Fractionation During Condensation of Vapor Mixtures

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Partial condensers of the reflux type are capable of producing substantial fractionation of vapor mixtures. For vapor products having low dew points they may be preferred to conventional equipment for adiabatic distillation plus total condensation.

Experimental studies of a condenser used to fractionate mixtures of ethylene dichloride and toluene show that observed mass transfer effects are in agreement with the Colburn-Drew film theory, which accounts for the influence of the net mass exchange on the relative mass transfer rates of the components. In an adaptation of the transfer-unit concept to partial condensation, new equations are derived relating the number of transfer units to liquid- and gas-phase resistances, surface area, and amount of condensation. Observed resistances to mass transfer agree qualitatively with values independently measured; the diffusional resistance of the liquid phase has a pronounced effect on the fractionation, which does not conform to the Rayleigh theory of equilibrium differential condensation.

Partial condensers appear to require more interfacial area than adiabatic distillation equipment in order to produce the same fractionation at the same heat load; for the same interfacial area condensers require more heat removal.

Although only the system ethylene dichloride–toluene was investigated here, the results of this work are believed pertinent to other binary liquid mixtures also. Knowledge of the vapor-liquid equilibrium relationship of the new system and of the liquid and vapor-phase transfer coefficients is required in order to employ the calculation methods introduced here.

Design of heat transfer equipment for the condensation of vapors is carried out according to well-established procedures in two extreme cases. In the first, the vapor phase is composed of a pure component, and only heat transfer considerations are involved, all the thermal resistance on the vapor side of the heat transfer surface being in a liquid condensate film that covers the surface. Here the problem is essentially that of estimating the thickness of this film and its effective thermal conductivity (*12*). In the second case the vapor is a mixture of components, one of which does not condense and is not soluble in the condensed phase. The problem still involves the estimation of the thermal resistance of the condensate layer, though the really important step in the design procedure is the estimation of the diffusional resistance offered by the gas phase to the mass transfer of the condensing component to the vapor-liquid interface. When only a single component condenses, the diffusion calculations are simple in principle (*2, 9, 10, 11*).

If more than one component condenses—a case intermediate between the two extreme cases—two new rate processes need to be considered carefully: the influence of the net flux of mass through the vapor phase on its diffusional resistance must be included, particularly when large concentrations of inert components are not present, and the diffusional resistance of the liquid mixture composing the condensate layer must be estimated and allowed for. Although the extended calculations are not expected to be difficult in principle, the necessary studies of diffusional mechanism having been partially worked out in previous investigations (*1*), no data on condensers have been available to determine whether computations made according to logical procedures would agree with observed performance.

The use of partial condensers in conjunction with distillation apparatus is not new. When the overhead product is composed of light and heavier components, reflux is provided for the fractionator by condensing mainly the heavier components, the distilled product being kept in the vapor state. In such concurrent-flow operations the vapor product and the condensed liquid leave the condenser together and even the apparatus that is most efficient in promoting mass transfer can do no better than cause the exit streams to reach phase equilibrium with each other. Thus the enrichment accomplished in such a device cannot exceed that equivalent to a single theoretical plate or equilibrium contact.

There are process situations, however, in which it may be advantageous to provide for as large a composition change in the condenser as can be achieved. This may occur, for example, if the condensation of even a portion of the vapor leaving a distillation column would require a refrigerated coolant. In this event it might be desirable to feed vapor containing appreciable quantities of heavy components to the bottom of a countercurrent partial condenser, sometimes referred to as a *backward-return* type of unit because the vapor and liquid products leave at opposite ends of the heat transfer surface. Under these conditions a very efficient condenser can produce a liquid stream that may be nearly at equilibrium with the entering vapor and the exit vapor may be much more concentrated in the volatile components. A substantial part of the heat removed from the condensing phase may be transferred to the coolant at a higher temperature than would be possible if the fractionation were done in a conventional adiabatic distillation unit producing the same light-distillate stream.

When a partial condenser of this type is to be designed to provide for efficient fractionation of components having comparable volatilities, presently available design procedures are incapable of determining the heat load or reflux requirements. Furthermore, the estimation of the required condensate surface appears difficult, as it depends both on the required heat load and on the specified composition change. What is apparently needed is a method of combining heat transfer and mass transfer computations in an extended version of the separate procedures that have been devised previously for the two extremes of condensers for pure components and for single condensable components mixed with inert gases.

THEORY

In the condensation of both components simultaneously from a binary vapor mixture there is a net flux of mass toward the interface which transports both types of molecules, assisting the diffusion of the less volatile component through the laminar fluid near the interface and hindering that of the more volatile component. The net rate of mass transport is of course proportional to the rate of heat transfer, and the problem under discussion is essentially that of describing the influence of the heat flux at the

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interface on the diffusional resistance of the liquid and vapor phases. The problem is not a new one. It was considered first by Colburn and Drew (*1*) in a paper on the condensation of binary vapor mixtures. Although this early work provided the mathematical methods needed to subdivide the total local mass flux into the portions due to the two kinds of molecules, no attempt was made by these authors to apply their equations to heat transfer surfaces of finite extent and no data were available from which the mass-transfer resistance of the liquid phase could be determined.

Using y to represent the local mole fraction of component A at a distance s and z for that in the net condensate stream, Colburn and Drew wrote the following equation for the total rate of transfer of component A owing to diffusion and to net mass flux:

$$N_A \equiv wz = -k_G(dy/d\eta) + wy \quad (1)$$

where k_G is equal to $D_V\pi/RTB_G$ and $\eta = s/B_G$, in which D_V is the diffusion coefficient and B_G is the equivalent laminar-film thickness.

The composition of the net condensate stream is

$$z \equiv N_A/(N_A + N_B) = N_A/w \quad (2)$$

in which N_A and N_B refer to the constant mass fluxes of A and B components, respectively. The solution of Equation (1) can be represented as

$$y - y_i \exp(-w/k_G) = z[1 - \exp(-w/k_G)] \quad (3)$$

in which y now refers to the mole fraction of component A in the bulk of the gas phase and y_i is the value at the interface.

Equation (3) can be put in a familiar form either when w is zero (no mass exchange) or when N_B is zero (no mass transfer of B, the "inert-gas component" when $N_B = 0$).

$$wz = N_A = k_G z \ln\left[\frac{z - y_i}{z - y}\right] \quad (4)$$

$$\lim_{z\to\infty} N_A = k_G(y - y_i) \quad (5)$$

$$\lim_{z\to 1} N_A = k_G \ln\frac{1 - y_i}{1 - y} = k_G\left(\frac{y - y_i}{1 - y}\right)_{log\ mean} \quad (6)$$

Equation (1) and the results derived from it do not appear to depend on the assumption of a stagnant film which offers the sole resistance to mass transfer; the equation would seem to remain unchanged when applied to turbulent diffusion in the core of the vapor stream. However, under some circumstances, such as those leading to the progressive development of a boundary layer, the problem is more complex. It has been solved, however, by Eckert and Lieblein (*4*) and discussed by Mickley et al. (*10a*); the results are qualitatively similar to those given here.

