A General Index of Fractional Distillation Power for Hydrocarbon Mixtures

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Results from precise calculations for fractionation of multicomponent hydrocarbon mixtures show that the relative separations between components are rationalized in a simple manner in terms of the relative volatilities. A quantitative criterion for sharpness of fractionation with complex mixtures, the Fractionation Index, is suggested. This function is useful for general correlation purposes. It also enables prediction of the detailed compositions of the products from a proposed fractionation and thereby simplifies the computation procedures.

With regard to computation of power of fractionation needed in separations of complex hydrocarbon mixtures, relatively little has been contributed in the past twenty-five years on one important problem: Given the required separation to be achieved between two selected feed components, how can an engineer predict the consistent distributions of all other components to distillate and bottoms before making detailed column computations to establish the number of plates and reflux needed to accomplish the specified fractionation? The literature is almost devoid of data which would give a reliable basis for speculations. The present paper will examine this question and present information which gives considerable clarification.

The derivations and the data presented refer to hydrocarbon mixtures for which the vapor-liquid equilibria are reconciled by the laws of ideal solutions. The conditions under which the conclusions are applicable to some other mixtures should become evident during the developments.

LIMITING CASES IN FRACTIONATION

An orientation can be obtained by considering the mathematical relations for two limiting cases in fractionation. The simplest, least powerful continuous fractionation is the equilibrium flash distillation. For each constituent the ratio of its concentration in the vapor to the concentration in the liquid is by definition $y_i/x_i = k_i$. Taking logarithms of both sides, one gets

$$\log (y_i/x_i) = \log (\alpha_i k_0) = \log \alpha_i + \log k_0 \qquad (1)$$

where k_0 refers to one of the constituents taken as a reference component and is a constant in the equation. By the definitions used, $\alpha_0 = 1.0$. Any component in the mixture may be taken as the reference component, or the reference component may be a hypothetical one having a volatility between those of two real components.

The significance of Equation (1) is that plots of $\log (y_i/x_i)$ vs. $\log \alpha_i$ for flash vaporizations are straight lines having unit slopes. In other words, a fundamental characteristic for this least powerful fractionation is that the logarithmic plots have the slope of 1.0; this is independent of the composition and of the ideality or nonideality of the mixture.

For the case of the fractionator operating at total reflux or infinite reflux ratio, the Fenske-Underwood equation (*2*, *6*)

$$n \log \alpha_i = \log \frac{(x_d/x_w)_i}{(x_d/x_w)_0} \qquad (2)$$

relates the terminal composition ratios for any pair of constituents to the relative volatilities and the number of theoretical stages in the fractionator. This may be rearranged to

$$\log (x_d/x_w)_i = n \log \alpha_i + \log (x_d/x_w)_0 \qquad (3)$$

and shows that a plot of $\log (x_d/x_w)_i$ vs. $\log \alpha_i$ will give a straight line having a slope equal numerically to the number of theoretical stages. The absolute values of $\log (x_d/x_w)_i$ depend upon the arbitrary value assigned to the reference component, identified in Equation (3) by the subscript zero. Any constituent in the mixture may be taken for reference, but there are advantages in using a constituent for which $x_d/x_w = 1$, and hence $\log (x_d/x_w)_0 = 0$; the reference component may be a hypothetical one having a volatility intermediate between those of two real components.

The relationships indicated by Equations (1) and (3) are illustrated graphically in Figure 6, with the reference constitutents selected such that the lines pass through the origin. The straight line at a 45-deg. angle, having unit slope, defines the terminal composition ratios x_d/x_w as a function of relative volatilities for all single-stage equilibrium vaporizations, at zero reflux or at infinite reflux. Lines are shown having slopes of 2, 3, 4, and 10, corresponding to increasingly sharper fractionation; these slopes are equal numerically to the number of theoretical plates used at infinite reflux ratio. The vertical line having infinite slope indicates the limiting condition for the most powerful fractionation obtainable by using infinite plates and infinite reflux ratio; it represents the hypothetical condition of completely sharp separation between constituents.

