FRACTIONAL DISTILLATION OF MULTI-COMPONENT MIXTURES—CALCULATION OF MINIMUM REFLUX RATIO.

By A. J. V. UNDERWOOD, D.Sc., M.I.Chem.E., A.M.I.Mech.E., F.R.I.C., F.Inst.F. (Fellow).

SUMMARY.

By extending a method which has been applied to ternary mixtures, equations are derived by which the minimum reflux ratio for multi-component mixtures can be readily calculated when the fractionation between the key components is a sharp one, relative volatilities and molal reflux being assumed constant. Numerical examples are given to illustrate the method of calculation.

THE calculation of minimum reflux ratio is an important problem. Several methods of calculation have been put forward such as those of Brown and Martin,[1] Brown and Holcomb,[2] Gilliland,[3] Hogan,[4] and Colburn.[5] Some of those methods involve a considerable amount of calculation and, as has been pointed out by Colburn,[5] are open to criticism in regard to the basic assumptions made. The most convenient method for most purposes is that of Colburn,[5] but it admittedly rests on an empirical basis.

By extending to multi-component mixtures the methods previously described by the author [6,7] in connection with ternary mixtures, the calculation of minimum reflux ratio can be made fairly simply for cases of ideal mixtures with constant relative volatilities and sharp separation between the key components. Where the relative volatilities vary in the column the same method of calculation can be used to give the minimum reflux ratio approximately.

By way of example a mixture of four components (w, x, y, z) will be considered, the relative volatilities, referred to component z, being δ, γ, β respectively. It has been shown previously [6] that an equation can be derived connecting the composition on any plate (w_0, x_0, y_0, z_0) with the composition (w_1, x_1, y_1, z_1) on the next plate below it, namely

$$\frac{\delta w_0}{\delta - \phi} + \frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi} = \frac{\phi\left\{\frac{\delta w_1}{\delta - \phi} + \frac{\gamma x_1}{\gamma - \phi} + \frac{\beta y_1}{\beta - \phi} + \frac{z_1}{1 - \phi}\right\}}{m(\delta w_1 + \gamma x_1 + \beta y_1 + z_1)} \quad (1)$$

where ϕ is given by the equation

$$\frac{a\delta}{\delta - \phi} + \frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} = 1 \quad . \quad . \quad . \quad (2)$$

As previously, for a rectifying column, $m = \dfrac{R}{R + 1}$, $a = \dfrac{w_D}{R + 1}$, $b = \dfrac{x_D}{R + 1}$,

etc., and for a stripping column, $m = \dfrac{S + 1}{S}$, where $S = \dfrac{RP + qF - W}{W}$

and $a = -\dfrac{w_W}{S}$, $b = -\dfrac{x_W}{S}$, etc.

Equation (2) gives four values of ϕ, which, in ascending order of magnitude, are denoted by ϕ_1, ϕ_2, ϕ_3, ϕ_4. These values of ϕ give four equations when substituted in equation (1). Applying these to n successive plates and dividing any one equation by any one of the others, there are obtained a set of equations such as

$$\frac{\dfrac{\delta w_0}{\delta - \phi_1} + \dfrac{\gamma x_0}{\gamma - \phi_1} + \dfrac{\beta y_0}{\beta - \phi_1} + \dfrac{z_0}{1 - \phi_1}}{\dfrac{\delta w_0}{\delta - \phi_2} + \dfrac{\gamma x_0}{\gamma - \phi_2} + \dfrac{\beta y_0}{\beta - \phi_2} + \dfrac{z_0}{1 - \phi_2}}$$

$$= \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{\dfrac{\delta w_n}{\delta - \phi_1} + \dfrac{\gamma x_n}{\gamma - \phi_1} + \dfrac{\beta y_n}{\beta - \phi_1} + \dfrac{z_n}{1 - \phi_1}}{\dfrac{\delta w_n}{\delta - \phi_2} + \dfrac{\gamma x_n}{\gamma - \phi_2} + \dfrac{\beta y_n}{\beta - \phi_2} + \dfrac{z_n}{1 - \phi_2}} \quad . \quad (3)$$

Any two of the four values of ϕ will give an equation of this type, so that six equations are obtained in all. Denoting, for convenience, the expression

$$\frac{\delta w_0}{\delta - \phi_1} + \frac{\gamma x_0}{\gamma - \phi_1} + \frac{\beta y_0}{\beta - \phi_1} + \frac{z_0}{1 - \phi_1} \text{ as } E(x_0, \phi_1) \quad . \quad . \quad (3a)$$

the six equations, of which equation (3) is the first, are

$$\begin{aligned}
&\frac{E(x_0, \phi_1)}{E(x_0, \phi_2)} = \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_2)}; & &\frac{E(x_0, \phi_1)}{E(x_0, \phi_3)} = \left(\frac{\phi_1}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_3)} \\
&\frac{E(x_0, \phi_1)}{E(x_0, \phi_4)} = \left(\frac{\phi_1}{\phi_4}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_4)}; & &\frac{E(x_0, \phi_2)}{E(x_0, \phi_3)} = \left(\frac{\phi_2}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_2)}{E(x_n, \phi_3)} \\
&\frac{E(x_0, \phi_2)}{E(x_0, \phi_4)} = \left(\frac{\phi_2}{\phi_4}\right)^n \cdot \frac{E(x_n, \phi_2)}{E(x_n, \phi_4)}; & &\frac{E(x_0, \phi_3)}{E(x_0, \phi_4)} = \left(\frac{\phi_3}{\phi_4}\right)^n \cdot \frac{E(x_n, \phi_3)}{E(x_n, \phi_4)}
\end{aligned} \right\} \quad (4)$$

These six equations represent only three independent relations. The last three can obviously be derived from the first three. The three independent relations, combined with the equation

$$w + x + y + z = 1$$

suffice to solve for the four variables, w, x, y, z.