On the assumption that the diffusion process in the liquid layer is also that of steady state mass transfer of two components through a condensed phase the velocity of which is not disturbed by the mass exchange, the same equations should apply to the liquid mass transfer resistance.

$$x_i - x \exp(-w/k_L) = z[1 - \exp(-w/k_L)] \quad (7)$$

$$wz = N_A = k_L z \ln\frac{z - x}{z - x_i} \quad (8)$$

where k_L is the liquid-phase mass transfer coefficient.

A somewhat more reasonable model of the liquid phase is that of a liquid layer that flows under the influence of gravity and on which incremental liquid condensate is deposited, the interface gradually moving toward the gas phase. The influence of molecular diffusion on the mass transfer rate in this situation can be estimated if it is assumed that the fluid motion is laminar (*8*). The results are somewhat involved but show that Equations (7) and (8) are very nearly correct, the deviations being a function of the ratio of the velocity of interface movement toward gas to the velocity of diffusion. For very wide limits of this ratio the deviations from the equations given are not more than a few per cent.

By use of Equations (4) and (8) the interfacial compositions y_i and x_i can be found if it is assumed that interfacial resistance is absent. For binary mixtures forming ideal solutions,

$$y_i = \frac{\alpha x_i}{1 + (\alpha - 1)x_i} \quad (9)$$

Equating the right sides of Equations (4) and (8) gives

$$\frac{z - x}{z - x_i} = \left[\frac{z - y_i}{z - y}\right]^{k_G/k_L} \quad (10)$$

which has to be solved simultaneously with Equation (9).

The procedure used for calculating the composition changes in liquid and vapor phases occurring as these fluids move past the heat transfer surface in a condenser involves the use of Equations (4), (8), (9), and (10) at each point on the surface, followed by differential energy and material balances to compute the changes in bulk composition. In principle such computations are simple, though they may be very time-consuming unless carried out by machine. If V and L represent the molar mass flow rates of vapor and liquid, respectively,

$$wz = -d(yV)/dA = -d(xL)/dA$$

or

$$w(z - y) = -V(dy/dA) \quad (11)$$

where dA represents a differential element of heat transfer area ($w = -dV/dA$).

Although Equations (4), (8), (9), (10), and (11) would be used in step-by-step computations for designing equipment, for understanding the principal features of the condensation phenomenon it is helpful to integrate the rate equations and the differential material balances approximately. This is done to determine how finite composition changes owing to fractionation in a condenser may be influenced by the rate of condensation. First an idealized unit is considered in which there is no liquid-phase resistance to mass transfer; i.e., k_L = infinity. Under these conditions Equations (4) and (11) give

$$V\,dy = (y_i - y)\frac{dV}{1 - \exp(w/k_G)} \quad (12)$$

or

$$\int_{y_1}^{y_2}\frac{dy}{y_i - y} = \int_{V_1}^{V_2}\frac{d\ln(V)}{1 - \exp(w/k_G)} \quad (13)$$

In view of the assumed absence of interfacial and liquid-phase resistance to diffusion $x - x_i$ and $y_i - y^* = \alpha x/[1 + (\alpha - 1)x]$. The integral on the left of Equation (13) is frequently referred to as the *number of transfer units* because its numerical value is a measure of the amount of composition change accomplished in a binary system, regardless of its particular phase-equilibrium characteristics. Numerical evaluation of the integral on the right shows the influence of partial condensation on the enrichment. In order to evaluate it precisely the functional dependence of k_G on the local value of V should be allowed for. Although exact numerical values can be found, it is sufficiently precise to assume that k_G is proportional to V and to use the logarithmic-mean value of k_G in the denominator of the integral.

$$\left[\frac{w}{k_G}\right]_{avg} \doteq \frac{(G_{M_1} - G_{M_2})(\pi D^2/4\pi Dh)}{(k_G)_{l.m.}} = \frac{(G_{M_1} - G_{M_2})}{\dfrac{(k_{G_1} - k_{G_2})ah}{\ln(k_{G_1}/k_{G_2})}} = \frac{(G_{M_1} - G_{M_2})}{ah\dfrac{k_{G_1}}{G_{M_1}}\dfrac{(G_{M_1} - G_{M_2})}{\ln(G_{M_1}/G_{M_2})}} = \frac{H_G}{h}\ln\left(\frac{G_{M_1}}{G_{M_2}}\right) = \frac{H_G}{h}\ln\left(\frac{V_1}{V_2}\right)$$

where $H_G = V_1/k_{G_1}a$ and a = interfacial area per unit volume of apparatus. With these approximations

$$N_G = \int_{y_1}^{y_2} \frac{dy}{y_i - y}$$

$$\doteq \frac{\ln (V_1/V_2)}{1 - [V_1/V_2]^{(-H_G/h)}} \quad (14)$$

Figure 1 shows a plot of N_G vs. V_1/V_2 according to Equation (14). It is interesting to notice that the normal value (h/H_G) of the number of transfer units is in the limit when V_1/V_2 approaches unity or when the rate of condensation is negligible. When V_1/V_2 is large, the number of transfer units is independent of the mass transfer resistance, as expressed by H_G, and can be computed from the Rayleigh equation, which assumes that the vapor stream is differentially condensed, each incremental quantity of condensate having a composition x^* at local equilibrium with the vapor stream. Diffusional mass transfer is assumed absent, each incremental condensate being isolated from the vapor as soon as it has been formed. The Colburn-Drew expressions thus are seen to provide the connecting link between the conventional expressions for the composition changes accomplished in adiabatic distillation and those calculated without regard for diffusional effects, according to the Rayleigh procedure.

In order to obtain a useful approximamate expression showing the effect of condensation on mass transfer when liquid-phase resistance is allowed for, it is helpful to approximate the true, curvilinear relationship expressed by Equation (9) by means of a straight equilibrium line,

$$y_i = m x_i \quad (15)$$

Substituting this into Equation (10) and assuming that the operation is at total reflux, so that $V = L$ at all points, the following equation can be derived in a form similar to Equation (14), as shown in the appendix:

$$N_{OL} \equiv \int_{x_1}^{x_2} \frac{dx}{x - x^*} \doteq \frac{\ln (V_1/V_2)}{m^{-1}[(V_1/V_2)^{(H_G/h)} - 1] + [1 - (V_2/V_1)^{(H_L/h)}]} \quad (16)$$

where $H_L = L/k_L a S$.

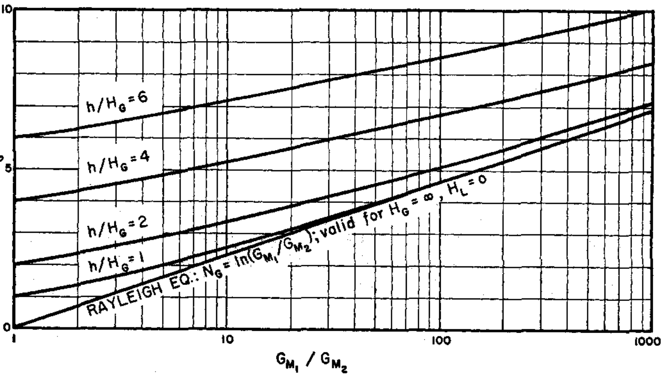

Fig. 1. Partial condensation in countercurrent column: gas-film resistance only.