When the relative fractionations between components for a given feed composition are defined by equations such as (1) or (3), or by other means, there is but one over-all material balance that will satisfy a given set of x_d/x_w values. The quantities and compositions of distillate and bottoms are determined by the over-all balance equations

$$\left\{\frac{Fx_f}{(D/W)(x_d/x_w) + 1}\right\}_i = (Wx_w)_i \qquad (4)$$

$$D = F - W = F - \sum (Wx_w)_i \qquad (5)$$

$$D/W \text{ (calculated)} = \{F - \sum (Wx_w)_i\}/\sum (Wx_w)_i \qquad (6)$$

$$(Dx_d)_i = (Fx_f)_i - (Wx_w)_i \qquad (7)$$

Equations (4) and (6) are solved by using various assumed values for D/W until a value of D/W is found which gives a consistent value for the calculated W.

Table 1. Conditions for Column Computations for Wide-Boiling-Range Hydrocarbon Mixture

	Theoretical plates		Bottom temperature,*		Molal flows	
Case	Rectifying	Stripping	°F.	D/W	Top L/V	Bottom V/L
A	7	0	440	3.6	0.48	
B	4	3	455	4.2	0.53	0.89
C	2	5	458	4.3	0.42	0.86
D	4	3	410	2.8	0.023	0.54
E	2	2	445	3.8	0.52	0.86
F	7		460	4.4	Total reflux	
G	2	2	400	2.8	0.033	0.45
H	2	5	420	3.0	0.044	0.60

*Top temperature is 322°F. in all cases.

Equation (4) is derived from Equation (7) and will be recognized as one form of the equations commonly used for evaluating flash vaporizations. In general, Equations (7) and (4) are the over-all material balance equations which apply to all fractionation problems.

EFFECT OF REFLUX RATIO AND FEED-PLATE LOCATION

In contrast with the simplicity of the variables for the single-stage equilibrium separation or the total reflux fractionation, the separations in the practical fractionator involve the effects of variable plates and variable reflux ratios in both rectifying and stripping sections. Both theory and experience show that the degree of removal of light components from the bottoms depends primarily upon the fractionating power in the stripping section and is influenced little by the power in the rectifying section, and that the degree of removal of heavy components from the distillate is dependent basically on the power in the rectifying section and but little on the power in the stripping section.

Some indication of the general relationships between the component distribution ratios for the practical fractionator is given by the distributions from a computation study cited by Thiele and Geddes (*5*). This case is of interest as it involved the fractionation of gasoline from a wide–boiling-range feed containing components boiling as high as 550°F. by use of a low-powered column having a reboiler and one theoretical plate in the stripping section and only two theoretical plates in the rectifying section. Hence there were wide overlappings of components appearing in both the distillate and bottoms in appreciable quantities. The distillate quantity corresponded to a molal D/F ratio of about 0.75; the top L/V ratio was 0.26, and the bottom V/L ratio was 0.85. The calculated top and bottom temperatures were 322° and 435°F. for operation at atmospheric pressure.

The calculated x_d/x_w ratios for all nineteen components are shown in Figure 1 which is plotted as a function of the relative volatilities taken at 380°F., approximately the mean of the column terminal temperatures. The component boiling at 393°F., for which x_d/x_w equaled 0.75, was taken as the reference component. The relative volatilities were calculated as the ratios of vapor pressures for the pure components.

Figure 1 shows that the curve reconciling the data points consists basically of two intersecting straight lines on the log-log plot, with some deviation of the points from the straight lines in the region near the intersection. The fractionating power of this column of four theoretical plates should be less than that for a four plate column operating at infinite reflux ratio and greater than the power for a single-plate equilibrium vaporization. The lines on Figure 1 have slopes consistent with these limiting conditions. The upper data points fall on a straight line having a slope of 1.95, this slope being related to the fractionating power in the column stripping section. The lower points fall on a line of slope 3.40, related to power in the rectifying section. Both these lines have slopes intermediate to the values 1.0 and 4.0 corresponding to the theoretical limiting values from Equation (3).

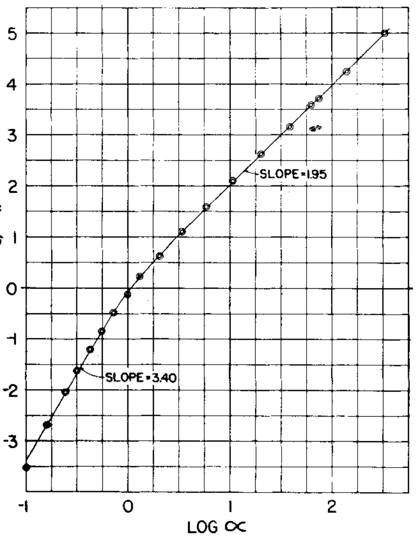

Fig. 1. Component distribution ratios for case given in reference (*5*).

