Experimental Transient Response of a Pilot-Plant Distillation Column: Part IV. Response of a Ten-Tray Column

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An important requirement in the design of automatic control systems for distillation columns is a knowledge of the dynamic behavior of the system. The purpose of this paper is to demonstrate the applicability and limitations of a set of linear, perturbation type of differential equations for characterizing this dynamic behavior. This may be done by comparing the transient response predicted by the mathematical model with that obtained in a series of experimental studies carried out in a 2-ft. diameter column.

The results of earlier research of this type with this same column have already been published. In Part I of these Delaware studies (*1*), step changes were made in the composition of the reflux returning to the top tray of a five-tray, total-reflux column. The resulting experimental changes in composition of the tray liquids varied with time in a manner almost identical to that predicted by the perturbation equations of Lamb, Pigford, and Rippin (*4*). Important conclusions from this work are that the tray liquid can be assumed to be perfectly mixed; tray efficiencies of less than 100% can be accounted for by use of a pseudoequilibrium curve; and tray efficiencies remain constant during the transient period.

The response to liquid rate and to vapor rate perturbations was evaluated in a second series of tests (*2*). In this case either the reflux rate was increased or the vapor rate was decreased in a stepwise manner to the five-tray column operating initially at total reflux. These studies showed that liquid rate changes were propogated rapidly down the column because of the small variation of liquid holdup on the trays with a change in liquid rate; that although liquid holdup in the downpipes was as large as 50% of that on the tray, its effect could be accounted for by combining it with the tray holdup; and that the use of cold reflux caused the transient response of the top tray to differ from that of the other trays. In the latter instance, use of two separate equations for the top tray, one to describe that part of the tray which acted only as a heat transfer device, and one to describe the remainder of the tray which acted normally, was required to characterize the experimental results.

The transient response results presented in this paper are for a ten-tray column fed at the center and operated in the normal manner producing both overhead and bottoms products; five additional trays were fabricated and added to the original five-tray column. The present studies appeared desirable to evaluate the effect of perturbations imposed at the feed tray and extending in both directions from the feed tray. Also it was desired to determine if any additional complexities arose in the propogation of liquid disturbances down the column and vapor disturbances up the column as the number of trays increased, factors which might be negligible in a five-tray tower but which might be important in a ten-tray situation. Another objective was to study the effects of making several simultaneous disturbances to the column. And finally, it was desired to determine the transient response of an entire distillation unit, one which contained reboiling and condensing systems which also contributed to the transient behavior of the trays. In Parts I and II of this series, the influence of the condensing system had been eliminated

Table 1. Design and Operating Conditions During Tests

Equipment

Column
Inside diameter: 2 ft.
Number of trays: 10
Feed entry: 5th tray from bottom
Caps: 17-3-in. round bubble caps per tray on 4.5-in. spacing in 2.45 sq. ft. area
Outlet weir height: 2 in.
Downpipes: 0.345 sq. ft. cross section
Tray spacing: 18 in.
Condenser
Downflow of vapor through 121 vertical tubes, ⅝-in. O.D., 75 in. long
Reflux drum: 100 gal.
Reboiler
Upflow of liquid through 163 vertical tubes, ¾-in. O.D., 122 in. long, discharging to 50 gal. separator; natural circulation, thermosiphon type

Average conditions during tests

System pressure: 25 lb./sq. in. gauge
Feed rate:
50-100 lb./min.
7.5-11.3 gal./min.
Vapor rate above feed:
100-150 lb./min.
5.6-8.4 cu. ft./sec.
50%-75% of flooding
Top tray temperature: 180°F.
Feed temperature: 100°F.
Fraction of feed tray used to preheat feed: 0.10

Average conditions during tests (cont.)

Reflux temperature: 100°F.
Fraction of top tray used to preheat reflux: 0.11
Average liquid condensate rate: 8-12 gal./min.
Average liquid rate to reboiler: 25-33 gal./min.
Increase in tray and downpipe holdup for each gal./min. increase in liquid rate: 0.049 gal.
Mixture employed: acetone-benzene
Tray efficiency: 70-90%
Slope of pseudoequilibrium curve
at 2 mole % acetone 2.70
at 50 mole % acetone 0.80
at 98 mole % acetone 0.64

Average liquid holdups under operating conditions

Each tray: 2.40 gal.
Each downpipe between trays: 1.20 gal.
Condenser: negligible
Piping between condenser and reflux drum: 3.6 gal.
Reflux drum: 50 gal.
Piping between reflux drum and entrance to column: 13.5 gal.
Piping between column and reboiler: 11 gal.
Reboiler-separator system: 56 gal.
Entire system: 171.3 gal.

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by supplying reflux from storage, and the influence of the reboiler had been minimized by operating it in a pinch region.

Before starting the present experiments, a comprehensive study was made of the transient behavior of the reboiling and condensing systems of the pilot-plant unit to be employed. These results, designated as Part III of the series, are described in references 7 and 8. These tests showed that the vertical, downflow, vapor-in-tube condenser had negligible lag time, and that the 100-gal. reflux drum which followed contained liquid which was perfectly mixed. The tests also showed that the contents of the vertical, thermosiphon reboiler and its associated vapor-liquid separator tank were perfectly mixed, and that the 30-sec. dead time of the liquid flowing in the pipe between the base of the tower and the base of the reboiler represented an important lag in the system. The liquid spilling over from the seal pan at the base of the tower, which was in contact with the vapor below the bottom tray, changed the vapor composition by the same amount as if it passed through a tray of 35% efficiency.