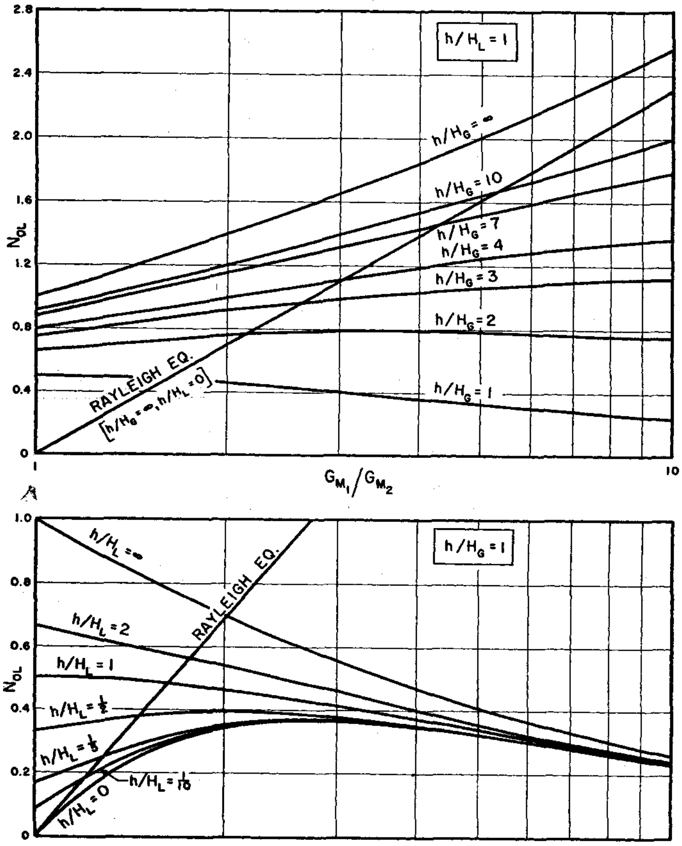

Fig. 2. Partial condensation in countercurrent column: gas- and liquid-film resistances ($m = 1.0$).

Figure 2 is a plot of this equation; it shows that in the limit when the condensation rate is negligible ($V_1/V_2 \rightarrow 1$) the number of transfer units according to Equation (16) agrees with the well-known expression,

$$N_{OL} = \frac{h}{(H_G/m) + H_L} \quad (17)$$

In contrast with Figure 1 and Equation (14), however, the Rayleigh line is no longer significant in the limit when the condensation is rapid unless gas-phase resistance is absent ($h/H_G = \infty$). In the extreme case of rapid condensation the liquid-phase resistance has a large effect and is capable of causing the enrichment to be much smaller than that given by the equation of equilibrium differential condensation.

The Rayleigh equation is derived on the assumption that the composition of the incremental condensate, z, is that in equilibrium with the bulk of the vapor, x^*; that is,

$$z = x^* = \frac{y}{\alpha - (\alpha - 1)y}$$

Figure 2 shows that the condensate is in equilibrium with the vapor from which it is produced only if the resistance of the vapor phase is negligible, i.e. $h/H_G = \infty$, and if the resistance of the liquid is large, i.e. $h/H_L = 0$.

APPARATUS

The apparatus used in this investigation is shown in Figure 3; it consisted essentially of a wetted-wall distillation column equipped with an annular jacket through which water could be circulated under carefully controlled conditions so as to produce known, nearly uniform rates of condensation. External reflux could be supplied from a total condenser operating on the exit vapor stream from the test section, so that the column could be operated as an adiabatic countercurrent distillation unit or as a partial condenser.

The wetted-wall section of the column was 1.063 in. I.D. and 6 ft. long. It was made from a piece of brass pipe of 1.315 in. O.D. around which a spiral of heavy copper wire was wound with a spacing of ½ in. between adjacent turns. Surrounding the copper spiral was a piece of 1⅝-in., 15-B.W.G. brass tubing which fitted snugly and formed a spiral channel for the passage of cooling water. This construction was used so that both a measurable temperature rise of the water and a high water velocity might be obtained. The temperature of the water in the annular space was measured by thermocouples located at 1-ft. intervals, and local values of the heat flux were computed from the known mass flow rate of the coolant and the slope of the experimentally observed plot of water temperature vs. position.

The column was wrapped with ⅝-in. asbestos rope on the outside of which thermocouples were mounted at three levels. When the readings of these thermocouples were compared with those of three similar thermocouples mounted outside a second layer of asbestos rope flow of heat through the insulation could be detected. Adiabatic conditions were achieved by adjusting the current through electrical resistance windings which were applied outside a third layer of asbestos rope.

Provision was made for withdrawing samples of the vapor stream at the center line of the wetted-wall section and at 1-ft. intervals along the axis. Short lengths of hypodermic tubing were inserted into the vapor space through the annular jacket. These tubes had their inner ends pointed upward so that any condensate formed inside the tubes could not drop out into the gas stream. The small copper tubes led to water-cooled condensers.

The test section was provided with electrically heated upper and lower calming sections. The external reflux was heated to its boiling point before being returned to the column and was distributed evenly to the wetted wall by means of a fine-mesh screen. The liquid stream was sent through a calcium-chloride drier before being returned to the column. Flow rates of external reflux and liquid returned to the boiler were measured with calibrated rotameters.

Only the system ethylene dichloride–toluene was distilled. Its composition was determined from measurements of refractive index made with an Abbé refractometer. Technical-grade materials were purified carefully by distillation before use. The refractive indexes (n_D) of the purified pure components were 1.4427 ± 0.0001 and 1.4941 ± 0.0001 at 25°C. for ethylene dichloride and toluene, respectively.

range of vapor Reynolds numbers extending approximately from 9,000 to 25,000.

The still pot, having a capacity of 4.9 gal., was charged with approximately 3 gal. of the liquid mixture; it was found that this amount was sufficient completely to cover the electrical immersion heaters during a run and at the same time to avoid bumping and carryover of liquid from the still pot into the column. The power input to the immersion heaters was adjusted to give the desired vaporization rate, and after about 30 min. the material in the still pot began to boil and the vapors started to flow through the lower calming section.

Adiabatic conditions were established and tameter. During this time the various heaters had to be adjusted frequently to keep pace with the warming of the column. After this time another hour of running followed during which no further adjustments were made on the column, and then the first set of four samples was taken, consisting of liquid and vapor samples from the top and the bottom of the wetted-wall section of the column.

Without any adjustments on the column, operation was continued for another hour. Then the second set of samples was taken at the same four points. These generally agreed very closely with the first set. Each run was made individually, always starting with cold equipment.

