$M = \alpha - \gamma$ (Freundlich) $M = \alpha$ (Temkin)

For ethane, M is always near 0 on nickel and the alloys (Table 2, column 7) thus $\alpha \sim \gamma$ (Freundlich) or $\alpha \sim 0$ (Temkin). In the latter case, the forward rate constant for

the first irreversible step is independent of S; that is, this irreversible step on a nonuniform surface is indistinguishable from an irreversible step on a uniform surface.

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Periodic Cycling of Plate Columns: Discrete Residence Time Distribution

The discrete residence time distribution applies to systems under periodic control. A system consisting of a plate column has been modeled to allow the generation of the discrete residence time distribution. The parameters in the model have been evaluated by measurements of entrainment, holdup, and the step response of the column under direct computer control. A least-squares minimization technique provided confirmation of the modeling procedures.

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SCOPE

Periodic cycling is a technique that can be applied to all separation processes taking place in plate columns. The vapor flow to the column is switched on and off in a regular cycle, and liquid drains from plate to plate during the brief time the vapor flow is zero. The theory of this unsteady state processing has been developed for a linear equilibrium relationship and predicts a major increase in separating ability. These increases have been observed in small distillation columns, but in experimental studies on large columns and in gas absorption columns reported in the literature, the increases predicted by the theory could not be obtained. The reason for this difference has been reported as due to mixing

of the liquid as it drains from plate to plate when the vapor flow is zero. Conventional mixing models from plug flow to a series of well-mixed stages have been used to account for the mixing. However, there is little physical significance in using a model consisting of well-mixed stages. An improvement in modeling of the liquid mixing during the draining period is proposed in this paper, which has real physical significance. It consists of liquid being transferred from a plate to the next two successive plates below. A fraction of the liquid is retained and mixed on each of these two plates. This improvement in the understanding of the draining phenomenon can lead to the minimization of the liquid mixing and a closer approach between theory and experiment.

CONCLUSIONS AND SIGNIFICANCE

We have proposed a new liquid mixing model for the liquid draining period for plate columns under periodic control. This (2S) model allows liquid to penetrate to the two neighboring plates below. The model allows for the prediction of the holdup distribution on the plates, and the response to an impulse is the discrete residence time distribution, which is a characteristic of systems under periodic control. The two parameters in the (2S) model were evaluated from the step response of a column controlled from a PDP11/45 computer

We can conclude that a significant fraction of the liquid holdup on a plate bypasses the plate immediately

below and is retained by the second plate below. In our investigations we found 63% of the holdup was transferred to the plate below and 12.5% to the second plate below.

This liquid bypassing of a plate during the liquid draining period has a significant effect on the separating ability of the column. It considerably reduces the separation that is predicted by the normal theory of periodic cycling. The inclusion of the (2S) mixing model into the mass transfer theory of periodic control results in a more complex treatment and will appear later.

Danckwerts (1953) introduced the residence time distribution for continuous systems and uses the C distribution for the impulse response and the F distribution for the step response. The distributions allow for the identification of plug flow and perfectly mixed regions in a system. Departures from these extreme flow conditions can be accommodated by dead water, bypass streams and the use of

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the Peclet number to characterize longitudinal mixing. The Laplace transform of the C distribution or the impulse response is the transfer function of the system. If the output of the system is observed at fixed time intervals only, we can generate the Z transform of the system. Both of these transfer functions apply only to systems which have the properties of a continuous variable.

If the system is under periodic control, then the output is discontinuous and the use of continuous system variables is not applicable. In this case, the residence time distribution and both transfer functions cannot be used. When a system is under periodic control, its output response is characterized by the discrete residence time distribution (DRTD). The DRTD allows for the identification of various flow regions existing in the system during those parts of a time cycle under periodic control. The DRTD is important in mass transfer processes, such as distillation, gas absorption, and liquid extraction, and in controlling contact times for chemical reactors. There are many advantages in using plate columns with periodic control, and the DRTD will be generated for this system.

LIQUID HOLDUP DISTRIBUTION

When the vapor flow rate is reduced to zero in a plate column, liquid drains from plate to plate throughout the column. The time interval before the vapor flow rate is returned to its normal value is the liquid drain time t_d . During this time, liquid originally on plate n can be transferred to plates n+1, n+2, n+3, etc., below. The ideal liquid draining mechanism is when all the liquid on plate η is transferred to plate n+1. Under these conditions, Horn (1967) and Furzer and Duffy (1974) have shown that the separation ability of the column is a maximum.