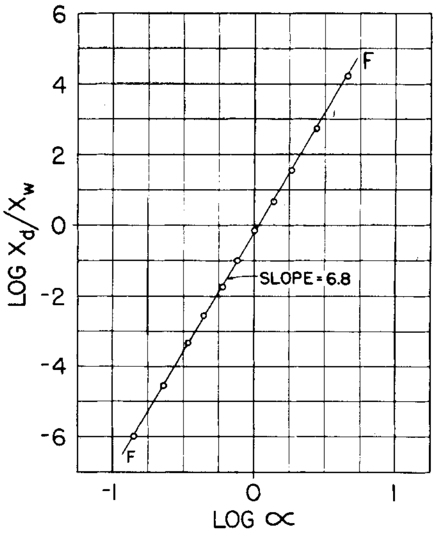

Fig. 2. Component distribution ratios for infinite reflux ratio fractionation.

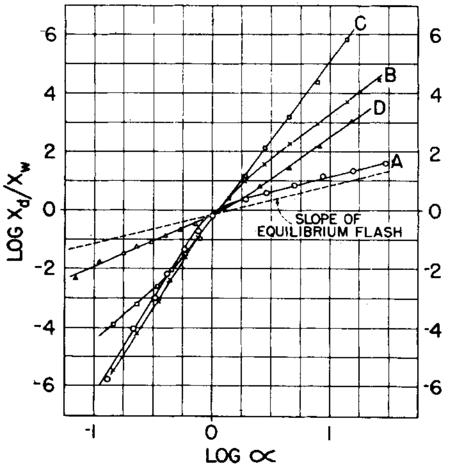

Fig. 3. Component distribution ratios obtained under various fractionation conditions (Table 1).

As there are no other published data having enough range and accuracy for the present purposes, some additional cases will be presented taken from computation work done at the same time as that on which Figure 1 is based. The feed composition and methods of computation were the same; cases were calculated for fractionators containing a reboiler plus either three or six theoretical plates, and various reflux ratios and feed plate locations were used. The important conditions are tabulated in Table 1, and the calculated distribution ratios are graphed in Figures 2, 3 and 4 as functions of the relative volatilities of the components. The relative volatilities were taken as the ratios of the vapor pressures of the pure hydrocarbons at average temperatures corresponding to the means of the column terminal temperatures; in each of the cases the selected reference component was that constituent for which x_d/x_w most closely approached unity.

On Figure 2 are shown the distribution ratios calculated for the case of infinite reflux fractionation of the wide boiling range mixture in a column consisting of a reboiler plus six theoretical plates and operating with terminal temperatures of 322° and 460°F. at atmospheric pressure. The relative volatilities were calculated at 390°F., the mean of the terminal temperatures. The x_d/x_w values for all components fall on the straight line *F* in accordance with the Fenske-Underwood relation [Equation (3)], the correlation line having a slope of 6.8 compared to the theoretical value of 7.0 for seven stages.

Plots of the distribution ratios for cases *A*, *B*, *C*, and *D* are given in Figure 3; these exhibit the same general characteristics as the case covered in Figure 1. The locus of points for each case consists of two intersecting straight lines, with some departure of the points in the transition region. Curves *A* and *B* bend downward, indicating relatively greater power in the rectifying sections than in the stripping sections; curves *C* and *D* bend upward, indicating relatively greater power in the stripping sections. The slopes of all straight line segments lie between the value 1.0 for a single stage equilibrium separation and 4.0 to 7.0 corresponding to operation of four or seven theoretical plates at infinite reflux ratio. Case *A* refers to a seven plate column having no stripping section, the feed being introduced directly to the reboiler; the upper characteristic line on Figure 2 for the stripping section has a slope only slightly greater than 1.0 corresponding to equilibrium solubility of distillate components in the heavier hydrocarbon bottoms.

Both theory and experience show that a definite fractionating power in a rectifying or stripping section may be obtained by means of various combinations of reflux ratio and number of plates and that the power in either section can be modified by appropriate changes in reflux ratio, number of plates, or both. This is illustrated well by the slopes of the curves in Figure 4 for cases *E*, *G*, and *H*. Reference to Table 1 will show that quite low L/V ratios were used in the rectifying sections for cases *G* and H; the stripping V/L ratios remained substantial, however, owing to the reboiler heat needed to complete the vaporization of the net distillate.

