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Transient Response of a Distillation Column Plate. Part III. Model Evaluation from Concentration Pulse Data on a Plate for the Benzene-Carbon Tetrachloride System

Chester N. Sittel Jr.[ab]; Gerald T. Fisher[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] Tennessee Eastman Company, Kingsport, Tennessee

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Transient Response of a Distillation Column Plate. Part III. Model Evaluation from Concentration Pulse Data on a Plate for the Benzene–Carbon Tetrachloride System

CHESTER N. SITTEL, JR.* and GERALD T. FISHER

DEPARTMENT OF CHEMICAL ENGINEERING
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37240

Abstract

A 3-plate distillation column was operated with the benzene–carbon tetrachloride system. The liquid composition entering the second plate was pulsed by direct injection of liquid into the downcomer. The output compositions of the two downcomers below the input were monitored. Vapor and liquid flow rates from 400 to 1000 ml/min were used, with the column at total reflux. The column was a 6-in. diameter column with one glass bubble cap tray on each plate.

The composition–time data were numerically Laplace transformed, and the frequency response form was statistically fit to four models; (1) perfectly mixed; (2) plug flow; (3) perfectly mixed with downcomer delay; and (4) dispersion. The composition–time data for each model were reconstructed using the best fit parameters, and are compared with experimental data.

The statistically best model was the dispersion model. A satisfactory model which is much simpler is the perfectly mixed tray with delay in the downcomer.

INTRODUCTION

Data were generated for testing the five models of a distillation column plate previously presented. A 3-bubble cap plate distillation column was operated with the benzene–carbon tetrachloride system, with a concentration pulse of pure benzene being injected into the downcomer from the

* Present address: Tennessee Eastman Company, Kingsport, Tennessee 37662.

first plate to the second, and the resulting concentration change was measured in the downcomer from the second plate.

The five models were compared for adequacy of fit, and appropriate parameters calculated using nonlinear least squares techniques. The model evaluation was performed using the F statistic and the Students' t test.

EXPERIMENTAL EQUIPMENT

The 3-plate distillation column is shown schematically in Fig. 1.

For good control of the boil-up rate, hot water was the reboiler heat transfer medium. An American Standard Model 302 BCF 7.4 ft^2 heat exchanger was the reboiler exchanger, HX-1.

The condenser accumulator and reboiler were initially charged with a 70 mole % carbon tetrachloride–30 mole % benzene mixture. The liquid return to the reboiler was measured with a calibrated rotameter. A drain line tap in the return line was a sediment trap and a density sample port. The vapor from the top plate was fed to the reflux accumulator–condenser.

A vertically mounted American Standard Model 502 BCF 16.0 ft^2 heat exchanger was the vapor condenser, HX-2.

Reflux flow rate was measured with a calibrated rotameter. The reflux liquid was fed to the top plate of the column, plate #3. The reflux and reboiler lines were wrapped with heating tape and lagged with $\frac{1}{4}$-in. gasket tape. Column pressure and pressure drop across the column were measured with a manometer.

The base and top of the column were Corning Glass 6 × $1\frac{1}{2}$ × $1\frac{1}{2}$-in. glass tees. The tees were connected to the reboiler and reflux systems with Teflon expansion joints. The column plates were Corning Glass Vicor plates with one $3\frac{1}{2}$-in. in diameter bubble cap in the center. The plates had liquid and vapor sample ports closed with drain spigots. Initially rubber gaskets with Teflon envelopes were used but were found unsatisfactory. The downcomer liquid sample lines, inserted through the gaskets, allowed the C_6H_6–CCl_4 mixture to attack the rubber gasket center, causing it to swell and rupture, filling the column with gasket material. Teflon gaskets, sealed with sodium silicate, were acceptable because the silicate did not damage the sample withdrawal system or contaminate the distilling solutions. All gaskets in the reboiler, condenser, and column were Teflon sealed with sodium silicate.