The (1S) model for nonideal draining is when a fraction n of the liquid holdup is transferred one plate below. The (2S) model is when fractions a and b of the liquid holdup are transferred to the next two stages, respectively. Such model building can be extended to 3S, 4S, and NS models to accommodate extensive transfer of liquid holdup deep into the column. The 2S model is the most satisfactory to account for small departures from ideal liquid transfer and will apply for short liquid drain periods.

The holdup will remain constant during the vapor-on period, when the weeping and entrainment rates are equal. The holdup on plate n at the end of a cycle is $h_{n,1}$ and must be equal to the holdup at the start of the next cycle $h_{n,0}$. The periodicity conditions which apply between the end of one cycle and the start of the next are

$$h_{1,0} = (1 - a - b) h_{1,1} + M$$

 $h_{2,0} = (1 - a - b) h_{2,1} + a h_{1,1}$
 $h_{n,0} = (1 - a - b) h_{n,1} + a h_{n-1,1} + b h_{n-2,1}$

The steady state conditions are

$$h_{1,0} = h_{1,1}$$

 $h_{2,0} = h_{2,1}$
 $h_{n,0} = h_{n,1}$

We define a dimensionless holdup as

A computer solution of this equation shows how the liquid holdup is distributed throughout the column and its functional dependence on the two parameters a and b in the (2S) model. Table 1 shows the results for a=0.75 and increments in b of 0.05, and a=0.5 and increments in b of 0.1. The latter result is also shown in Figure 1. It should be noted that the maximum holdup occurs on plate 1, and the successive maxima occur on odd numbered plates. The minimum occurs on plate 2, and successive minima occur on even numbered plates. The reduction in the holdup on plate 2 can be highly significant as b increases; when b=0.5 the holdup is only 0.5 compared with 1.0 on plate 1. The main characteristic of the liquid holdup distribution is the nonuniform holdup throughout the column, although as we progress down the column the holdup becomes more even.

DISCRETE RESIDENCE TIME DISTRIBUTION

We can define the discrete residence time distribution DRTD as the response of a system under periodic control to an impulse in the input. A unit impulse is one in which a unit mass of inert nonvolatile tracer is admitted to plate 1 at time zero. The output from the system which occurs only at integer values of the cycle time is the DRTD of the system. If a unit step change in tracer composition is the input to the system, then the output is the summation of the DRTD.

For the (2S) model, there will be a unique DRTD for each set of the parameters a and b. The most general form of the DRTD would also account for the effects of entrainment and weeping. The liquid streams that occur during the vapor-on period are shown on Figure 2. For constant mass balances, it is necessary to return any entrainment from plate 1 back to plate 1, and no weeping can occur from the bottom plate. A mass balance around a control volume which cuts the column between plates and passes around the end of the column (see Figure 2) at steady state leads to

$$e_1 = e_2 = \dots e_n$$

 $w_1 = w_2 = \dots w_{n-1}$
 $e = w$

If we divide the vapor-on period t_v into j equal time intervals of length Δt , then the mass balance for a tracer at time interval i is given by

$$h_{1}x_{1}(t_{i+1}) = (h_{1} - e\Delta t - w\Delta t)x_{1}(t_{i})$$

$$+ e\Delta t x_{2}(t_{i}) + w\Delta t x_{1}(t_{i})$$

$$h_{n}x_{n}(t_{i+1}) = (h_{n} - e\Delta t - w\Delta t)x_{n}(t_{i})$$

$$+ e\Delta t x_{n+1}(t_{i}) + w\Delta t x_{n-1}(t_{i})$$

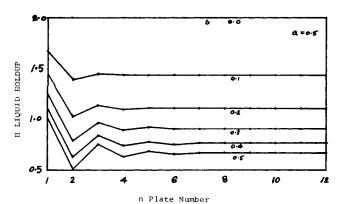


Fig. 1. Liquid holdup distribution.

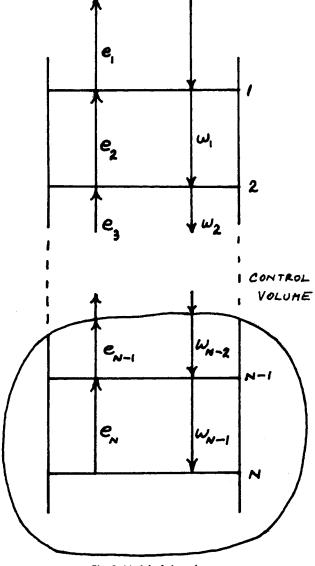


Fig. 2. Model of the column.

