Batch Distillation of Binary Mixtures at Minimum Reflux

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In this note, analytical formulas are derived to describe the separation that can be achieved and the vapor requirement when a binary mixture is to be separated by batch distillation with rectification. The results obtained are formally for the case where the batch column operates with an infinite number of stages (corresponding to minimum reflux). However, practically speaking, the results obtained in this work often will give a close approximation to operation with a small, finite number of stages. Under normal circumstances the design equations for batch distillation must be integrated numerically after evaluation of the integrand using a McCabe-Thiele graphical procedure. Implementation of the analytical formulas derived in this note avoids this tedious procedure.

Results are obtained here for each of the two common modes of operation of batch distillation columns: operation with a constant distillate composition and operation with a constant reflux ratio. In deriving these results, it is assumed that the McCabe-Thiele assumptions are valid and that the vapor-liquid equilibrium can be described by a constant relative volatility over the concentration range of interest.

Development of Equations

Figure 1 is a diagram of a batch distillation column. An overall material balance for the system shown, neglecting any holdup in the column, gives

$$dW = -dD \tag{1}$$

A material balance for the light component on the same system gives

$$d(x_w W) = -x_D dD \tag{2}$$

Combining Eqs. 1 and 2 results in

$$\frac{dW}{W} = \frac{dx_w}{x_D - x_w} \tag{3}$$

Equation 3 may be integrated between the initial charge conditions, x_{w_1} and W_1, and some later condition, x_{w_2} and W_2.

$$\ln \frac{W_2}{W_1} = \int_{x_{w_1}}^{x_{w_2}} \frac{dx_w}{x_D - x_w} \tag{4}$$

Equation 4 relates the total moles in the still at any time, W_2, to the mole fraction of the light component in the still, x_{w_2}. This is the basic design equation that describes the separation that the column can achieve. For the constant distillate composition mode of operation, x_D is constant and Eq. 4 can readily be integrated. However, if the column is operated under the constant reflux ratio mode of operation, x_D varies and a numerical integration of Eq. 4 is usually necessary (Perry and Chilton, 1973). In this case, a McCabe-Thiele diagram can be used to relate x_D to x_w. Figure 2 illustrates the relationship for this situation when the batch column is equivalent to three stages. For decreasing x_D, values for x_w are located on the diagram for three stages.

It is often necessary, for design calculations, to know the vapor requirement for a specified separation. A differential bal-

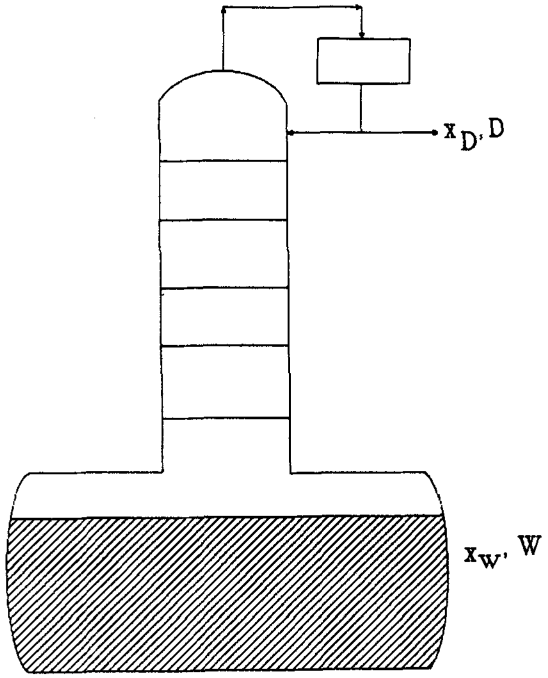

Figure 1. Batch distillation column.

