Part II: Experimental Results and Comparison with Simulation During Start-Up at Total Reflux

Experimental concentration profiles throughout a fourteen plate column approaching steady state at total reflux were obtained for mixtures of benzene, toluene, and ethylbenzene. The concentration profiles are characterized by a large movement of the middle component, toluene, through the column so that its maximum concentration shifts from plate to plate until steady state is reached.

Computer runs were made in which the column variables were specified to be, as nearly as possible, those observed or calculated for the experimental runs. The computer results indicated the same behavior as the experimental runs, and the concentration profiles were in fair agreement. Thus, the computer model and calculation procedure used could replace the real column for many purposes. Inaccuracies in the computer simulation are due more to inadequate information about the characteristics of the real column than to deficiencies of the computer model.

There are several reports in the literature of mathematical models and simulation schemes to be used in describing the unsteady state behavior of multicomponent distillation columns. However, there is virtually no experimental work available to permit the results of computer simulations to be compared with the operations of a real column. Rosenbrock (7) compared computer and experimental results for several successive changes in column-operating conditions and showed that the plate temperature profiles had essentially the same shape. Peiser and Grover (5) reported that their computer simulation had represented a real column well enough to indicate design changes which had to be made to correct actual operating difficulties. Renfroe (6) has done the most extensive experimental work. He distilled a mixture of benzene, toluene, xylene, and *n*-heptane in a semicommercial scale column. Two experiments were performed in which the column was operated with feed, distillate, and bottom product streams. The column was allowed to come to steady state and was then disturbed by a step change in benzene concentration in the feed and by a pulse of benzene in the feed. Hand samples were taken of vapor and liquid at several locations. These results and extensive data on heat and material balance are reported. Simulation on a small digital computer showed the same trend as the actual test but could not duplicate the concentration values observed in the column. In addition to these three reports, there is undoubtedly a great deal of industrial work which has not been published.

The computer columns give a picture of the general nature of the behavior of real distillation columns in unsteady state operation. Their ability to represent specific real columns has not been demonstrated. No one has really assessed just how hard it is to get any agreement at all between a theoretical and a real column. It is not known what particular properties of a column must be known very well and which may be only roughly approximated when simulating its behavior. A part of this question really concerns the validity and effect of the simplifying assumptions which are normally made in setting up a mathematical model. The range of these assumptions, as pointed out by Williams (8) and others, is very great, but the effect on a particular simulation of taking one or another of them has not usually been determined. The purpose of this work was to try to answer some of these questions by comparing the results of actual experiments on a real distillation column with the results of a digital computer simulation by using the general technique described in Part I (4). The unsteady state period during start-up was chosen as the one of interest primarily because the large concentration changes during this period provide a very stern test for the computer modeling procedure.

EXPERIMENTAL APPARATUS AND PROCEDURE

Mixtures of benzene, toluene, and ethylbenzene were distilled in an uninsulated, fourteen plate bubble cap column. The reboiler was a 40 gal. pot heated by steam in a stainless steel coil with an effective heating area of 6.05 sq. ft. A pressure regulator controlled the inlet steam pressure, and a thermostatic type of steam trap regulated the steam condensate discharge. The condensate rate was determined by weighing the discharge. An 8 in. I.D. section of stainless steel pipe served as the support for the plates and as a bottom reservoir. The plates were 8 in. in diameter and contained five 2⅛ in. bubble caps. The overflow weir was a 1½ in. pipe with a height of 1.19 in. The plate spacing was 6 in. The condenser had an effective area of 15 sq. ft. and was operated with two liquid passes and the vapor on the shell side. The reflux flow rate and the reboiler return flow rate were measured by turbine flowmeters; combined with a frequency to D.C. converter, these meters give a millivolt signal which is linearly proportional to volume flow rate. The cooling water flow rate was set with a rotameter, but the actual water rate was measured by weighing.

There is no generally accepted procedure for starting a distillation column. Most methods are designed to reach steady state as quickly as possible and are tailored to the specific process and equipment to be operated. The purpose of the start-up procedure used in this work was not to minimize the time but, rather, to maximize the information that could be obtained during the start-up time. The concentration profile in the column was made as distorted as possible when the collection of data was begun. This distortion was obtained by using a vapor bypass from the reboiler directly to the overhead vapor line. In this way, vapor was fed into the bottom of the column in the usual manner and also directly into the condenser where it formed a liquid stream to fill the column. When the column was completely filled with hot vapor and liquid, the vapor bypass was closed. It took about 5 min. after this for the top and bottom flows to stabilize. Composition sampling was begun at this time, and the complete datum record was started.

