$\mu$ = dynamic viscosity, lb./ft.-hr.
$\nu$ = kinematic viscosity, sq. ft./hr.
$\rho$ = density, lb./cu. ft.
$\phi$ = $k$ variable density/$k$ constant density = $\left(\ln \frac{M_w}{M_x}\right) \Big/ \left(\frac{M_w}{M_x} - 1\right)$

**Subscripts**

1 = diffusing component
$w$ = evaluated at wall
$o$ = approach conditions
$\infty$ = evaluated at outer edge of boundary layer

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# Performance of a Packed Distillation Column with Electrically Heated Packing

**TARIK G. SOMER**
**Middle East Technical University, Ankara, Turkey**

**Electric current was applied across the coke packing of a glass column, distilling carbon tetrachloride-benzene at total reflux. Heat generated by electricity boiled the liquid on the packing surface. Bubbles rising across the liquid film reduced its resistance to mass transfer, improving the column efficiency.**

**Theoretical analysis and experimental results are presented.**

Attempts to improve the efficiency of a packed distillation column have been directed mostly to the development of new packing materials and to methods providing better distribution of the liquid. The literature contains numerous recommendations as to the best types of packing elements and distributors to use. Little or no work seems to have been directed toward inducing turbulence to the liquid layer on the packing surface. If a suitable method were devised in this respect, it would help reduce the liquid film resistance and improve the efficiency. The results of Furnas and Taylor (*6*) on a water-ethanol system and Yoshida et al. (*12*) on a benzene-toluene system and using ordinary packed columns at various reflux ratios, show that in the rectifying section of a packed column, the rate of mass transfer is controlled by the liquid film resistance. This conclusion is supported further by the results of Hands and Whitt (*7*) and Edye (*4*) on columns packed with small rings. It is, therefore, reasonable to assume that the mixing of the liquid layer should improve the efficiency, particularly in the rectifying section.

The simplest method to induce turbulence to the liquid in a packed column is to increase its flow rate. The net effect, however, is rather small, as can be seen from the empirical expressions for the liquid film coefficient presented by Brown and Rosenberg (*1*) and Morris (*11*) for design purposes.

An interesting paper by Kafarov (*8*) describes another method by which a violent mixing of the liquid is achieved by *emulsification* through the penetration of bubbles of vapor. This condition is said to have provided, at the same time, a fast equalization of liquid concentration, an even distribution, and a longer residence time, all of which helped to raise the efficiency. Unfortunately, the operating limits for such a column appear to be narrow.

In an attempt to induce turbulence to the liquid layer without increasing its flow rate, the writer considered passing electrical current through a conductive packing. This current would generate heat to be transferred from the packing to the liquid. Since the liquid in a rectification column would be at its boiling point at all locations, the heat absorbed would actually boil the liquid by generating minute bubbles, first formed on the packing surface, then gradually rising across the liquid layer. The motion of these bubbles, along with the convection current set up owing to the temperature difference between the inner and the outer surfaces of the liquid layer, would provide certain mixing while increasing the vapor-liquid interfacial area. The packing material for this purpose had to be electrically conductive with fairly high resistance in order to generate sufficient heat at moderate current ratings.

It should be noted that the heating of the packing has also a reverse effect as far as the column efficiency is concerned. Since any boiling of the liquid causes the depletion of its more volatile component, the driving force for mass transfer is reduced. Furthermore, a slight rise of the liquid temperature due to boiling will lessen the chances for condensation of the contacting vapor, which is normally at a lower temperature. This phenomenon in distillation and its contribution to efficiency is outlined in detail by Danckwerts et al. (*3*). Thus, for a column with electrically heated packing, the efficiency should increase because of the induced turbulence in the liquid and increased interfacial area, but, at the same time, should decrease because of the reduction of the driving force between the vapor and the liquid phases and also because of the slight rise of the liquid temperature. Unless the overall effect is on the positive side, the heating of the packing may serve no useful purpose.

## THEORETICAL

It is possible to derive an equation that shows the effect of the reduction of driving force as a result of electrical heating. Before presenting its derivation, it will be interesting to point out the expected differences between the operations of such a column and a conventional one.