Under certain conditions the composition on a plate may be exactly equal to the composition on the plate above or below it, and a plate-to-plate calculation leads to an infinite number of plates. For such conditions of "constant composition" or "limiting composition," denoting such a composition by (g, h, k, l), equation (1) gives

$$\phi = m(\delta g + \gamma h + \beta k + l) \quad . \quad . \quad . \quad . \quad (5)$$

As shown previously [6]

$$g = \frac{a\phi}{m(\delta - \phi)}; \quad h = \frac{b\phi}{m(\gamma - \phi)}; \quad k = \frac{c\phi}{m(\beta - \phi)}; \quad l = \frac{d\phi}{m(1 - \phi)} \quad . \quad (6)$$

There are four values of ϕ, and consequently four limiting compositions which may be denoted by the suffix attached to the corresponding value of ϕ. Thus g_1, h_1, k_1, l_1 are obtained by using ϕ_1 in equations (6).

The expression $E(x_n, \phi_1)$ can be shown to become zero if g_2, h_2, k_2, l_2 are substituted for w_n, x_n, y_n, z_n. The condition for this is that

$$\frac{\delta g_2}{\delta - \phi_1} + \frac{\gamma h_2}{\gamma - \phi_1} + \frac{\beta k_2}{\beta - \phi_1} + \frac{l_2}{1 - \phi_1} = 0$$

or, from equations (6),

$$\frac{a\delta}{(\delta - \phi_1)(\delta - \phi_2)} + \frac{b\gamma}{(\gamma - \phi_1)(\gamma - \phi_2)} + \frac{c\beta}{(\beta - \phi_1)(\beta - \phi_2)}$$
$$+ \frac{d}{(1 - \phi_1)(1 - \phi_2)} = 0 \quad . \quad (7)$$

From equation (2)

$$\frac{a\delta}{\delta - \phi_1} + \frac{b\gamma}{\gamma - \phi_1} + \frac{c\beta}{\beta - \phi_1} + \frac{d}{1 - \phi_1}$$
$$= \frac{a\delta}{\delta - \phi_2} + \frac{b\gamma}{\gamma - \phi_2} + \frac{c\beta}{\beta - \phi_2} + \frac{d}{1 - \phi_2} = 1$$

or

$$\frac{a\delta}{(\delta - \phi_1)(\delta - \phi_2)} + \frac{b\gamma}{(\gamma - \phi_1)(\gamma - \phi_2)} + \frac{c\beta}{(\beta - \phi_1)(\beta - \phi_2)}$$
$$+ \frac{d}{(1 - \phi_1)(1 - \phi_2)} = 0$$

which is the same as equation (7).

Similarly it can be shown that $E(x_n, \phi_1)$ also becomes zero for the values g_3, h_3, k_3, l_3 and g_4, h_4, k_4, l_4. It does not become zero for the values g_1, h_1, k_1, l_1, as may be seen by putting $\phi_2 = \phi_1$ in equation (7). All the terms on the left-hand side are positive for a rectifying column and negative for a stripping column, and the sum of them can in neither case be zero.

Similar relations can be obtained for the other expressions similar to $E(x_n, \phi_1)$. The various equations are satisfied as follows. (The suffix n is here dropped for the sake of generality.)

$$E(x, \phi_1) = 0 \text{ by } (g_2, h_2, k_2, l_2), (g_3, h_3, k_3, l_3) \text{ and } (g_4, h_4, k_4, l_4)$$
$$E(x, \phi_2) = 0 \text{ by } (g_1, h_1, k_1, l_1), (g_3, h_3, k_3, l_3) \text{ and } (g_4, h_4, k_4, l_4)$$
$$E(x, \phi_3) = 0 \text{ by } (g_1, h_1, k_1, l_1), (g_2, h_2, k_2, l_2) \text{ and } (g_4, h_4, k_4, l_4)$$
$$E(x, \phi_4) = 0 \text{ by } (g_1, h_1, k_1, l_1), (g_2, h_2, k_2, l_2) \text{ and } (g_3, h_3, k_3, l_3)$$

If any three of these equations are simultaneously satisfied, they have one common solution.

Thus
$$E(x, \phi_1) = E(x, \phi_3) = E(x, \phi_4) = 0$$

have (g_2, h_2, k_2, l_2) as the common solution. The suffix attached to g, h, k, l is the one which does not appear in the values of ϕ involved in the three equations.

If any two of the equations are simultaneously satisfied, they have two common solutions.

Thus
$$E(x, \phi_3) = E(x, \phi_4) = 0$$

have (g_1, h_1, k_1, l_1) and (g_2, h_2, k_2, l_2) as common solutions. Here again the suffixes attached to g, h, k, l are those which do not appear in the values of ϕ.