Samples were taken at twenty-six points throughout the column. The locations of these points were: reflux line, plates 1, 2, 3 vapor and liquid, 4 liquid, 6 and 7 vapor and liquid, 8 liquid, 9 and 10 vapor and liquid, 11 liquid, 12 and 13 vapor and liquid, 14 (the bottom plate) liquid, the vapor to plate 14, the liquid return to the reboiler, and the reboiler liquid. No sample could be taken from plate 5 owing to its location next to a beam. The first five sets of samples were taken at 3 min. intervals; the time periods were then gradually lengthened during the rest of the run. The composition of the samples from the column was determined by averaging replicate analyses obtained by using a gas chromatograph equipped with a thermal conductivity detector.

More complete details about the experimental equipment, analytical procedures, and experimental procedures are given by Howard (3).

EXPERIMENTAL RESULTS

Three start-up experiments were performed in which composition profiles through the column were obtained as it approached steady state. In addition, many experiments were performed to determine the steady state operating characteristics of the column. In general the steady state results were quite variable and could not be used to predict the exact operating characteristics for a particular experiment. Trends could be observed, but no general correlations were obtained to relate subsidiary column variables such as heat losses, holdups, and efficiencies to the operating conditions of the column. This paper presents the results of the calculations made by using the data of the unsteady state runs which are sufficient to completely describe the column operating variables.

The main object of the experimental work was to obtain concentration profiles during the unsteady state period. The amount of benzene charged to the system in all runs was small, so that the whole column would be utilized for separation. In the runs designated 816 and 817 the toluene charge was made about four times that of the ethylbenzene. The run designated 830 reversed the relative amounts of ethylbenzene and toluene. The measured liquid concentrations of each component during run 830 are plotted against time in Figures 1 to 3.

After the data had been taken and analyzed, it was discovered that the vapor samples were not representative of the vapor passing to the next plate. The vapor compositions on a given plate were always different from the liquid compositions and changed in the same manner as the liquid as steady state was approached. In this way the vapor data at least tend to substantiate the behavior of the liquid compositions.

The flow rates of the reflux and the reboiler return liquid were measured by using the turbine flow meters. When the samples were taken, the reflux flow dropped to almost nothing. The flow returned to its previous value in 15 sec., surged slightly, and recovered completely within a minute. The reboiler return flow was not affected at all. Investigation showed this behavior to be caused by the loss of pressure when the vapor sample on the top plate was taken. None of the other samples affected either flow rate.

Energy balances were made based on the flow rates and on the measured steam and cooling water flows for the steady state conditions. Heat losses were calculated for the major sections of the column, and these were assumed to be constant during a run. The plates lost at least 25% of the net heat flow into the bottom of the column.

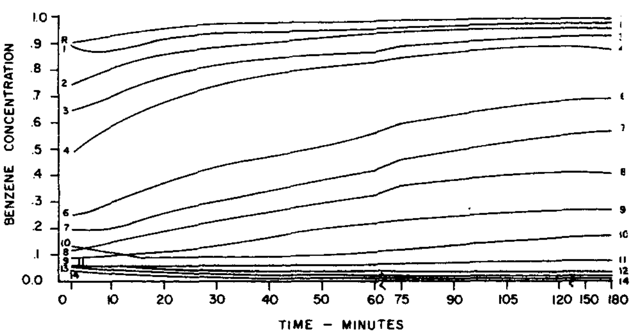

Fig. 1. Benzene concentration profile for run 830.

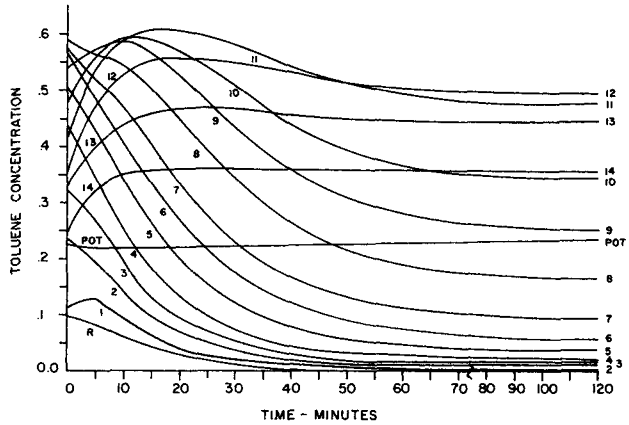

Fig. 2. Toluene concentration profile for run 830.

