17) also apply here. The average error is 4.2%.
3. A region of intermediate separation (overhead > 0.80 and bottoms < 0.20) which still exhibits nonlinear behavior. The method developed here does not produce the desired degree of accuracy for this condition, the average error being 23.0%.
4. A region of low separation (overhead < 0.80 and bottoms > 0.20) where the columns studied approached linear behavior. Equations (18) apply here, the average error being 6.1%. For regions (1), (2), and (3) the % error refers to the slower responding end and the method for inventory time developed here predicts which end this is. In region (4) the error refers to both the slower and faster responding ends with the corresponding errors of 3.8 and 8.3%, respectively. The errors produced by the method of Moczek et al. (1965), the original version of inventory time, Equation (4), are 8.5, 13.5, 22.8, and

16.3% for regions (1) to (4), respectively. Their method only predicts the slower responding end and does not indicate which end this will be.

The nonlinear behavior of regions (1), (2), and (3) listed above is reflected in both the dependance of response time with the size and direction of the step input from a given initial steady state. The nonlinear behavior is also shown to be asymmetric, the ratio of leaving to returning transients for a given steady state are shown to vary from 1.14 to 0.094 in Table 7 for a particular column.

Some significant advances towards developing an approximate but accurate model based only on steady state and design data have been made in this work. The calculation method developed here accurately predicts the 60% response time. This, in future work, will be used to determine the parameter values for approximate dynamic models proposed for the column response. These models will eventually be used for the adaptive feedforward digital control of distillation columns operating over a wide range of separations.

SOME ASPECTS OF APPROXIMATE COLUMN MODELS

Distillation is a complex multivariate nonlinear process. Many models based on linearization of the fundamental equations have been developed. These models are adequate for small disturbances for columns producing a low separation. Another approach commonly taken is to develop transfer function type relationships from either experimental data or computed transient data. Such models, however, lack generality and are apt to be limited to particular columns over a special range of operating conditions. However, there have been attempts to represent the overall dynamics of a distillation column by a more general approach. The objective is to define a single unified variable which is a characteristic quantity depending upon the column, the operating conditions and the particular type of upset.

Rosenbrock (1960) introduced the concept of a disturbance function to study departures from equilibrium of distillation columns. As defined by the author this is given for a binary system by the equation

$$\frac{1}{2} DF = \sum_{n=0}^{N+1} \left[\frac{d}{dt} U_n x_n \right] \tag{1}$$

The rate of change of the lighter material is summed over all the trays, the reboiler and the condenser. The author compares DF with the kinetic energy of a dissipative system, whereby after the external disturbance has ceased the amount of disturbance within the column is being reduced by the action of the column itself. It is shown to be a Lyapunov function for the column. However, this concept has not been developed to the point where it is used for the prediction of column behavior to various upsets.

Another attempt at defining a single unified variable was the introduction of the concept of change of *inventory time* by Moczek et al. (1965). The present work is based on the inventory time concept. The set of nonlinear differential equations which rigorously describe the process were solved on a digital computer. The program was based on the relaxation method developed by Ball (1961) with the θ method of convergence of Holland (1963). Although our rigorous simulation can handle mixtures of several components, only binary systems were investigated in this work. Multicomponent mixtures will be the topic of future studies.

As defined by the Moczek et al. (1965) inventory time is given by the equation

$$T_{INV} = \frac{(INV)_f - (INV)_i}{(F_v x_{Fv} - F_i x_{Fi}) - (D_v - D_i) x_{Di} - (W_v - W_i) x_{Wi}} \tag{2}$$

One can define the initial and final inventory as the total amount of light material in the column initially and following an upset. Thus Equation (2) becomes

$$T_{INV} = \frac{U_C(x_{Df} - x_{Di}) + U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni})}{(F_v x_{Fv} - F_i x_{Fi}) - (D_v - D_i) x_{Di} - (W_v - W_i) x_{Wi}} \tag{3}$$

Using an overall material balance for the light material for the initial and final steady states and assuming that the liquid and vapor rates change quickly compared to compositions, the denominator of Equation (3) can be simplified to produce the following form for inventory time

$$T_{INV} = \frac{U_C(x_{Df} - x_{Di}) + U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni})}{D_f(x_{Df} - x_{Di}) + W_f(x_{Wf} - x_{Wi})} \tag{4}$$

The terms in Equation (4) are obtained from only initial and final steady state data and can be interpreted as follows:

$U_C(x_{Df} - x_{Di})$ = change in storage in condenser (5a)

$U_W(x_{Wf} - x_{Wi})$ = change in storage in reboiler (5b)

$\sum_{n=1}^{N} U_n(x_{nf} - x_{ni})$ = change in storage summed over all the plates (5c)

$D_f(x_{Df} - x_{Di})$ = change in flow out with distillate (5d)

$W_f(x_{Wf} - x_{Wi})$ = change in flow out with bottoms (5e)

Thus,

$$T_{INV} = \frac{\text{total change in storage for whole column}}{\text{total change in flow out of whole column}} = \frac{\Delta(\text{storage})}{\Delta(\text{flow})} \tag{6}$$

This definition of inventory time is the definition for the time constant of a well-stirred first-order mixing tank. Thus, the change of inventory time has physical meaning as a pseudo first-order time constant for the complete holdup of the column.

Inventory time, when it applies, gives only the response time of one end of the column, the most affected end. A well-stirred first-order mixing tank with two outlet streams would have the same response time for both streams. Thus, a one-tank model can lead to the approximation of only one, the larger, response time when used as the approximate model for a distillation column.