One-half inch copper pipe was used for the downcomers. Machined Teflon was the insert between the downcomer and the plate. Check valves,

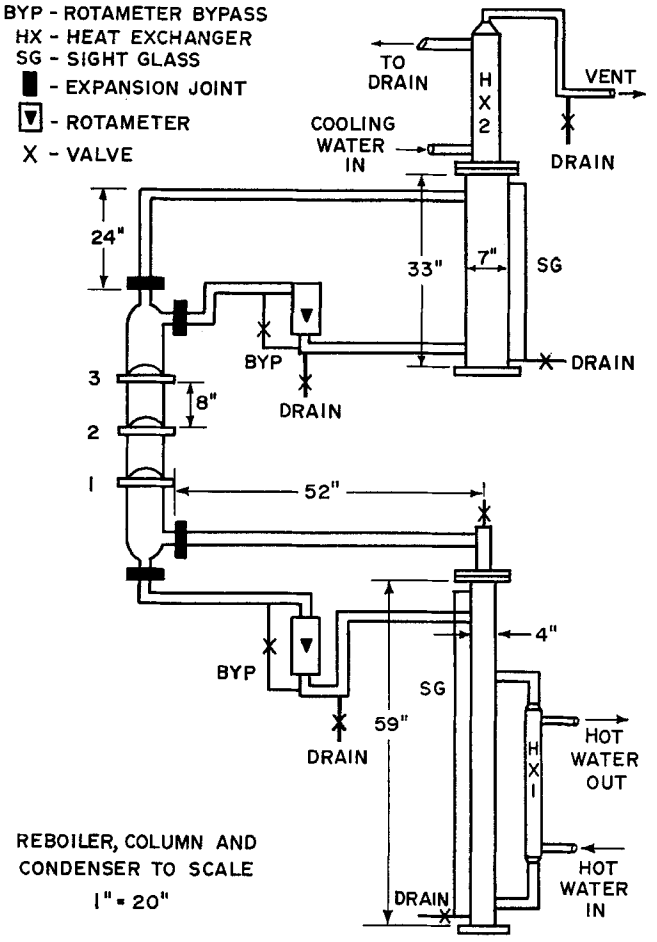

FIG. 1. Schematic of distillation column.

similar in construction to those of the distillation simulator, were used in the distillation column. In the distillation column, a $\frac{1}{4}$-in. nylon ball was used instead of polyethylene because of the better chemical resistance of nylon to carbon tetrachloride–benzene mixtures.

The sample withdrawal system is shown schematically in Fig. 2. A #17 hypodermic needle was silver soldered in the downcomer $8\frac{1}{2}$ in. from the top. The needle point was placed bevel up in the downcomer center.

Thin-wall Teflon tubing was connected from the downcomer to a

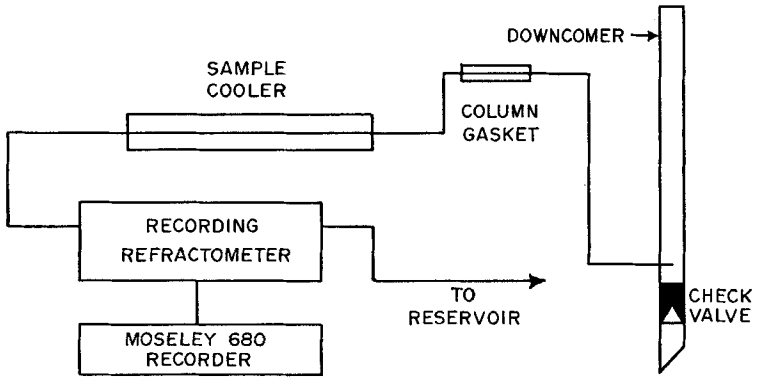

FIG. 2. Schematic of sample withdrawal system.

hypodermic needle inserted through the column gasket. Teflon tubing was connected from the gasket needle to the sample cooler. The sample flowed through 18 in. of 1/8-in. diameter copper tubing. The sample was cooled with water. The sample flowed from the cooler through the recording refractometer to a collection reservoir.

Waters Associates Inc., Miniature Liquid Chromatography Monitor, Model 34H, recording refractometers measured the composition. The refractometer output signal was the input to a Moseley 680 recorder. A benzene–carbon tetrachloride system was chosen because of its relative volatility, chemical stability, and nearly equal molar latent heats of vaporization, molar heat capacities, and molar densities. Equilibrium data for CCl_4 mole fractions greater than 0.7334 were not available. The column operated in a range of 0.60 to 0.70 CCl_4 mole fractions because of the higher flash point and the lower relative volatility in this range. Pure benzene was the tracer material. The refractometers were calibrated with C_6H_6–CCl_4 solutions in 0.05 mole fraction intervals from 0.0 to 1.0. Plotting the millivolt output of the recording refractometers, which measured the concentrations on plates n and $n - 1$, versus the millivolt output of the refractometer on plate $n + 1$, at the same concentration, gave the cross calibration constants. The cross calibration constants were temperature insensitive.