ance around the condenser leads to

$$dV = dL + dD \tag{5}$$

Equation 5 may be rearranged to

$$dV = \frac{dD}{1 - \frac{dL}{dV}} \tag{6}$$

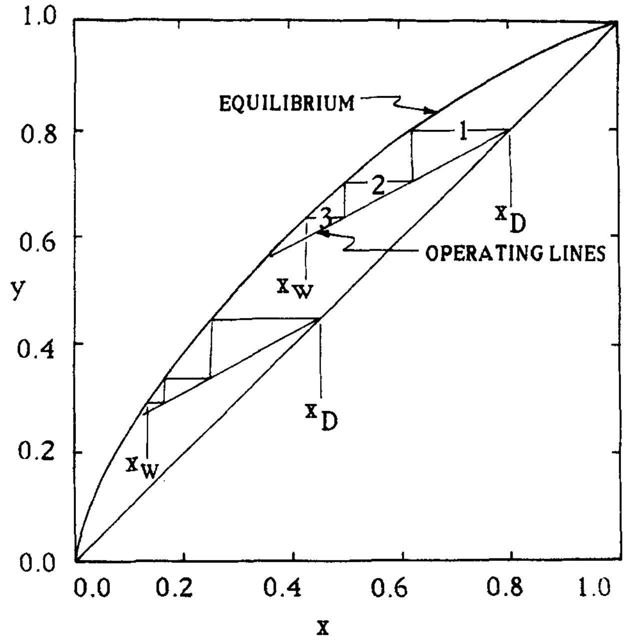

Figure 2. McCabe-Thiele plot to relate x_D and x_w for constant reflux operation.

where dL/dV is the instantaneous slope of the operating line, which may be related to the external reflux ratio:

$$\frac{dL}{dV} = R/(R + 1) \tag{7}$$

For operation with a constant reflux ratio, Eq. 6 may be simply integrated. However, for operation under the constant distillate composition mode, R varies and Eq. 6 cannot be integrated directly. In this case, an overall component balance gives an equation for the liquid remaining in the still at any time

$$W = \frac{W_1 (x_{w_1} - x_D)}{x_w - x_D} \tag{8}$$

Equations 6 and 8 may be combined with Eq. 3 to give

$$V = \int_0^v dV = W_1 (x_D - x_{w_1}) \int_{x_{w_2}}^{x_{w_1}} \frac{dx_w}{(x_D - x_w)^2 \left(1 - \frac{dL}{dV}\right)} \tag{9}$$

A McCabe-Thiele diagram may be used to relate x_w and dL/dV, as shown in Figure 3 for the case of a column equivalent to three stages.

Integration of Equations

For the case of an infinite number of stages corresponding to minimum reflux it is possible to avoid the tedium of numerical integration and to integrate the design equations, Eqs. 3 and 9, analytically. For this situation the operating line ends in a pinch zone, and x_w will be located on the equilibrium curve in Figures 2 and 3. If y_w is defined as the vapor phase mole fraction in equilibrium with x_w, then the slope of the operating line is given by

$$\frac{dL}{dV} = \frac{x_D - y_w}{x_D - x_w} \tag{10}$$

Under conditions where the equilibrium may be expressed by a constant relative volatility, y_w is related to x_w by

$$y_w = \frac{\alpha x_w}{1 + x_w (\alpha - 1)} \tag{11}$$

Constant reflux ratio operation

For the constant reflux ratio mode of operation, Eq. 6 may easily be integrated to give the vapor requirement.

$$V = (R + 1) D = (R + 1)(W_1 - W_2) \tag{12}$$

The material balance equation, Eq. 4, may be integrated by relating the compositions at opposite ends of the operating line, i.e., the instantaneous value of x_D as a function of x_w, through combination of Eqs. 7, 10, and 11:

$$x_D = \frac{(R + 1) \alpha x_w - R x_w - R x_w^2 (\alpha - 1)}{1 + x_w (\alpha - 1)} \tag{13}$$