Moczek, et al. (1965) simulated a high-purity Benzene-Toluene-Xylene column and applied their model to it with remarkable success. However, when Bhat and Williams (1969a, b) simulated other systems, particularly ones that were not such high-purity columns, this model was found to be inadequate.

Bhat and Williams modified the equation of Moczek et al. with the addition of a term which made it applicable over a larger range. By graphical integration of the terms on the right-hand side of the unsteady state material balance for a column with constant holdups, that is,

$$U_C \frac{dx_D}{dt} + U_W \frac{dx_W}{dt} + \sum_{n=1}^{N} U_n \frac{dx_n}{dt} = Fx_F - Dx_D - Wx_W \qquad (7)$$

they obtain modified expressions for the inventory time. This leads to the equations

$$\tau_1 = \frac{U_C(x_{Df} - x_{Di}) + U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni}) - (\tau_2 - \tau_1)(W_f x_{Wf} - W_f x_{Wi})}{D_f(x_{Df} - x_{Di}) + W_f(x_{Wf} - x_{Wi})} \qquad (8a)$$

$$\text{for } \tau_1 > \tau_2$$

and

$$\tau_2 = \frac{U_C(x_{Df} - x_{Di}) + U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni}) - (\tau_1 - \tau_2)(D_f x_{Df} - D_f x_{Di})}{D_f(x_{Df} - x_{Di}) + W_f(x_{Wf} - x_{Wi})} \qquad (8b)$$

$$\text{for } \tau_2 > \tau_1$$

where τ_1 and τ_2 are the response times the distillate and bottoms, respectively. These equations are actually not independent but one and the same equation put in two forms, depending upon which is the larger response time.

They present results which show significant improvements over the equation of Moczek et al. However, Equations (8) do not yield the response times from steady state alone as did the original equation of Moczek et al. and, as the authors themselves point out, prior knowledge of $(\tau_2 - \tau_1)$ is necessary in order to use the above equations. They could find no way to predict $(\tau_1 - \tau_2)$ a priori from the steady state data at hand. They overcame this difficulty by first running the transient simulations to obtain $(\tau_2 - \tau_1)$. This essentially amounts to knowing the answers before embarking upon a method of solution for the problem. This, of course, renders Equations (8) useless for the actual prediction of τ_1 and τ_2 as first envisaged by Moczek et al., that is, by using steady state design only. However, the form of Equations (8) permits a modified version of the inventory time concept to be developed.

An analysis of the modified inventory time equation leads to a two noninteracting tanks model shown in Figure 1. Although not thought of in these terms by Bhat and Williams, after some contemplation one can arrive at the two tanks model. As in the case of the Moczek et al., Equation (4), we can interpret the Bhat and Williams equations in terms of changes in storage and flow. Using the same definitions as before, we can write Equations (8a) and (8b) as

$$\tau_1 = \frac{\Delta(\text{Total storage}) - (\tau_2 - \tau_1)\,\Delta(\text{Flow out bottoms})}{\Delta(\text{Total flow out})} \qquad (9a)$$

$$\text{for } \tau_1 > \tau_2$$

and

$$\tau_1 = \frac{\Delta(\text{Total storage}) - (\tau_1 - \tau_2)\,\Delta(\text{Flow out distillate})}{\Delta(\text{Total flow out})} \qquad (9b)$$

$$\text{for } \tau_2 > \tau_1$$

We can now derive Equations (9a) and (9b) considering the two non-interacting tanks model as shown on Figure 1. A material balance for each tank yields

$$q_{10}x(t) - q_{10}y_1(t) = V_1 \frac{dy_1}{dt} \qquad (10a)$$

$$q_{20}x(t) - q_{20}y_2(t) = V_2 \frac{dy_2}{dt} \qquad (10b)$$

By definition, we obtain from Equations (10)

$$\tau_1 = \frac{V_1}{q_{10}} = \frac{V_1 y_1}{q_{10} y_1} = \frac{\Delta(\text{Storage in tank 1})}{\Delta(\text{Flow out of tank 1})} \qquad (11a)$$

$$\tau_2 = \frac{V_2}{q_{20}} = \frac{V_2 y_2}{q_{20} y_2} = \frac{\Delta(\text{Storage in tank 2})}{\Delta(\text{Flow out of tank 2})} \qquad (11b)$$

Also, we know

$$\Delta(\text{Total storage}) = V_1 y_1 + V_2 y_2 \qquad (12)$$

$$\Delta(\text{Total flow out}) = q_{10} y_1 + q_{20} y_2 \qquad (13)$$

Equations (9a) and (9b) can be derived from Equations (11), (12), and (13) by an overall material balance in the following manner

$$\tau_1 = \frac{V_1 y_1}{q_{10} y_1} = \frac{(V_1 y_1 + V_2 y_2) - V_2 y_2}{q_{10} y_1} = \frac{\Delta(\text{Total storage}) - \tau_2(q_{20} y_2)}{q_{10} y_1} \qquad (14)$$

Adding $\tau_1(q_{20}y_2/q_{10}y_1)$ to both sides of Equation (14) we obtain

$$\tau_1 = \frac{\Delta(\text{Total storage}) - (\tau_2 - \tau_1)(\text{Flow out bottoms})}{\Delta(\text{Total flow out})} \qquad (15a)$$

Similarly we can derive

$$\tau_2 = \frac{\Delta(\text{Total storage}) - (\tau_1 - \tau_2)(\text{Flow out distillate})}{\Delta(\text{Total flow out})} \qquad (15b)$$

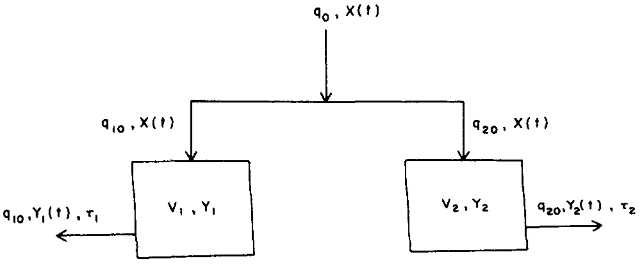

Fig. 1. Two noninteracting tanks model.