 $h_N x_N(t_{i+1}) = (h_N - e\Delta t) x_N(t_i) + w\Delta t x_{N-1}(t_i)$

Define a dimensionless time T and a dimensionless entrainment E as

$$T = \frac{t}{t_v}$$

$$E = \frac{et_v}{M}$$

TABLE 1. LIQUID HOLDUP DISTRIBUTION

2S Model

a = 0.75										
b	0.0	0.05	0.10	0.15	0.20	0.25				
n										
1	1.3333	1.2500	1.1765	1.1111	1.0526	1.0001				
2	1.3333	1.1719	1.0381	0.9259	0.8310	0.7502				
3	1.3333	1.1768	1.0543	0.9568	0.8777	0.8126				
4	1.3333	1.1765	1.0524	0.9516	0.8679	0.7970				
5	1.3333	1.1765	1.0527	0.9525	0.8699	0.8009				
6	1.3333	1.1765	1.0526	0.9524	0.8696	0.7999				
7	1.3333	1.1765	1.0526	0.9524	0.8696	0.8002				
8	1.3333	1.1765	1.0526	0.9524	0.8696	0.8001				
9	1.3333	1.1765	1.0526	0.9524	0.8696	0.8001				
10	1.3333	1.1765	1.0526	0.9524	0.8696	0.8001				
			a = 0.5	.						
b	0	0.1	0.2	0.3	0.4	0.5				
n										
1	2.0000	1.6667	1.4286	1.2500	1.1111	1.0000				
2	2.0000	1.3889	1.0204	0.7812	0.6173	0.5000				
3	2.0000	1.4352	1.1370	0.9570	0.8368	0.7500				
4	2.0000	1.4275	1.1037	0.8911	0.7392	0.6250				
5	2.0000	1.4288	1.1132	0.9158	0.7826	0.6875				
6	2.0000	1.4285	1.1105	0.9066	0.7633	0.6563				
7	2.0000	1.4286	1.1113	0.9100	0.7719	0.6719				
8	2.0000	1.4286	1.1111	0.9087	0.7681	0.6641				
9	2.0000	1.4286	1.1111	0.9092	0.7698	0.6680				
10	2.0000	1.4286	1.1111	0.9090	0.7690	0.6660				

Note that E is the mass of liquid entrained per cycle per unit mass of input liquid. The set of equations becomes

$$H_{1}x_{1}(T_{i+1}) = (H_{1} - E\Delta T) x_{1} (T_{i}) + E\Delta T x_{2} (T_{i})$$

$$H_{n}x_{n}(T_{i+1}) = (H_{n} - 2E\Delta T) x_{n} (T_{i})$$

$$+ E\Delta T x_{n+1} (T_{i}) + E\Delta T x_{n-1} (T_{i})$$
(2)
$$H_{N}x_{N}(T_{i+1}) = (H_{N} - E\Delta T) x_{N} (T_{i}) + E\Delta T x_{N-1} (T_{i})$$

$$0 \le T \le 1$$

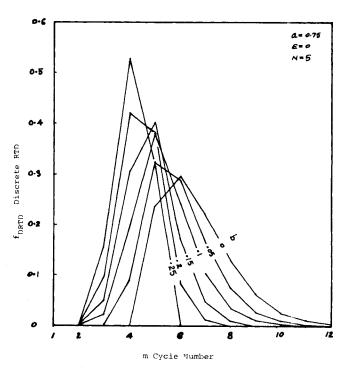


Fig. 3. Discrete residence time distribution.

This set of equations contains the holdups H_1 , H_2 , H_N which are already available from Equation (1). The initial conditions for an impulse at time zero correspond to a unit mass of tracer on plate 1 at the start of the first cycle and the first time interval.

