

BATCH DISTILLATION.

by

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ABSTRACT

The previous literature is critically discussed. A concise and efficient method is given for operating a batch distillation column. Experimental results are given to show the validity of the theory. Suggestions are made for further mechanical improvements on the column.

BATCH DISTILLATION.

Introduction.

Batch distillation, while it is not as important commercially as continuous distillation, is an exceedingly important unit process.

A batch column can rectify a large number of components, each to a high degree of purity, whereas a continuous column can only ~~separate~~ two components into their pure states.

As always, a mathematical analysis of the problem gives a clearer understanding of the physical-chemical mechanism and indicates the most efficient manner of operating a column.

In 1931 Bogart² developed a theory of batch distillation in which he postulated that the composition of the distillate would remain constant. He arrived at the following equations:

$$D = \frac{M(x_0 - x_n)}{(x_D - x_n)}$$

where D = amount distilled

M = amount of feed

x_D = composition of distillate

x_0 = composition of feed

x_n = composition of liquid in still-pot,

(compare this equation with equations 21 and 23), and

$$T = - \frac{M(x_D - x_0)}{V} \int_{x_0}^{x_D} \frac{dx_n}{(1 - L/V)(x_D - x_n)^2}$$

where T = time

V = vapour velocity

L = reflux velocity,

(compare this equation with equations 27 and 32).

Both of Bogart's equations involve a large amount of graphical work with McCabe-Thiele⁴ diagrams, and the latter equation can only be integrated by plotting it graphically. It should be pointed out that these equations, while they are ideal,

give no indication of how the composition of the distillate is to be kept constant.

Edgeworth-Johnstone³ extended this idea to take into account the column hold-up and also presented equations for the variation of the reflux ratio with the fraction distilled which can be applied in certain cases. His equations become rather complex and a simpler method is to be desired.

Smoker and Rose⁶ have developed a method of analysis for columns operated at a constant reflux ratio. This involves the use of the Rayleigh⁵ equation. A constant reflux ratio, while it is very simple to operate, is very inefficient because at low reflux ratios a very poor separation is obtained and at high reflux ratios a great deal of heat and time is wasted.

From a study of all these methods, it is seen that the best way to operate a batch column is to keep the composition of the distillate constant but this is exceedingly hard to accomplish. Either some automatic controller must be made that will take into account all the variables or some limiting curve must be developed which can be easily approximated.

In what follows, a limiting curve is developed, and also a method is indicated from which an automatic controller can be built.

For the sake of completeness, the following theory is developed from first principles.

Theory.

General.

In the following discussion, let us consider two liquids, A and B, which do not form a constant boiling mixture, A having the lower boiling point. (The same discussion would apply, with certain modifications, to liquids which form such mixtures.)

Boiling Point Curve.

The boiling point curve, which is found experimentally, is the starting point for all further work. Figure 1 shows the boiling point curve for benzene and toluene.

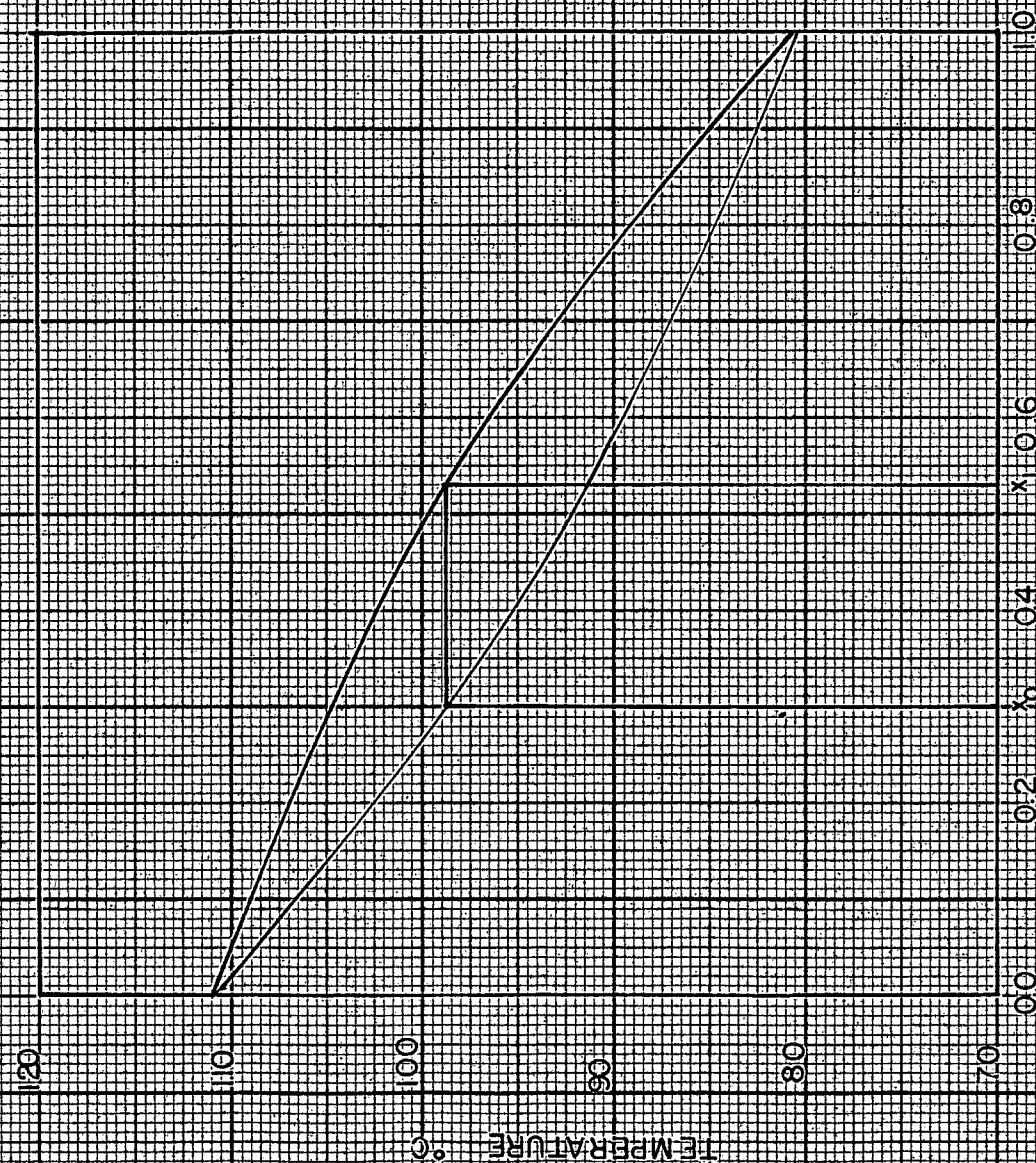
When a liquid of any composition x_0 is boiled the vapour which is given off is not x_0 but instead x_1 (see figure 1). This fact allows distillation to take place.

Equilibrium Diagram.