EXPERIMENTAL TECHNIQUES

At the start of the distillation column runs the reboiler and reflux accumulator were charged with a mixture of approximately 70 mole % carbon tetrachloride and 30 mole % benzene. The condenser and sample

cooling water were turned on. The hot water heater was filled and the steam pressure to the heating coils was set at 30 psig. The Honeywell 24 point temperature recorder was turned on. When the vapor ring reached the top of the column, the sample lines were blown clear and the refractometers and recorders were turned on to "warm up." When the heating water began to boil freely, the steam pressure was decreased to 12 psig to conserve the water. The recycle line around the heating water pump was opened and adjusted to approximate the desired boilup rate. When reflux was observed flowing from the return line, the heating tape was turned on. Two to 4 hr were allowed for the column to attain steady state. During this time the heating water flow rate was adjusted to give the desired reflux flow rate. When steady state was attained, sample flow was diverted through the refractometers for at least 30 min until the recorded traces became constant.

The recording refractometers were checked for significant dynamics. The response was examined by step testing. The response was examined at 0.5, 1, 2, 3, and 4 time constants. The response fit a first-order system with a 0.768 sec time constant. This gave a breakpoint frequency of 1.3 rad/sec which was high enough so that no correction was needed for the refractometer response.

Reflux flow rates ranged from 1000 to 400 ml/min in approximately 100 ml/min intervals. Duplicate runs were attempted at each flow rate. For each run, reflux and bottoms flow rates, froth height, base refractometer settings, and sample line flow rates were recorded along with the pulse tracer curves. At the end of a set of runs, liquid and vapor samples were taken from the plates and condenser vapor line. Vapor and liquid samples were corked tightly. The compositions were determined with a Bausch and Lomb precision refractometer. Samples for density determinations were taken from the drains on the reflux and reboiler return lines.

The reboiler heating water pump was shut off and the clear liquid holdup on each plate was determined.

RESULTS AND DISCUSSIONS

The distillation sample withdrawal system was checked for dynamics. The system consisted of the downcomer tubing, the gasket hypodermic needle, the tubing to the sample cooler, the sample cooler, the refractometer tubing, and the refractometer associated with the system. The system volume from pulse tests differed from the volume calculated from manufacturers information by less than 9%. Sample system response corrected

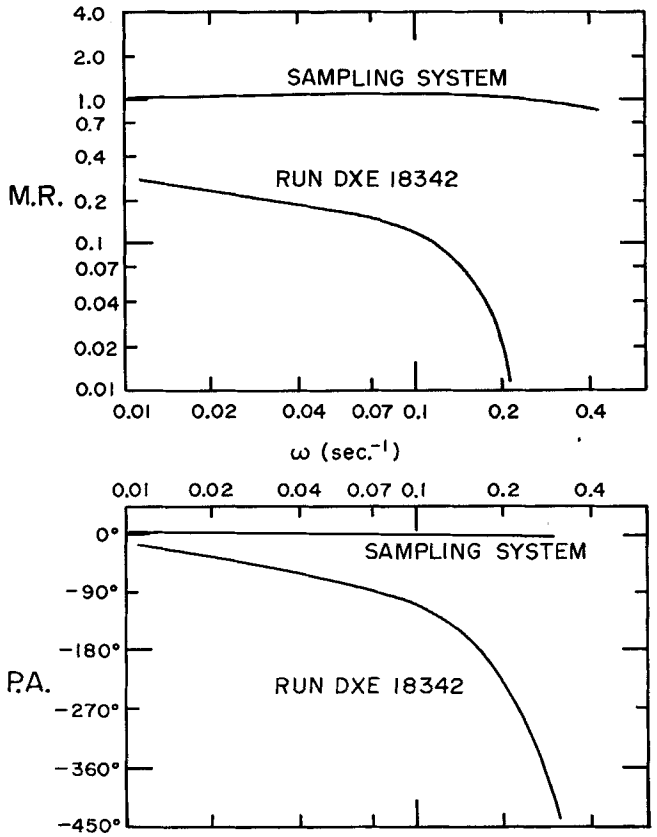

FIG. 3. Sample system response.

by Eq. (128) and (129), Ref. *1*, is shown in Fig. 3. The response of run DXE 18342 is also included for comparison.