Impulse
$$x_1(T_1) = \frac{1}{H_1}$$

 $x_n(T_1) = 0 \quad n = 2, 3, ... N$

Iteration on Equation (2) through j steps leads to the tracer composition at the end of the first cycle at T=1; that is, $x_1(1)$, $x_2(1)$, $x_3(1)$ $x_N(1)$. Liquid draining then takes place, and the 2S model leads to the following mass balances:

$$H_1x_1(0) = H_1 (1 - a - b) x_1(1)$$

$$H_2x_2(0) = H_2 (1 - a - b) x_2(1) + H_1a x_1(1)$$

$$H_nx_n(0) = H_n (1 - a - b) x_n(1)$$

$$+ H_{n-1} a x_{n+1}(1) + H_{n-2}b x_{n-1}(1)$$
 (3)

Here, $x_1(0)$, $x_2(0)$ $x_n(0)$ are the initial conditions for the start of the next cycle. This process of repeated iteration and the establishing of new initial conditions can continue for M cycles.

The output from the system is $X_{N,m}(1)$ for each cycle number m from 1 to M, is the DRTD, or is

$$X_{N,m}(1) = (a+b) H_N x_N + b H_{N-1} x_{N-1}$$

$$x_{N,m}(1) = f_{DRTD}(a, b, E, N, M)$$
(4)

It should be noted that the $f_{\rm DRTD}$ is a discrete function with values at integer values of the cycle number, which may be joined by straight lines for better interpretation. Figure 3 and Table 2 show values of $f_{\rm DRTD}$ for a five-plate column for the first twelve cycles as

$$x(1) = f_{DRTD} (0.75, b, 0.0, 5, m)$$

The maxima in the distribution move from cycle number 6 through to 5 and 4 as the parameter b is increased from 0 to 0.25.

The DRTD can be characterized by its moments, which leads to the mean cycle number and its variance. The mean as defined by Equation (6) allows for a fractional part to the cycle number:

$$\sum_{i=1}^{M} f_i = 1 \tag{5}$$

$$\overline{m} = \sum_{i=1}^{M} m_i f_i \tag{6}$$

$$\sigma_m = \sum_{i=1}^M (m_i - \overline{m})^2 f_i / \sum_{i=1}^M f_i$$
 (7)

$$\theta = \frac{m}{\overline{m}}$$

$$\overline{\theta} = \frac{\sum_{i=1}^{M} \theta_i f_i}{\sum_{i=1}^{M} f_i}$$

$$\frac{1}{\sum_{i=1}^{M} f_i} f_i$$

$$\overline{\theta} = \frac{\frac{1}{m} \sum_{i=1}^{M} m_i f_i}{\sum_{i=1}^{M} f_i}$$

$$\overline{\theta} = 1 \tag{8}$$

$$\sigma = \sum_{i=1}^{M} (\theta_i - \overline{\theta})^2 f_i \left| \sum_{i=1}^{M} f_i \right|$$

$$\sigma = (\overline{m})^2 \sigma_m \tag{9}$$

The DRTD using θ has the important properties of the summation of DRTD = 1, and the mean cycle time $\overline{\theta}=1$. The mean cycle number \overline{m} is shown on Figure 4a for a five-plate column. The variance σ about $\overline{\theta}=1$ is shown on Figure 4b for a five-plate column and shows that the parameter a is an important variable which controls the spread of the DRTD. It is valuable to compare the variance of the DRTD with the variance of n well-stirred tanks in series. It can be shown that if the time θ is made dimensionless, so that the mean dimensionless time is 1, then the variance about the meantime is given by

$$\sigma_n = \frac{1}{n} \tag{10}$$

For equal variances of the DRTD and n tanks in series

$$n = \frac{1}{\sigma} \tag{11}$$

TABLE 2. DISCRETE RESIDENCE TIME DISTRIBUTION

2S Model

$$a = 0.75$$
 $E = 0.0$ $N = 5$
 $f_{DRTD}(0.75, b, 0.0, 5, m)$

b	0.0	0.05	0.10	0.15	0.20	0.25
m						
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0.575×10^{-2}	0.235×10^{-1}	0.540×10^{-1}	0.980×10^{-1}	0.156
4	0	0.920×10^{-1}	0.196	0.307	0.420	0.527
5	0.237	0.325	0.383	0.404	0.383	0.317
6	0.297	0.289	0.244	0.172	0.854×10^{-1}	0.158×10^{-3}
7	0.222	0.166	0.103	0.486×10^{-1}	0.123×10^{-1}	$0.475 imes 10^{-7}$
8	0.130	0.759×10^{-1}	0.351×10^{-1}	0.110×10^{-1}	0.140×10^{-2}	0.111×10^{-10}
9	0.649×10^{-1}	0.299×10^{-1}	0.103×10^{-1}	0.216×10^{-2}	0.139×10^{-3}	0.221×10^{-14}
10	0.292×10^{-1}	0.107×10^{-1}	0.275×10^{-2}	0.383×10^{-3}	0.124×10^{-4}	0.399×10^{-18}
11	0.122×10^{-1}	0.354×10^{-2}	0.682×10^{-3}	0.633×10^{-4}	0.102×10^{-5}	0.664×10^{-22}
12	$0.478 imes 10^{-2}$	0.111×10^{-2}	0.160×10^{-3}	0.988×10^{-5}	0.801×10^{-7}	0.104×10^{-25}