In the ordinary rectification of a binary system at total reflux, assuming there are no heat losses to the surroundings and the molal latent heat of vaporization of the mixture is independent of its composition, the vapor and liquid rates remain constant throughout the column. When current is applied, however, to the packing, the liquid begins to boil within the column itself. As a result, the vapor rate increases upward. The liquid rate by a material balance must increase as well in the same direction. Although at total reflux the mass flow rates of the vapor and liquid are equal, they both increase linearly from the bottom to the top of the column. In the upper sections, therefore, the packing is better irrigated, both phases possess greater turbulence, and the average liquid layer over the packing is thicker. Consequently, each section of the column should exhibit different performances, and therefore, different efficiencies. Since it is not practicable to express mathematically the exact effects of the vapor-liquid flow rates on the wetted area and the mass transfer coefficient, it seems necessary to speak only in terms of their average values. Although for ordinary packed columns similar averages are also assumed (*9, 10*), the effect of minor variations in the vapor-liquid rates should be much less significant in comparison to electrically heated packing.

In the derivation of an expression to estimate the height of a transfer unit for such a column at total reflux, the following assumptions are made: (1) The electrical heating is uniform; that is, the resistance of packing per unit height is constant. (2) Molal latent heat of vaporization of the binary system is independent of its composition. (3) Boiling of the liquid in the column produces a vapor in equilibrium with the liquid.

Considering a differential section $dz$ of the column, $Z$ feet from the base, a portion of the more volatile component is transferred from the liquid to the vapor phase both by diffusion and liquid evaporation. If the amount of vapor formed by evaporation is $dV$ moles/hr., then a familiar material balance based on the transfer rate of the more volatile component can be written as follows.

$$K_{ya}\, S(y^* - y)dz + y^* dV = d(Vy) \qquad (1)$$

Since the vapor rate at any level in the column is nearly the summation of the vapors generated both in the boiler and within that section of the column, $V$ at any $Z$ can be represented approximately by

$$V = V_o + \frac{qZ}{\lambda} \qquad (2)$$

Differentiating Equation (2) for a constant boiler heat load

$$dV = \frac{q}{\lambda}\, dz \qquad (3)$$

substituting the values of $V$ and $dV$ from Equations (2) and (3) into Equation (1)

$$K_{ya}\, S(y^* - y)dz + y^* \frac{q}{\lambda} dz = \left( V_o + \frac{qZ}{\lambda} \right) dy + y \frac{q}{\lambda} dz \qquad (4)$$

and rearranging

$$\left( K_{ya}S + \frac{q}{\lambda} \right)(y^* - y)dz = \left( V_o + \frac{qZ}{\lambda} \right) dy \qquad (5)$$

is obtained.

Integration of Equation (5) yields

$$\frac{1}{K_{ya}S + \dfrac{q}{\lambda}} \int_{y_a}^{y_b} \frac{dy}{y^* - y} = \frac{\lambda}{q} \ln\left( 1 + \frac{qH}{\lambda V_o} \right) \qquad (6)$$

since $qH/\lambda$ corresponds to the moles of vapor generated in the column due to electrical heating, the following relationship can be written

$$\frac{qH}{\lambda V_o} = \alpha \qquad (7)$$

Substituting Equation (7) into Equation (5), also noting that by definition $V_o/S = G_{oy}$

$$\frac{1}{\dfrac{K_{ya}H}{G_{oy}} + \alpha} \int_{y_a}^{y_b} \frac{dy}{y^* - y} = \frac{\ln(1 + \alpha)}{\alpha} \qquad (8)$$

By the use of $N_{oy}$ and $H_{oy}$ for a conventional packed column (*2*), Equation (8) can be written in these terms

$$N_{oy} = \left( \frac{H}{H_{oy}} + \alpha \right) \frac{\ln(1 + \alpha)}{\alpha} \qquad (9)$$

Equation (9) is the relationship between $N_{oy}$, $H_{oy}$, and $\alpha$ for a packed distillation column with electrically heated packing.

The limiting value of $N_{oy}$ as $\alpha$ approaches zero may be obtained from Equation (9).

$$\lim_{\alpha\to 0} N_{oy} = \frac{H}{H_{oy}} \lim_{\alpha\to 0} \frac{\ln(1+\alpha)}{\alpha} + \lim_{\alpha\to 0} (1+\alpha) \tag{10}$$

Since by L'Hospital's rule

$$\lim_{\alpha\to 0} \frac{\ln(1+\alpha)}{\alpha} = \lim_{\alpha\to 0} \frac{1/(1+\alpha)}{1} = 1$$