Noting the identity of Equations (8), (9), and (15) we see that the equations of Bhat and Williams can be derived from the noninteracting tanks model. We therefore see that Equations (11) can be used to find τ_1 and τ_2. It is simple to identify the flow out of tank 1 as the distillate stream and the flow out of tank 2 as the bottoms stream. However, it is not obvious how to divide the column holdup so that we can identify two separate tanks and the change in storage of each. A method for this last task is developed in the sequel.

Equations (8) do not require dividing column holdup into two parts but they cannot be used since $(\tau_2 - \tau_1)$ could not be predicted a priori. We avoid the need to determine $(\tau_2 - \tau_1)$ by appropriately dividing the column holdup into two parts.

METHOD OF MINIMUM CHANGE OF STORAGE

Of the several arbitrary choices for a suitable location to divide the column, one obvious location is the feed plate. Unfortunately, it is quickly found that this technique does not work in general, except at low separations.

Some consideration of the approximate model, Figure 1, leads one to the conclusion that the location for column division should be where the interaction between the two parts would be at a minimum. Some typical profiles of Δ(storage) versus plate number are shown in Figure 2. Figure 2 is the same column, that is, column III, operating at both high and low separations. The operating conditions for the results on this figure are given in Tables 1 and 5. Examination of this figure illustrates that these profiles do show a point along the column where the Δ(storage) is an absolute minimum. A high degree of success was achieved in predicting the larger response time for a column using this approach as is shown in Tables 2 to 4 and 6. It proved at least as good or better than the original equation of Moczek et al. for very fine separations. Over other ranges of separation it proved far superior.

It was observed that most of these minimum changes of storage occurred at one of the ends of the column for fine separations and the feed plate for columns producing poor separation. This is also shown on Figure 2.

COLUMNS OPERATING WITH FINE SEPARATIONS AT BOTH ENDS

Considering for the moment fine separations, if the minimum occurs at the top end of the column, in the context of the above definitions of inventory time we define

$$\tau_1 = \frac{U_C(x_{Df} - x_{Di})}{D_f(x_{Df} - x_{Di})} = \text{Minor time constant} \quad (16a)$$

$$\tau_2 = \frac{U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni})}{W_f(x_{Wf} - x_{Wi})}$$

$$= \text{Major time constant} \quad (16b)$$

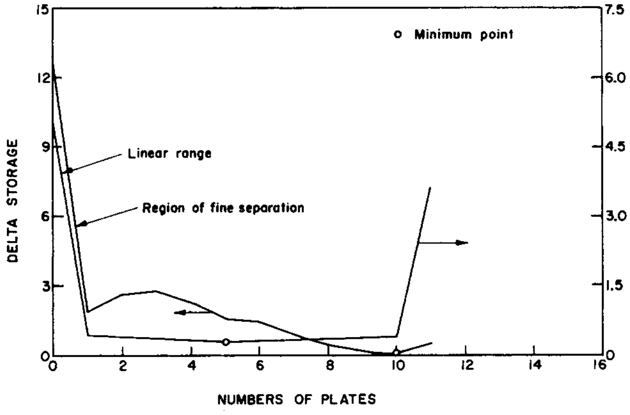

Fig. 2. Delta storage versus plate number. Column III, nonlinear range and linear range.

TABLE 1. SUMMARY OF COLUMN PARAMETERS AND CHARACTERISTICS

Chemical system	Column I Benzene-toluene	Column II Toluene-*n*-octane	Column III Water-acetone	Column IV Benzene-toluene	Column V Benzene-toluene	Column VI Benzene-toluene
Average rel. volatility	2.42	1.667	3.4	2.42	2.42	2.42
Average column pressure	760 mm	760 mm	760 mm	760 mm	760 mm	760 mm
No. of plates	25.0	40.0	10.0	25.0	40.0	25.0
Feed plate location	13.0	20.0	5.0	13.0	20.0	13.0
Condenser holdup	300.0	7,000.0	150.0	300.0	300.0	300.0
Plate holdup	60.0	1,500.0	10.0	15.0	15.0	60.0
Reboiler holdup	300.0	7,000.0	150.0	300.0	300.0	300.0
Total column holdup	2,100.0	74,000.0	400.0	975.0	1,200.0	2,100.0
Initial feed rate	25.0	850.0	8.0	15.0	25.0	25.0
Initial distillate rate	10.0	460.0	3.5	7.0	12.0	10.0
Top reflux ratio	0.60	0.80	0.75	0.6667	0.6075	0.60
Initial liquid rate	15.0	1,840.0	10.5	14.0	18.57	15.0
Initial bottoms rate	15.0	390.0	4.5	8.0	13.0	15.0
Bottom reflux ratio	0.616	0.85	0.73	0.72	0.70	0.62
Initial vapor rate	25.0	2,300.0	14.0	21.0	30.57	25.0
Initial feed composition	0.45	0.53	0.45	0.50	0.48	0.377
Initial distillate composition	0.96969	0.96915	0.99391	0.99762	0.99700	0.89682
Initial bottoms composition	0.10354	0.01075	0.02696	0.06459	0.00284	0.03076
Separation achieved	0.86615	0.95840	0.96695	0.93303	0.99416	0.86606
Maximum separation possible	0.86615	0.96594	0.96695	0.98502	0.99416	0.91257

1. The reflux ratios are internal reflux ratios.
2. All flow rates are in g-moles/min.
3. All holdups are in g-moles.
4. All compositions are in mole fractions.