Case E on Figure 4 involved the use of two rectifying and two stripping stages with a top L/V ratio of 0.52; the slopes for the curve were 3.3 and 2.3 for the rectifying and stripping sections, respectively, indicating the greater power in the rectifying section. Reducing the top L/V to 0.033 in case G caused more reduction in rectifying slope than in stripping slope; this almost resulted in a single straight correlation line with slopes of 1.6 and 1.8 for the curve segments. For case H three added stripping plates were used, resulting in the marked increase for the stripping section slope to the value 4.7.

Figure 5 is a plot of the calculated component distribution ratios for a gasoline debutanizer tower taken from computations made by the procedure of Thiele and Geddes. The partially vaporized feed entered a column consisting of a reboiler plus four stripping and ten rectifying theoretical plates operating with terminal temperatures of 150° and 340°F. at 100 lb./sq. in. gauge. The relative volatilities were taken as the ratios of the y/x values at 250°F., approximately the average of the terminal temperatures. The straight correlation line indicates a good balance between the fractionating powers in the stripping and rectifying sections.

These examples are sufficient to show that there is a simple, orderly pattern for the relative separations achieved between components in a complex mixture of hydrocarbons. When the distributions of only a few selected components to the terminal products are known, the distributions of all the other components become definite, conforming with the linear relations illustrated in Figures 1 to 5. In other words there are interrelations in the complex fractionation process which reduce markedly the number of independent composition variables which must be considered; these simplifying relations are associated closely with the important fundamental variable, the relative volatilities of the components.

Much more data must become available before all the secondary questions and implications can be settled. It seems logical that the intersection of a pair of characteristic lines should occur near the point where x_d/x_w equals unity (Figures 1, 3, and 4). It is evident that the slope of a characteristic line depends to some extent upon the arbitrary selection of the temperature at which relative volatilities are taken.

The present examination indicates that relative volatilities evaluated at approximately the mean of the column terminal temperatures have the most significance. For example the component distributions for the infinite reflux ratio fractionation shown in Figure 2 conform to a single straight line having a slope of 6.8 compared to the theoretical value of 7.0 for seven plates. Single straight correlation lines also were obtained when the relative volatilities were taken at the terminal temperatures of 322° or 460°F., but the slopes were 5.9 and 7.7, respectively.

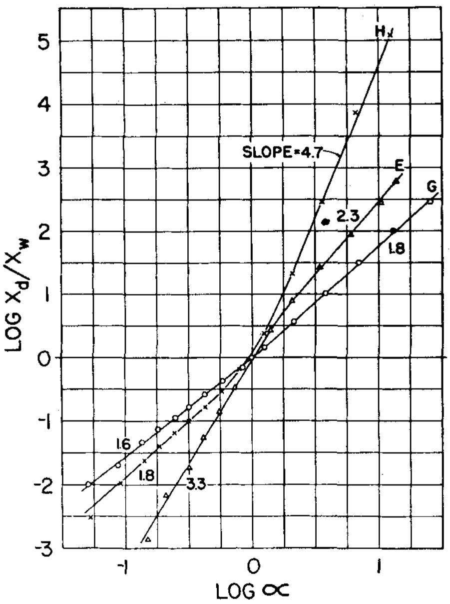

Fig. 4. Effect of changes in number of plates and reflux ratios (Table 1).

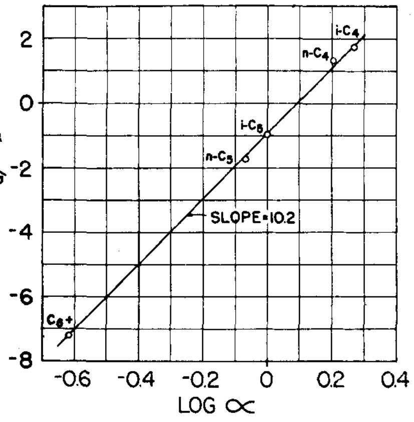

Fig. 5. Component distribution ratios for gasoline debutanizer.