All analyses were made by determining

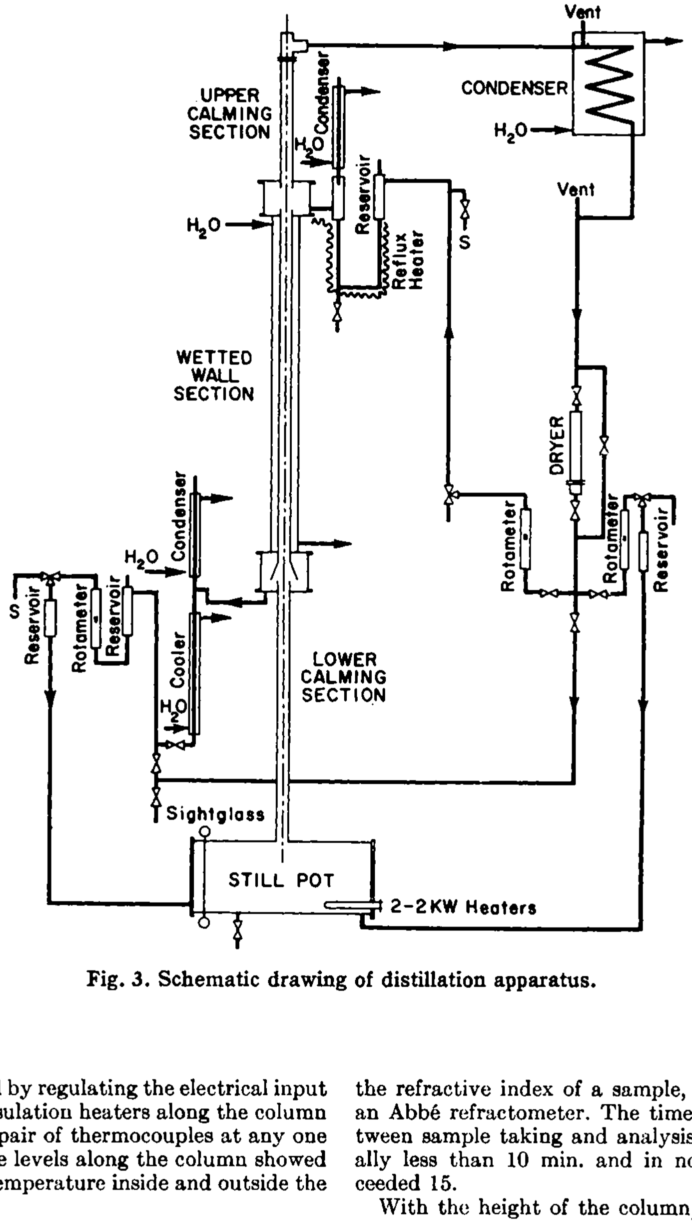

Fig. 3. Schematic drawing of distillation apparatus.

RESULTS*

Adiabatic Distillation Experiments

Ordinary distillation tests were carried out at total and at finite reflux by use of three different average levels of liquid composition, in each case covering a maintained by regulating the electrical input to three insulation heaters along the column until each pair of thermocouples at any one of the three levels along the column showed the same temperature inside and outside the insulation.

As soon as the reflux was flowing at a fairly uniform rate, the reflux heater was turned on and adjusted to assure the return of liquid reflux at its boiling point.

It was found that approximate equilibrium was established about 2 hr. after the reflux began to flow through the reflux rotameter.

the refractive index of a sample, by use of an Abbé refractometer. The time lapse between sample taking and analysis was usually less than 10 min. and in no case exceeded 15.

With the height of the column, the relative volatility, and the compositions of the vapor and liquid streams at the top and at the bottom of the column known, the overall height of a gas-phase transfer unit was computed by use of standard relationships. A series of about ten runs each was made at total reflux for three conditions representing

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*A complete description of the experimental procedure is given in reference (8). Tables of original data are on file as document number 4954 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $5.00 for photoprints or $2.25 for 35-mm. microfilm.

high, medium, and low ethylene dichloride concentration; similar series of runs were made for adiabatic operation at finite reflux and for the condensation experiments.

Material and energy balances were computed for the adiabatic runs as well as for those in which condensation occurred. In the adiabatic runs the average of the absolute deviations from perfect balances were 0.2 and 1.2%, respectively, expressed in each case as the error divided by the net mass or energy transported into the column. For operation as a condenser the corresponding figures were 0.3 and 8.1%, respectively.

Since the principal object of these runs was to determine the extent of the liquid-phase resistance, it was necessary to estimate the vapor-phase diffusional resistance and to calculate the liquid-phase value by difference. By use of a vapor Reynolds number computed from the vapor velocity relative to the falling interface, the friction factor for a smooth tube was calculated from the empirical equation of Drew, Koo, and McAdams (*3*). Next this was corrected for the roughness of the liquid-vapor interface, on which ripples were invariably present, by use of an empirical equation due to Kamei (*7*),

$$\frac{f_r}{f_0} = 1 + 0.00397(Re_L)^{0.476}\left(\frac{\mu_L}{\mu_G}\right)^{0.271} \tag{18}$$

in which the Reynolds number of the liquid layer is expressed as

$$Re_L = 4\Gamma/\mu_L \tag{19}$$

where Γ = liquid-mass flow rate, lb./(hr.)(ft. wetted perimeter) and μ_L = liquid viscosity, lb. mass/(hr.)(ft.). Kamei's result is based on careful measurements of interfacial friction in wetted-wall columns of various diameters, water and aqueous solutions having a wide range of viscosities being used. The values of the ratio of friction factors estimated for the conditions of these experiments were in the range $1.1 < f_r/f_0 < 1.25$. In estimating H_G it was assumed that

$$j_M = f_r/2 \tag{20}$$

and the usual relationship between j factor and the height of a transfer unit was employed.

$$H_G = (D/4j_M)(Sc_V)^{2/3} \tag{21}$$

The Schmidt number of the vapor phase was calculated from a diffusivity that had been estimated from the empirical equation of Gilliland (*6*). The numerical values of other physical properties were interpolated from experimental data reported in standard references. In the standard equation for the addition of individual resistances of the phases,

$$H_{OG} = H_G + (mV/L)H_L \tag{22}$$

from which H_L was computed, the average value of the slope of the equilibrium curve, m, was calculated for the particular range of compositions encountered in each experiment following the procedure suggested by Sherwood and Pigford (*13*).

Figure 4 shows the values of H_L derived from the over-all composition changes in distillation plotted against the Reynolds number of the liquid phase. The drawing of the line in Figure 4 requires some explanation: It has been observed visually that when the liquid Reynolds number fell below approximately 250, uniform wetting along the entire length of the column no longer occurred. Operation of the column with dry spots along its wetted wall gave erratic results and the two points at the lowest Reynolds numbers must therefore be ignored.