Table 2. Summary of Calculated Inventory Times and Actual Response Times

Column	Actual response time			Prediction of inventory time % error		
	Run	τ_{Top} (60%)	τ_{Bot} (60%)	Moczek et al.	Bhat, Williams	Minimum method
Column I	1	187.5	105.2	36.3	−11.0	47.0
	2	228.0	86.8	47.3	−8.7	6.6
	3	154.1	99.2	26.7	−11.1	32.0
	4	216.2	94.8	27.2	−1.8	17.5
	5	147.1	132.6	13.8	6.3	51.0
	6	167.0	59.2	58.6	8.9	14.6
Column II	1	161.8	406.8	22.1	6.1	4.8
	2	220.6	106.6	7.5	3.7	2.6
	3	114.3	263.6	16.8	6.5	1.2
	4	169.5	83.1	7.4	5.2	4.1
	5	84.4	273.4	20.0	7.3	5.2
	6	153.3	56.5	10.5	7.7	6.7
Column III	1	42.7	71.0	1.9	5.7	0.7
	2	157.0	34.9	23.3	−13.1	4.3
	3	32.0	59.3	0.3	−0.6	0.3
	4	107.5	20.5	13.7	2.4	5.7
	5	35.4	60.2	7.1	6.1	1.6
	6	125.7	27.0	22.6	6.9	7.6
Column IV	1	58.5	74.4	19.0	18.8	0.9
	2	446.6	73.4	57.2	2.6	90.0
	3	54.0	68.5	−0.8	−0.9	1.0
	4	204.1	45.6	28.9	2.6	2.7
	5	44.7	67.7	7.7	0.8	0.9
	6	462.1	79.0	59.2	3.4	91.0
Column V	1	80.4	122.5	5.8	−2.5	4.0
	2	147.3	40.3	6.6	4.7	4.5
	3	67.3	91.4	13.6	13.0	2.7
	4	100.9	31.1	3.6	2.6	2.6
	5	55.3	141.8	14.4	7.3	6.8
	6	155.8	39.8	9.2	6.5	6.4
Column VI	1	162.0	143.1	1.5	4.5	1.1
	2	165.1	113.8	6.1	2.4	23.0
	3	147.4	133.6	−4.2	10.4	17.9
	4	144.7	82.2	8.0	1.2	5.2
	5	125.3	115.1	−3.9	−6.6	0.5
	6	105.6	98.9	−3.3	−5.0	12.0

Run 1— + 5% feed composition change.
2— −5% feed composition change.
3— + 10% feed composition change.
Run 4— −10% feed composition change.
5— + 5% reflux rate change.
6— −5% reflux rate change.

If the minimum occurs at the bottom end of the column, the inventory times are given by

$$\tau_1 = \frac{U_C(x_{Df} - x_{Di}) + \sum_{n=1}^{N} U_n(x_{nf} - x_{ni})}{D_f(x_{Df} - x_{Di})}$$
$$= \text{Major time constant} \qquad (17a)$$

$$\tau_2 = \frac{U_W(x_{Wf} - x_{Wi})}{W_f(x_{Wf} - x_{Wi})} = \text{Minor time constant} \qquad (17b)$$

Examination of the above equations reveals that the expressions for the major response time in each case are similar to the equation of Moczek et al., Equation (4). However, Equations (16) and (17) indicate which is the slower end. This cannot be done with Equation (4).

Further insight into the behavior of columns at high separations was obtained by interpreting the responses in terms of changes which cause transients which further increase or decrease the separation. It was observed that Equation (4) worked well when both ends of a column were at a very fine separation. Any upset to such a column has the effect of lowering the separation at one end while further increasing it at the other end. Invariably it was found that the end with the decreased separation in terms of concentration change was the most affected and also had the slower response. The criterion for classifying a column in terms of purity of separation was observed to correspond to the manner in which a column responded to changes in input. Any change in feed rate, feed composition, reflux rate, or vapor rate from the steady state value causes the distillate, bottoms and plate compositions all along the column to change. Externally, the column reflects the effect of the input in terms of new distillate and bottoms compositions or, in other words, in terms of different lighter material outflow rates in the distillate and bottoms streams. Internally, the total holdup in terms of the lighter material changes resulting in a storage change as a function of plate number.