The significance of the four limiting compositions can be shown as follows, a rectifying column being considered by way of example. It is readily shown, as in the case of ternary mixtures, that putting $w_0 = w_D, x_0 = x_D$, etc., makes any of the expressions on the left-hand side of equations (4) equal to (1). We then have, by selecting the three appropriate equations,

$$\frac{E(x_n, \phi_2)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_2}\right)^n; \quad \frac{E(x_n, \phi_3)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_3}\right)^n; \quad \frac{E(x_n, \phi_4)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_4}\right)^n$$

Now $\phi_1 < \phi_2 < \phi_3 < \phi_4$ and therefore, when n becomes infinite,

$$E(x_n, \phi_2) = E(x_n, \phi_3) = E(x_n, \phi_4) = 0.$$

These equations are satisfied by (g_1, h_1, k_1, l_1), which, in addition, does not make the denominator $E(x_n, \phi_1)$ zero. Thus a calculation proceeding down the column from the top finally reaches the limiting composition (g_1, h_1, k_1, l_1).

If we put $n = -N$, where N is positive, the composition can be obtained for an imaginary plate located N plates above the top of the column. From equations (4) we have

$$\frac{E(x_{-N}, \phi_1)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_1}{\phi_4}\right)^N; \quad \frac{E(x_{-N}, \phi_2)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_2}{\phi_4}\right)^N; \quad \frac{E(x_{-N}, \phi_3)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_3}{\phi_4}\right)^N$$

When n becomes infinite

$$E(x_{-N}, \phi_1) = E(x_{-N}, \phi_2) = E(x_{-N}, \phi_3) = 0$$

and the solution is (g_4, h_4, k_4, l_4), which is the limiting composition reached when a calculation is carried upwards from the top of the column.

The other two limiting compositions (g_2, h_2, k_2, l_2) and (g_3, h_3, k_3, l_3) have particular practical significance when certain components are only present in small amount in the top product.

There are three cases to be considered :—

   Case I. z is the heavy key component and is present in the top product in small amount.

   Case II. y is the heavy key component and both y and z are present in the top product in small amounts.

   Case III. x is the heavy key component and x, y and z are present in the top product in small amounts.

For case I, since d in equation (2) is approximately zero, ϕ_1 is approximately equal to 1. Substituting this value in equations (6) gives g_1, h_1, k_1, l_1 the last of these by difference. These are the values of the limiting composition reached by calculating downwards from the top of the column with all four components in the calculation.

For case II, since both d and c in equation (2) are approximately zero, $\phi_1 = 1$ and $\phi_2 = \beta$ approximately. Using the value $\phi_1 = 1$, the values of g_1, h_1, k_1, l_1 can be calculated when the values of d and c, although very small, are specified. The method of calculation is similar to that given for

Example 3 of the previous paper.[7] Using the value $\phi_2 = \beta$ in equations (6) gives g_2, h_2, k_2, l_2. l_2 has a very small negative value which, as explained in connection with ternary mixtures,[7] may be neglected for practical purposes. k_2 is indeterminate in equation (6) when $c = 0$ and $\phi = \beta$, but can be found by difference, or by the method of approximation described in connection with ternary mixtures. This limiting composition thus contains the three components w, x, y, and is the one reached by calculating down from the top of the column using these three components. It can also be calculated by the usual method based on the small amount of the heavy key component.

For Case III, since d, c, and b are all small in equation (2), $\phi_1 = 1$, $\phi_2 = \beta$, and $\phi_3 = \gamma$ approximately. Using $\phi_3 = \gamma$ in equation (6) gives $\phi_2 = \beta$, and $\phi_3 = \gamma$ approximately. Using $\phi_3 = \gamma$ in equation (6) gives $k_3 = l_3 = 0$. After finding g_3, then h_3 is found by difference. The limiting composition contains only the two components w and x, and is the one obtained by calculating down the column from the top using these two components. It represents the limiting composition that would be reached with a binary mixture.

Thus, when making a calculation downwards from the top (g_1, h_1, k_1, l_1) is reached if z is the heavy key. If y is the heavy key, (g_2, h_2, k_2, l_2) is reached. If x is the heavy key, (g_3, h_3, k_3, l_3) is reached.

For a rectifying column, superimposed on a stripping column, minimum reflux conditions prevail (in the rectifying column) when a calculation made downwards from the top and a calculation made upwards from the feed-plate both meet at the appropriate limiting composition which, as shown above, depends on which are the key components. It is possible to specify what composition or range of compositions can exist at the feed-plate if the downward and upward calculations are to meet in this way.