The sample withdrawal system response was flat to about 0.4 rad/sec and it may have been flat beyond that but the pulse frequency content was too low (less than 0.01) for reliability. Because of the lower frequency content of the system dynamics, the effect was negligible. The maximum deviation in the phase angle was 7° in 480°.

The effect of pulse injection on the column response was examined. Fifty cubic centimeters of the solution on plate $n + 1$ were withdrawn and the output of plates $n + 1$, n, and $n - 1$ were examined. The 50 cc were then injected onto plate $n + 1$ and the response was checked. No

change in base levels was observed for the tests, so no pulse flow rate correction factor was necessary.

In the distillation column work the original plan was to use the response of plates $n + 1$ and $n - 1$ to calculate the output response of plate n. This approach was unsatisfactory because the pulse height on plate $n - 1$ was on the order of 0.02 mole fraction and the base line fluctuations were about 0.0005 mole fraction, making the data unreliable. The small concentration change on plate $n - 1$ validates the boundary condition

$$\lim_{z \to \infty} x_n(t,z) = 0 \tag{1}$$

and in addition the assumption of negligible concentration below plate $n - 1$

$$X_{n-2}(\zeta,s) = 0 \tag{2}$$

Figures 4–7 show the fitting of the distillation column data from run DXE 18342 with the perfectly mixed, plug flow, perfectly mixed plate with time lag, and dispersion models. For comparison purposes, Fig. 8 shows the data fit with the dispersion model without mass transfer (*2*). In order of increasing ability to fit the data, the models were the plug

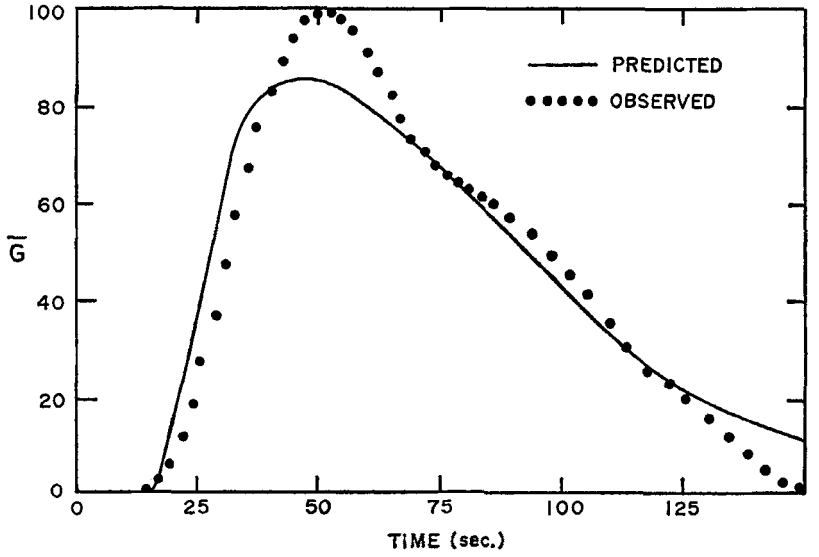

FIG. 4. Fitting of the data from run DXE 18342 with the perfectly mixed model.