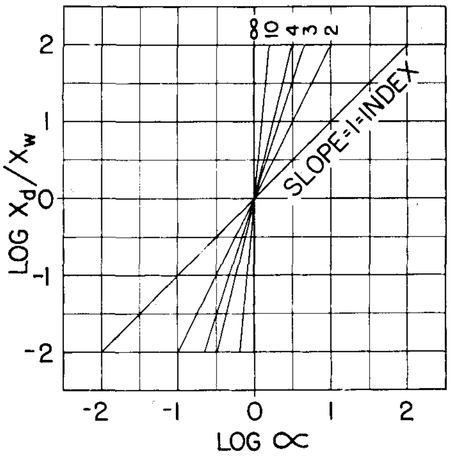

Fig. 6. Component distribution ratio vs. relative volatilities, fractionation index.

On theoretical grounds one might speculate that it would be more sound to take relative volatilities for the light constituents at the bottoms temperature and relative volatilities for the heavy constituents at the top temperature or to use the average temperatures in the stripping and in the rectifying sections. For the cases cited in the present paper, pairs of straight correlation lines still result. The slopes of the straight lines vary with the changes in relative volatilities of constituents at different temperature levels.

GENERAL INDEX OF FRACTIONATION POWER

The data presented indicate that the characteristic straight lines obtained from plots of log x_d/x_w vs. log α give simple identifications for the manner in which multicomponent mixtures separate in fractional distillation. The slopes of these lines also provide a rational criterion for power of fractionation in distillation systems. In view of the fundamental nature and the usefulness of the slope function it is proposed that the natural descriptive term *fractionation index* be used to designate the logarithmic slopes of the straight characteristic lines.

Figure 6 gives the graphical definition of the fractionation index with separate lines shown for index numbers of one, two, three, four, ten, and infinity. The plot is based on the use of Equation (3), with the constant term log $(x_d/x_w)_0$ for the reference component taken equal to zero (i.e., $x_d/x_w = 1.0$). This reference component can be a normal component, a trace component, or a hypothetical component.

PRACTICAL USES

The concept of the fractionation index is useful in condensing the results of computation studies, since it is a means of conveying much information in a brief way. For a fractionator having balanced power in the stripping and rectifying sections a single value of the index plus one x_d/x_w value for a reference component fully define the yields and detailed compositions of distillate and bottoms from a given feed stock. If the known separation is characterized by a pair of intersecting straight lines, only the two values of the Index plus the value of x_d/x_w at the point of intersection are required. In other words in each case there is but one yield and composition of distillate which will satisfy these conditions and the over-all component balances defined by Equations (4) to (7). Cataloguing this way should be helpful in comparing new fractionation problems with ones that have been evaluated previously.

The calculation of a fractionator by plate to plate methods can be done more conveniently by making use of the fractionation index, whether the computations are carried out by the Lewis-Matheson (*4*) or the Thiele-Geddes (*5*) procedure. Persons familiar with the Thiele-Geddes method will recognize that the characteristic slopes of the index lines are fairly well established after the first trial solutions, and that these slopes

TABLE 2. DEVELOPMENT OF PRODUCT YIELDS AND COMPOSITIONS

Assumed: Index = 6.0 in rectifying section, 2.0 in stripping section; index lines to intersect at log $x_d/x_w = 0$

1	2	3	4	5	6	7	8	9	10
	Feed,				D/W assumed equal to 1.03				
Component	Fx_f	Log α	Log x_d/x_w	x_d/x_w	Dx_d/Wx_w	Wx_w	Dx_d	x_w	x_d
1	15	0.5	1.0	10	10.3	1.33	13.67	0.027	0.270
2	20	0.3	0.6	3.98	4.10	3.92	16.08	0.079	0.317
3	25	0.1	0.2	1.59	1.63	9.50	15.50	0.193	0.306
(reference)	Trace	0	0	1.0					
4	25	−0.1	−0.6	0.252	0.259	19.82	5.18	0.403	0.102
5	15	−0.3	−1.8	0.0159	0.0164	14.75	0.25	0.298	0.005
						49.32	50.68	1.000	1.000

generally do not change substantially with further trial solutions. The first index lines often enable estimation of the final compositions of the product streams without the need to complete the plate to plate computations rigorously.