EXPERIMENTAL

A description of the equipment employed and a summary of the average operating conditions is given in Table 1. A more complete description of the unit and its steady state performance is contained in reference 3.

Scope of Experiments

All tests were made with the acetone-benzene system at a total pressure of 40 lb./sq. in. abs. At these conditions the relative volatility varies with composition from 1.8 to 2.2. This binary system has enthalpy properties such that equal molar overflow prevails within the column except at the top tray and at the feed tray, which were fed with liquid at around 100°F., a temperature well below that of the liquid on the trays.

The transient response of the system was measured when subjected to four different types of disturbances: changes in feed composition, feed rate, reflux rate to the top tray, and vapor rate to the bottom tray. A number of runs was also made in which feed rate, reflux rate, and vapor rate were changed at about the same time. Both step changes and pulse changes of the input perturbations were made, and the magnitude and direction of these changes were varied. The tests were made at two different levels of reflux ratio which in effect varied the steady state change in composition across each tray. Except for the specific disturbance introduced, the initial steady state conditions were maintained constant during the transient period; variables held constant included feed rate, feed composition, feed temperature, reflux rate, reflux temperature, vapor rate from the reboiler, and tower pressure; overhead and bottoms products were withdrawn at a rate such that levels in the reflux drum and reboiler remained constant. Average values for the steady state variables employed in all of the runs are shown in Table 1, while specific conditions for each of the twenty-nine runs are tabulated in reference 6. Conditions for the runs shown graphically in this paper are given in Table 2.

Changes in the composition of the liquid from every other tray of the column and from key positions of the reboiling and condensing systems were measured as a function of time after introduction of the disturbance for a period of about 20 min., the full transient period usually lasted for about 40 min., but nearly all of the composition changes had occurred at the end of 20 min.

Operating Procedure

The unit was operated initially under steady state conditions until all temperatures, pressures, flow rates, and compositions remained constant. Temperatures were determined from small-gage, bare-wire thermocouples; the tower pressure was held constant by nitrogen supplied from a cylinder to the upper part of the reflux drum. Flows of the process streams were obtained from precision rotameters. The steam flow to the reboiler was from a calibrated Brown orifice-meter body-recorder assembly. Compositions were determined accurately by refractive index. Steady state material and enthalpy balances were made for each run and these checked within a few percent. Enthalpy balances were also used to compute local vapor and liquid flow rates within the tower.

During the initial steady state, the overhead and bottoms products were combined and returned to the feed tank. To change the feed composition, feed from a separate tank was introduced in place of the original feed; the change was made in a few seconds through use of quick-operating solenoid valves. When the feed rate was changed, the same scheme was used so that the original feed tank could be used as storage for the products of changing composition. Changes in reflux rate were accomplished almost instantaneously by manipulating the valve from the reflux pump; the withdrawal rate of the overhead product was also changed to maintain a constant level in the reflux drum. The vapor rate was changed by changing the set point of the controller in the steam line to the reboiler; a lag of 30 sec. occurred between the set point change and the vapor rate change.

To measure the changes in composition during the transient period, small bleed streams from various locations were continuously withdrawn through fine-bore stainless tubing.

TABLE 2. OPERATING CONDITIONS FOR RUNS SHOWN GRAPHICALLY

		Initial flow rates, lb. moles/min.			Initial external reflux ratio,	Initial compositions, mole % acetone			
Run no.	Type of perturbation	Feed	Overhead product	Vapor below feed tray	L/D	Feed	Overhead product	Bottoms product*	Feed tray
7	Feed composition increased in step by 6.5 mole % acetone	1.487	0.801	2.19	1.125	49.4	80.8	11.6	47.0
12	Feed rate increased in step by 17.6%	0.948	0.513	2.23	2.60	51.0	86.5	5.4	44.7
15	Feed rate increased in step by 19.6%	1.455	0.778	2.22	1.35	53.8	84.9	16.6	53.0
16, 17	Feed rate increased for 2 min. by 54.0%	1.450	0.774	2.23	1.31	50.5	82.5	10.7	47.4
18	Reflux rate increased in step by 24.1% from 1.034 to 1.284 mole/min.	1.446	0.793	2.27	1.31	49.6	81.0	8.2	44.3
19	Reflux rate increased for 2 min. by 54.0% from 0.940 to 1.446 mole/min.	1.447	0.784	2.18	1.20	49.6	81.1	10.5	46.4
10-V	Vapor boilup increased in step by 6.72%†	1.549	0.774	2.35	1.25	48.7	83.1	11.1	50.1
16-V	Step decrease in feed rate by 17.5%, followed in 1 min. by step decreases in reflux rate by 5.7% and in vapor boilup rate by 7.7%	1.197	0.559	2.17	1.92	45.5	84.4	6.0	47.4

* For runs 2 to 20, bottoms product was withdrawn from liquid stream entering reboiler; for runs 4-V to 16-V, bottoms product was withdrawn from stream of unvaporized liquid leaving reboiler.