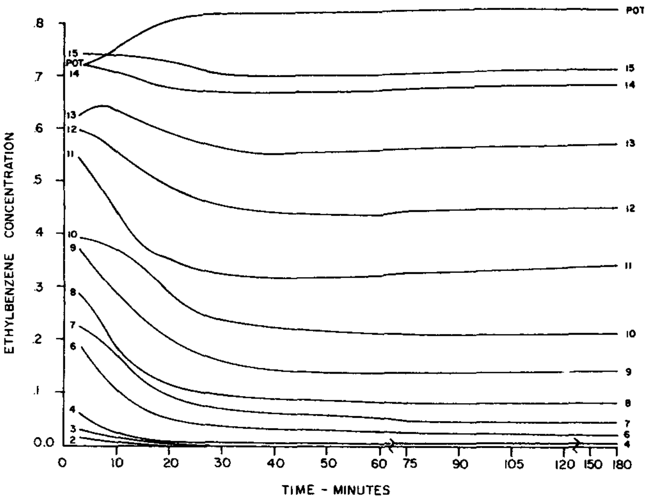

Fig. 3. Ethylbenzene concentration profile for run 830.

The amount of holdup on the plates could not be measured directly; in fact, the holdup on a particular plate could not be found at all. The average holdup per plate may be calculated from overall system component balances at any time during a run. The steady state holdups for runs 830 and 817 were calculated to be 1.39 and 1.42 lb./plate, respectively, while the average value found by weighing material drained from the column after many preliminary runs was 1.42 lb. The holdups increased with time to the steady state value in an exponential manner similar to that of a first-order system subjected to a step input.

It was hoped that efficiencies during the unsteady state period could be found from the vapor and liquid concentration measurements taken during the course of a run. As discussed previously, however, the vapor data were not satisfactory and could not be used to find unsteady state efficiencies. Steady state efficiencies were calculated by assuming that true steady state was reached. Efficiency values for run 830 are given in Table 1. The values associated with plates 4, 5, and 6 are based on an estimate of the plate 5 liquid composition. Murphree efficiencies calculated by the AIChE method are quite a bit higher than these experimental values in the range 0.76 to 0.85.

Table 1. Experimental Plate Efficiencies for Run 830

Plate	Vaporization efficiency			Murphree efficiency		
	BZ	TOL	EBZ	BZ	TOL	EBZ
1	0.9949	1.4786	1.0000	0.6925	0.6925	1.0000
2	0.9916	1.4401	1.0000	0.7105	0.7105	1.0000
3	0.9830	1.5413	1.0000	0.6382	0.6313	1.2133
4	0.9735	1.4961	1.0777	0.6540	0.6411	0.9826
5	0.9676	1.3086	1.3806	0.7590	0.7461	0.9060
6	0.9162	1.4557	2.6956	0.5634	0.5667	0.5340
7	0.8884	1.3601	2.0100	0.5849	0.5684	0.6741
8	0.8880	1.1605	1.7222	0.7011	0.7027	0.6964
9	0.8071	1.1329	1.7201	0.5807	0.5658	0.6040
10	0.7434	1.0773	1.5643	0.5143	0.3720	0.5931
11	0.9606	0.9588	1.1892	0.9350	0.5063	0.7918
12	0.7227	0.9295	1.2682	0.5707	0.6203	0.6032
13	0.7547	0.9079	1.1660	0.6390	0.6603	0.6568
14	0.8484	0.8868	1.1086	0.7852	0.6658	0.6741
Pot	0.3608	0.9844	1.0175			

COMPARISON OF COMPUTED AND REAL EXPERIMENTAL RESULTS

The simulation model and computer programs described in Part I (*4*) were used to try to duplicate the experimental concentration profiles. The computer column was set up to match the experimental column as closely as possible. The condenser was considered to have a well-mixed, constant mass holdup. Its only input stream was the vapor from the top plate, and its output was the reflux flow. The column itself consisted of fourteen plates, with the holdup on each plate specified by the exponential relationship developed from the data of run 830. The heat loss from each plate was considered constant and equal to an average steady state value. The bottom reservoir was considered to have a well-mixed, constant mass holdup equal to the steady state value calculated from measuring the fluid level. The input to this reservoir was the liquid flow from the bottom plate, and the output was the flow to the reboiler. The vapor from the reboiler was considered to pass directly to the bottom plate and had no effect on the reservoir. The pressure throughout the column was assumed constant at the atmospheric pressure observed during the experimental run. The reflux flow rate was specified constant at the steady state value measured during the experimental run. The reflux temperature was also considered constant at the experimental value.