The use of the fractionation index has a distinct value in the computation of a column by the Lewis-Matheson procedure. In the common problem, where a balanced fractionator is desired, a single value of the index plus a value of x_d/x_w for one component will define precisely the relative separations of components and the concentrations of every component in the products; this enables plate to plate calculations to be made from each end of the column with the minimum of trial and error work continued until composition matches indicate that the feed plate has been reached.

The setting of the component distributions by use of a single, straight index line is consistent with the most efficient usage of plates and leads to the simplest column computation procedures. In effect this was the distribution Hengstebeck (*3*) used for reduction of a multicomponent feed to an equivalent binary mixture in the application of his graphical computation procedure.

There are conditions however where the engineer has practical justification for the design of an unbalanced fractionator. The predetermination of consistent product compositions and yields can be done by a calculating procedure similar to that used in the case of a single, straight index line. This will be illustrated by considering the case of a fractionation to be accomplished in a column where the rectifying section would have three times as much fractionating power as that of the stripping section. Table 2 gives the premises and derivations of product yields and compositions. It was arbitrarily assumed that the feed would be split so that a hypothetical constituent (or a trace component) having a relative volatility midway between those for components three and four would appear in distillate and bottoms in equal concentrations, or $x_d/x_w = 1.0$. It was also assumed that a fractionation index of 2.0 would be used for the stripping section and of 6.0 for the restifying section, with intersection of the index lines at log $x_d/x_w = 0$. The consequent composition ratios based on the relative volatilities of column 3 are tabulated in columns 4 and 5 and plotted in Figure 7.

Equation (4) was then used to determine the yields and compositions of products consistent with the assumed composition ratios in column 5 by using trial values for D/W. Columns 6 to 10 summarize the calculations for the correct trial value $D/W = 1.03$. Column 6 gives the product of D/W and x_d/x_w, and column 7 gives the values of Wx_w evaluated by means of Equation (4). The component quantities in the distillate Dx_d were calculated by difference, with Equation (7) used, and are tabulated in column 8. The derived compositions of distillate and bottoms are given in columns 9 and 10. These terminal compositions then could be the starting point for the Lewis-Matheson type of plate to plate calculations by using reflux ratios greater than the minimum reflux ratio required for this separation.

Years ago Docksey (*1*) gave an ingenious algebraic solution for the plate to plate enrichment equations in terms of the relative volatilities of the components, thus avoiding the trial and error methods of Lewis and Matheson for reconciling vapor-liquid equilibria and temperature on successive plates. The practical use never developed however since it was necessary to know accurately the concentration of every component in the products from a proposed fractionator to start the computations. With the means available for estimating these rather accurately engineers should find the Docksey equations particularly helpful for some computation studies. Docksey's solution is similar to that developed by Underwood (*6*), but it is somewhat simpler in execution.

While the present study has been concerned with hydrocarbon mixtures, the conclusions are applicable to mixtures of other organic molecules where the departures from the laws of ideal solutions are small; they should apply also to some nonideal mixtures in special cases where the activity coefficients of the components change only moderately over the concentration ranges existing within a fractionator.

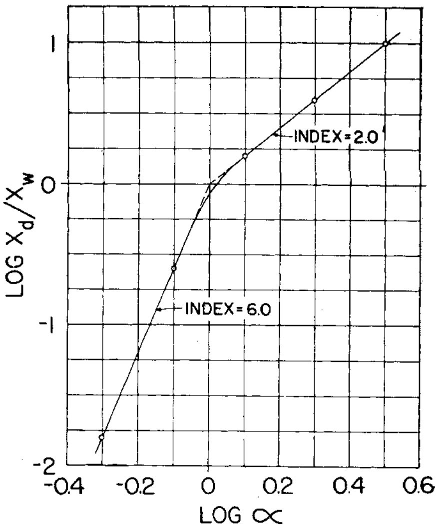

Fig. 7. Component distribution ratios for unbalanced fractionator problem (Table 2).

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NOTATION

F = total moles of feed
D = total moles of distillate
W = total moles of bottoms
L = moles of liquid overflow within column
V = moles vapor flowing within column
n = number of theoretical plates
x = mole fraction of a constituent in the liquid (x_d in distillate, x_w in bottoms)
y = mole fraction of a constituent in the vapor
k = y/x

Greek Letters

α = relative volatility of a constituent ($\alpha_i = k_i/k_0$)
$\sum$ = summation

Subscripts

0 = reference constituent
i = constituent i
d = distillate from column
w = bottoms from column
f = feed

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