If z is the heavy key, the composition at the feed-plate will be (g_1, h_1, k_1, l_1), and the downward and upward calculations actually meet at the feed-plate. The composition at the feed-plate is thus defined by the three equations

$$E(x, \phi_2) = 0; \quad E(x, \phi_3) = 0; \quad E(x, \phi_4) = 0 \quad . \quad . \quad (8)$$

If y is the heavy key, the limiting composition (g_2, h_2, k_2, l_2) is reached by the downward calculation. If the upward calculation is to reach this point, $E(x_n, \phi_2)$ must not be equal to zero. (Here w_n, x_n, y_n, z_n is taken to be the feed plate composition.) From equation (1) it will be seen that, if $E(x, \phi_2)$ is zero for any given plate, it will also be zero for all successive plates. From equations (4) we have, for a plate 0 which is n plates above the feed plate,

$$\frac{E(x_0, \phi_1)}{E(x_0, \phi_2)} = \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_2)}.$$

When n becomes infinite, $E(x_0, \phi_1)$ becomes zero. At (g_2, h_2, k_2, l_2), in addition to $E(x_0, \phi_1) = 0$ we must also have $E(x_0, \phi_3) = 0$ and $E(x_0, \phi_4) = 0$. If these two equations are satisfied by the feed-plate composition, they will also be satisfied by the compositions on all plates above it, as will be seen from equation (1). Thus, where y is the heavy key, there is a possible range of compositions at the feed-plate, and this range is defined by the equations

$$E(x, \phi_3) = 0; \quad E(x, \phi_4) = 0 \quad . \quad . \quad . \quad (9)$$

From these equations it is also clear that the upward calculation will not pass through (g_3, h_3, k_3, l_3) or (g_4, h_4, k_4, l_4).

If x is the heavy key, the limiting composition reached by the downward calculation is (g_3, h_3, k_3, l_3). This composition must also be reached by the upward calculation. Then $E(x_n, \phi_3)$ must not be zero. From equations (4),

$$\frac{E(x_0, \phi_1)}{E(x_0, \phi_3)} = \left(\frac{\phi_1}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_3)} \text{ and } \frac{E(x_0, \phi_2)}{E(x_0, \phi_3)} = \left(\frac{\phi_2}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_2)}{E(x_n, \phi_3)}.$$

When n becomes infinite, $E(x_0, \phi_1) = 0$ and $E(x_0, \phi_2) = 0$. At (g_3, h_3, k_3, l_3), we must also have $E(x_0, \phi_4) = 0$. If the feed-plate composition satisfies this equation, the upward calculation will reach (g_3, h_3, k_3, l_3). Thus, where x is the heavy key, the possible range of compositions at the feed plate is defined by the equation

$$E(x, \phi_4) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From equations (8), (9), and (10) it will be seen that the composition at the feed-plate, for minimum reflux conditions, is defined by three, two or one equations according as z, y, or x is the heavy key.

Conditions for minimum reflux in the stripping column can be defined in a similar manner. When calculating upwards from the reboiler, the limiting composition $(\bar{g}_4, \bar{h}_4, \bar{k}_4, \bar{l}_4)$ is reached when w is the light key. When x is the light key, $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ is reached. When y is the light key, $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_1)$ is reached. By calculating downwards below the reboiler $(\bar{g}_1, \bar{h}_1, \bar{k}_1, \bar{l}_2)$ is reached.

For the stripping column it is convenient to write ψ instead of ϕ. Also $\psi_1 < \psi_2 < \psi_3 < \psi_4$. Let $(\bar{w}_0, \bar{x}_0, \bar{y}_0, \bar{z}_0)$ refer to the feed-plate and $(\bar{w}_n, \bar{x}_n, \bar{y}_n, \bar{z}_n)$ to a plate n plates below the feed-plate. When y is the light key, $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ is reached by calculating upwards from the bottom, and must also be reached by calculating downwards from the feed-plate. Then $E(\bar{x}_0, \psi_2)$ is not zero.

From equations (4)

$$\frac{E(\bar{x}_n, \psi_3)}{E(\bar{x}_n, \psi_2)} = \left(\frac{\psi_2}{\psi_3}\right)^n \cdot \frac{E(\bar{x}_0, \psi_3)}{E(\bar{x}_0, \psi_2)} \text{ and } \frac{E(\bar{x}_n, \psi_4)}{E(\bar{x}_n, \psi_2)} = \left(\frac{\psi_2}{\psi_4}\right)^n \cdot \frac{E(\bar{x}_0, \psi_4)}{E(\bar{x}_0, \psi_2)}.$$

When n becomes infinite, $E(\bar{x}_n, \psi_3) = 0$ and $E(\bar{x}_n, \psi_4) = 0$. For $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ to be reached it is also necessary that $E(\bar{x}_n, \psi_1) = 0$, and this will be the case if the feed-plate composition satisfies the relation

$$E(x, \psi_1) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If x is the light key, $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ has to be reached by calculating down from the feed-plate.

$E(\bar{x}_0, \psi_3)$ is not zero. From equations (4)

$$\frac{E(\bar{x}_n, \psi_4)}{E(\bar{x}_n, \psi_3)} = \left(\frac{\psi_3}{\psi_4}\right)^n \cdot \frac{E(\bar{x}_0, \psi_4)}{E(\bar{x}_0, \psi_3)}.$$

When n becomes infinite, $E(\bar{x}_n, \psi_4) = 0$. In addition, for $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ it is necessary that $E(\bar{x}_n, \psi_1) = 0$ and $E(\bar{x}_n, \psi_2) = 0$. This will be the case if the feed-plate composition satisfies the relations

$$E(x, \psi_1) = 0 \text{ and } E(x, \psi_2) = 0 \quad . \quad . \quad . \quad (12)$$

If w is the light key, the limiting composition $(\bar{g}_4, \bar{h}_4, \bar{k}_4, \bar{l}_4)$ is reached at the feed-plate and the relations to be satisfied are

$$E(x, \psi_1) = 0; \quad E(x, \psi_2) = 0; \quad E(x, \psi_3) = 0 \quad . \quad . \quad . \quad (13)$$

Relations have now been derived which specify the composition or range of compositions at the feed-plate if minimum reflux conditions prevail in the rectifying column or in the stripping column. If minimum reflux prevail throughout the whole column, the conditions for feed-conditions prevail derived from the rectifying column and those derived plate composition derived from the stripping column must be satisfied simultaneously. Collecting together the results which have been obtained, the conditions to be satisfied for the various separations are shown in Table I.