A more convenient diagram to use in distillation calculations is the equilibrium diagram. This diagram is made from the boiling point curve by plotting y , the composition of the vapour, against x , the composition of the liquid. Figure 2 shows this diagram for benzene and toluene.

Material Balance on a Perfect Plate.

Now, let us consider a perfect plate in a fractionating column as represented in figure 3.



MOLE FRACTION BENZENE

FIGURE 1

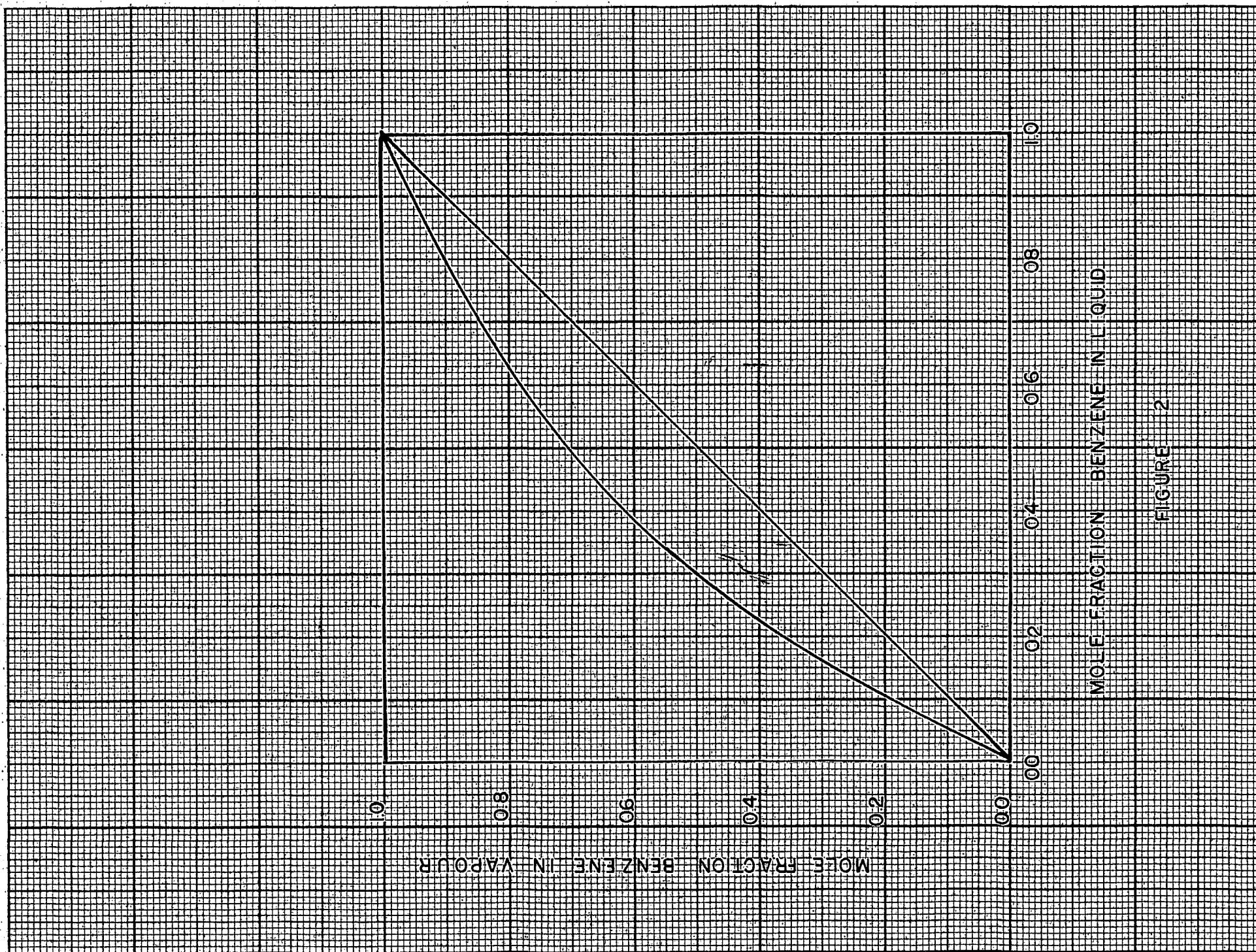


FIGURE 2

In figure 3, V = vapour

Y = composition of vapour

L = reflux

x = composition of liquid.

The subscripts refer to the plate at which the flow originates.

Taking a material balance over the n^{th} plate,

$$L_{n-1} + V_{n+1} = L_n + V_n \quad \text{—————} \quad (1).$$

also,

$$L_{n-1} x_{n-1} + V_{n+1} y_{n+1} = L_n x_n + V_n y_n \quad \text{—————} \quad (2).$$

It can be shown, by taking an overall heat balance and using Trouton's rule¹, that

$$L_n = L_{n-1} \quad \text{and} \quad V_n = V_{n+1} \quad \text{—————} \quad (3).$$

$$\therefore V y_{n+1} + L x_{n-1} = V y_n + L x_n \quad \text{—————} \quad (4).$$

Material Balance on Head of Column.

Now, let us consider a material balance over the head of the column as shown in figure 4.