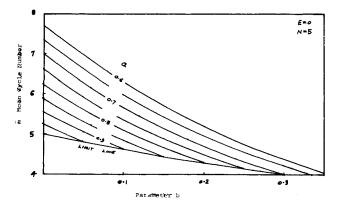


Fig. 4a. Mean cycle number.

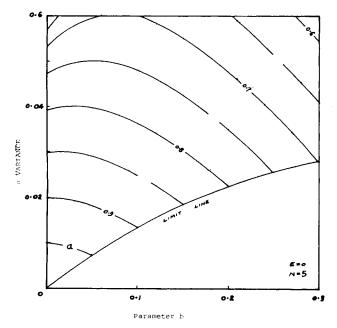


Fig. 4b. Variance.

Figure 5 shows values of n the importance of the parameter a. When $a=1,\ b=0$, the DRTD is simply an impulse occurring at cycle number N, and $n\to\infty$. This control over the spread of the DRTD is one of the major advantages of periodic control.

For a unit step change input to the column, the output on cycle number m is given by

$$F_m = \sum_{i=1}^m f_i \tag{12}$$

$$F = F(a, b, E, N, m) \tag{13}$$

Figure 6 shows the effect of the parameter a on the step response for b=0. When a=1, the output jumps to 1 at cycle number 5 for a five-plate column. As the parameter a decreases, the response becomes more sluggish.

The entrainment parameter E has a similar effect to back mixing in the column. However, the need to balance weeping with entrainment leads to short residence times in the column. Figure 7a shows the DRTD for a five-plate column with a=0.75, b=0.225, and Figure 7b shows the step change response for a=0.75, b=0. The number of well-mixed tanks n with the same variance is considerably reduced by entrainment as shown in Figure 8.

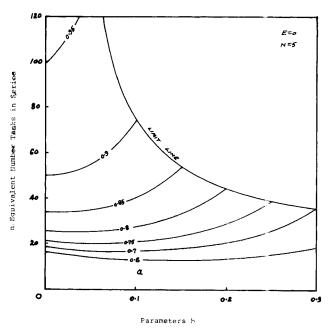


Fig. 5. Equal variances: n tanks in series.

APPARATUS AND EXPERIMENTS

A 600 mm diameter column containing five plates was operated under periodic control by direct digital control to a PDP11/45 computer. A simplified drawing of the apparatus is shown in Figure 9. Air from a centrifugal compressor enters the column through a three-way valve and then passes through sieve plates with 5% free area and 6 mm diameter holes. Water is pumped through a three-way valve to the top plate and is discharged from the bottom plate. Electrical connections to the three-way valves pass to an interface and through the MINIBUS system to the PDP11/45 computer. The pressure drop over the top plate is measured by a DP cell with an electrical output which is connected to the interface. Programs in the computer monitor the liquid holdup on the top plate and control the mass of liquid pumped onto the column each cycle. These programs also control the vapor-on and liquid drain times. Highly reliable and reproducible control could be achieved with this control scheme. Full details of the apparatus and column operation are given by Duffy (1976).

Three experiments were completed on this apparatus to

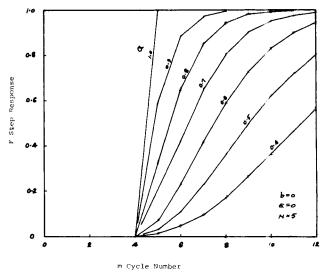


Fig. 6. Step response of a five-plate column.