TABLE I.

Light key.	Heavy key.	From rectifying column.	From stripping column.
y	z	$\begin{cases} E(x, \phi_2) = 0; \ E(x, \phi_3) = 0 \\ \text{and } E(x, \phi_4) = 0 \end{cases}$	$E(x, \psi_1) = 0$
x	y	$E(x, \phi_3) = 0; \ E(x, \phi_4) = 0$	$E(x, \psi_1) = 0; \ E(x, \psi_2) = 0$
w	x	$E(x, \phi_4) = 0$	$\begin{cases} E(x, \psi_1) = 0; \ E(x, \psi_2) = 0 \\ \text{and } E(x, \psi_3) = 0 \end{cases}$

In each case there are four equations to be satisfied. Each of these equations is of the type

$$\frac{\delta w}{\delta - \phi_1} + \frac{\gamma x}{\gamma - \phi_1} + \frac{\beta y}{\beta - \phi_1} + \frac{z}{1 - \phi_1} = 0$$

and involves only three independent variables such as $\frac{w}{z}$, $\frac{x}{z}$, and $\frac{y}{z}$. (In addition, there is, of course, the equation $w + x + y + z = 1$ for finding the actual values of the components from their ratios.) There must, therefore, be a relation between the four equations which reduces them to three independent equations. A relation which obviously meets this requirement is that any two of the values of ϕ or ψ involved in the equations should be equal.

From equation (2) it is readily shown that, for a rectifying column where a, b, c, d are positive

$$0 < \phi_1 < 1; \quad 1 < \phi_2 < \beta; \quad \beta < \phi_3 < \gamma; \quad \gamma < \phi_4 < \delta.$$

Similarly for a stripping column where a, b, c, d are negative

$$1 < \psi_1 < \beta; \quad \beta < \psi_2 < \gamma; \quad \gamma < \psi_3 < \delta; \quad \delta < \psi_4.$$

Thus none of the values of ϕ can be equal and none of the values of ψ can be equal. To satisfy the conditions for minimum reflux it is therefore necessary that one of the values of ϕ involved should be equal to one of the values of ψ involved.

For the case where y and z are the light and heavy keys respectively, ψ_1 must then be equal to ϕ_2 or ϕ_3 or ϕ_4. From the ranges of the values of

ϕ and ψ, it is obvious that the only possibility is $\phi_2 = \psi_1$. Both these lie between 1 and β—that is, between the relative volatilities of the key components y and z. The limiting composition in the rectifying column in this case is (g_1, h_1, k_1, l_1) which satisfies $E(x, \phi_2) = 0$. The limiting composition for the stripping column is $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ which satisfies $E(x, \psi_1) = 0$. Since $\phi_2 = \psi_1$, both limiting compositions satisfy the same equation.

Where x and y are the light and heavy keys, ψ_1 or ψ_2 must be equal to ϕ_3 or ϕ_4. The only possibility is $\phi_3 = \psi_2$, as both lie between β and γ, the relative volatilities of the key components. Here again it can be shown, as before, that the limiting compositions for the rectifying and stripping columns both satisfy the same equation $E(x, \phi_3) = 0$ or $E(x, \psi_2) = 0$.

Where w and x are the light and heavy keys, ϕ_4 must be equal to ψ_1 or ψ_2 or ψ_3. Thus ϕ_4 must be equal to ψ_3, as both lie between γ and δ.

The condition for minimum reflux in both the rectifying column and the stripping column is therefore

$$\phi_{n+1} = \psi_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where n and $(n+1)$ represent the numbers to be attached to the values of ϕ and ψ when counting up from the lowest values, and also represent the numbers to be attached to the heavy and light keys components when counting up from the least volatile component. Also ϕ_{n+1} and ψ_n have a value which lies between the relative volatilities of the key components.

When equation (14) is satisfied, a stepwise calculation starting from the reboiler will reach a limiting composition in the stripping column and an infinite number of plates will be required to pass through this composition. The calculation will then pass up through the feed plate and will reach a limiting composition in the rectifying column and an infinite number of plates will again be required to pass through this composition to reach the composition at the top of the column.

Equation (2) for the rectifying column and the corresponding equation for the stripping column thus have a common root, which will be denoted by θ. This root has a value lying between the relative volatilities of the key components. Substituting for a, b, c, d in equation (2), the appropriate values for a rectifying column and for a stripping column, there are obtained the two equations which define θ

$$\frac{\delta w_D}{\delta - \theta} + \frac{\gamma x_D}{\gamma - \theta} + \frac{\beta y_D}{\beta - \theta} + \frac{z_D}{1 - \theta} = R + 1 \quad . \quad . \quad (15)$$

and

$$\frac{\delta w_W}{\delta - \theta} + \frac{\gamma x_W}{\gamma - \theta} + \frac{\beta y_W}{\beta - \theta} + \frac{z_W}{1 - \theta} = -S \quad . \quad . \quad (16)$$

Now $\quad Pw_D + Ww_W = Fw_F; \quad Px_D + Wx_W = Fx_F;$ etc.

where w_F, x_F, etc., denote the composition of the feed.