A positive composition or reflux upset will raise the compositions of both the distillate and the bottoms. But, as the distillate composition is already very high there is very little room for it to increase further. On the other hand, the bottoms composition is very low in the lighter component and, therefore, it readily increases. Consequently we see that the distillate end is further moved towards a purer product while the bottoms moves to a less pure product. Following a similar line of analysis we see that a negative composition or reflux upset will produce the in-

TABLE 3. MODIFIED COLUMN CHARACTERISTICS AND RESPONSE TIMES

Column	I	IV	VI
Distillate rate	11.0	7.5	9.5
Top reflux ratio	0.70	0.70	0.75
Bottoms rate	14.0	7.5	15.5
Bottom reflux ratio	0.72	0.764	0.70
Vapor rate	36.66	25.0	38.0
Distillate composition	0.99788	0.99715	0.98957
Bottom composition	0.01953	0.00285	0.00185
Separation achieved	0.97835	0.99430	0.98772
Maximum separation possible	0.97835	0.99430	0.98772

	Actual response time			Prediction of Inventory time, % error	
	Run	τ_{Top} (60%)	τ_{Bot} (60%)	Moczek et al.	Minimum method
Column I	1	100.5	174.5	6.55	5.7
	2	541.0	101.0	26.5	4.34
	3	64.5	155.5	7.16	6.55
	4	495.0	87.5	22.6	6.06
Column IV	1	123.0	424.0	13.7	7.55
	2	271.5	67.0	7.93	7.0
	3	86.0	368.0	13.04	8.96
	4	221.5	48.0	8.35	7.45
Column VI	1	65.0	165.0	7.45	6.25
	2	186.5	44.0	8.31	6.7
	3	48.0	138.0	7.4	6.52
	4	154.5	33.0	8.1	6.93

Run 1— + 5% feed composition change.
2— − 5% feed composition change.
3— + 5% reflux rate change.
4— − 5% reflux rate change.

TABLE 4. COLUMN IV OPERATING AT LOWER REFLUX RATIO

	$R = 0.642$
Distillate rate	7.5
Bottoms rate	7.5
Vapor rate	20.95
Distillate composition	0.992535
Bottoms composition	0.007465
Separation ($x_D - x_B$)	0.985070

	Actual times		Prediction of inventory time			
Run	τ_{Top} (60%)	τ_{Bot} (60%)	τ_{MOW}	% error	τ_{MIN}	% error
1	77.5	146.5	134.33	8.3	139.23	4.96
2	169.0	49.5	152.39	9.83	159.21	5.80
3	63.0	109.0	103.20	5.32	105.06	3.77
4	120.5	36.5	113.54	5.84	115.88	3.84
5	46.0	101.5	94.53	6.90	95.93	5.50
6	109.0	30.0	101.15	7.20	102.60	5.87

Run 1— + 5% feed composition change.
2— − 5% feed composition change.
3— + 10% feed composition change.
4— − 10% feed composition change.
5— + 5% reflux ratio change.
6— − 5% reflux ratio change.

verse effect. This naturally leads us to the conclusion that for positive upsets the bottoms end is the more affected end and has the slower response; for negative upsets the distillate end has the slower response. Thus the method of minimum change of storage works well with columns producing a fine separation when the upsets have an effect as outlined above.

The above discussion indicates a method which enables one to know beforehand whether the method of minimum change of storage will apply. This method was successful over a wider range of operating conditions for high separations than the equation of Moczek et al. (1965), Equation (4).

EFFECT OF VERY SMALL INPUTS

One consequence of the above analysis was the investigation of the so-called "linear" behavior of the column. It seems reasonable to expect that as the upsets were made smaller and smaller the column would approach linear behavior. Such an investigation was carried out on Column III and the results (not shown here) were that the response time asymptotically approached a certain value and eventually became independent of the magnitude or direction of upset. Also, as the inputs become smaller the inventory time as defined by Equation (4) or Equations (16) or (17) approach the value of the actual response time. This indicates that, in addition to predicting the response time for columns producing fine separations, the inventory time of Moczek et al. (1965) and the minimum method of inventory time presented here applies for the case of infinitesimal small inputs. Of course, the case of such small inputs is of no concern in practical terms since the changes they produce will also be extremely small.

COLUMNS OPERATING AT LOW SEPARATIONS AT BOTH ENDS

Another possibility which follows from the above is that if a column were to be operated in a condition such that both ends of the column were free to move in response to an input (as opposed to the behavior at high separations), then the column response should approach linear behavior. Such would be the case for a column producing a poor separation. Luyben et al. (1963) made an extensive experimental study in this region of operation and concluded that the response behavior could be adequately repre-

TABLE 5. COLUMN PARAMETERS FOR THE LINEAR REGION

Column	I	II	III	IV	V	VI
Distillate comp.	0.7839	0.7847	0.7812	0.8017	0.9029	0.7729
Bottoms comp.	0.2273	0.2283	0.1924	0.1983	0.0897	0.2075
Separation achieved	0.5566	0.5564	0.5888	0.6034	0.8132	0.5654
Liquid rate	5.25	687.25	0.37	3.14	11.82	6.02
Vapor rate	15.38	1,150.0	3.89	10.71	24.0	13.64
Top reflux ratio	0.35	0.60	0.10	0.30	0.50	0.45
Bot. reflux ratio	0.50	0.74	0.45	0.58	0.64	0.43
Max. sep. possible	0.57303	0.73529	0.5888	0.60731	0.81805	0.59114
Distillate rate	10.0	460.0	3.50	7.5	12.0	7.5
Bottoms rate	15.0	390.0	4.50	7.5	13.0	17.5

Table 6. Calculated Inventory Times and Actual Response Times for the Linear Region