$$V = L + D \quad \text{—————} \quad (5).$$

$$V y_{n+1} = L x_n + D x_p \quad \text{—————} \quad (6).$$

eliminating V ,

$$y = \frac{L}{L + D} x_n + \frac{D}{L + D} x_p \quad \text{—————} \quad (7).$$

By definition,

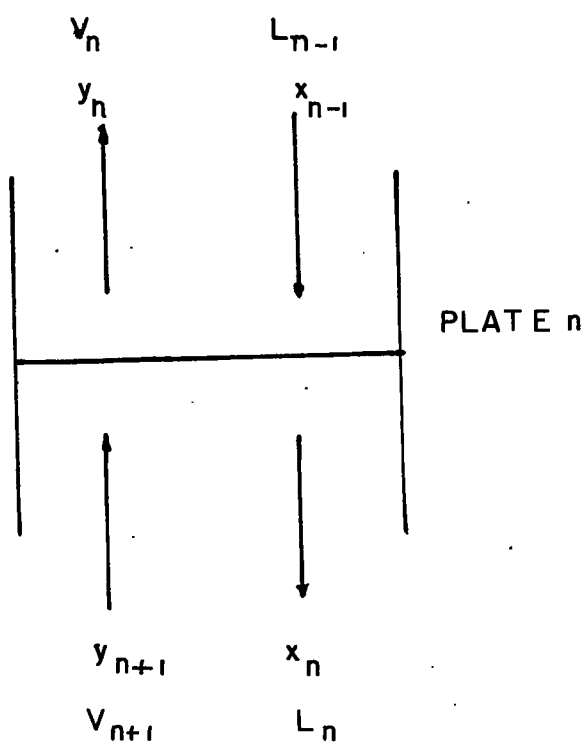


FIGURE 3

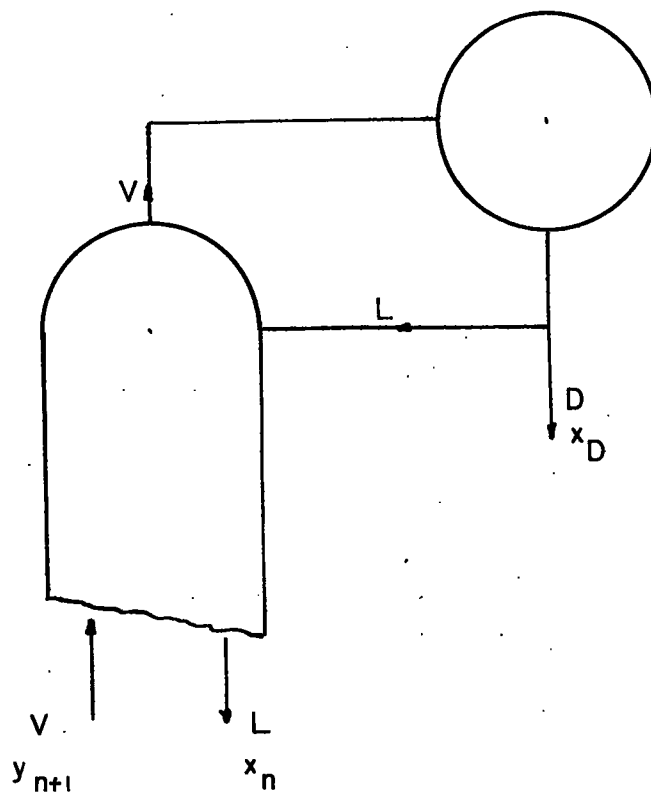


FIGURE 4

$$R = \frac{L}{D} = \frac{V - D}{D} \quad (8).$$

Substituting R in equation (7),

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \quad (9).$$

Equation 9 is a straight line and is known as the operating line. It can be plotted on the equilibrium diagram from the fact that it crosses the diagonal at x_D and crosses $x = 0$ at $y = \frac{x_D}{R+1}$. This line gives the composition of the liquid on the plates when a particular reflux ratio is being used.

When columns with a large number of plates are used, such diagrams become very cramped and it is often found advantageous to skew the coordinate system to an angle of 45° .

Calculation of Number of Theoretical Plates.

The number of theoretical plates in a batch column may be determined by considering the conditions that exist when the maximum separation has been obtained. A skewed diagram has been used in figure 5 to calculate the number of theoretical plates in a column which is capable of separating C_6H_6 and C_7H_8 to the extent that there is only 0.2% toluene in the overhead product and only 0.5% benzene in the liquid in the still-pot when the reflux ratio is 198. It may be seen that this column has 14 theoretical plates.

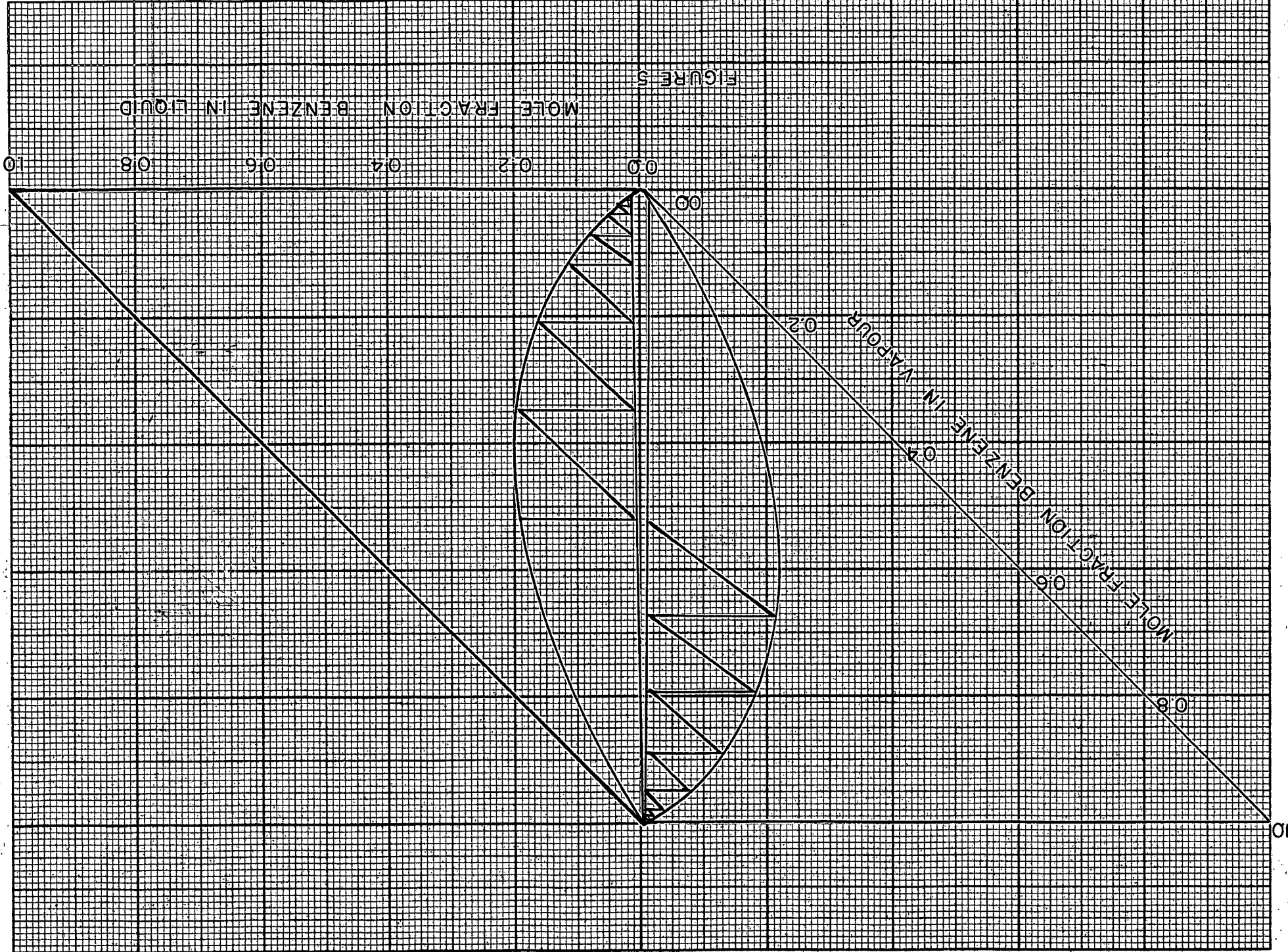


FIGURE 5

MOLE FRACTION BENZENE IN LIQUID

MOLE FRACTION BENZENE IN VAPOR

Derivation of Rayleigh's⁵ Equation.

Let us consider figure 6 which is essentially an equilibrium curve where w = total amount of liquid and
 u = total amount of A in liquid.