Computer run 30 was an attempt to duplicate experimental run 830. The initial concentrations in the computer column were those of run 830 at 3 min. The calculated total amount of material in the system was 2.99 moles. The plate efficiencies were those given in Table 1. One nonexperimental value was used. The vaporization efficiency of the benzene in the reboiler was taken as 0.99 instead of the calculated value of 0.3608. This was done because all the other reboiler efficiencies in all the runs were very nearly 1.0.

The toluene concentration profiles for computer run 30 and experimental run 830 are shown in Figure 4. The computer column shows the same general behavior as the experimental column. The toluene moves both up and down the column and has a maximum value at some intermediate plate. But, the maximum value is shifted down two plates and is much less than that observed in the experimental column. The computer data show that the benzene concentrations are all much higher in the computer run than in the experimental run. The ethylbenzene concentrations are somewhat smaller.

The high benzene concentrations may be explained in part by the high reboiler efficiency. The benzene concentration on the bottom plate is nearly three times what it would be if the actual value of the efficiency had been used. A more important factor is the total charge of material to the system. The charge for the experimental run was about 2.92 moles instead of the 2.99 in the computer column. If even half of this extra material were benzene, the additional 0.03 moles could easily account for the difference in the two concentration profiles by raising the benzene levels throughout the column.

Computer run 31 was also an attempt to duplicate experimental run 830. In this case the simulation started from the conditions measured at 90 min. The reboiler

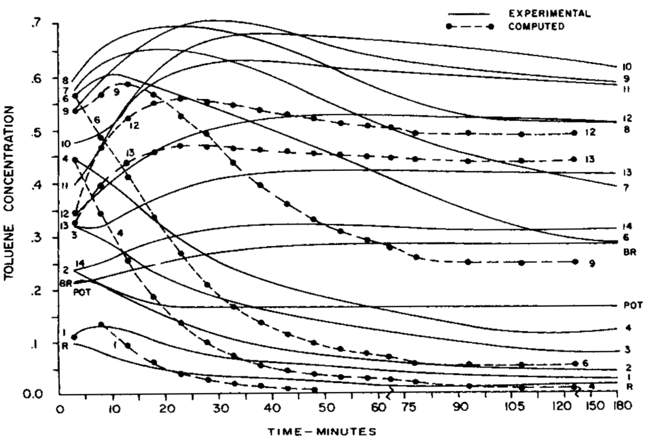

Fig. 4. Toluene concentration profiles for run 830 and Computer run 30, initial conditions at 3 min.

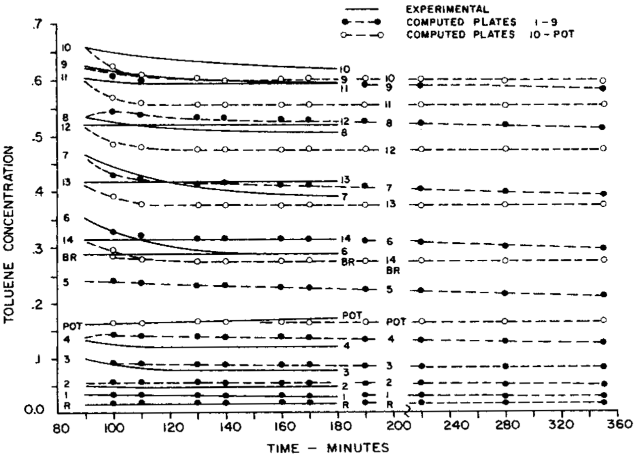

Fig. 5. Toluene concentration profiles for run 830 and Computer run 31, initial conditions at 90 min.