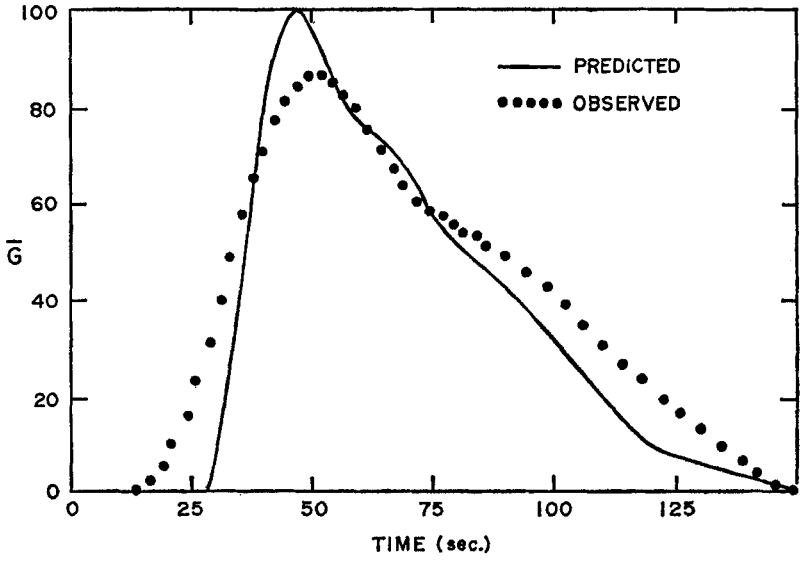

FIG. 5. Fitting of the data from run DXE 18342 with the plug flow model.

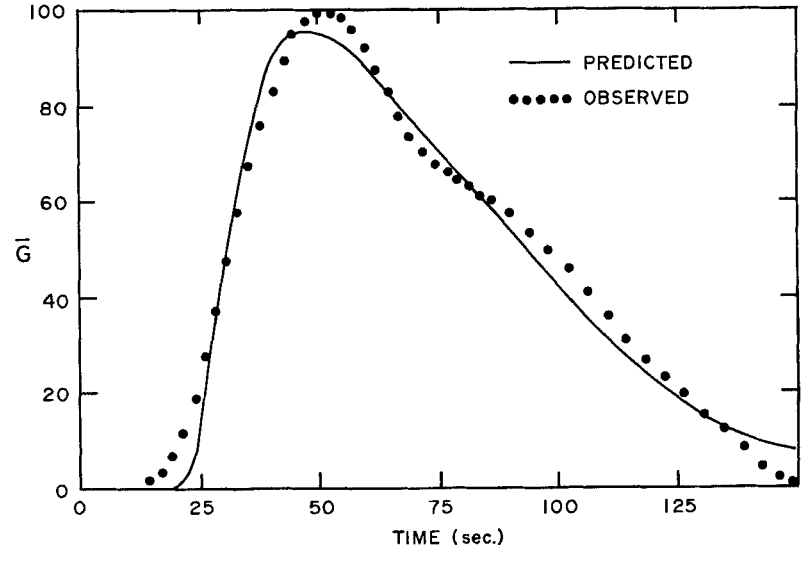

FIG. 6. Fitting of the data from run DXE 18342 with the perfectly mixed plate with time lag model.

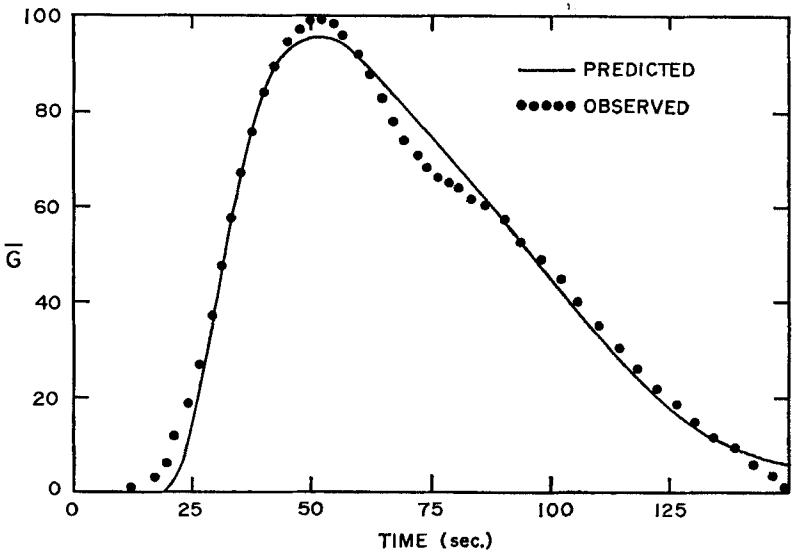

FIG. 7. Fitting of the data from run DXE 18342 with the dispersion model.