† Magnitude of vapor perturbation was not measured with high precision; values which gave best analog predictions were taken as correct. See reference 2.

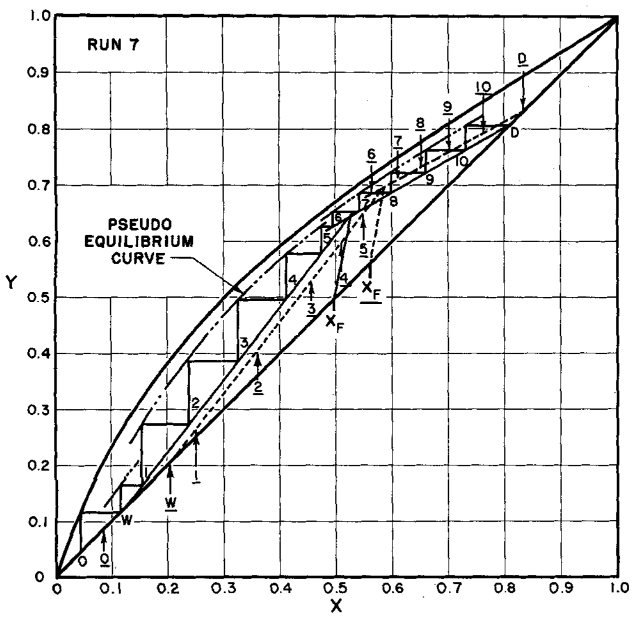

Fig. 1. McCabe-Thiele diagram for run 7. Operating lines and tray compositions at initial steady state shown as solid lines and steps. Final steady state, after feed composition has been increased in a step by 6.5 mole % acetone (from x_F to $\underline{x_F}$), shown by dashed operating lines and arrowed compositions.

Streams were taken from trays 1, 3, 5 (the feed tray), 7, and 9 (counting from the bottom upwards); from the vapor leaving the reboiler and leaving the top tray; and from the feed, reflux, and bottoms. The sample streams flowed at a rate of 1 cc./sec. and were cooled before discharging into the atmosphere. All ten sample lines were brought to a common point where a simultaneous collection of all samples was made. This was done with a series of racks, each containing ten sample vials. Each rack collected samples for 2 to 3 sec. and then was replaced by the next. Samples were collected every 30 sec. for the first 4 min. of the transient; then every minute for the next 4 min., every 2 min. for the next 6 min., and finally every 3 min. The samples were analyzed later for composition with a five-place refractometer. As acetone and benzene have considerably different indexes of refraction, the precision of the analytical method was better than 0.1 mole percent. The composition-time data were corrected to account for the lag time in the sample lines, which was about 1 min.

EXPERIMENTAL RESULTS

The complete results of this study are too voluminous for presentation with this paper, but all of the data and results are available in a separate publication (*6*). The present paper, however, does contain many of the results in graphical form.

Experimental results are typified by those obtained for run 7, as shown in Figures 1 and 2. Figure 1 shows that the tray efficiencies were around 75%, a value found to hold for the other runs as well. Efficiencies for the top tray and the feed tray tended to be somewhat lower, as discussed later, because of the introduction of cold reflux or cold feed to these trays. The pseudoequilibrium curve shown on this figure connects the actual (rather than the equilibrium) compositions of the vapor leaving each tray; use of this curve directly relates the compositions of vapor and liquid leaving a given tray, and is thus more convenient than employing separate relationships for the efficiency and the true vapor-liquid equilibrium. Figure 1 shows the small enrichment obtained by the liquid discharging from the seal pan at the base of the tower. It also shows that the efficiency of the reboiler is essentially 100% and that the bottoms product was withdrawn (in this particular run) from the liquid stream entering the reboiler. In some of the other runs, the bottoms was withdrawn from the liquid stream leaving the reboiler.

MATHEMATICAL PREDICTIONS

Prediction of the experimental transient responses was made using a system of simultaneous perturbation type of linear differential equations. The equations were originally developed by Lamb, Pigford, and Rippin (*4*) and were shown to apply for a five-tray stripping column in Parts I and II, and for the condensing and reboiling systems in Part III of this study (*1*, *2*, *7*). The equations were applied in the present situation for a column containing five rectifying and five stripping trays, a total condenser, and a thermosiphon reboiler. The following assumptions were made in developing the equations: (1) negligible vapor holdup; (2) equal molar overflow except at feed tray and at top tray; (3) reboiler and reflux drum contents perfectly mixed; (4) negligible holdup in condenser; (5) dead time in piping between base of column and entrance to reboiler and between reflux drum and tower; (6) tray liquids perfectly mixed; (7) tray holdup includes actual holdup plus downpipe holdup; (8) linear relationship between compositions of vapor and liquid leaving each tray; and (9) special model for feed tray and top tray as described later. The first five of these assumptions were shown to apply closely either by calculation (assumptions 1 and 2) or by experimental observation (assumptions 3, 4, and 5). Perfect mixing of liquid on each tray was known not to exist (3), but analog predictions described in reference *1* showed that the degree of liquid mixing did not greatly affect the predicted transient response. Proper treatment of downpipe holdup was evaluated in reference 2, where analog predictions were made with downpipe holdup treated either as a separate dead time, as a holdup to be combined with the tray holdup, or as being absent completely. The first two cases were shown to give essentially the same predicted result. Assumption 8 implies that the slope of the pseudoequilibrium curve is constant during the transient period. Although separate values for this slope were used for each tray, the slope for some of the trays did vary sufficiently to require special consideration in choice of a proper average value. This is discussed later.