Equation (9) reduces to the familiar form

$$\lim_{\alpha\to 0} N_{oy} = \frac{H}{H_{oy}} \tag{11}$$

By means of Equation (9), the effect of $\alpha$ on the column efficiency, due only to the reduction of the driving force for mass transfer, can be estimated for a fixed height and constant $H_{oy}$. Actually $H_{oy}$ depends on $\alpha$, since any increase in column heating would also increase the interfacial area $a$ in the $H_{oy}$ expression. If there were no increase in interfacial area, or if $H_{oy}$ remained fixed for all heating rates, then, by assigning various values to $\alpha$ in Equation (9), percent reduction in $N_{oy}$ could be calculated in comparison to a nonheated conventional packed column. The results indicate that as $\alpha$ ranges from 0.1 to 1.0, the percent decrease in $N_{oy}$ ranges from 4.7 to 30.6.

The overall effect of $\alpha$ on column efficiency has to be determined, of course, experimentally. The results of such experiments will be presented later.

It should be noted that the $K_ya$ appearing in Equation (1) was taken as an average for the entire column. For that reason, in the integration of Equation (5) it was considered independent of Z, the column height. If the local value of $K_ya$ were taken, then it would be a function of Z, since the vapor and liquid velocities both increased linearly from the base to the top. It would also depend on the extent of electrical heating which would proportionally produce bubbles and set up convection currents stirring the liquid film. Furthermore, appreciable variations in the vapor and liquid rates would affect distribution, channeling, and wetted area. Since all these factors cannot be evaluated separately, an average value for $K_ya$ had to be chosen.

## EXPERIMENTAL

### Apparatus

To evaluate the performance of an electrically heated packing, an experimental column was built as shown schematically in Figure 1. It included a 12-liter copper boiler of cylindrical shape. A calibrated glass float in a perforated metal enclosure was installed in the boiler for reading the liquid level through a glass cover on the outside. The metal enclosure was used to prevent surface ripples of the boiling liquid from reaching the float for an accurate reading. A 4-kw. electric immersion heater was installed in the boiler through a potentiometer.

A 146 cm. long glass column (I.D. = 8.8 cm.) was packed with coke. The height of the packed section was 132 cm. The packing was supported by a perforated brass plate. In order to prevent the coke particles from plugging the holes, a copper wire was soldered on the upper surface of the plate, diagonally across the holes.

The packing was hard, metallurgical coke of about 14% porosity. It was crushed, screened, and washed repeatedly to remove dust. Particles between 6.7 and 5.7 mm. were collected by screening. The average of these two (6.2 mm.) was taken as the particle size. The column was filled by hand while holding vertically on a vibrator. At this stage, the free volume was about 44%. Under normal operating conditions, the electrical resistance of the packing was around 9 ohms. The top plate over the packing was similar in construction to the bottom support plate, except that its center rod was spring-loaded to provide electrical contact by pushing onto the coke.

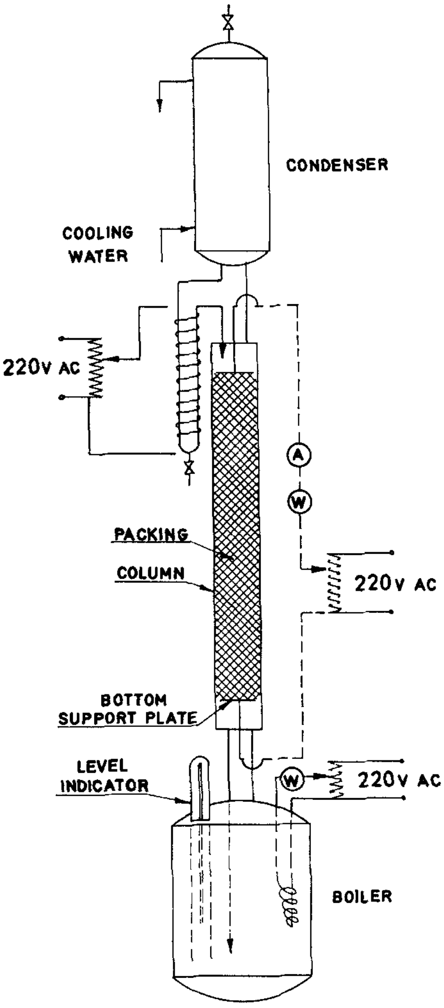

Fig. 1. Schematic diagram of experimental packed column with electrically heated packing.