Also $SW = RP + qF - W = (R + 1)P - (1 - q)F$ since $W = F - P$. Then multiplying equation (15) by P and equation (16) by W, and adding, we obtain

$$\frac{\delta w_F}{\delta - \theta} + \frac{\gamma x_F}{\gamma - \theta} + \frac{\beta y_F}{\beta - \theta} + \frac{z_F}{1 - \theta} = 1 - q \quad . \quad . \quad (17)$$

When the feed is liquid at boiling-point, $q = 1$. When the feed is vapour at dew point, $q = 0$.

From equation (17) is found the appropriate value of θ which is the one lying between the relative volatilities of the key components. On substituting this value of θ in equation (15), the minimum reflux ratio is obtained. Similarly the minimum reboil ratio can be obtained from equation (16).

When R and S have thus been found, equations (19) and (20) can be used to find the other values ϕ and ψ required in the equations for the feed-plate composition listed in Table I. These equations can then be used to solve for the feed-plate composition.

In equations (15), (16), (17) the relative volatilities are all referred to the least volatile component. The relative volatilities can, however, be referred to any component. Thus, if y is the heavy key, and it is desired to refer the relative volatilities to it, equation (17) takes the form

$$\frac{\frac{\delta}{\beta} \cdot w_F}{\frac{\delta}{\beta} - \frac{\theta}{\beta}} + \frac{\frac{\gamma}{\beta} \cdot x_F}{\frac{\gamma}{\beta} - \frac{\theta}{\beta}} + \frac{y_F}{1 - \frac{\theta}{\beta}} + \frac{\frac{1}{\beta} \cdot z_F}{\frac{1}{\beta} - \frac{\theta}{\beta}} = 1 - q \quad . \quad . \quad . \quad (18)$$

Equations (15) and (16) can be written in the same form. The variable is now $\frac{\theta}{\beta}$, which may be written θ'. Its value lies between 1 and $\frac{\gamma}{\beta}$—i.e., between the relative volatilities of the key components. The value obtained for the minimum reflux ratio is obviously the same whichever form of the equations is used.

The general equations corresponding to equations (15) and (16) for conditions other than minimum reflux are

$$\frac{\delta w_D}{\delta - \phi} + \frac{\gamma x_D}{\gamma - \phi} + \frac{\beta y_D}{\beta - \phi} + \frac{z_D}{1 - \phi} = R + 1 \quad . \quad . \quad . \quad (19)$$

and

$$\frac{\delta w_W}{\delta - \psi} + \frac{\gamma x_W}{\gamma - \psi} + \frac{\beta y_W}{\beta - \psi} + \frac{z_W}{1 - \psi} = -S \quad . \quad . \quad . \quad (20)$$

By differentiating these equations it will be seen that ϕ increases as R increases, while ψ decreases as S increases. R and S must obviously increase together. When R and S become infinite, the roots of both equations (19) and (20) are obviously 1, β, γ, δ. As R decreases from infinity to a finite value, the values of ϕ decrease and the values of ψ increase. As R is gradually decreased there will come a point when a value of ϕ and a value of ψ (lying between the relative volatilities of the key components) will become equal, and this will correspond to minimum reflux conditions.

The analysis has been given in detail for a four-component mixture. It can be made in exactly the same way for a mixture of any number of components, and equations exactly similar to equations (15), (16), (17) are then obtained. For instance, for a six-component mixture there will be six equations to be satisfied at the feed-plate for minimum reflux conditions. The ratios of the components constitute five independent variables. Two

of the equations must be the same, and this condition is found to be equation (14)

$$\phi_{n+1} = \psi_n$$

where n and $(n + 1)$ refer to the heavy and light key components and the common value of ϕ and ψ lies between the relative volatilities of those components. The relation is quite a general one, and also holds good for binary mixtures.

The root of equation (17) which is normally required is the one lying between the relative volatilities of the key components. In some cases it is useful to obtain the other roots. For instance, if a mixture of four components is to be separated into the four pure substances, three fractionating columns are required. There are five different ways of using these three columns to produce the four pure substances, as illustrated diagrammatically by Thormann.[8] In such a case it is useful to calculate the heat requirements for the different ways of effecting the total separation. Equation (17) is then used to find the three values of θ corresponding to the cases where one, two, or three components are taken as the top product of the first column. Equation (15) is then used to obtain the corresponding minimum reflux ratios, it being noted that equation (15) varies with the composition of the top product, while equation (17) does not. The minimum reflux ratios for the other two columns, which may be separating either ternary mixtures or binary mixtures, are calculated similarly for the various cases.

The relative ease with which the calculation of minimum reflux ratio for multi-component mixtures can be made is illustrated by the following numerical examples.