Column		Process response times			Predicted response times				
		τ_1 (60%)	τ_2 (60%)	τ_{MOW}	% Error	τ_{Top}	Error	τ_{Bot}	Error
I	1.	122.5	73.0	88.1	28.0	124.8	−1.9	70.6	3.3
	2.	113.5	76.0	89.4	21.2	112.1	1.2	75.8	0.3
	3.	127.0	71.5	87.6	31.0	131.7	−3.7	68.6	4.1
	4.	109.5	77.5	90.2	17.6	106.2	3.0	79.4	−2.5
II	1.	98.0	94.75	95.4	2.7	100.2	2.2	91.7	3.2
	2.	93.0	100.25	96.9	3.3	91.2	2.0	102.3	−2.0
	3.	100.5	92.5	94.8	5.7	105.4	−4.9	87.6	5.3
	4.	90.5	102.75	97.9	4.7	87.1	3.8	109.5	−6.6
III	1.	63.5	41.0	51.06	19.70	63.32	0.28	44.9	9.4
	2.	63.5	41.0	52.26	17.70	60.36	4.95	46.8	14.0
	3.	64.4	42.0	50.58	21.5	64.81	0.62	44.3	3.1
	4.	64.05	39.9	52.92	17.2	58.84	8.1	48.0	19.3
IV	1.	72.25	62.75	68.1	5.8	74.6	−3.2	64.5	−2.8
	2.	69.0	65.25	69.2	−0.3	70.3	−1.9	68.4	−4.8
	3.	74.25	62.0	67.8	8.7	76.9	−3.6	63.1	−1.8
	4.	68.0	66.25	70.1	−3.1	68.2	−0.3	71.6	−6.6
V	1.	67.75	49.50	56.1	17.2	72.9	−7.6	48.1	2.8
	2.	60.75	57.75	61.8	−1.6	62.0	−2.0	61.7	−6.9
	3.	72.0	47.25	55.8	22.6	80.9	−12.3	45.6	3.5
	4.	70.0	51.25	74.0	−5.7	56.5	19.3	94.8	85.0
VI	1.	14.45	67.5	90.2	37.4	152.2	−5.3	64.0	5.2
	2.	132.5	69.5	91.2	31.2	133.9	−1.1	68.3	1.7
	3.	150.5	66.0	89.8	40.4	162.7	−8.1	62.4	5.5
	4.	127.0	70.5	91.9	27.6	125.9	0.9	71.0	−0.7

Run 1— +5% feed composition change.
2— −5% feed composition change.
Run 3— +10% feed composition change.
4— −10% feed composition change.

Table 7. Reverse Response for Column III

Feed composition changes		Response times		
Upset	Column end	Going away	Coming back	Ratio
+5%	Distillate	42.7	138.0	0.31
	Bottoms	71.0	57.5	1.24
−5%	Distillate	157.0	68.5	2.30
	Bottoms	34.9	280.5	0.12

Reflux ratio changes		Response times		
Upset	Column end	Going away	Coming back	Ratio
+5%	Distillate	35.36	135.5	0.26
	Bottoms	60.20	53.0	1.14
−5%	Distillate	125.7	63.0	1.99
	Bottoms	27.0	288.0	0.094

sented by linear models. The method of minimum change of storage also confirmed this and again proved superior to Equation (4) as is shown by the results in Table 6.

When considering columns operating with low purity product streams the minimum change of storage usually occurs somewhere near the middle of the column rather than towards any end. For the columns studied here this occurred at the feed plate. In such a case, if the minimum occurs in general at the Mth plate the equations for inventory time are

$$\tau_1 = \frac{U_C(x_{Df} - x_{Di}) + \sum_{n=M+1}^{N} U_n(x_{nf} - x_{ni})}{D_f(x_{Df} - x_{Di})} \tag{18a}$$

$$\tau_2 = \frac{U_W(x_{Wf} - x_{Wi}) + \sum_{n=1}^{M} U_n(x_{nf} - x_{ni})}{W_f(x_{Wf} - x_{Wi})} \tag{18b}$$

REVERSE RESPONSE CHARACTERISTICS

Another interesting problem occurs when trying to predict inventory time from steady state data alone. Consider the case of a column operating at any given initial steady state. In response to an upset the column moves to a new steady and we can calculate the inventory time for this response. Now, if the upset is removed the column would again settle back to its original initial steady state. For both these responses all the steady state data would be identical, only reversed in sign. This then yields the same value for the inventory time. But, as shown in Table 7, the response times are usually not the same. De Lorenzo et al. (1970) and Bernardi et al. (1971) studied this problem and came up with some plots to predict this type of asymmetry in the distillate product response of distillation columns to upsets in reflux or vapor rate. They do not, however, deal with the problem of predicting the response time from steady state data.

DISCUSSION

The present study was initiated to find a way of priori predicting $(\tau_2 - \tau_1)$ from steady state data alone. During the course of this work it appeared that $(\tau_2 - \tau_1)$ was not a fundamental quantity and no general method could be developed to predict this. Instead considerable insight was gained into various regions of operation of distillation columns and a method was developed which improved considerably over the original Moczek et al. (1965) Equation (4).

Table 2 shows that the inventory time as determined by the method of minimum change of storage is superior in predicting the response time for every run in Columns II, III, and V. Column IV has low prediction errors in all runs except 2 and 6. In a majority of these cases it is also significant that this method is superior to the Bhat and Williams (1969a,b) prediction which relies upon information from the transient runs. Column VI has low errors for runs 1, 4, and 5 but large errors for runs 2, 3, and 6; all runs of Column I except for run 2 have large prediction errors. It was found that one key to the problem lay in explaining how Columns IV and VI, had large errors for small upsets, (−5%), whereas for larger upsets in the same direction, (−10%), the errors were small.

The conclusion reached after examining the data was that these columns were not producing a high purity product at one end or the other. The smaller upsets consequently do not have the effect of producing small composition changes one end and large changes at the other. However, the larger upset is great enough to have the effect of producing the type of composition changes described above. To confirm this idea, some of the operating conditions for these columns were changed so as to bring these to a condition where both ends were producing a pure product. For any given column and feed composition, changes in the reflux rate and vapor rate could be made to produce the desired effect. Table 3 shows the changes that were made and the effect these had on the distillate and bottoms compositions. The results in Table 3 confirm the idea stated above.