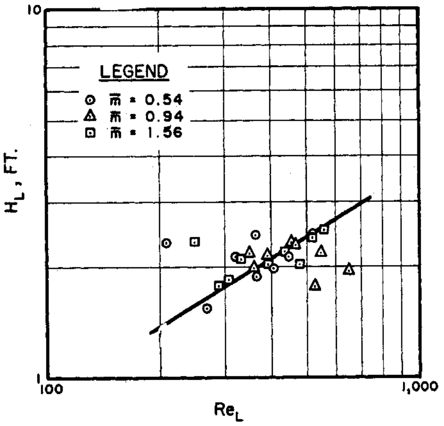


Fig. 4. H_L as function of liquid Reynolds number.

The trend toward higher values of H_L with increasing Reynolds numbers is normal, the general direction of the line following the diffusion theory for falling liquid films. Previous data obtained by Emmert and Pigford (*5*) and shown on Figure 9 also indicate an upward trend with increasing Reynolds number.

The H_L values shown on Figure 4 are more accurate and reliable than previous values obtained by Johnstone and Pigford (*13*), who published the only previous information on H_L values in adiabatic distillation.

On Figure 4 the H_L line for the high and low concentration ($\bar{m}$ = 0.54 and $\bar{m}$ = 1.56, respectively) is rather clearly defined, and it was thought unlikely that a line at intermediate concentration ($\bar{m}$ = 0.94) would show any drastic change in direction from the other two. It is interesting to observe that a single line could be drawn for the values at the three different concentration levels.

In a preliminary attempt to calculate H_L values from estimates of H_G based on friction factors for smooth tubes, a large variation of H_L with liquid composition appeared to be present. These variations were eliminated when Kamei's roughness correction was introduced according to Equation (18). Whether the true values of the friction factor have been used and whether Equation (20) is valid for the rippling interface cannot be determined with certainty, though it would appear significant that the H_L values given on the figure show approximately the same small influence of composition that would have been expected from the liquid physical properties.

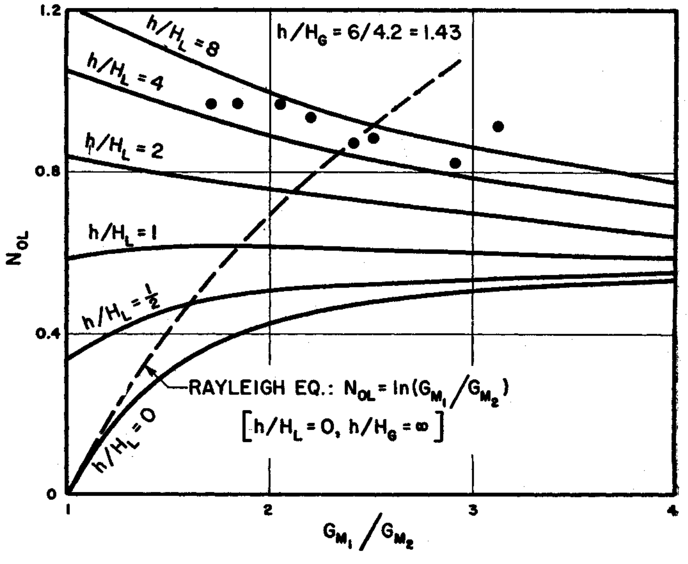
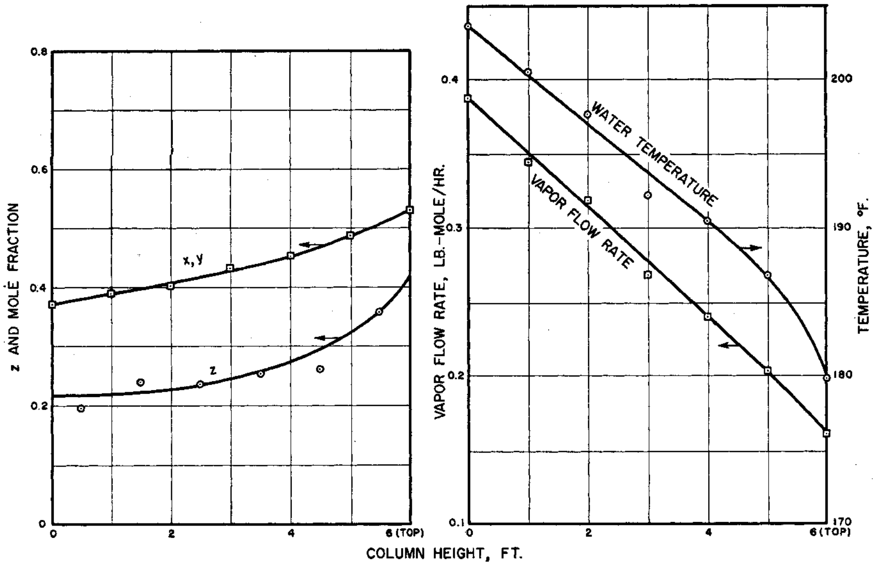


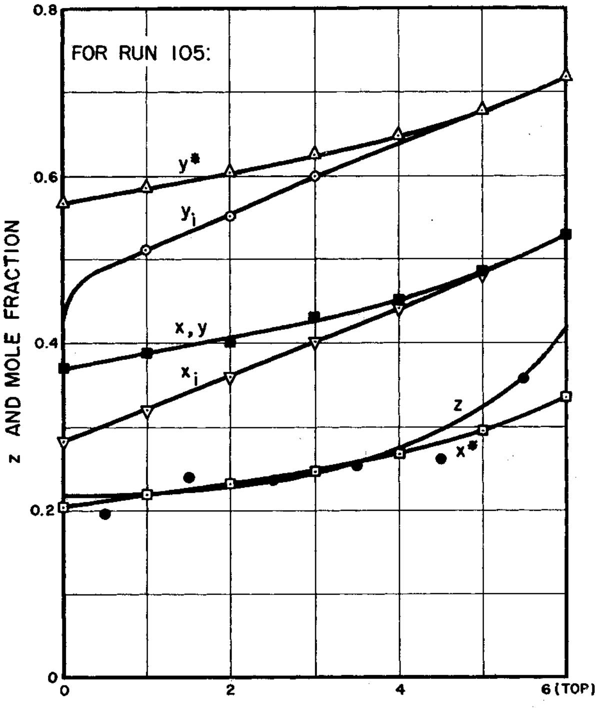
Fig. 5. Comparison between experimental and theoretical results.

Condensation Experiments

Figure 5 compares the effect of condensation on the apparent number of transfer units computed from the terminal compositions with the theory in its approximately integrated form according

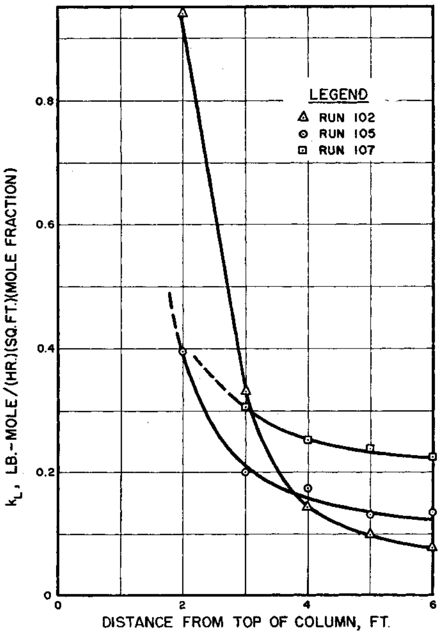


↑ **Fig. 6. Point conditions in column (for run 105).**



← **Fig. 7. Interfacial compositions.**

↓ **Fig. 8. Local values of k_L.**



to Equation (16). The theoretical lines on the figure are similar to those on the lower part of Figure 2; they apply to a different value of the h/H_G parameter, however, this time corresponding to the height of the experimental column and the value of H_G expected at the vapor flow rate used in the condensation runs. Like Figure 2, Figure 5 shows lines corresponding to various assumed values of the h/H_L parameter, though only a single value of this parameter applied to the condensation experiments.