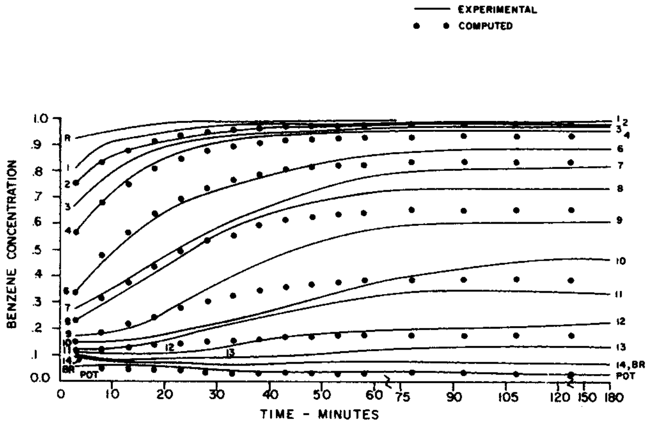

Fig. 6. Benzene concentration profiles for run 816 and Computer run 16, initial conditions at 3 min.

efficiency for the benzene was the measured value of 0.3608. The toluene concentrations for this computer run and the experimental run are shown in Figure 5. The agreement between the computer and experimental values is very good. The top nine plates correspond almost exactly. The bottom five plates show slightly lower concentrations and reach lower steady state values in the computer than they do in the real column.

Computer run 16 was planned to duplicate experimental run 816. The initial conditions were taken as those of experimental run 816 at 3 min. The reboiler holdup and the total charge were best guess type of estimates, since the total charge to the experimental system was not known exactly. The plate efficiencies were those calculated from the experimental data at 180 min. The benzene concentration profiles for the computer and experimental run are shown in Figure 6. The agreement between the two is generally good. The amount of benzene in the computer system is slightly too small, since the concentrations near steady state are all too low. The concentration profiles all drift downward during the last 60 min. of the computer run in order to reach these lower steady state values. The fact that the bottom plate and reservoir have the same concentrations at the experimental steady state indicates that the computer model of the bottom reservoir is correct.

It would be possible to obtain an exact match between computer and experimental results by adjusting the computer column specifications until the match was obtained. The great amount of computer time required to do this, however, did not seem justified in order to fulfill the aims of this work, since the computer specifications would no longer be comparable to the experimental ones. The ratio of computer time to real time depends upon the size of the time increment. The computer took about 3.27 sec. to go through one time step. If the time step is 0.1 min., the computer operates at 0.54 of real time. The 135 min. simulation of run 30 took about 75 min. on the computer. Only serious questions about the operation of a large industrial column would justify this type of simulation of the column. These conclusions and other reached during the course of this work are summarized in the next section.

CONCLUSIONS

The general questions raised at the beginning of this paper have not been answered. They may not have general answers, since the purpose for which a simulation is made will determine the accuracy required of the results. In this case the purpose was academic, to check a computation and modeling procedure and to see what experimentally determined parameters were necessary for a computer model to be able to generate the same composition profiles as a real column. The three comparisons presented in this paper show that the calculation procedure and general mathematical model used can replace the real column for many purposes. Inaccuracies in the computer simulation are due more to inadequate information about the characteristics of the real column than to deficiencies of the computer model.

The completely mixed pool plate assumption seems to be satisfactory. The rigorous method of calculating the unsteady state flow rates is valid, although in this case the flow rates could have been calculated from the steady state equations. The flexibility in choosing the holdup specification is necessary to represent the varying holdups actually observed. No attempt was made to simulate the fluid dynamic behavior, but equations to describe this aspect of column operation could easily be included in the model if this were desirable.

This simulation would be satisfactory to show the general nature of the movement of the components through the column, to show the time required to reach steady state, or to indicate the temperature fluctuations that would be observed on an intermediate plate. The predicted composition profiles are in only fair agreement with those that were observed and are very dependent upon information obtained experimentally from the real column.

In general, adequate values of column specifications such as holdups and plate efficiencies can probably not be obtained by direct calculations or by the use of general correlations. The idiosyncrasies of a real column are such that the predicted values would probably be enough in error to cause the simulated behavior to be quite inaccurate.

The simulation of a closed system (one at total reflux) is much more difficult than the simulation of an open system in which there is continuous addition and removal of material. The reason for this is that unless the exactly correct amount of all components is charged to the column as initial conditions, it can never reach the correct steady state values, and the approach to steady state will be correspondingly distorted. The open system on the other hand can always reach the correct steady state values despite incorrect initial conditions.

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