The data in Tables 2, 3, and 4 clearly illustrate the response of distillation columns producing a fine separation. The response times change by a factor of 2 to 8 for a change in direction for an input of given magnitude. As an example we look at runs 3 and 4 of Modified Column I of Table 3: a +5% reflux upset results in a top response time of 64.5 minutes whereas a −5% reflux upset has a response time of 495.0 minutes, a factor of almost 8 between these two runs. On the other hand, columns producing a distillate stream mole fraction of around 0.80 and the bottoms stream mole of fraction around 0.20 do approach linear behavior as shown in Table 6. This is in agreement with the results of Luyben et al. (1963). The effect of the regions of operation for distillation columns on the dynamic behavior of the column, that is, linear or nonlinear dynamics, can be depicted on a composition scale.

Four regions of operation are indicated for the distillation columns investigated in this study. The region of very fine separation is identified as that initial steady state condition where the distillate composition is 0.99 to 1.00 and the bottoms composition is 0.00 to 0.01. Much of the data presented by Moczek et al. (1965) are in this region. They indicate Equation (4) to be accurate under these conditions. In this study we had four columns in this condition, namely Column V of Table 2, Columns IV and VI of Table 3, and Column IV of Table 4 all of which verify their conclusion. However, we note that even for these columns the minimum method yields more accurate results. The average error produced by the minimum method, Equations (16) and (17), being 5.7% while the average error from Equation (4) is 8.5%.

In the next region of separation, namely steady state distillate composition from 0.97 to 0.99 and bottoms from 0.01 to 0.03, we find the prediction errors for the minimum method are much less than those for the method of Moczek et al. See Columns II and III of Table 2 and Column I of Table 3. The average error from Equations (16) and (17) being 4.2% while the average error of Equation (4) is 13.5%. The next region of separation, a region where the separation is not very fine but which still exhibits nonlinear dynamic behavior, has initial steady state distillate composition in the range of 0.80 to 0.97 and initial bottoms composition of 0.03 to 0.20. Columns I, IV, and VI of Table 2 are in this region. Neither Equation (4) or the minimum method produce satisfactory results for all of these columns for this region. The average error from the minimum method being 23.0% while the original method of inventory time produces an average error of 22.8%. Lastly the region of operation between 0.80 and 0.20 is the linear region where many of the linear models found in the literature should apply. This region was studied in this work by changing the liquid and vapor rates in all six columns so that the distillate and bottoms compositions would be in the proper range. The operating conditions are given in Table 5. The results for this operating region are presented in Table 6 and indicate linear behavior for upsets as large as 10%. In particular we note that the response time does not change greatly with either the magnitude or direction of the input as opposed to the other column responses we observe in Tables 2, 3, and 4. These properties are characteristic of linear systems and most approximate linear models will have these features. As indicated in Table 6 the minimum method is also applicable in this region producing an average error of 6.1% while Equation (4) of Moczek et al. yields an average error of 16.3%. We also note that Equation (18) of the minimum method predict both the slower and faster responses while Equation (4) can predict only one. Considering the error produced by Equation (18) for the slower and faster responding ends we have 3.8 and 8.3%, respectively.

Using the approach DeLorenzo et al. (1970) and Bernardi et al. (1971) we investigated a broad range of reflux rates, holding the vapor rate constant. This led to Figure 3 for Columns IV and V and to corresponding figures for the other columns not shown here. It is observed that Columns I, II, III, and V of Table 2 are operating at the point of maximum separation, while Columns IV, and VI are not. Also, the separation achieved in Columns II, III, and V was much greater than that obtained for Columns I, IV and VI.

Also when Columns I, IV, and VI are modified to achieve a higher separation they then were predicted well by the method of minimum change of storage as shown in Tables 3 and 4. In modifying the columns two things were achieved. Namely, the maximum possible separation was increased and the columns were operated at these conditions. Upon close examination of Column IV on Figure 3 and Tables 1 and 4, it was noticed that reduction of the reflux ratio from 0.666 to 0.642 would raise the separation achieved. This would also be the maximum separation possible for a vapor rate of 21.0 moles/minute through the

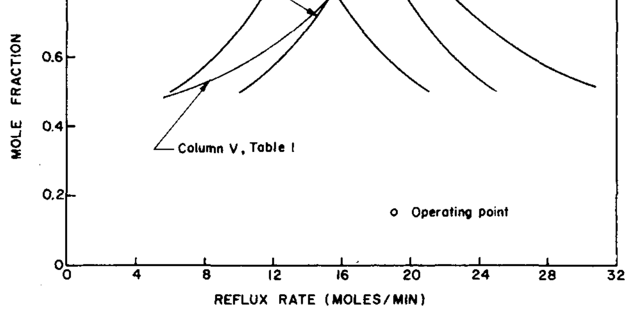

Fig. 3. Composition change versus reflux rate changes, Columns IV and V.

column. As indicated by the foregoing discussion, Column IV now became even more amenable to analysis by the minimum method as can be seen by an inspection of Tables 2 and 4. These Tables indicate that both an increase in reflux ratio, Tables 1 and 3, and a decrease in reflux ratio, Tables 1 and 4, produce conditions in the column at which the minimum method works very well. Both changes from the original condition moved the column to operation at the maximum possible separation. This condition also improved the accuracy of Equation (4).