By definition,

$$x = \frac{u}{w} \quad (10).$$

As soon as any vapour leaves the still-pot, u changes by $-du$ and w changes by $-dw$.

$$y = \frac{du}{dw} \quad (11).$$

$$y = f(x) \quad (12).$$

but

$$y = \frac{du}{dw} = \frac{d(xw)}{dw} = \frac{xdw + wdx}{dw} \quad (13).$$

$$\frac{dw}{w} = \frac{dx}{f(x) - x} \quad (14).$$

$$\ln \frac{w}{w_0} = \int_{x_0}^x \frac{dx}{f(x) - x} = \int_{x_0}^x \frac{dx}{y - x} = \int_{x_0}^x \frac{dx}{x_D - x} \quad (15).$$

Minimum Reflux Ratio.

If the hold-up is negligible and the column is operated to give an overhead product which is very pure (say between 99.8 and 100%) x_D may be considered a constant equal to 1.

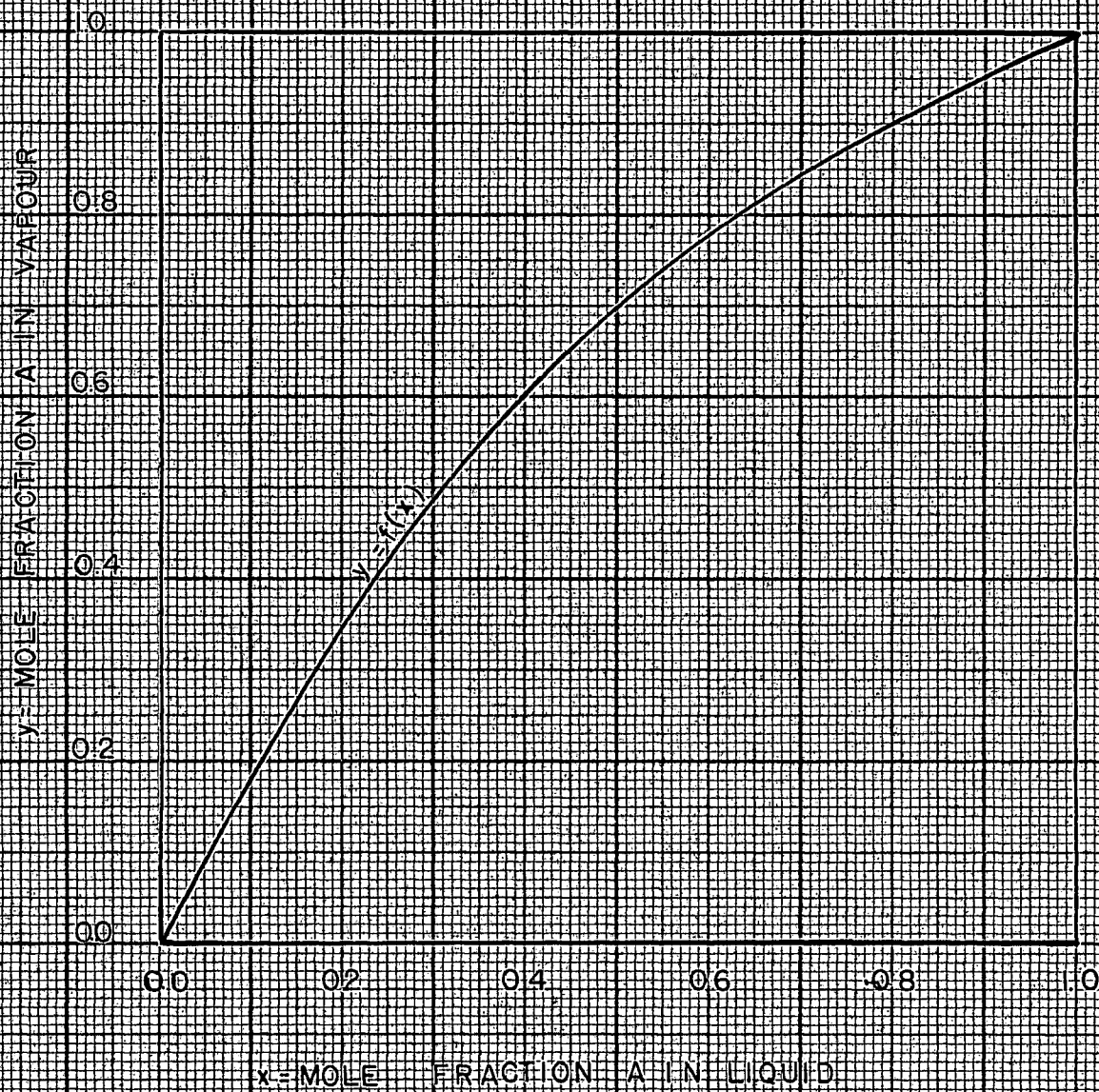


FIGURE 6

$$\ln W_n = \int_{x_{n-1}}^{x_n} \frac{dx}{1-x} \quad (16).$$

and
$$W_n = \frac{1-x_{n-1}}{1-x_n} \quad (17).$$

At any time the fraction in the still-pot is the product of all the intermediate fractions up to that point.

$$W_{Tn} = W_1 \times W_2 \times W_3 \times \dots \times W_n \quad (18).$$

Each intermediate fraction in turn satisfies equation (17).

$$W = \frac{1-x_0}{1-x_1} \frac{1-x_1}{1-x_2} \frac{1-x_2}{1-x_3} \dots \frac{1-x_{n-1}}{1-x_n} \quad (19).$$

$$W = \frac{1-x_0}{1-x_n} \quad (20).$$

By definition,

$$D = \frac{1-W_{Tn}}{1-x_n} = \frac{1-x_0}{1-x_n} = \frac{x_0-x_n}{1-x_n} \quad (21).$$

where D is the total fraction distilled and x_n is the composition of the liquid in the still-pot at any stage of the distillation and is a function of the reflux ratio only, for any particular liquid pair.

For any given reflux ratio, the corresponding x_n may be found by using a McCabe-Thiele diagram as in figure 7.