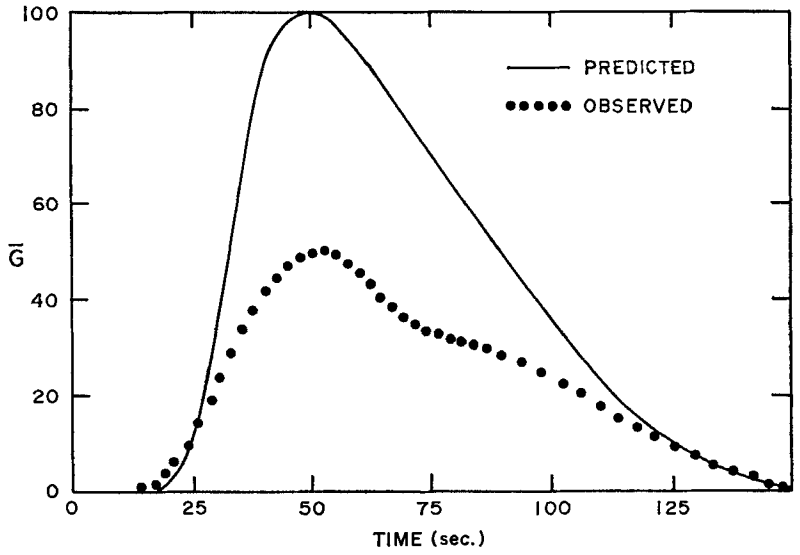

FIG. 8. Fitting of the data from run DXE 18342 with the dispersion model without mass transfer.

flow, perfectly mixed, perfectly mixed plate with time lag, and the dispersion model. These results were identical to those of the distillation simulator.

For correlating the data from the mixing apparatus (*2*) and the distillation column, the equation

$$(D_L/X^2)^{\frac{1}{2}} = 0.08393 + 0.001936F + 0.07435L - 0.1488W + 0.001784\rho_L \tag{3}$$

was used. The range of variables covered was: F, from 0.0 to 0.492 (ft^3) (square root of gas density in lb/ft^3)/(sec) (tray bubbling area, ft^2); L, from 0.355 to 0.755 gal/(min) (average tray width, ft); W, from 7/8 to 11/8-in.; and ρ_L from 62.2 to 83.2 lb/ft^3. The average error in fitting the dispersion function was 15%. The correlating equation along with the data from all runs is shown in Fig. 9. The confidence limits on Eq. (3) included the coefficients of Eq. (6), Ref. (*2*), and that from the American Institute of Chemical Engineers' study (*3*) modified to the form of Eq. (3). From this fact it was concluded that the simulator could predict the dispersion function for a distillation column.

The mass transfer function $(\beta/m)^{\frac{1}{2}}$ was correlated by the equation

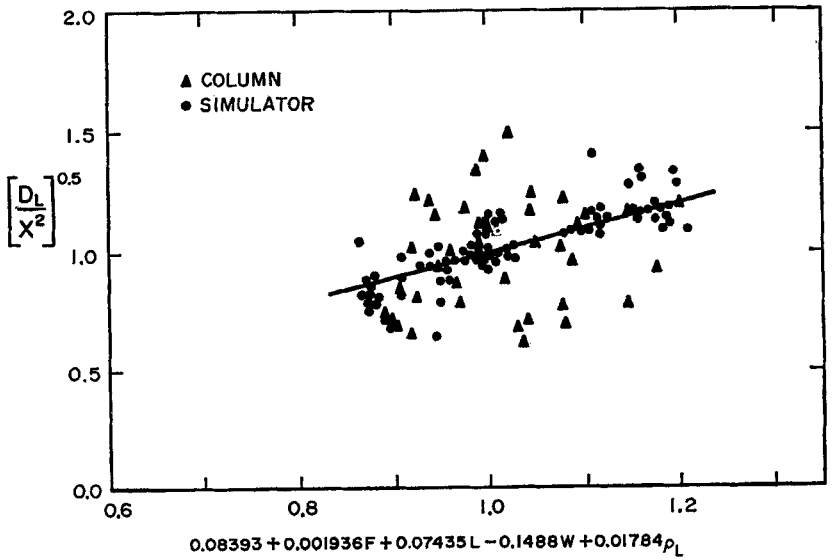

FIG. 9. Correlation of the dispersion function.