Example 1 (from Colburn [5])

w and x are the key components

$$w_F = x_F = y_F = z_F = 0.25; \quad w_D = 1$$
$$\delta = 8; \quad \gamma = 4; \quad \beta = 2. \quad q = 1.$$

Equation (17) gives

$$\frac{2}{8 - \theta} + \frac{1}{4 - \theta} + \frac{0.5}{2 - \theta} + \frac{1}{1 - \theta} = 0 \quad . \quad . \quad . \quad (21)$$

The value of θ required lies between 4 and 8. It is found by trial solution to be 5.58.

From equation (15),

$$\frac{8}{8 - 5.58} = R + 1 \qquad \therefore R = 2.31$$

Example 2 (from Colburn [5])

As in Example 1, but with x and y as key components

$$w_D = x_D = 0.5.$$

Equation (21) is used again, the value of θ now required being that between 2 and 4. It is found to be 2.556.

From equation (15),

$$\frac{4}{8 - 2.556} + \frac{2}{4 - 2.556} = R + 1 \quad \therefore R = 1.12$$

Example 3 (From Colburn[5]).

As in Example 1, but with y and z as key components

$$w_D = x_D = y_D = 0.3333.$$

Equation (21) is used again, the value of θ now required being that between 1 and 2. It is found to be 1.196.

From equation (15)

$$\frac{2.667}{8 - 1.196} + \frac{1.333}{4 - 1.196} + \frac{0.333}{2 - 1.196} = R + 1 \quad \therefore R = 0.698.$$

Example 4 (from Gilliland[3]).

	Feed.	Distillate.	Residue.	Relative volatility to o-cresol.
Phenol	0.35	0.95	0.0524	1.26
o-Cresol	0.15	0.05	0.199	1.0
m-Cresol	0.30	—	0.449	0.663
Xylenols	0.15	—	0.224	0.394
Residue	0.05	—	0.075	0.087

Here there are five components. Relative volatilities are referred to o-cresol. Instead of recalculating them relative to the heaviest component, an equation of the type of equation (18) can be used with the variable changed to θ'. An appropriate term for the fifth component is brought into the equation. $(q = 1)$

$$\frac{1.26 \times 0.35}{1.26 - \theta'} + \frac{0.15}{1 - \theta'} + \frac{0.663 \times 0.3}{0.663 - \theta'} + \frac{0.394 \times 0.15}{0.394 - \theta'}$$
$$+ \frac{0.087 \times 0.05}{0.087 - \theta'} = 0 \quad . \quad (22)$$

The value of θ' required lies between 1 and 1.26. By trial solution it is found to be 1.0798. Successive approximations and interpolations are not laborious, as, when an approximate solution has been obtained, only the first two terms in the equation change appreciably with small variations in the assumed value of θ'.

The equation corresponding to equation (15) for the modified variable θ' is

$$\frac{1.26 \times 0.95}{1.26 - 1.0798} + \frac{1 \times 0.05}{1 - 1.0798} = R + 1 \text{ and } R = 5.02.$$

Gilliland[3] states that " detailed stepwise calculations indicate that the true minimum reflux ratio is approximately 5.2." The difference between this and the figure calculated above is thus 3-4 per cent. In this example the amounts of the heavy key in the distillate (0.05) and of the light key in

the residue (0.0524), though small, are not negligible. This may affect the accuracy of the method used in this paper, which is based on negligible amounts of the heavy and light keys in the distillate and residue respectively. On the other hand, plate-to-plate calculations are not easy to carry out with a high degree of accuracy, owing to the possibility of small errors being cumulative.

This example may be used to illustrate the effect on the minimum reflux ratio of a comparatively small change in the relative volatilities of the key components when these are fairly close to each other. Assume that the relative volatility of phenol to o-cresol is 1.28 instead of 1.26, all other data remaining unchanged. Equation (22) then gives $\theta' = 1.0856$ instead of 1.0798, and R is found to be 4.67 instead of 5.02. Thus a difference of about $1\frac{1}{2}$ per cent in the relative volatility makes a difference of about 7 per cent in the minimum reflux ratio. This is approximately the same difference as for a binary mixture where $R = \dfrac{1}{(\alpha - 1)x_F}$ and the effect on R is proportional to $(\alpha - 1)$. It appears that a high degree of accuracy in the method of determining minimum reflux ratio is unwarranted unless the relative volatilities, particularly of the key components, are known to a correspondingly high degree of accuracy. Especially is this the case when the relative volatilities of the key components are not greatly different.

Example 5 (From Jenny[9]).

	Feed.	Distillate.	Bottoms.	Relative volatilities at—		
				63° F.	175° F.	300° F.
C_1	0.26	0.434	—	514.5	100	30.25
C_2	0.09	0.150	—	100.3	24.6	12.95
C_3	0.25	0.411	0.010	34.1	10	5.51
nC_4	0.17	0.005	0.417	10.69	4.85	2.96
nC_5	0.11	—	0.274	3.35	2.08	1.67
nC_6	0.12	—	0.299	1	1	1

The feed is 66 per cent vapour and 34 per cent liquid, so that $q = 0.34$. The temperatures at the top and bottom of the column are 63° F. and 300° F. respectively. The temperature of the feed is 175° F.

Jenny gives relative volatility data for all components at the feed temperature, but only for some components at the top and bottom temperatures. The additional data used have been taken from those published by Kirkbride.[10] The relative volatilities vary considerably through the column. For the key components the variation is from 1.86 at the bottom to 3.19 at the top.