The vapor condenser was a single-pass, countercurrent, tube-and-shell heat exchanger made of ¼-in. brass tubes, 1.2 m. long. The total cooling area was 2.1 sq. m., almost three times the required minimum.

All of the condensate returned to the column (total reflux) through a copper gooseneck at the center of the top perforated plate, which acted also as a liquid distributor. The reflux before entering the column was heated in the gooseneck by a resistance wire ribbon, up to the temperature of the outlet vapor, controlling the heat by a potentiometer.

Electric current to the packing was applied through the top and bottom brass plates. To measure the power input both to the boiler and the packing, separate watt meters were connected in the respective circuits. The power supply to the potentiometers was 220 v. a.c.

The boiler and the column were insulated by glass wool and asbestos cloth to an approximate thickness of 3 in. Through two suitable openings in the insulation, the ends of the column could be observed to check for loading and flooding.

### Procedure

Since the purpose of the experimental work was to evaluate the performance of an electrically heated packing, only one binary liquid system was chosen, in order to eliminate side effects due to variations in surface tension, viscosity, polarity, and wetting properties. The system chosen was benzene-carbon tetrachloride for the following reasons. The vapor-liquid equilibrium curve for this system was very close and parallel to the 45 deg. line within the experimental range, thus requiring a large $N_{oy}$ for a small enrichment. Both components were

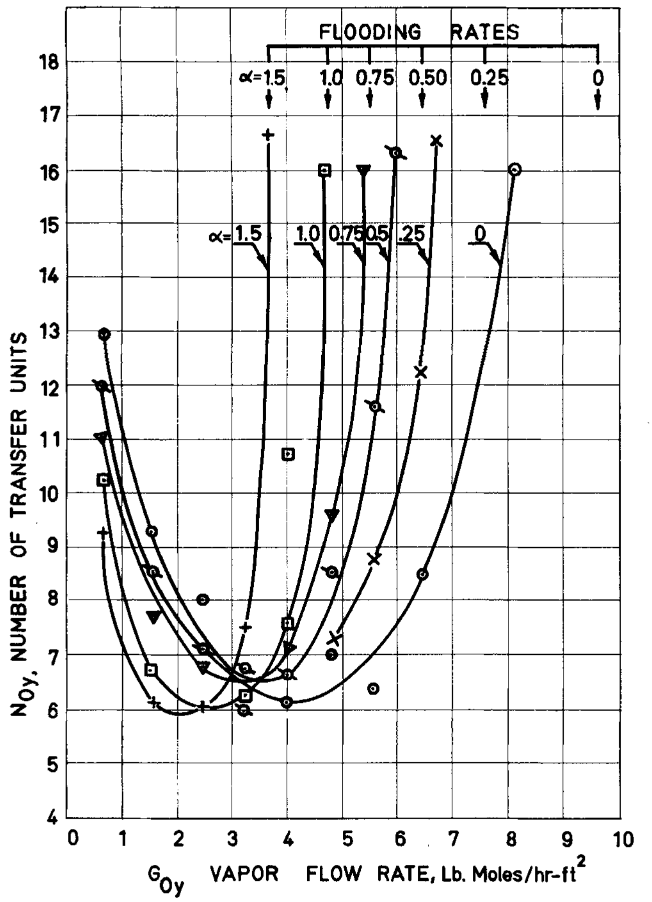

Fig. 2. Effect of boiler and column heat loads on $N_{Oy}$.

nonpolar, quite different in molecular weight for better accuracy in material balances. Since there was an appreciable difference between the refractive indices of the individual components, the composition of the mixture could be accurately determined by measuring the refractive index. Before the experiment the entire fractionating equipment was evacuated down to about 2 mm. Hg. Then, about eight liters of the benzene-carbon tetrachloride mixture was transferred into the boiler by suction. With no cooling water in the condenser, heat was applied to the boiler until the mixture began to boil and the pressure rose slightly above atmospheric. Then the needle valve above the condenser was opened to drive off air in the system. The needle valve was closed, and the condenser cooling water was turned on at the same time. The heat loads to the boiler and the column were both adjusted while controlling the cooling water rate in order to keep an atmospheric pressure in the system.

The operation was continued at steady state for at least 3 hr. Liquid samples were then taken from the condenser and the boiler for refractive index measurement using an Abbe refractometer. Three sets of samples taken at 15-min. intervals had to check within 3% before the operating conditions were adjusted for a new run.