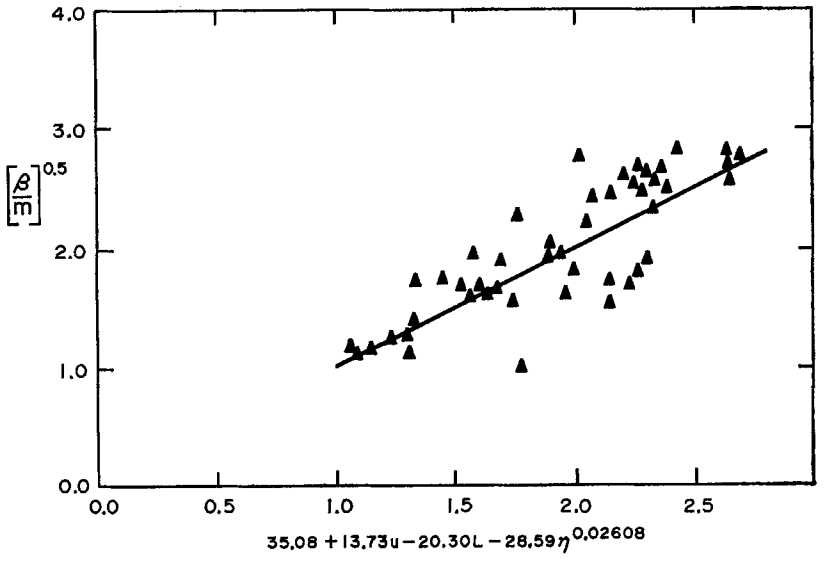

FIG. 10. Correlation of the mass transfer function.

$$(\beta/m)^{\frac{1}{2}} = 35.08 + 13.73u - 20.30L - 28.59\eta^{0.02608} \quad (4)$$

where m is the volatility of the most volatile component.

The average error in fitting the data was 15%. The correlation covers the range of variables was: u, from 0.363 to 0.937 $ft^3/(sec)$ (tray bubbling area, ft^2); L, from 0.261 to 0.706 gal/(min) (average tray width, ft); and η from 48 to 264 sec. The mass transfer data correlation is shown in Fig. 10. During transient runs, Martin (*4*) observed an error between the theoretical and the actual enriching factors of 200%.

With the range of variables investigated and the plate system described, Eqs. (3) and (4) correlated the data from this study.

The F statistic for the 95% confidence limit, 1.60, was applied to the sum of the squared error in each data fitting. The F statistic was used to find the best predictive model. Table 1 gives the number of times the model in the column is statistically better than the model of the row for all data. These results indicated that the dispersion model was the best model investigated. However, a more conclusive analysis was desired.

The sum of the squared error is a measure of the model fit to the data, and the model having the smallest squared error was defined to be the one that gave the best fit. Hald (*5*) suggests the use of Students' t test on the difference, d_i, of paired observations. If the hypothesis that the observa-

TABLE 1

Statistical Comparison of the Model Results from the Distillation Simulator and Column

	Perfectly mixed	Plug flow	Perfectly mixed plate with time lag	Dispersion
Perfectly mixed	*	9	104	109
Plug flow	99	*	111	111
Perfectly mixed plate with time lag	1	0	*	41
Dispersion	2	0	7	*
Total number of cases	120			

tions are from the same population is valid, then the difference variable should be a population with a zero mean. The data could be meaningfully grouped in pairs since the data were fit with each of the four models. The comparison of the squared error could be made for any two models for the same data run. This approach appeared to be a satisfactory method of data analysis.

Table 2 gives the t statistic value when the model in the column is compared to the model in the row. If the entry is positive and greater than $t_{0.95}$, then the column model has a statistically significant smaller squared error than the model of the row. From an examination of Table 2 it is seen that in increasing order of ability to fit the data the models were: plug flow, perfectly mixed, perfectly mixed with time lag, and dispersion.