With liquids such as benzene and toluene, it is

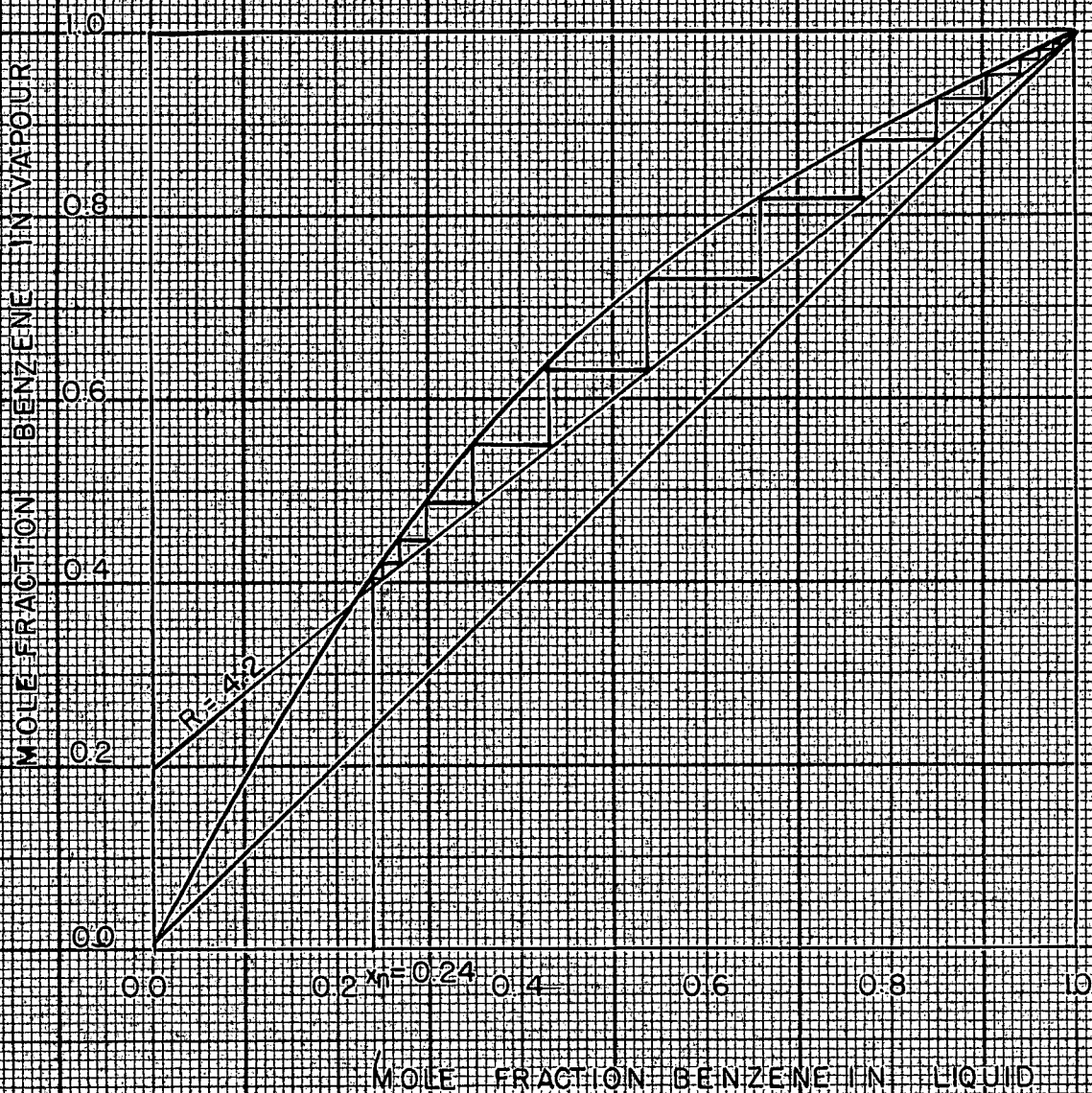


FIGURE 7

found that this function may be represented by the equation

$$x_n R^a = b \quad (22).$$

where a and b are constants and can be found by plotting $\log x_n$ against $\log R$ on a graph as in figure 8. For a 14 plate column separating benzene and toluene, $a = .836$ and $b = .795$.

Now, combining equations (21) and (22) to eliminate x_n

$$D = \frac{x_0 R^a - b}{R^a - b} \quad (23).$$

Equation (23) is plotted in figure 9 and represents the minimum reflux ratio which gives 100% overhead where a fraction D has been distilled.

It is easily seen that the most efficient method of operating a column is to duplicate this curve exactly. This, however, is not easily done. One method which might be used to accomplish this would be by turning a valve or divided wier in a prearranged way.

Derivation of the Time Curve.

In order to do this it is necessary to know the relationship between the time and the minimum reflux ratio.