The amount of the liquid remaining in the boiler could be determined at all times by reading off the float level indicator. This was a quick and useful check, since a rapid depletion of the boiler holdup indicated the beginning of a column loading and eventual flooding.

## RESULTS AND DISCUSSIONS

As soon as the electric current was applied to the packing, boiling of the liquid could be observed. The bubbles forming ranged from minute to large sizes, rising to the surface and often producing a foam. The largest bubbles appeared where two packing units touched, obviously due to the high electrical resistance generating more heat in this location.

To determine the overall effect of column heating on the efficiency, the $N_{oy}$ for each run was determined by graphical integration, using the vapor-liquid equilibrium for benzene-carbon tetrachloride (5) between the limits of the boiler and reflux compositions. Since the column operated at total reflux and the equilibrium curve was almost parallel to the 45 deg. line, the $N_{oy}$'s could also be determined by a stepwise procedure. These two were practically identical.

$H_{oy}$ for each run was calculated from Equation (9) by substituting the respective values of $N_{oy}$ and $\alpha$.

The $N_{oy}$'s and $H_{oy}$'s are plotted[*] as a function of $G_{oy}$ in Figures 2 and 3, respectively.

Before the interpretation of these curves it should be noted that the vapor and liquid rates at any point in the column were the same (total reflux) and equal to $G_{oy}$ at the base and gradually increasing up to $G_{oy}$ $(1 + \alpha)$ at the top.

In the low $G_{oy}$ region, the column efficiency is high; this is believed to be due to the high residence time and large surface area of the liquid that spreads through the capillaries of the porous packing. Heating the packing does not seem to improve the efficiency in this region, since little liquid forms a layer on the surface of the packing. In fact, it has a slight reverse effect on the efficiency by reducing the liquid residence time, the driving force for mass transfer and surface area due to vapor formation inside the capillaries. In Figure 2, the curves in the low $G_{oy}$ region approach to a minimum around $N_{oy} = 6$, indicating that the improvement of the mass transfer coefficient is now balancing the factors that reduce the efficiency. From here on the curves begin to rise, more steeply at higher $\alpha$. Near the flooding rates, indicated at the upper right corner of Figure 2, the rising curves are almost vertical. The results in this region resemble those obtained by Kafarov (8) in the so called *emulsification stage* of a packed column operation.

Figure 3 shows the variation of the height of a transfer unit with respect to $G_{oy}$ and $\alpha$. The results are similar,

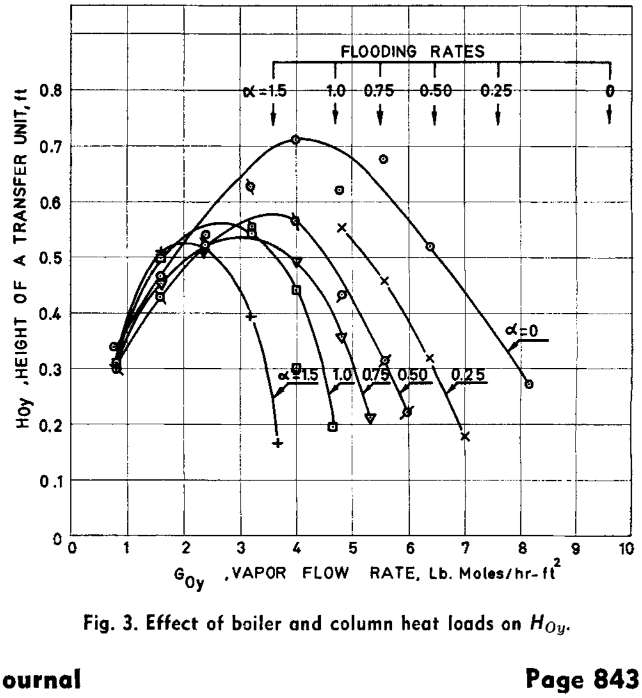

Fig. 3. Effect of boiler and column heat loads on $H_{Oy}$.