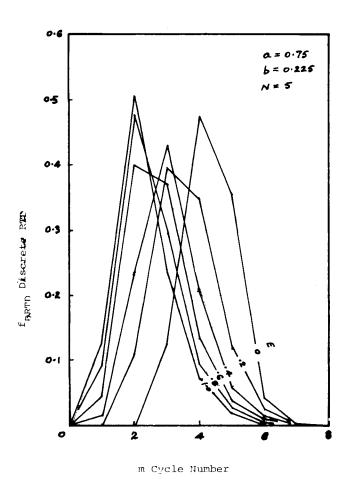


Fig. 7a. Entrainment effect on DRTD.

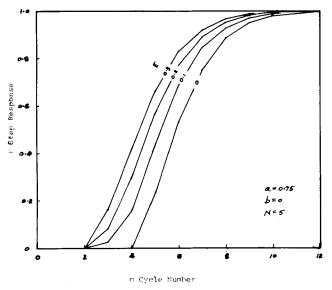


Fig. 7b. Entrainment effect on step response.

obtain the parameters a, b, and E. The first experiment consisted of an entrainment measurement, whereby a salt solution was placed on one plate and the salt concentration monitored on the plate above, which originally contained salt free water. This provides an accurate and independent method for the evaluation of E. The second experiment involves measuring the total liquid holdup in the column, which can be obtained by simply draining the column. The parameters a and b affect the total liquid holdup. The third experiment involves a step change in salt concentration on the top plate and monitoring the salt con-

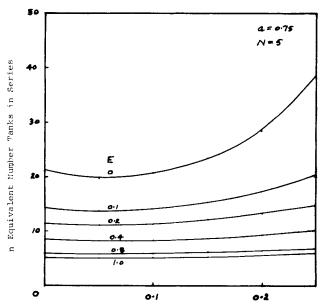
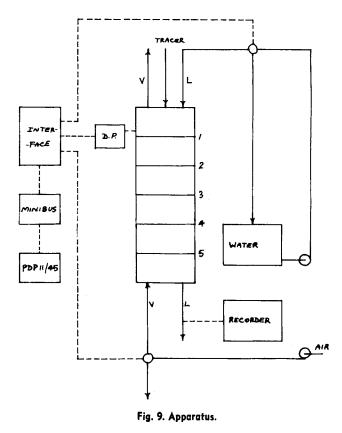


Fig. 8. Equivalent perfectly mixed tanks.



centration of the liquid leaving the column at the end of each cycle. The parameters a, b, and E affect the step response of the column.

RESULTS

From the first experiment, E=0.044. An analysis of the second experiment leads to the total liquid holdup, the mean liquid holdup \overline{H} , and the mean liquid fraction dropped $\overline{\eta}$ per plate.

$$H_T = \sum_{n=1}^5 H_n$$

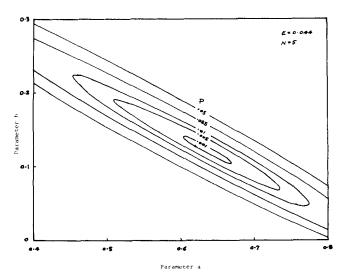


Fig. 10. Contours of constant P.

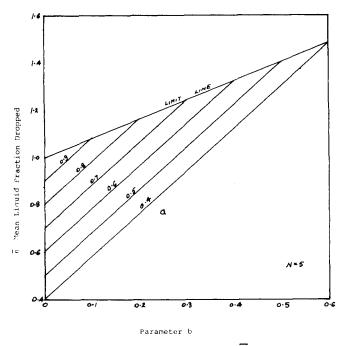


Fig. 11. Mean fraction dropped η .

$$\overline{H} = \frac{1}{5} \sum_{n=1}^{5} H_n$$

$$\overline{\eta} = \frac{5}{\sum_{n=1}^{5} H_n}$$

$$\overline{\eta} = \overline{\eta} (a, b)$$

The experimental value of $\overline{\eta}$ was $\overline{\eta}_e = 0.88$. Figure 11 is a plot of $\overline{\eta}$ for various values of a and b, and many sets of (a, b) will satisfy $\overline{\eta}_e = 0.88$.

The third experiment leads to experimental values of F_m at cycle number m, that is, F_{me} . A least-squares objective function P can be defined as

$$P = \sum_{m=1}^{11} (F_m - F_{me})^2$$

$$P = P(a, b, E)$$

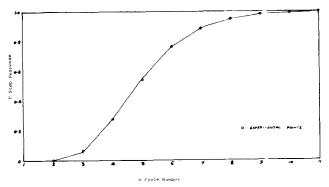


Fig. 12. Step response of a five-plate column

$$a \ge 0$$
; $b \le (1.0 - a)$; $E \ge 0$

A search technique using quadratic convergence was used to locate particular values of P on the a, b plane for E=0.044. Contours of P are shown on Figure 10 and indicate that the global minimum lies at the base of a deep channel function.