Now, since

$$P = \frac{V}{1 + R} \quad (24).$$

where P = rate of product
V = vapour velocity,

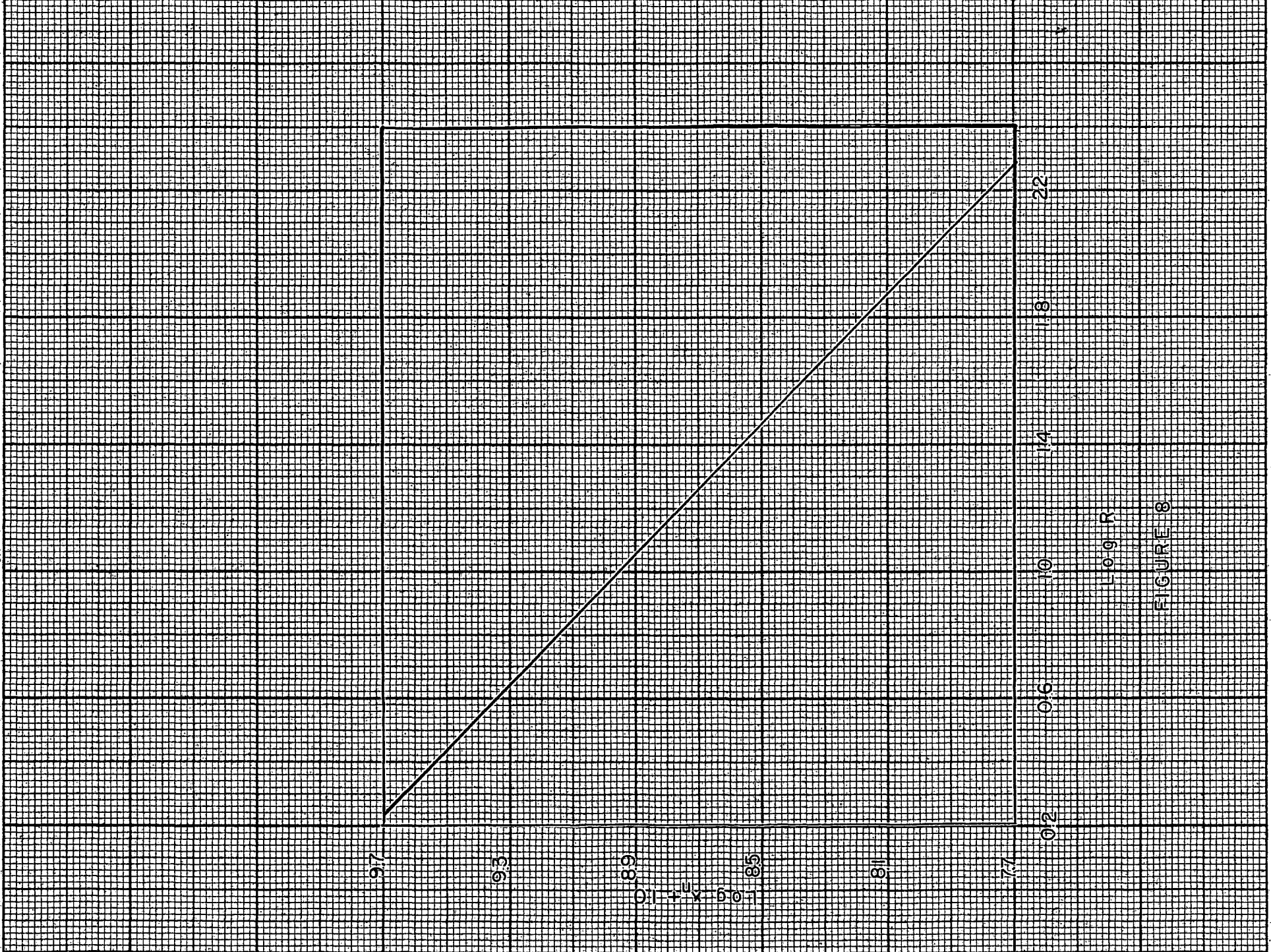


FIGURE 8

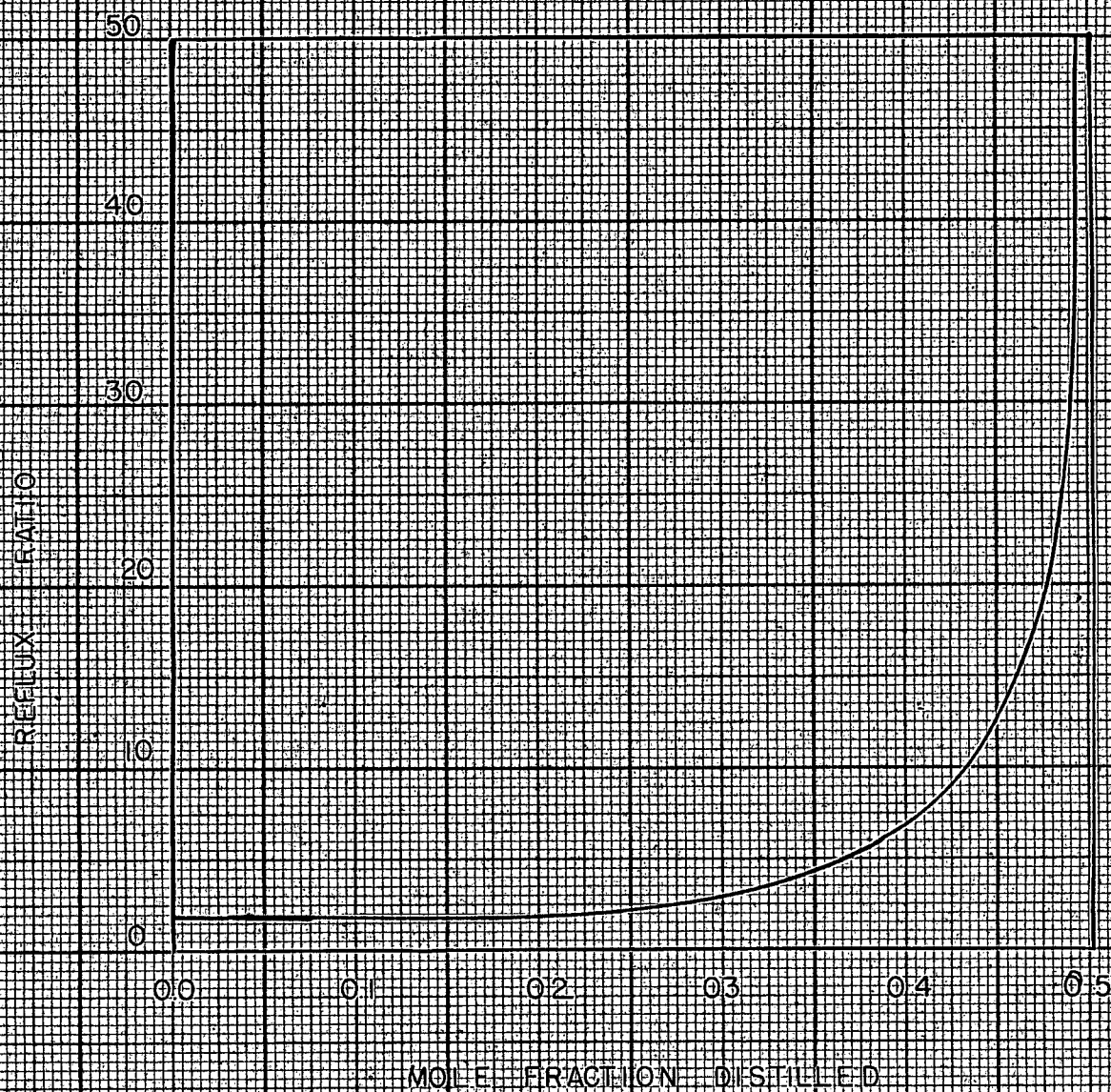


FIGURE 9

and also

$$P = \frac{dD}{dT} \text{ ————— (25).}$$

where T = the time per unit charge.

Combining (24) and (25)

$$VdT = (1 + R)dD \text{ ————— (26).}$$

$$VT = D + \int_{D=0}^{D=D} RdD = D + RD - \int_{R=R_0}^{R=R} D dR \text{ ————— (27).}$$

The integral in equation (27) can be evaluated graphically by using figure 9 or in the following manner. Consider the integral by itself.

$$\int_{R=R_0}^{R=R} D dR = \int_{R=R_0}^{R=R} x_0 \frac{R^a - b}{R^a - b} dR = x_0 \int_{R=R_0}^{R=R} \frac{R^a}{R^a - b} dR - b \int_{R=R_0}^{R=R} \frac{dR}{R^a - b} \text{ — (28).}$$

now,

$$x_0 \int \frac{R^a}{R^a - b} dR = x_0 R + x_0 b \int \frac{dR}{R^a - b} \text{ ————— (29).}$$

$$VT = D(1+R) - x_0 R + b(x_0 + 1) \int_{R=R_0}^{R=R} \frac{dR}{R^a - b} \text{ ————— (30).}$$

Expanding $(R^a - 1)^{-1}$ by the binomial theorem

$$\int \frac{dR}{R^a - b} = \int \frac{dR}{R^a} + b \int \frac{dR}{R^{2a}} + b^2 \int \frac{dR}{R^{3a}} + \text{ — (31).}$$

$$\therefore VT = \frac{x_0 R^a - b}{R^a - b} (1+R) + x_0 R + b(x_0 + 1) \left\{ \frac{1}{(1-a)R^{a-1}} + \frac{b}{(1-2a)R^{2a-1}} + \dots \right\} + C \text{ (32).}$$