The resulting equation for any given tray n is as follows:

$$\frac{dx_n}{d\theta} = (\overline{x}_{n+1} - \overline{x}_n)(L_{n+1}/\overline{L}_n) - \overline{y}_n(V_n/\overline{L}_n) + \overline{y}_{n-1}(V_{n-1}/\overline{L}_n) + x_{n+1}(\overline{L}_{n+1}/\overline{L}_n) + m_{n-1}x_{n-1}(\overline{V}_{n-1}/\overline{L}_n) - x_n(m_n\overline{V}_n/\overline{L}_n) - x_n \qquad (1)$$

A bar over a variable indicates that it is a steady state value, while variables lacking the bar are the deviations or perturbations from the steady state value; for example, the liquid composition on tray n at any instant is $\overline{x}_n + x_n$.

It will be noted in Equation (1) that not only is a single, average value required for m, the slope of the pseudoequilibrium curve for a given tray, but that suitable steady state values are required for compositions and flow rates at the tray considered. If the tray is moving from an initial steady state to a new, final steady state, some average steady state value is required. Thus the smaller the magnitude of the changes involved, the more exact these linear, perturbation type of equations become; a major objective of this study was to determine the extent to which these equations apply.

Liquid perturbations on adjacent trays are related to each other by the relationship

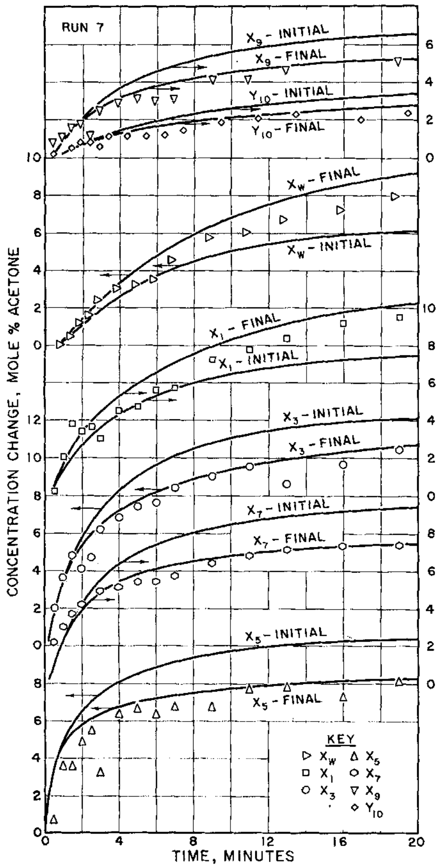

Fig. 2. Rate at which tray liquids change from initial to final steady state for run shown in Figure 1. Trays are numbered from bottom (1) to top (10). Points are experimental values; solid lines are analog predictions with steady state parameters in Equation (1) evaluated either at initial steady state or at final steady state.

$$\frac{dL_n}{d\theta} = (1/\beta_n)(L_{n+1} - L_n) \qquad (2)$$

where β is a constant, $(\bar{L}_n/\bar{H}_n)(d\bar{H}_n/d\bar{L}_n)$; this implies a linear relationship between tray holdup, H, and liquid rate, $\bar{L}$.

Equations for Top Tray and Feed Tray

The model used for the top tray or the feed tray was to assume that it consists of two parts: a portion which totally condenses vapor to raise the entering cold liquid to the boiling point, and a portion which receives and discharges saturated liquid and vapor streams as a normal tray. Each portion consists of its own pool of well-mixed liquid. As shown in the Part II studies (*2*), this model was necessary and sufficient for the top tray of the five-tray stripping column, and should be adequate for the feed tray of the present column. The actual equations are contained in reference 2.

Solution of Equations by Analog Computer

To predict the transient response of the ten-tray unit, one must first write Equations (1) and (2) for each tray plus two additional differential equations for the heat transfer parts of the top tray and the feed tray. Two more differential equations must be written to relate input-output compositions for the reflux drum and the reboiler. These twenty-four differential equations must then be solved simultaneously.

The most convenient way to solve these equations is with an analog computer. However, the university's analog computer contains only twenty integrators, sufficient to solve only twenty simultaneous equations, and it was also desirable to use two of these integrators to approximate dead time between reflux drum and tower and between tower base and reboiler; an integrator was also required to generate the time scale. To overcome the deficiency of seven integrators, it was decided not to delay the liquid perturbation on every tray, but rather to apply Equation (2) only once; namely, after the liquid had flowed down the top five trays. Thus changes in reflux rate were assumed to be felt simultaneously on the top five trays, and changes in liquid rate on the bottom five trays were felt at the same time as the liquid perturbation reached the feed tray. This restriction in the analog circuit did not cause much of a deviation in the predicted result because only about 0.1 min. was required for a perturbation in liquid rate to travel through the column, as compared with the 20-min. period required for most of the composition changes to occur.

A drawing of the analog circuit is included in reference *6*; eighty potentiometers and ten summers were required along with the integrators to describe the system. Calculation of the proper values of the coefficients for each of the potentiometers was made on a digital computer. This saved time because of the large number of runs involved and tended to eliminate errors in any particular value.