The experimental values of F_{me} have an estimated error of 1%, so that any point inside the contour $P=1\times 10^{-3}$ would be acceptable. The global minimum on Figure 10 lies inside this particular contour. From the independently determined value of E=0.044, a point can be located on Figure 10, inside the $P=1\times 10^{-3}$ contour, with the following values for a and b:

$$a = 0.63$$
 $b = 0.125$
 $E = 0.044$

We can independently confirm that these values of a and b have physical significances from the experimental value of $\overline{\eta}_e = 0.88$, which compares favorably with $\eta = 0.86$ from Figure 11. The accuracy obtained with this set of parameters can be observed by comparing the step response with the theoretical response as shown on Figure 12.

It should be noted that the (1S) model predicts the first breakthrough following a step change in the input, on cycle number 5, whereas the (2S) model predicts a breakthrough on cycle number 3. The experimental step response as shown on Figure 12 demonstrates the early breakthrough on cycle number 3. A parameter evaluation to provide the best fit to the step response for the (1S) model provides a larger sum of the errors than the (2S) model. Thus we can reject the (1S) model as being inadequate.

DISCUSSION

The two-stage (2S) dropping model predicts the liquid holdup distribution and the discrete residence time distribution for a plate column under periodic control. This model provides a basic understanding of the liquid transfer processes, occurring during the drain period of a cycle, and will lead to improvements in studying the mass transfer processes occurring in the column. The single-stage (1S) dropping model has been used in mass transfer studies by Horn (1967), May and Horn (1968), Robinson and Engel (1967), Chien et al. (1966), Furzer (1973), and Furzer and Duffy (1974). A (1S) model with perfect liquid mixing on each plate during the drain period has been used in mass transfer studies by Horn and May (1968), McWhirter and Lloyd (1963), and Gerster and Scull (1970). The (2S) model will be an improvement on these previous attempts to model the mass transfer procThe experiments completed on the total liquid holdup and the step response of a column under periodic control have not been reported previously in the literature. The analysis of these experiments in terms of the (2S) model has provided the basic liquid transfer mechanism in the column.

ACKNOWLEDGMENT

A part of this research project was supported by the Australian Atomic Energy Commission.

NOTATION

a = parameter in the 1S model

A = matrix with elements composed of a and b

b = parameter in the 1S model e = entrainment rate, kg s⁻¹

E = dimensionless entrainment

f = discrete residence time distribution

F = step response of the system
 h = liquid holdup on a plate, kg

H = dimensionless holdup

 $\frac{m}{m}$ = mean cycle number

m = cycle number

M = mass of liquid admitted to the column per cycle

n = number of perfectly mixed tanks; or plate number
 N = number of plates in the column

P = objective function

t = time

T = dimensionless time w = weeping rate, kg s⁻¹

X = output response

Greek Symbols

 η = fraction of liquid dropped from a plate in the 1S

model

 θ = dimensionless cycle number

 σ_n = variance for n tanks

 $\sigma_m = \text{variance about } \overline{m}$ $\sigma = \text{variance about } \overline{\theta}$

Subscripts

d = drain period v = vapor period

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An Analysis of Carrier Facilitated Transport in Heterogeneous Media

A theoretical model is developed for steady state diffusion in reactive heterogeneous media in which simultaneous reversible chemical reactions occur between diffusible carrier species and the transported species. The heterogeneous systems analyzed are those for which one phase is dispersed as uniform spheres in a second continuous phase, and either or both phases may be reactive. The results have a simple physical interpretation in terms of additivity of resistances. The theory is applied to oxygen diffusion in blood.

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SCOPE

Transport processes in heterogeneous media pose an important problem in science and engineering. This paper is concerned with the problem of diffusion with reversible chemical reaction in such systems. Previous work has dealt separately with diffusion in nonreactive hetero-

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geneous media and with diffusion and chemical reaction in homogeneous media, but the combined problem has not been studied in depth. The theoretical framework presented here provides a model for heterogeneous reactive systems and serves as a cohesive link between the two subjects. The heterogeneous media considered are those for which one phase is dispersed as uniform spheres