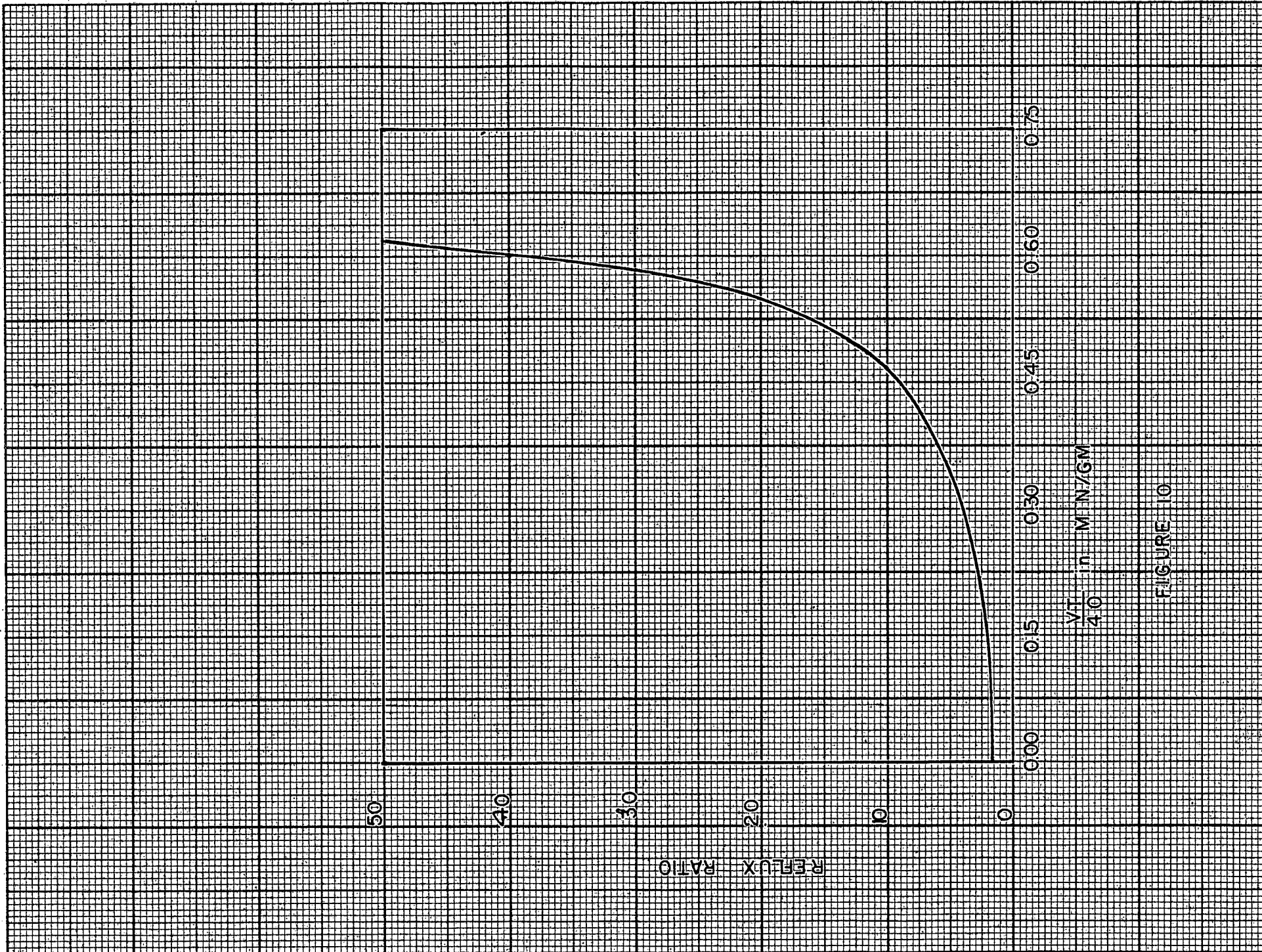


FIGURE 10

By dividing equation (32) by V and plotting it on a graph, figure 10 is obtained.

Experimental Work.

Apparatus Used.

The apparatus used was the jack-chain packed column built in 1935 by Williamson and McGinn⁷ which they have fully described in their thesis. It was this column that was referred to before and, as was shown, it contains 14 theoretical plates.

Determination of Vapour Velocity.

The column was operated as adiabatically as possible and the vapour velocity was determined by a heat balance on the head of the column. The following equation was used:

$$V = \frac{(T_2 - T_1)W}{L_v} \quad (33).$$

where W weight of water through the condenser per minute,

T_1 = temperature of the water entering,

T_2 = temperature of water leaving, and

L_v = latent heat of vapourization.

In the initial runs the water was collected and measured for one minute. In later runs, however, a rotameter was used and the flow of water was adjusted to 1000 grams per minute. By doing this, the vapour velocity became a linear function of the temperature difference and could be very easily read from a

graph.

Determination of Reflux Ratio and Fraction Distilled.

The product was collected and weighed for a given length of time. The reflux ratio was calculated from the relation

$$R = \frac{V}{P} - 1 \quad (34).$$

Results.

The reflux ratios actually used for the fraction distilled are plotted on figure 11. For purposes of comparison equation (23) is also plotted on figure 11.

That this method does give a pure product is shown by figure 12, on which is plotted the purity of product versus the fraction distilled.

Suggestions for Further Work.

It was attempted to make a controller to regulate the reflux ratio according to the time (equation (32) and figure 10). This attempt was made on the basis of the characteristics of the valve used. When the vapour velocity was kept constant, the reflux ratio was found to vary with the position of the valve stem indicator as shown in figure 13.

Since figure 13 and figure 10 are of approximately the same shape, it would appear that by turning the valve at