The method of calculation described in this paper is based on constant relative volatilities. To apply it to this example it appeared a reasonable approximation to take relative volatilities at a temperature midway between the top and bottom temperatures. Actually the feed temperature (175° F.) has been taken instead of the true mean (181.5° F.), owing to the data being readily available for the former temperature.

Using these data in equation (17) with two additional terms, since there are six components, we have

$$\frac{100 \times 0.26}{100 - 0} + \frac{24.6 \times 0.09}{24.6 - 0} + \frac{10 \times 0.25}{10 - 0} + \frac{4.85 \times 0.17}{4.85 - 0}$$
$$\times \frac{2.08 \times 0.11}{2.08 - 0} + \frac{0.12}{1 - 0} = 0.66 \quad . \quad (23)$$

The value of 0 required lies between 4.85 and 10. It is found by trial solution to be 6.73. Substituting in the equation corresponding to equation (15) gives

$$\frac{100 \times 0.434}{100 - 6.73} + \frac{24.6 \times 0.150}{24.6 - 6.73} + \frac{10 \times 0.411}{10 - 6.73} = R + 1$$

from which $R = 0.93$.

Jenny [9] obtained a value of 0.95 and Colburn a value of 0.96. The agreement with these values is quite good. The general validity of the basis assumed in the above calculation—namely, taking relative volatilities at the mean temperature in the column—requires, however, to be checked by a larger number of examples.

The limits between which the true minimum reflux must lie can be found by making two calculations, one based on the relative volatilities at the top of the column and the other based on the relative volatilities at the bottom. The first calculation assumes that the relative volatilities throughout the column are equal to the high values at the top and obviously gives too low a value for the minimum reflux ratio. Similarly, the other calculation obviously gives too high a value.

The value of R found by the first calculation is 0.53 and that found by the second calculation is 1.15. The mean of these is 0.84, compared with the true value of 0.95 or 0.96. As this mean value is obtained by averaging two substantially different values, the approximation can only be regarded as a rough one.

For many practical purposes the higher limit for the minimum reflux ratio, obtained by taking the low relative volatilities at the bottom of the column, provides a useful figure for guidance and, as shown, it can be quite readily calculated.

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THE TENDENCY TO SMOKE OF ORGANIC SUBSTANCES ON BURNING. PART I.

By A. E. CLARKE, Ph.D., T. G. HUNTER, D.Sc., A.R.T.C., M.I.Chem.E. (Fellow), and F. H. GARNER, O.B.E., Ph.D., F.R.I.C. (Fellow).

SUMMARY.

The British incendiary bomb, used in very large quantities by the R.A.F. for the bombing of German towns and cities, was essentially a 30-lb. bomb filled with a special benzol gel together with white phosphorus. The benzol gel filling produced, on burning, a large amount of black carbon smoke which obscured the target, and resulted also in an appreciable portion of the filling being wasted as unburned carbon. In addition, copious white smoke produced by the burning phosphorus increased the obscuring effect over the target. The possibility of replacing this benzol gel–phosphorus combination with a smokeless filling of a satisfactory nature was therefore investigated.

Towards this end the smoking tendency of a large number of organic compounds was assessed by flame-height measurements in a special lamp based on the I.P. smoke lamp.

A burning organic substance has a flame-height at, and above which, smoking occurs, and this height is a measure of the tendency to smoke. A new form of lamp was devised to measure flame-heights, from about 9 to 450 mm, of liquid compounds burning freely in air.

A wide range of hydrocarbons, alcohols, ketones, esters, and nitro-compounds was examined—115 compounds in all. In general, a compact molecule was found to give a smoky flame. The order for increasing tendency to smoke for hydrocarbons is: n-paraffins (in which increased chain length or chain branching gave increased smoke), naphthenes, olefines, and aromatics (in which appreciable aliphatic side chains on the benzene ring appeared to give no marked reduction in smoke).

In general, increased oxygen content of an organic compound resulted in decreased smoking tendency and compounds, such as methyl acetate, containing high percentages of oxygen only smoked at very large flame-heights. Some compounds, such as allyl alcohol, although having appreciable oxygen contents, had relatively high smoking tendencies, due to the nature of the carbon–hydrogen portion of the compound.

Of the aliphatic alcohols, the tertiary compounds were more smoky than the primary compounds. This also applied to nitro-paraffins. For each set of isomeric aliphatic esters, the flame-height at which smoking began increased with the chain length attached directly to the carboxylic carbon atom.

At equal oxygen content, the general order for increasing tendency to smoke was: n-primary alcohols, n-primary nitro-paraffins, propionates, acetates, lactates, and formates, although the order varied slightly for different oxygen contents.

WHEN an organic substance burns under fixed conditions there is a particular critical flame-height at and above which smoking occurs. It would appear that the tendency to smoke is determined by the amount of oxygen (required by the flame on the one hand and by the amount of oxygen) available to the flame on the other. At the critical flame-height the two quantities are equal.

It has been observed by Bancroft [1] that a luminous flame can be regarded as a colloidal suspension of carbon in a gaseous medium. Further, Minchin [2] suggests that through coagulation the charged carbon particles vary in size through the flame, being smallest towards the base and largest at the tip. Thus, in certain instances this coagulation may proceed to such an extent that the particles at the tip of the flame are too large to be