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[*] Deposited as document 8441 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

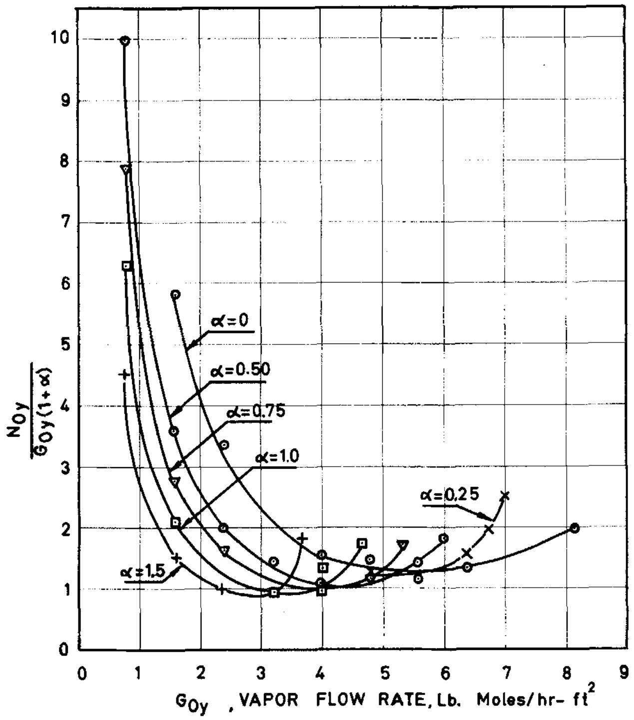

**Fig. 4. Effect of boiler and column heat loads on $N_{Oy}$ per mole of total vapor generated.**

except that at the low $G_{oy}$ region the effect of $\alpha$ on $H_{oy}$ is practically insignificant.

The sudden rise of efficiency by electrical heating of the packing, especially near the flooding rate, is apparent from Figures 2 and 3. This is achieved, however, by expenditure of energy, which, in turn, increased the vapor rate. From an economic point of view, therefore, it is interesting to see the contribution of column heating to column efficiency per mole of the total vapor generated. This is shown in Figure 4 by plotting $N_{oy}$ per mole of vapor vs. $G_{oy}$. The curves in Figure 4 show that the column heating begins to indicate an advantage for values of $G_{oy}$ exceeding 3.6 lb. moles/hr.-sq.ft. The improvement of column efficiency is the highest for $\alpha = 0.25$. This is an interesting result, since it reveals that compared to a conventional column, if the packing is electrically heated and the energy thus supplied is 25% of the boiler heat load, $N_{oy}$ per mole of total vapor generated would increase from 1.5 to 2.5, an improvement of efficiency by 66%. For values of $\alpha$ above 0.25, the advantage diminishes gradually, such that for $\alpha = 1.5$, $N_{oy}$ per mole of total vapor is the same as $\alpha = 0$, condition for a nonheated packing. These analyses are presented on the assumption that the main cost in operating a distillation column is the cost of energy. Otherwise, heating of the packing definitely improves the efficiency as seen from Figures 2 and 3.

## CONCLUSIONS

The experimental results show that the principle of mixing liquids with streams of gas bubbles can be successfully applied to packed distillation columns in order to mix the liquid film on the packing surface and reduce its resistance to mass transfer. The bubbles can be generated by electrical heating for which the energy supplied to the packing should not exceed 25% of the boiler heat load in order to achieve maximum efficiency.

For such an operation the product of $N_{oy}$ and $H_{oy}$ is no longer equal to the column height. For an average mass transfer coefficient there exists a relationship between these terms and the degree of column heating [Equation (9)].

Since the packing must conduct electricity and possess appreciable resistance, coke, graphite rings, metal-coated particles, and similar materials can be used.

The writer hopes that this subject will create sufficient interest among researchers for further study and application to various mass transfer operations.

## SUMMARY

A glass column packed with coke particles was used to investigate the distillation of a mixture of carbon tetrachloride-benzene at total reflux. Electric current was applied to the packing through the ends of the column. Heat produced by the electricity boiled the liquid, generating minute bubbles first on the packing surface, then rising across the liquid film. This motion of the bubbles mixed the liquid, decreasing the film resistance to mass transfer.

The results indicated a definite improvement of column efficiency due to the heating of the packing. The effect on efficiency was greater at higher liquid rates, increasing rapidly near the flooding range.

NTU's at various heat loads of the boiler and the column were determined and plotted. An equation was derived to show the relationship between NTU, HTU, column height, and $\alpha$, defined as that fraction of the total heat supplied to the packing.