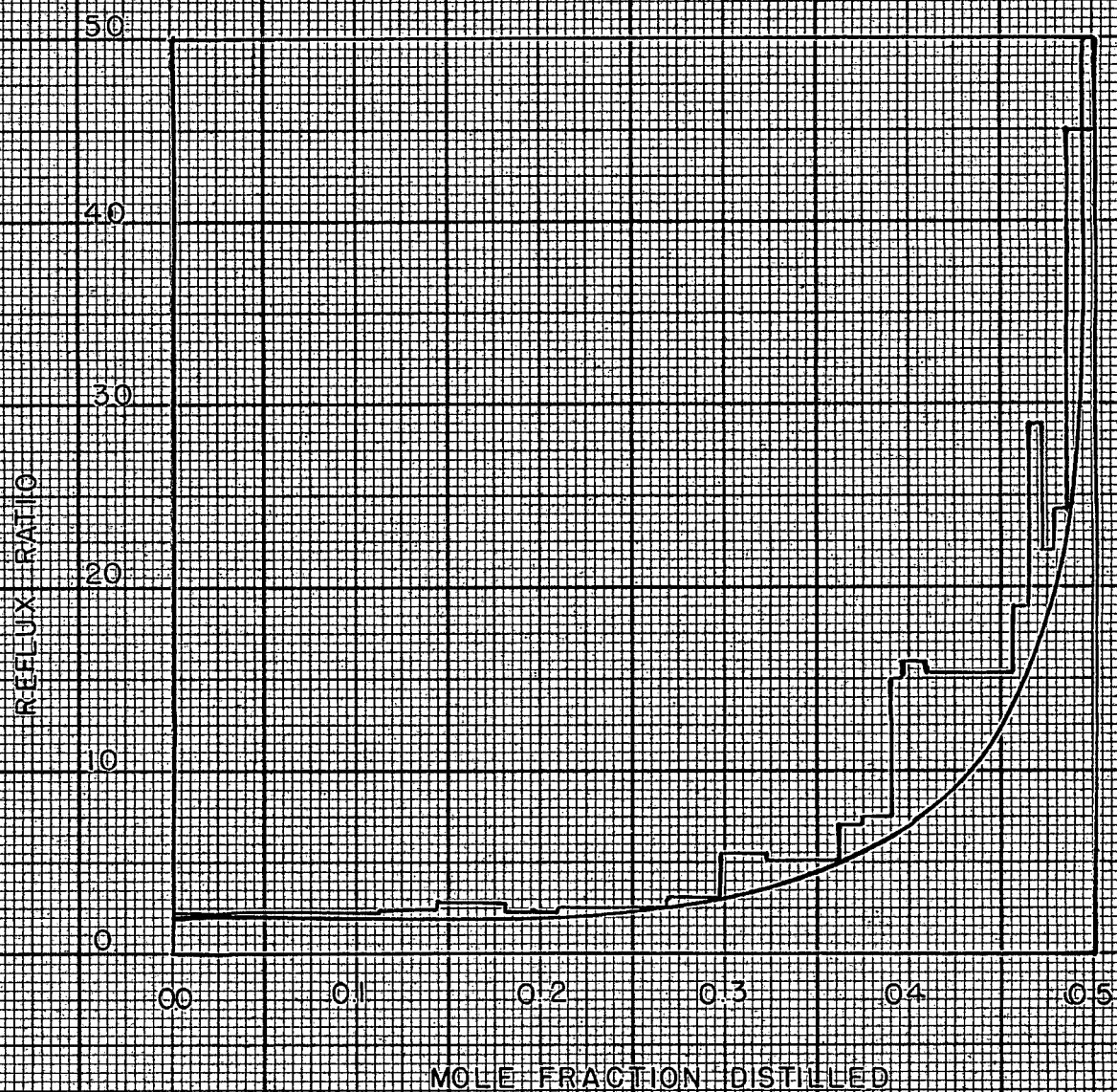


FIGURE 4

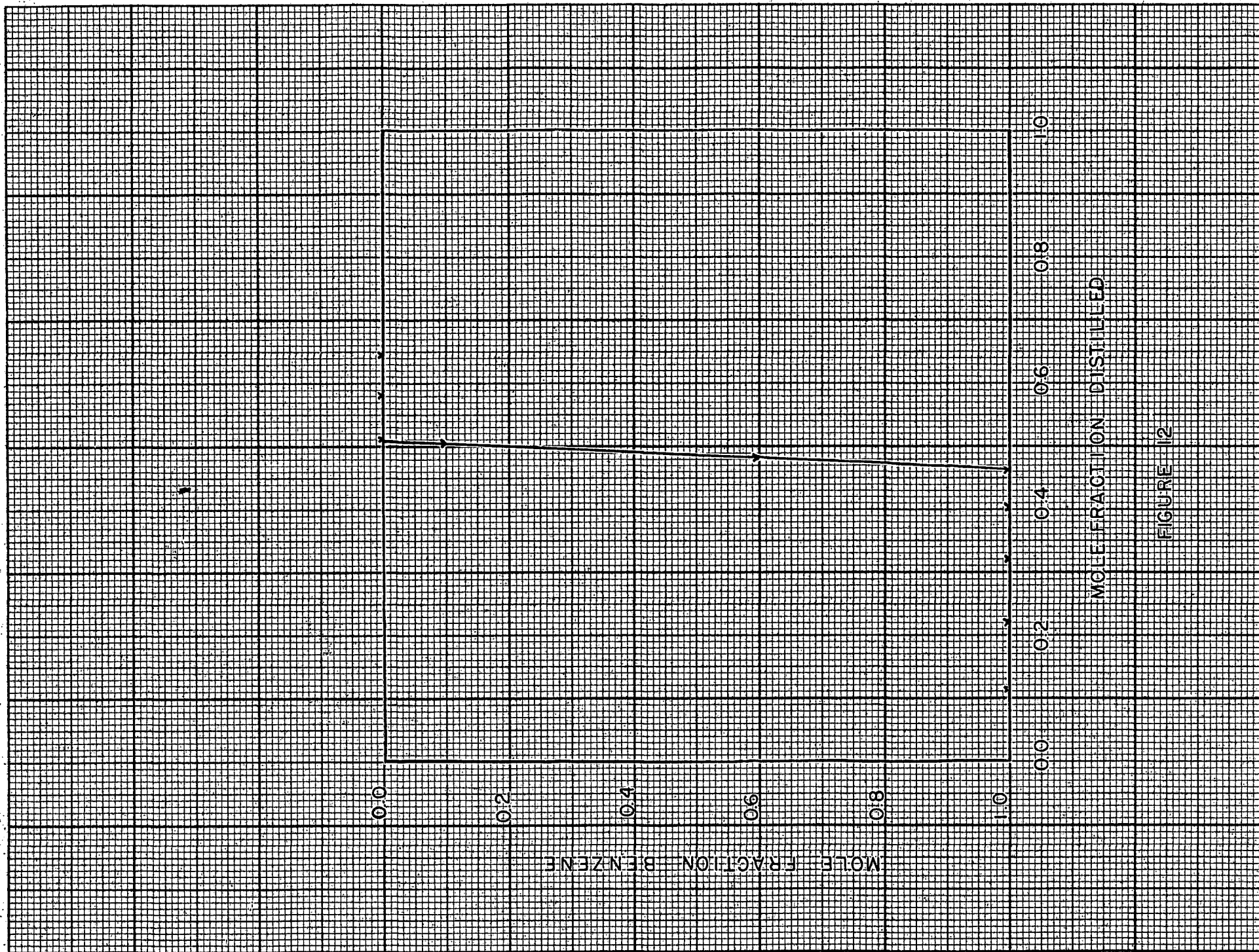


FIGURE 12



VALVE SETTING
($v = 40 \text{ gm/min}$)

FIGURE 113

a constant speed a good approximation of equation (32) could be obtained. This was found to be the case but it was still very much an approximation and needed further improvement. The valve mechanism could be improved in either of two ways. First, by turning the valve at a varying speed and second, by redesigning the valve to modify the flow characteristics.

Instead of using a valve it might be better to use a divided weir and turn it at a varying speed. A method which would probably be the simplest of all would be to design a valve operated by a sensitive temperature controller which would close the valve automatically.

In any method used provision must be made to keep the vapour velocity constant. This would involve using a temperature controller in the still-pot which would increase the power as the temperature increased.

Conclusions and Summary.

The preceding pages have outlined a concise and efficient method for operating a batch distillation column when the hold-up can be considered negligible.

Experimental results are given to show the validity of the theory.

Suggestions are made for further improvements in the manner of operation.

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