RESULTS

Changes in Feed Composition

Figure 2 typifies the results obtained for a step change in feed composition to the column. Two different analog predictions are shown: in one case, the steady state values were evaluated at the initial steady state, while in the other, final steady state values were employed. The most important difference in these two sets of steady state values was that owing to the change in slope of the pseudoequilibrium curve in the lower trays of the column. Because the acetone concentration of the feed was increased, the m-values became smaller as the column moved from its initial to its final steady state; thus, as shown on the figure, the predicted composition changes are less when the final steady state m-values are employed. It might be expected that the experimental data would lie more nearly intermediate between the two predicted curves in Figure 2, but reference to the figure shows that in this instance the experimental data follow the final steady state predictions rather closely. This is probably because the assumption of complete liquid mixing on the trays predicts responses which are slightly greater than those found experimentally. In tests where the feed composition was decreased in a step change, the initial m-values, and the predicted responses were both smaller when evaluated at the initial steady state instead of at the final steady state; in such cases, the experimental data followed the initial predictions quite closely, confirming that the data tend to follow the slowest of the predicted responses.

Changes in Feed Rate

Results for three runs are shown in Figures 3, 4, and 5. Because a change in feed rate causes changes in compositions as well as in flow rates within the column, the prediction equations are more complex; in Equation (1), the term involving L as well as those terms involving x are used in the stripping section. And, because the feed is cold, a change in feed rate causes a small vapor perturbation in the rectifying section.

Runs 12 and 15, shown in Figures 5 and 3, are similar in that in both cases the feed rate was increased in a

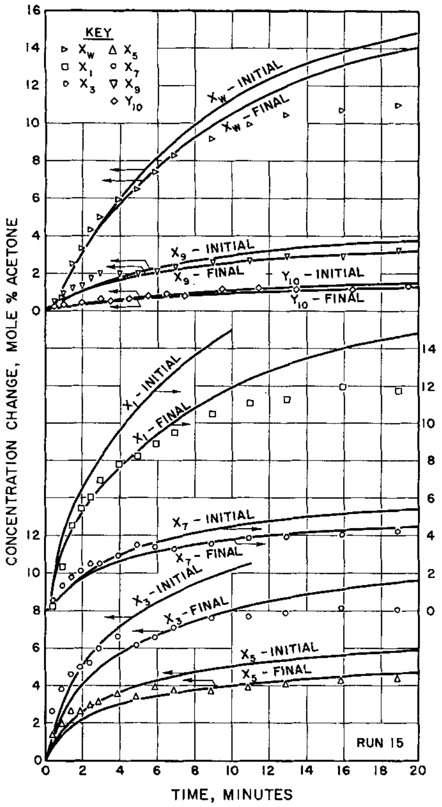

Fig. 3. Transient response of column plotted as in Figure 2 but for run 15 where feed rate is increased in step by 19.6%.

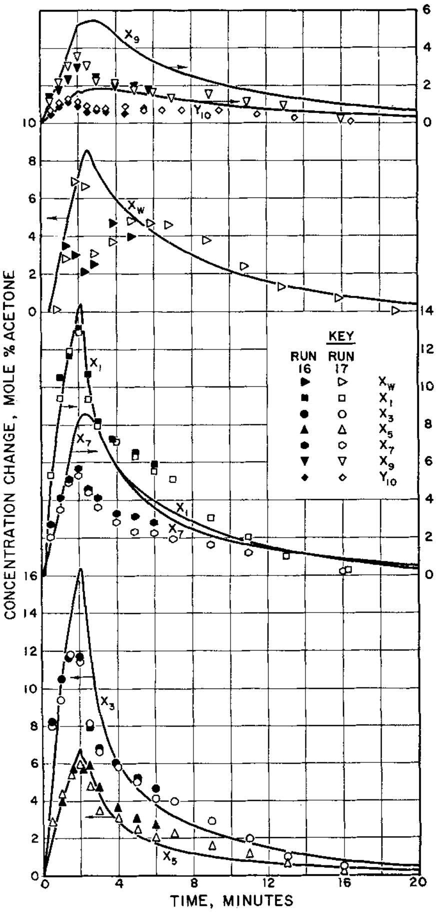

Fig. 4. Transient response of column subjected to a 54% increase in feed rate for 2 min. Points are experimental values, solid lines are analog predictions based upon initial steady state parameters.

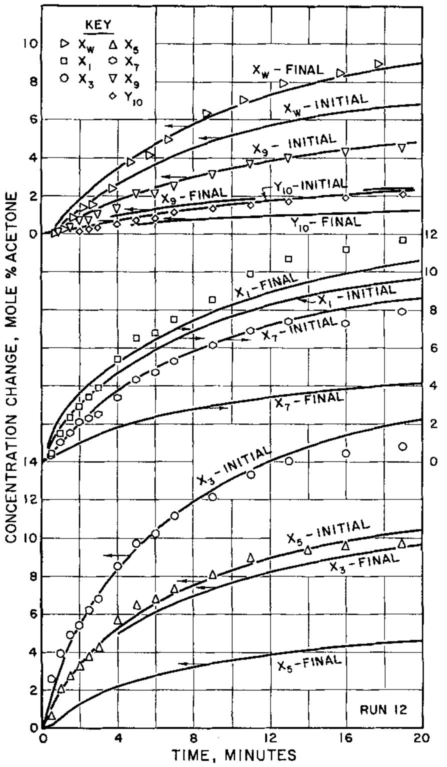

Fig. 5. Transient response of column plotted as in Figure 2 but for run 12 where feed rate is increased in step by 17.6%.