As may be seen on the figure, the observed influence of the rate of condensation is the same as that expected from the theory, and it is significant that the points fall approximately along a line of constant h/H_L. When this line is extrapolated backward to the left-hand margin of the figure, it intersects the vertical axis at a value of N_{OG} equal to the value expected from the adiabatic-distillation tests. Apparently, as expected from the theory, the liquid-phase resistance has a large influence and causes the experimental points to cross the Rayleigh differential-distillation line, which is often used (incorrectly) for the estimation of fractionation that can be accomplished in a partial condenser.

As far as the quantitative use of the Colburn-Drew theory is concerned, it is of greater interest to study the effect of condensation on the local changes in composition within the column. Figure 6 is a plot of the observed local vapor compositions and cooling water temperatures at 1-ft. intervals along the condenser. The figure also shows other quantities, such as the vapor rate V and the composition of the incremental condensate z derived from the experimental observations. The values of V were computed from the following equation expressing a differential energy balance:

$$(dV/dh) = (Wc_P/\lambda)(dT/dh) \quad (23)$$

where W = cooling-water rate, lb./hr.; c_p = specific heat of water; T = local water temperature at position h; and λ = latent heat of condensation, B.t.u./lb. The composition of the incremental condensate was computed from the differential material balance, as expressed by Equation (11) and written in the form

$$z = y + V(dy/dV)$$
$$= y + (V\lambda/Wc_P)\frac{(dy/dh)}{(dT/dh)} \quad (24)$$

The differential quotients in Equation (23) and (24) were evaluated by means of a least-squares procedure based on five equally spaced points.

The fact that z is everywhere smaller than y, as shown in Figure 6, corresponds to the enrichment of the vapor stream as it flows upward. Thus the less volatile component, toluene, is condensed relatively faster than the more volatile one, ethylene dichloride.

Having available values of y and z at each point in the condenser makes it possible to compute the interfacial compositions y_i and x_i from Equations (3) and (9) if k_G/w is known. It was assumed that in spite of the progressive change in vapor velocity the local Reynolds number could be used to compute k_G from Equations (18), (20), and (21) and the smooth-tube friction factors. (This computation also neglects the probable distortion of the normal turbulent-velocity profile in the vapor phase owing to the transport of momentum to the interface by the condensing vapor.) The resulting values of interfacial compositions are shown by Figure 7. It is interesting to observe that at the top of the column, where the liquid layer is freshly formed, the values of x and x_i are very nearly equal. Thus only a very small concentration across the liquid phase is capable of producing a finite rate of mass transfer of each component. Doubtless this is due to the sudden creation of a sharp concentration gradient in a relatively quiet liquid mass; a similar end effect probably is present in the vapor phase at the bottom of the column, where the vapor stream is first exposed to the liquid layer and where the local gas-phase mass transfer coefficient is probably very large. In all probability, however, this end effect in the gas phase disappears very quickly, and so the steady state values of k_G computed from Equation (20) should be nearly equal to the local ones throughout most of the test section.

Figure 8 shows local values of k_L computed from the estimated interfacial compositions by means of Equation (8). It is evident that, in agreement with the discussion just given, the value of k_L is very large at the top of the column and undergoes a progressive decrease as the liquid flows down the column.

In order to compare the values of k_L computed from the condensation data with the values previously obtained in the adiabatic distillation runs it is necessary to compute an average of the local values of k_L. This was done by means of the following equation, which is suggested by theoretical relations for mass transfer into purely laminar liquid layers.

$$(k_L)_{avg} = \int_0^1 k_L \, d(t/\theta)$$

$$= 2 \int_0^1 k_L (t/\theta)^{1/2} \, d(t/\theta)^{1/2} \quad (25)$$

in which (t/θ) refers to the ratio of time of exposure of the liquid surface at any point to the total time of flow of surface layers down the column, as computed from the well known relations for laminar, gravitational flow of liquid layers. Figure 9 shows values of H_L [$= L_{avg}/(k_L)_{avg} aS$] from three of the condensation runs. The agreement with the adiabatic data is considered to be good in view of the uncertainties in the estimation of local conditions.

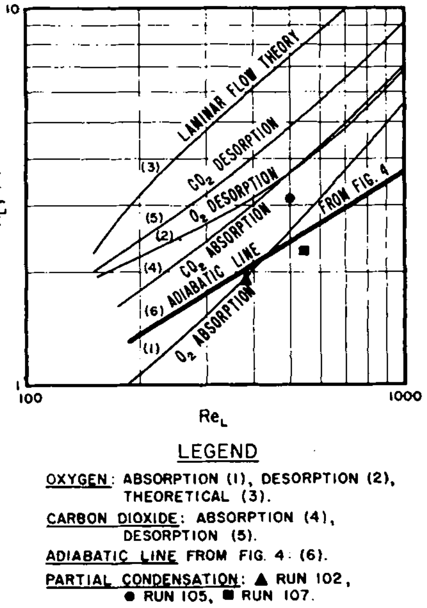


Fig. 9. H_L for distillation, condensation, and absorption. Curves (1) and (5) are from reference *5*.

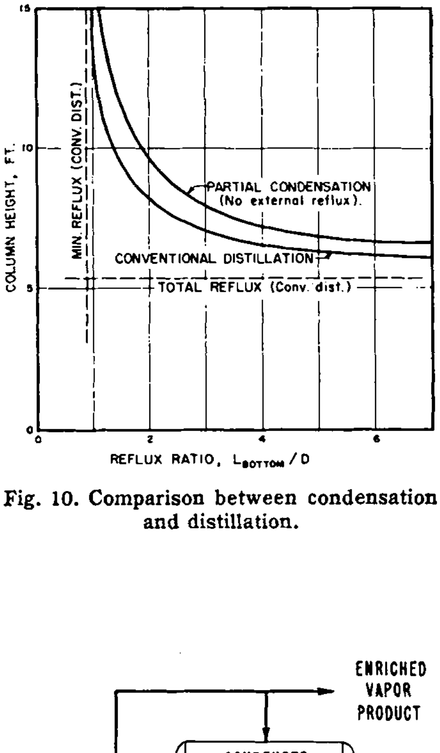


Fig. 10. Comparison between condensation and distillation.