Inventory Time, Equation (4), when it is applicable approximates only one response time, that is, the slower responding end of the column. Also, it does not indicate which end this would be. The later work of Bhat and Williams (1969 a,b) also possessed this shortcoming. The method of minimum change of storage successfully estimates the larger response time for a broad range of separations and also indicates which end of the column this would be. With is in mind it would seem feasible to estimate the smaller response time be rearranging Equations (9). For instance if τ_1 were the larger response time then

$$\tau_2 = \frac{\Delta S_T}{\Delta F_W} - \frac{\Delta F_D}{\Delta F_W} \tau_1 \qquad (19)$$

In Equation (19) it occurs that in almost every case if $\tau_1 > \tau_2$, then

$$\Delta F_D > \Delta F_W \qquad (20)$$

However, for the vast majority of the cases of high purity product at both ends, the inequality Condition (20) becomes much more pronounced and we have

$$\Delta F_D >>> \Delta F_W \qquad (21)$$

Such a condition makes the estimation of the smaller inventory time very difficult for even if there are small errors in estimating τ_1, say 5% to 10%, the corresponding errors introduced in estimating τ_2 are very large. In the linear region, though, that is, for a column operating in the range of overhead < 0.80 and bottoms > 0.20, the Condition (20) holds rather than (21). Consequently, it is possible to estimate the smaller inventory time as well in this region. Results for operation in the linear region summarized in Table 6 show that the method of minimum storage Equations (18) predict the response time for both ends of the column.

ACKNOWLEDGMENT

This research was supported by the Purdue Laboratory for Applied Industrial Control. Computer time was supplied by Purdue University.

NOTATION

D = distillate rate, moles/min.
DF = Rosenbrock's disturbance function
F = feed rate, moles/min.
INV = inventory of material in the column, moles
M = plate number at which the minimum occurs
N = total number of plates
n = plate number
q = flow rate, moles/min.
t = time, min.
T_{INV} = inventory time, min.
U = holdup, moles
V = holdup in two tank model, mole
W = bottoms rate, moles/min.
x = liquid composition
y = vapor composition

Greek Letters

τ_1 = top response time, time for 60% point for a step input, min.
τ_2 = bottom response time, time for 60% point for a step input, min.
ν = condition immediately after imposition of a step change

Subscripts

C = condenser
D = distillate
F = feed
f = final
i = initial
MOW = Moczek, Otto, and Williams
n = plate number
Top = Top end
W = bottoms
1 = Tank 1
2 = Tank 2
0 = outflow

LITERATURE CITED

Ball, W. E., "Computer Programs for Distillation," paper presented at 44th National Am. Inst. Chem. Engrs. Meeting, New Orleans (1961).

Bernardi, M., D. Belgeri, and G. Fronza, "On the Asymmetrical Transient Behavior of Binary Plate Distillation Columns: Step Changes of Vapor," Int. Rep. Inst. di Elettrotecn. Elittronica, Politec. Milane L.C.A. 71-6 (1971).

Bhat, P. V., and T. J. Williams, "Approximate Mathematical Models for Distillation Columns," Report No. 18, Purdue Lab. of Applied Ind. Control, Purdue University, Lafayette, Ind. (1969).

——————., "Approximate Mathematical Models of Distillation Operations and Their Relation to Overall Column Control Methods," *Inst. Chem. Engrs. Symp. Ser.*, No. 32, Session 6, 22 (1969).

DeLorenzo, et al., "On the Asymmetric Behavior of Distillation Systems," Int. Rep. Inst. di Elettrotecn. Elettronica, Politec. Milane L.C.A. 70-21 (1970).

Distefano, G. P., et al., "Transient Response and Feedforward Control of a Distillation Tower Subject to a Sequence of Upsets," *AIChE J.*, 13, 125 (1967).

Gilliland, E. R., and C. M. Mohr, "Transient behaviour in plate-tower distillation of a binary mixture," *Chem. Eng. Progr.*, 58, 59 (1962).

Holland, C. D., *Multicomponent Distillation*, Prentice-Hall Englewood Cliffs, N. J. (1963).

Lamb, D. E., et al., "Dynamic Characteristics and Analogue Simulation of Distillation Columns," *Chem. Eng. Progr. Symp. Ser. No. 57*, 132 (1961).

Luyben, W. L., et al., "Transient Response of Ten-Tray Distillation Column: Complete Data and Results," Report from Univ. Delaware, Newark (1963).

Moczek, J. S., et al., "Approximate Models for the Dynamic Response of Large Distillation Columns," *Chem. Eng. Progr. Symp., Ser. No. 61*, 136 (1965).

Mohr, C. M., "Effect of the Equilibrium Relationship on the Dynamic Characteristics of Distillation Column Sections," *AIChE J.*, 11, 253 (1965).

Rosenbrock, H. H., "A Theorem of Dynamic Conservation for Distillation," *Trans. Inst. Chem. Engrs.*, 38, 279 (1960).

Thal-Larsen, H., "Dynamics of Heat Exchangers and Their Models," *Trans. ASME J. Basic Eng.*, 82, 489 (1960).

Wahl, Edward F., and P. Harriott, "Understanding and Prediction of the Dynamic Behavior of Distillation Columns," *Ind. Eng. Chem. Process Design Develop*, 9, 396 (1970).

Williams, T. J., "What's Next for Process Control Computers?", *Chem. Eng. Progr.*, 68, 45 (1972).

Manuscript received May 9, 1972; revision received July 6, 1972; paper accepted July 7, 1972.