step by nearly 20%. However, reference to the figures shows that in the first instance, agreement between predicted and experimental values is best when initial steady state values are used in the analog predictions; in the second instance, the final steady state values are the optimum. The reason for this is, as just mentioned, the inclusion of the term involving the liquid perturbation L in the prediction equation for each tray. The coefficient for L in Equation (1) is $(\bar{x}_{n+1} - \bar{x}_n)$, which is the difference in steady state liquid compositions on adjacent trays. This difference can change in magnitude to a large degree in proceeding from an initial steady state to a final steady state, and the direction of the change depends not only upon whether the feed rate is increased or decreased, but also upon the absolute value of the tray compositions at the start. For example, in run 12 the difference in composition between trays 1 and 3 was 18.1 mole % initially, and it was 21.3% at the final steady state; in run 15, the initial difference was 20.2 mole %, but it decreased to 16.2 mole % at the final steady state. The main reason for this is that the initial composition on tray 3 for run 12 was 25.9 mole % acetone, whereas for run 15 this value was 41.7%; thus, because of pinching at the feed in this latter case, this composition had less opportunity to change in run 15. This fact, plus the fact that the composition increases on tray 1 were about the same in the two runs, explains the result obtained.

Thus in cases having only composition changes, nonlinearities are caused only by nonlinear variations in the slope of the equilibrium curve during the transient. It is a simple matter to increase or to reduce the predicted composition changes by increasing or reducing the average slopes within the limits of the initial and final steady state values. However, in the general case where both rate and composition perturbations occur, evaluation of the optimum steady state parameters becomes more uncertain as the perturbations from an initial steady state increase in magnitude.

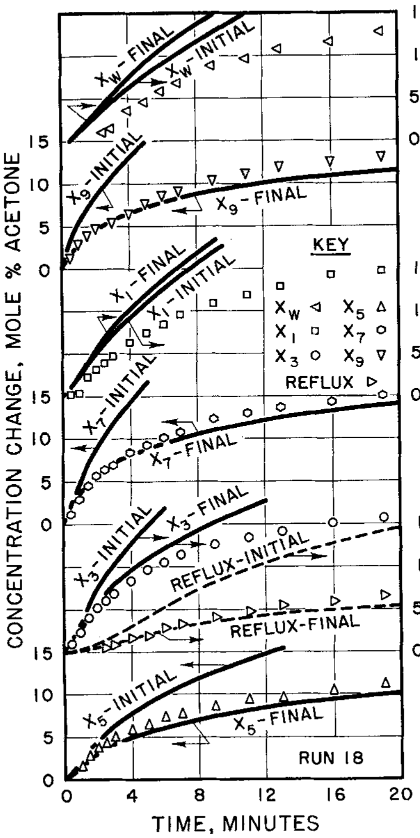

Fig. 6. Transient response of column plotted as in Figure 2 but for run 18 where reflux rate is increased in step by 24.1%.

To eliminate uncertainties in evaluating steady state parameters, a number of modified pulse-input runs were carried out. In runs 16 and 17, the feed rate was increased by 54% for 2 min., then returned to its initial value. As shown in Figure 4, the experimental and analog-predicted results agree fairly well. A very close agreement is shown between the experimental results of these two runs which were carried out on different days but under identical conditions.

Changes in Reflux Rate

More extensive tests with feed-rate perturbations were not made because the liquid rate changes occurred on only the lower five trays of the column. Instead, a good number of tests were made in which the reflux rate to the column was changed. Results for two of the nine runs completed are shown in Figures 6 and 7. The predicted responses are fairly close to the experimental values for this series of runs except for a small tendency for the predicted results to be too fast in the lower trays.

Changes in Vapor Rate

The transient situation which results when a perturbation in the vapor rate is introduced to the base of the column is similar to that when a reflux perturbation is introduced onto the top tray: a corresponding composition change occurs which may be predicted by a series of equations involving as parameters the average slopes of the equilibrium curve, the average composition changes, and average flow rates. In both cases when perturbations are not small, it is difficult to choose the proper averages to be employed in the predictions, especially in the first two instances.

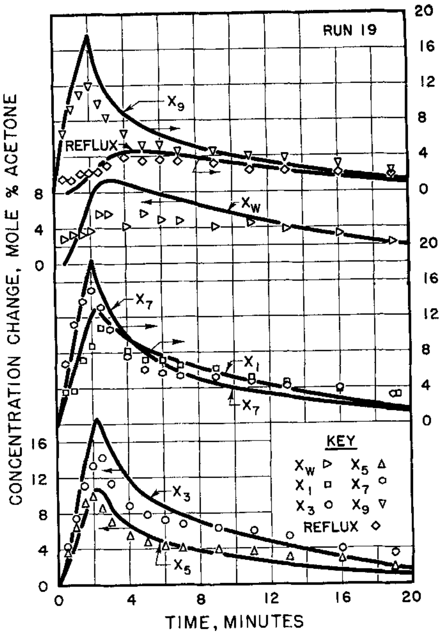

Fig. 7. Transient response of column subjected to a 54% increase in reflux rate for 2 min. Points are experimental values, solid lines are analog predictions based upon initial steady state parameters.