The dispersion model with the boundary condition of equal derivatives

TABLE 2

Student's t Test for the Models Distillation Simulator and Column

	Perfectly mixed	Plug flow	Perfectly mixed plate with time lag	Dispersion
Perfectly mixed	*	−8.97	11.70	11.94
Plug flow	8.97	*	9.64	9.69
Perfectly mixed plate with time lag	−11.70	−9.64	*	4.54
Dispersion	−11.94	−9.69	−4.54	*

$t_{0.95} = \pm 1.98$

with respect to distance at the point of measurement was derived. Using the t-test, this model was compared with the infinite boundary condition model, and no significant difference was found. Also the series of perfectly mixed tanks model was compared to the dispersion model, and the t-test indicated that the dispersion model was statistically superior in fitting the data.

All the models have the same magnitude ratio and phase angle at zero frequency, and then diverge from each other as the frequency increases. The data pulses dropped to a low frequency content at low frequencies (maximum frequency approximately 0.35 rad/sec); this made model discrimination more difficult.

All these models are empirical descriptions of the actual situation on a distillation plate. This empiricism will remain until an accurate and useful model of turbulent transport is available. A better understanding of turbulent mass flux is needed. Defining the turbulent mass flux analogous to Fick's law was suspected to be one reason for the imperfect fit of the dispersion model. This approximation is valid for turbulent pipe flow (*6–8*), but its use in a vapor agitated open system, such as a distillation plate, may be inadequate. Large eddies were observed on the distillation mixing apparatus; this observation would make Fick's law analogy uncertain.

CONCLUSIONS AND RECOMMENDATIONS

(1) In order of increasing statistical goodness of fit, the models were: plug flow, perfectly mixed, perfectly mixed with time lag, and the dispersion model. It was concluded that the dispersion model gave the best empiric representation of the dynamic data and therefore was the best of all the models investigated in describing distillation column concentration dynamics.

(2) The dead zone model did not provide a significant improvement in data fitting because the parameters θ and τ were superfluous.

(3) The dispersion model with the infinite boundary condition was a physically impossible situation, but it was not significantly different, in a statistical sense, from the dispersion model with continuous derivatives. In addition, the infinite boundary condition case was computationally easier.

(4) The series of perfectly mixed tanks was a statistically poorer model when compared to the dispersion model.

(5) The dispersion model was better from a physical viewpoint because

it allowed pulse concentration to vary with distance and time along the plate. The concentration gradients which existed on the plates experimentally verified this viewpoint.

(6) The distillation mixing apparatus and column were comparable in discriminating between dynamic models and in predicting dispersion coefficient values.

A microscopic study of turbulence, such as Taylor's (*6–8*) for pipe flow, should be performed for distillation plates. The prediction of the degree of turbulent mixing in cases where flow geometry and turbulent inducing mechanisms are complicated should be the objective of such an investigation. Also, a microscopic study on the effect of mixing turbulence on distillation mass transfer would prove valuable.

Also, dynamic studies should be made on the combined effects of temperature, reflux flow rate, boilup rate, feed rate, and feed enthalpy and composition. These investigations would more nearly determine the parameters important to distillation dynamics.

SYMBOLS

D_L	longitudinal dispersion coefficient (ft^2/sec)
F	F factor, $u\sqrt{\rho_V}$, [ft^3 square root of gas density in lbm/ft^3/sec (square feet of bubbling area)]
L	L factor, liquid flow rate [gal/min (average feet tray width)]
$\tilde{L}$	molar liquid flow rate (lb moles/sec)
m	constant in equilibrium relationship $y = mx + b$
n	plate number
s	Laplace transform variable
t	time (sec)
u	u factor, linear gas velocity [ft^3/sec (square feet of tray bubbling area)]
V	molar gas flow rate (lb moles/sec)
W	outlet weir height (in.)
$x_n(t,z)$	liquid mole fraction on plate n as a function of time t and distance z
$X_{n-2}(\zeta,s)$	transformed liquid mole fraction on plate $n-2$ as a function of reduced length ζ and transform variable s
X	total length of travel on a distillation plate (ft)
z	coordinate length on a tray (ft)
β	mass transfer term on tray n, $m\tilde{V}/\tilde{L}$
ζ	reduced length, $\zeta = z/Z$

η dispersion coefficient function, D_L/X^2, on plate n (sec)
ρ_L liquid density (lbm/ft^3)
ρ_V gas density, (lbm/ft^3)

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