## ACKNOWLEDGMENT

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## NOTATION

$dz$ = differential height of a packed section at a height Z ft. from the base
$G_{oy}$ = superficial vapor flow rate at the column base, moles/hr.-sq.ft. (defined as $Vo/S$)
$H$ = height of packed column, ft.
$H_{oy}$ = height of a transfer unit, overall, based on vapor phase, ft.
$K_{ya}$ = overall mass transfer coefficient, lb. moles/hr.-cu. ft. (unit mole fraction)
$N_{oy}$ = number of transfer units, overall, based on vapor phase
$q$ = heat supplied to packing by electrical energy, B.t.u./hr.-ft. (packing)
$S$ = column cross section, sq.ft.
$V$ = vapor rate, moles/hr.; $Vo$, the rate of vapor generated in the boiler
$x$ = liquid composition, mole fraction of more volatile component in liquid
$y$ = vapor composition, mole fraction of more volatile component; $y^*$, composition of vapor in equilibrium with a liquid of composition $x$

### Greek Letters

$\lambda$ = latent heat of vaporization, B.t.u./lb. mole
$\alpha$ = ratio of the heat supply of the packing to that of the boiler

### Subscripts

$a$ = column base
$b$ = column top

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# Adsorption Kinetics in Fixed Beds with Nonlinear Equilibrium Relationships

**CHI TIEN**
**Syracuse University, Syracuse, New York**

**GEORGE THODOS**
**Northwestern University, Evanston, Illinois**

**Previous work by the authors on ion exchange kinetics for systems having nonlinear equilibrium relationships has been extended. Computer studies have produced additional concentration—bed length–time relationships for values of $\alpha_0 = 5$, 10, and 50. This information and the results obtained previously for values of $\alpha_0 = 100$ and 1,000 provide an extensive variation of the parameter $\alpha_0$ for design applications. The composite results are represented graphically.**

Separation processes in fluid-solid systems have recently become increasingly important. The design of processes conducted in fixed beds requires accurate prediction of the concentration history of the effluent stream.

For the analytical study of the kinetic behavior of a fixed-bed system, the initial task is to express the bed operation mathematically in terms of the continuity equation, the rate of adsorption, and the equilibrium relationship that describes the system. Although the continuity equation is general, the exact form of the rate relationship depends on the individual case. In general, there are two types of such relationships. In the first case the rate is expressed in terms of the fluid concentration and the average concentration within the adsorbent. Here the diffusion resistance in the solid phase is assumed negligible. Most of the investigations reported in the literature are based on this model, notably the comprehensive studies of Goldstein (*1*, *2*), Goldstein and Murray (*3* to *5*), and Vermeulen (*12*). The second type of rate relationship is that in which the solid diffusion resistance is as significant as the resistance in the fluid phase. Rosen (*6*) studied this case for systems having a linear equilibrium relationship. Tien and Thodos (*9*) generalized Rosen's study to include systems having nonlinear equilibrium relationships. The concentration history of the effluent stream expressed in terms of $c/c_0$ was presented as a function of parameters representing time, bed length, and relative resistance.

Although the mathematical treatment of this problem was presented in detail previously (*9*), this study considers the final equations used in the computations and the definitions of the pertinent parameters. The parameters $\alpha$, $\alpha_s$, and $\beta$ are related through the following relationships:

$$\beta_{si}^{j+1} = C_1 \left[ (\alpha_i^j - \alpha_{si}^j) + C_2 \sum_{k=1}^{j} K_{j-(k-1)} \beta_{si}^k \right] \quad (1)$$

$$\alpha_{i+1}^j = \alpha_i^j + (\alpha_{si}^j - \alpha_i^j)\Delta x \quad (2)$$

$$\beta_s = \alpha_s^a \quad (3)$$

The subscript $i$ and the superscript $j$ refer to $x$ and $\theta$, respectively. The initial and boundary conditions for this problem are

$$\alpha = \alpha_s = \beta_s = 0 \quad \text{for} \quad x \geqq 0 \quad \text{and} \quad \theta \leqq 0 \quad (4)$$

and

$$\alpha = \alpha_0 \quad \text{for} \quad x = 0 \quad \text{and} \quad \theta > 0 \quad (5)$$

In Equation (3) the exponent $a$ is a constant dependent upon the appropriate equilibrium relationship. In this study $a$ has been assumed to be 0.5. The constants $C_1$, $C_2$, and $K_{j-(k-1)}$ are defined as

$$C_1 = \frac{1}{\dfrac{3}{\pi\sqrt{\Delta\theta}} - \dfrac{3}{4\pi}} \approx \frac{\pi\sqrt{\Delta\theta}}{3} \quad (6)$$

$$C_2 = \frac{3}{\pi\sqrt{\Delta\theta}} \quad (7)$$