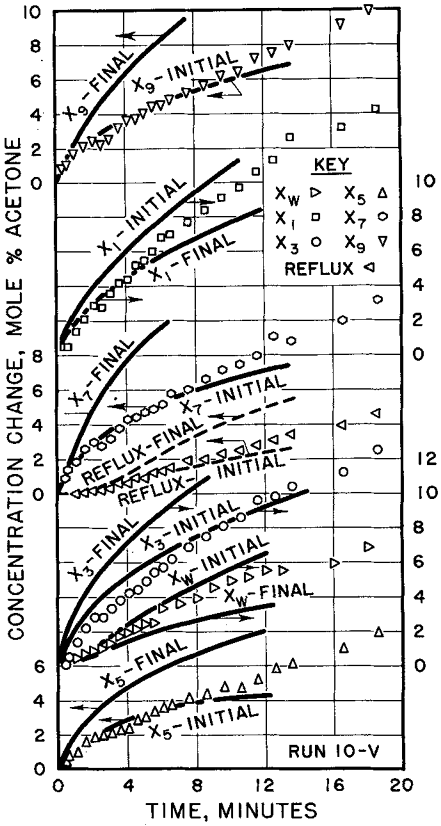

Fig. 8. Transient response of column plotted as in Figure 2 but for run 10-V where vapor boilup rate to tower is increased in step by 6.72%.

Results for one of the four runs completed is shown in Figure 8. In all four cases, agreement between predicted and experimental results is better than when changes in reflux rate are made.

Applications in Control

As mentioned earlier, a primary purpose of this work is to demonstrate experimentally the applicability of the

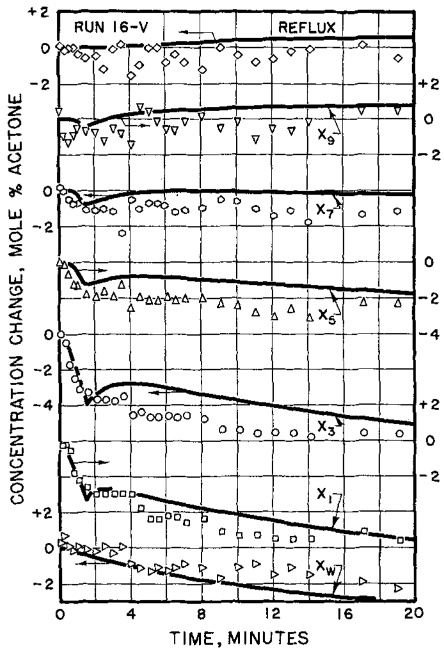

Fig. 9. Transient response of column for step decrease in feed rate by 17.5%, followed in 1 min. by step decreases in reflux rate by 5.7% and in vapor boilup by 7.7%.

linear model chosen to characterize the transient response of a column to various types of inputs. Once these equations have been shown to apply with sufficient accuracy, they may be used with confidence to design optimum automatic control systems for distillation columns. The earlier tests of this paper have shown that the model is suitable for four different types of input changes, but it remains to be demonstrated that the response resulting from a simultaneous change in more than one input can be predicted satisfactorily.

A simultaneous change in more than one input occurs in the control situation where the effects of an uncontrollable feed rate or feed composition are corrected by manipulating the reflux rate and the vapor rate to the column. To study such simultaneous input changes, a series of four tests was carried out in which step changes in the feed rate, reflux rate, and vapor rate to the tower were made at the same time or within a few minutes of each other.

In run 14-V, the feed rate, reflux rate, and vapor boilup were all changed simultaneously. The feed rate was decreased by 7.15%, and changes in the other two variables were such that the final steady state compositions would be just about the same as at the initial steady state. The experimental data showed very little change in composition both during the first several minutes after the upset, and over the rest of the time period as well.

More important, the data also showed that the column responds very fast to corrective action: if the change in feed rate had been sensed or known in advance, and if the proper corrective action (change in reflux rate and vapor boilup) had been taken when the feed change reached the column, there would be essentially no transient period during which the product compositions would be off-specification. The predictions show a transient period of about 2 min., but the data do not bear this out.

In run 13-V, where the feed rate was increased by 5.54% and corrective action was taken simultaneously by increasing reflux rate and vapor boilup accordingly, compositions within the column and of the products again did not change to any extent. The predictions showed composition increases of about 1 mole % acetone for the first 30 sec., but by the end of 2 min., the predicted compositions were nearly the same as those at the initial steady state.

In run 16-V, the feed rate was decreased by 17.5%, and the corrective action was delayed for 1 min. This was done to resemble an actual control situation where time would be required to sense the feed rate change, to compute the required changes in reflux rate and vapor boilup to maintain constant product purities, and to carry out the corrective action. Figure 9 shows the experimental and predicted result, where rapid changes occur (especially at trays 1 and 3) during the first minute, after which compositions rapidly line out to uniform values. The predicted vapor boilup change did not reach the system until a minute and a half, so the predicted responses show no corrective effect for 1.5 min. Predicted and experimental responses compare well in this instance, reflecting the high precision obtainable from the prediction equations when the departure from a steady state condition is small in magnitude. The reason for the drift in the compositions from the initial steady state in this instance is that the reflux rate and vapor boilup were not changed during the test by exactly the proper amount.