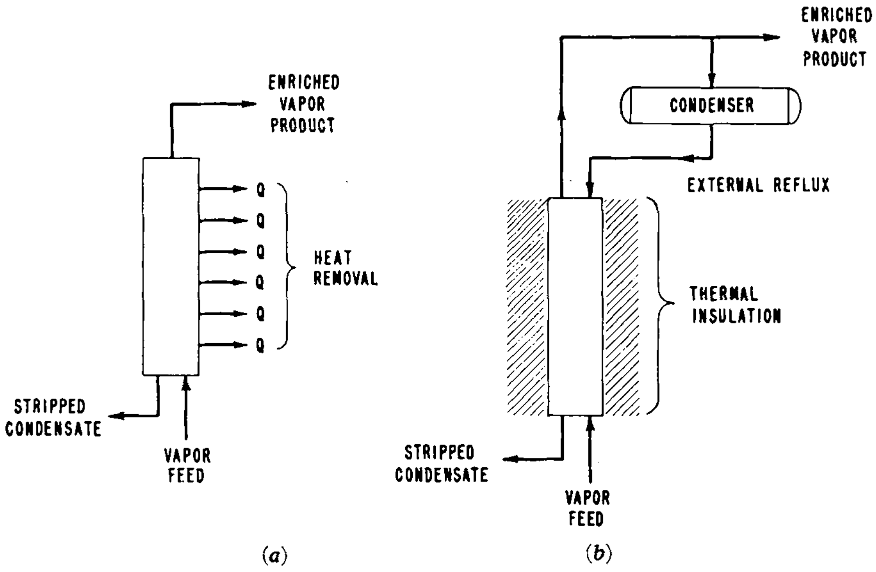


Fig. 11. Flow sheet for fractionation (*a*) with partial condenser, (*b*) with adiabatic distillation column plus ordinary condenser.

DISCUSSION OF RESULTS

The agreement shown on Figure 9 between values of H_L measured independently in distillation and in condensation experiments suggests that the Colburn-Drew analysis of mass transfer during condensation can be applied successfully by point-to-point calculation, by use of diffusional-resistance parameters evaluated from experiments in which condensation did not occur. This conclusion is further borne out when the H_L values are compared with data from gas-absorption studies. Figure 9 also shows a line representing the data of Emmert and Pigford (*5*) for liquid-phase resistances in the absorption and desorption of oxygen and carbon dioxide in water at room temperature, a wetted-wall column being used which is somewhat smaller than that employed in the condensation work. When it is remembered that H_L should decrease with increasing temperature, owing to the increase in the diffusion coefficient, the comparison appears to be a good one. A further explanation of the differences between the two sets of data may be the influence of interfacial resistance, which probably contributed to the total resistance to transfer of the slightly soluble gases in water but may have had less effect in the hydrocarbon system.

With the data just described it is possible to carry out a numerical design calculation for a reflux type of condenser and for an adiabatic-distillation column so that the two operation may be compared at equal capacities or at equal rates of heat removal. At equal values of the ratio of the liquid rate at the bottom of the apparatus, L_{bottom}, to the vapor-product rate at the top, D, the total heat transferred in fractionator or auxiliary condenser is the same, as indicated by Figure 11. The conditions assumed for an illustrative calculation are as follows:

System: ethylene dichloride–toluene
Bottom vapor rate: 0.400 lb.-mole/hr. at dew point

Vapor composition given: 0.400 mole fraction ethylene dichloride at bottom of column
Vapor composition desired: 0.550 mole fraction ethylene dichloride at top of column
Inside diameter of condenser tube: 1 in.
Coolant liquid: water, introduced at top of condenser, single pass on shell side

It is desired to determine the height of the tubes or the surface required. The calculations are made solely from the point of view of mass transfer, the assumption being that the correct heat transfer rate will be obtained by adjusting the cooling-water temperature.

For conventional distillation without heat transfer from the column, the required tube height is computed in the customary way by use of the values of H_G and H_L found in this work. The influence of the reflux ratio on the height is indicated in Figure 10.

For partial condensation a trial-and-error computation is required. A tube length is assumed so as to get a value of condensation rate (w, assumed constant here) and the Colburn-Drew equations are applied stepwise starting at one end until the composition at the other end of the column is reached. If it does not agree with the composition desired, another length is assumed and the calculations are repeated. After the extent of the surface is known, the required cooling-water temperatures are found from conventional heat transfer calculations. If these temperatures cannot be obtained, the specified vapor compositions must be altered. Thus it is not possible to specify fractionation, heat requirements and coolant temperatures independently; only two of the three can be fixed independently.

Under finite reflux in partial condensation the condenser operates in such a fashion that all condensation takes place inside the column, and no external reflux is returned to it. Thus the overhead product is all the vapor leaving at the top. For example, at a reflux ratio of $(L_{bottom}/D) = 1.50$, the first trial, with a column height of 8 ft. assumed and Equations (4), (8), (9), (10), and (11) applied for a stepwise integration over eight 1-ft. increments, gave $y_1 = 0.432$ (which compares with the given value of $y_1 = 0.400$); a second trial, with a column height of 11 ft. assumed, gave $y_1 = 0.405$. A detailed sample calculation for the design of a reflux condenser is given in reference *8*.

Figure 10 shows the computed results in the illustrative example. It is seen that at a given ratio of the liquid flow rate from the bottom of the tube to the rate of flow of the vapor product from the top of the tube the partial condenser requires slightly greater transfer surface in the fractionator to accomplish the same enrichment. To produce reflux in conventional distillation, on the other hand, heat transfer surface is required in an external condenser, which is not needed for the partial condenser, as shown by Figure 11. Conversely, for the same surface and the same enrichment conventional distillation requires a smaller reflux ratio, i.e., a smaller heat load per unit of product. Though an exact statement cannot be made, it appears from the numerical work that the minimum reflux ratio in a partial condenser is the same as that in ordinary distillation or that the same amount of liquid must be condensed to provide reflux whether the condensation takes place in a separate condenser or in the condenser fractionator.

In spite of the disadvantages in heat consumption and in required transfer surface the partial condenser does of course have the advantages of eliminating the need of a separate condenser when a vapor product is acceptable and of permitting heat removal partly at a higher temperature.

ACKNOWLEDGMENT

The financial assistance of the Research Corporation of New York, New York, is gratefully acknowledged. N. A. Copeland and R. D. Rice contributed valuable assistance and preliminary data. One of the authors received a generous fellowship award from the Socony Mobil Oil Company.