Run 15-V was carried out in the same was as run 16-V, except the feed rate was changed by a greater amount (increased by 24.7%). In this instance agreement between predicted and experimental values was not as satisfactory, partly because of a more rapid departure from steady state during the first 1.5 min. before corrective action was made, and partly because of a difference of as much as 12 mole % between initial and final steady states caused by use of insufficient corrective action.

More extensive studies are being completed on applicability of feed-forward controllers for distillation columns (5).

CONCLUSION

This study has shown that a set of linear, perturbation type of differential equations predicts the unsteadystate performance of a ten-tray distillation column with reasonably good precision. The equations are less precise as the magnitude of the perturbations from steady state increases, but should be applicable and useful in automatic control situations where deviations from the steady state are never allowed to become too large.

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NOTATION

$\bar{H}$ = steady state liquid holdup on tray, lb. moles
$\bar{L}$ = steady state liquid rate, lb. moles/hr.
L = perturbation in liquid rate, lb., moles/hr.
m = slope of vapor-liquid equilibrium curve or of pseudoequilibrium curve
$\bar{V}$ = steady state vapor rate, lb. moles/hr.
V = perturbation in vapor rate, lb. moles/hr.
$\bar{x}$ = steady state liquid composition, mole fraction
x = perturbation in liquid composition, mole fraction
$\bar{y}$ = steady state vapor composition, mole fraction
y = perturbation in vapor composition, mole fraction
β = $(\bar{L}/\bar{H})(d\bar{H}/d\bar{L})$
θ = ratio of elapsed time to time required for liquid to traverse a tray

Subscripts

n = any tray in distillation column
$n + 1$ = tray above tray n
$n - 1$ = tray below tray n
w = bottoms product

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Activity Coefficients at Infinite Dilution: 2-Propanol — Water System

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Activity coefficients at infinite dilution in the liquid phase are of interest both to physical chemists and chemical engineers. Physical chemists study them because they represent a direct macroscopic measure of the degree of interaction between a molecule of one species and an environment consisting entirely of a second species. Chemical engineers are interested in them because of their utility in the prediction of vapor-liquid equilibria for use in the design of absorbers, distilling columns, and heterogeneous reactors. This paper will illustrate a method of obtaining activity coefficients at infinite dilution from the terminal slopes of binary vapor-pressure curves. It will also illustrate the use of these data to predict equilibrium vapor and liquid compositions, including azeotrope compositions, in the concentrated region. While the methods used are not new, they are not very commonly employed at present, and it is hoped that this paper will stimulate a more general realization of the utility of these techniques.

THEORETICAL BACKGROUND

Vapor-liquid equilibrium data are most frequently correlated in terms of activity coefficients. The activity coefficient of component i in a liquid phase is defined by the relation

$$\gamma_{iL} = \frac{f_{iL}}{x_i f^\circ_{iL}} \tag{1}$$

The standard state commonly chosen for an activity coefficient in a liquid phase is the pure liquid at the temperature and pressure of the solution. Similarly for a vapor phase

$$\gamma_{iV} = \frac{f_{iV}}{y_i f^\circ_{iV}} \tag{2}$$

Equation (2) implies that the standard state for an activity coefficient in a vapor phase is the pure vapor at the temperature and pressure of the solution.

Since a pure compound at a given temperature and pressure can be stable in only one phase, it is apparent that the quantities f°_{iL} and f°_{iV} appearing in Equations (1) and (2) will refer to fictitious states for one or more components in each of the phases. This difficulty is removed in practice by some suitable extrapolation of the properties in question into the fictitious region. The derived values of the activity coefficients are thus seen to be defined both by appropriate forms of Equations (1) and (2) and by the extrapolation method selected.

The present discussion will be confined to systems with one vapor and one liquid phase.

If a liquid and a vapor phase are at equilibrium, the expression

$$f_{iL} = f_{iV} \tag{3}$$

may be written for each of the i components. Hence from Equations (1) and (2)

$$\gamma_{iL}\, x_i\, f^\circ_{iL} = \gamma_{iV}\, y_i\, f^\circ_{iV} \tag{4}$$

for each of the i components. All of the activity coefficients are unity in any phase behaving as an ideal solution. At low pressures $f^\circ_{iL} = P^\circ_i$ (when the very small effect of total pressure on vapor pressure is neglected) and $f^\circ_{iV} = P$, and Equation (4) reduces to

$$\gamma_{iL}\, x_i\, P^\circ_i = y_i P \tag{5}$$

Ibl and Dodge (9) have derived the following equation for a binary system at constant temperature:

$$\frac{d \ln \gamma_1}{d \ln x_1} - \frac{d \ln \gamma_2}{d \ln x_2} = \frac{1}{RT}\,(V - x_1 V^\circ_1 - x_2 V^\circ_2)\,\frac{dP}{dx_1} \tag{6}$$

The term $V - x_1 V^\circ_1 - x_2 V^\circ_2$ is the volume change on mixing the pure components at the temperature and pres-

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