NOTATION

A = interfacial area, sq. ft.
a = interfacial area per unit volume of apparatus, sq. ft./cu. ft.
B_G = equivalent film thickness, ft.
c_P = specific heat at constant pressure, B.t.u./(lb.)(°F.)
D = diameter of column, ft.
D_V = diffusion coefficient of vapor, sq. ft./hr.
f_0 = friction factor for smooth tube, dimensionless
f_r = friction factor corrected for roughness, dimensionless
G_M = molar rate of gas flow, lb.-mole/(hr.)(sq. ft.)
h = height of wetted-wall column, ft.
H_G = height equivalent to a transfer unit, based on gas-phase resistance, ft.
H_L = height equivalent to a transfer unit, based on liquid-phase resistance, ft.
H_{OG} = height equivalent to a transfer unit, based on over-all gas-phase resistance, ft.
j_M = j factor for mass transfer
k_G = mass transfer coefficient for gas phase, lb.-mole/(hr.)(sq. ft.)(mole fraction)
k_L = mass transfer coefficient for liquid phase, lb.-mole/(hr.)(sq. ft.)(mole fraction)
L = molar mass flow rate of liquid, lb.-mole/hr.
L_M = molar rate of liquid flow, lb.-mole/(hr.)(sq. ft.)
m = slope of equilibrium curve, dy^*/dx
N_A = rate of diffusion of component A, lb.-mole/(hr.)(sq. ft.), taken positive when A diffuses from gas toward interface
N_B = rate of diffusion of component B, lb.-mole/(hr.)(sq. ft.), taken positive when B diffuses from gas toward interface
N_G = number of transfer units based on gas-phase driving force, dimensionless
N_{OG} = number of transfer units based on over-all gas-phase driving force, dimensionless
N_{OL} = number of transfer units based on over-all liquid-phase driving force, dimensionless
n_D = refractive index, dimensionless
R = universal gas constant, 1,544 (ft.)(lb.-force)/(lb.-mole)(°F.)
Re = Reynolds number, dimensionless
S = cross section of vapor channel, sq. ft.
s = distance, ft., measured positively from gas phase toward the interface; $s = 0$ at gas side of equivalent laminar film
Sc = Schmidt number, dimensionless
T = absolute temperature, °*R*.
t = time, hr.
V = molar mass flow rate of vapor, lb.-mole/hr.
w = total molal rate of condensation on unit area, lb.-mole/(sq. ft.)(hr.)
x = mole fraction of more volatile component in liquid phase
x^* = mole fraction of more volatile component in liquid phase existing in equilibrium with vapor of mole fraction y
y = mole fraction of more volatile component in vapor phase
y^* = mole fraction of more volatile component in vapor phase existing in equilibrium with liquid of mole fraction x
z = ratio of the rate of condensation of the more volatile component to the net rate of condensation

Greek Letters

α = relative volatility, dimensionless
Γ = liquid mass flow rate, lb./(hr.)(ft. wetted perimenter)
η = fractional distance through film, $= s/B_G$
θ = time, hr.
λ = latent heat of vaporization, B.t.u./lb.-mole
μ = viscosity, lb.-mass/(ft.)(hr.)
π = 3.14159

Subscripts

G = gas
i = interface
L = liquid
V = vapor
1 = the bottom of the column
2 = the top of the column

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APPENDIX

Partial Condensation for Gas- and Liquid-film Resistances

In the derivation of Equation (14) it was shown that

$$\left[\frac{w}{k_G}\right]_{\text{avg}} \doteq \frac{H_G}{h}\ln\left[\frac{V_1}{V_2}\right] \quad (1A)$$

Similarly,

$$\left[\frac{w}{k_L}\right]_{\text{avg}} \doteq \frac{H_L}{h}\ln\left[\frac{L_1}{L_2}\right] \quad (2A)$$

Since by definition $h/H_G = N_G$ and $h/H_L = N_L$, Equations (1A) and (2A) may be written as

$$\frac{w}{k_G} = \ln\left[\left(\frac{V_1}{V_2}\right)^{N_G^{-1}}\right] \quad (3A)$$

and

$$\frac{w}{k_L} = \ln\left[\left(\frac{L_1}{L_2}\right)^{N_L^{-1}}\right] \quad (4A)$$

Le

$$G = e^{w/k_G} = (V_1/V_2)^{N_G^{-1}} \quad (5A)$$

and let

$$£ = e^{w/k_L} = (L_1/L_2)^{N_L^{-1}} \quad (6A)$$

Solving the Colburn-Drew equation—Equation (3)—for z in terms of both the liquid and vapor phase gives

$$z = \frac{£x_i - x}{£ - 1} = \frac{Gy - y_i}{G - 1} \quad (7A)$$

and replacing y_i by mx_i results in

$$x_i = \frac{G(£ - 1)y + (G - 1)x}{£(G - 1) + m(£ - 1)} \quad (8A)$$

and

$$x_i - x \quad (9A)$$

$$= (£ - 1)\frac{Gy - (G - 1 + m)x}{£(G - 1) + m(£ - 1)}$$

or

$$\frac{x_i - x}{x^* - x}$$

$$= \frac{[Gy - (G - 1 + m)x](£ - 1)}{[£(G - 1) + m(£ - 1)](y/m - x)}$$

$$= \frac{m(£ - 1)}{£(G - 1) + m(£ - 1)}$$

$$\cdot\frac{G(y - x) - (m - 1)x}{(y - mx)} \quad (10A)$$

From Equation (7A)

$$z - x = \frac{£}{£ - 1}(x_i - x)$$

or

$$\frac{dx}{z - x} = \frac{£ - 1}{£}\frac{dx}{x_i - x} \quad (11A)$$

but $dx/(z - x) = dL/L$; therefore, according to Equation (11A)

$$\frac{dx}{x_i - x} = \frac{£}{£ - 1}\,d\ln L \quad (12A)$$

For the over-all resistance

$$\frac{dx}{x - x^*} = \frac{x_i - x}{x^* - x}\cdot\frac{dx}{x - x_i}$$

which upon substitution by Equations (10A) and (12A) gives

$$dN_{OL} = \frac{dx}{x - x^*} = \left[\frac{1}{\dfrac{G - 1}{m} + \dfrac{£ - 1}{£}}\right][-d\ln L]$$

$$= \frac{-d\ln L}{\dfrac{1}{m}[(V_1/V_2)^{N_G^{-1}} - 1] + [1 - (L_1/L_2)^{-N_L^{-1}}]}$$

Upon integration this becomes Equation (16) in the text, i.e.

$$N_{OL} \equiv \int_{x_1}^{x_2}\frac{dx}{x - x^*} = \frac{\ln(V_1/V_2)}{m^{-1}[(V_1/V_2)^{(H_G/h)} - 1] + [1 - (V_2/V_1)^{(H_L/h)}]}$$

Presented at A.I.Ch.E. Louisville meeting

ERRATA

Below is the list of references cited in John W. Delaplaine's paper "Forces Acting in Flowing Beds of Solids," which appeared in the March, 1956, issue of the *Journal* on page 127. The list was omitted from the published paper.

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In the paper "Entrainment Removal by a Wire-mesh Separator" by C. LeRoy Carpenter and Donald F. Othmer, which appeared in the December, 1955, issue of the *Journal*, on page 554 the equation

$$k = \frac{36{,}856\times 9.4167\times 10^{-4/3}}{3.2739} = 10.601$$

should be

$$k = \frac{36{,}856\times 9.4167\times 10^{-4}}{3.2739} = 10.601$$

and Equation (8) on page 556, which appeared as $E_s = 1 - (1 - (E_M/c))^N$, should be $E'_s = 1 - [1 - (E_M/c)]^N$.