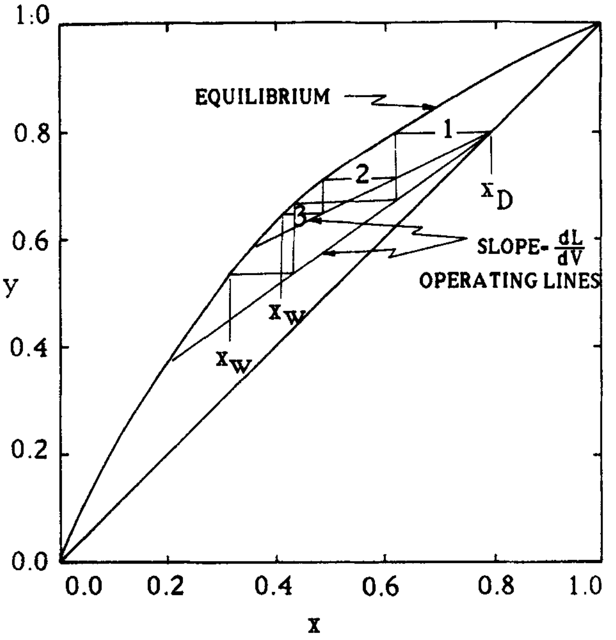

Figure 3. McCabe-Thiele plot to relate x_w and dL/dV for constant x_D operation.

Substitution of Eq. 13 into Eq. 4 and integrating gives

$$\ln\frac{W_2}{W_1} = \frac{1}{(R+1)(\alpha-1)}\ln\left[\left(\frac{1-x_{w_1}}{1-x_{w_2}}\right)\left(\frac{x_{w_2}}{x_{w_1}}\right)\right] + \frac{1}{(R+1)}\ln\left(\frac{1-x_{w_1}}{1-x_{w_2}}\right) \quad (14)$$

Equation 14 relates the moles remaining in the still to the composition in the still.

Constant distillate composition operation

For the constant distillate composition mode of operation, the material balance relation, Eq. 4, may be integrated directly to give:

$$\frac{W_2}{W_1} = \left(\frac{x_D - x_{w_1}}{x_D - x_{w_2}}\right) \quad (15)$$

To integrate Eq. 9 for the vapor requirement it is necessary to relate the instantaneous slope of the operating line, dL/dV, to the mole fraction in the still, x_w. Substitution of Eq. 11 into Eq. 10 results in

$$\frac{dL}{dV} = \frac{x_D + x_D x_w(\alpha-1) - \alpha x_w}{(x_D - x_w)\,[1 + x_w(\alpha-1)]} \quad (16)$$

Substitution of Eq. 16 into Eq. 9 and integration gives an equation for the vapor requirement.

$$V = \frac{W_1(x_D - x_{w_1})}{(1-x_D)(x_D)(\alpha-1)}\left\{(1-x_D)\ln\left[\left(\frac{x_D - x_{w_2}}{x_D - x_{w_1}}\right)\left(\frac{x_{w_1}}{x_{w_2}}\right)\right] + x_D\,\alpha\ln\left[\left(\frac{x_D - x_{w_2}}{x_D - x_{w_1}}\right)\left(\frac{1-x_{w_1}}{1-x_{w_2}}\right)\right]\right\} \quad (17)$$

Implementation of Design Equations

Equations 12 and 14 are the design equations for batch distillation when the column is operated under constant reflux ratio conditions. Equations 15 and 17 are the corresponding design equations for the constant distillate composition mode of operation. Equations 14 and 17, which are the contributions of this note, are strictly valid only for an infinite number of stages in the column. However, it is often the case that even a small finite number of stages will result in a near pinch zone. Under these conditions the approximation made by Eq. 10 is valid, and Eqs. 14 and 17 will give good results and will permit considerably simplified design calculations. Inspection of Figures 2 and 3 shows that for these examples, a column equivalent to five or more stages would readily satisfy the approximation made by Eq. 10. A similar quick inspection of the equilibrium of a binary system under study will indicate if a small, finite number of stages will place x_w essentially on the equilibrium line. It should be pointed out that when implementing Eq. 14 for a finite number of stages, the reflux ratio should be such that the pinch zone occurs at the still end of the column rather than the distillate end, since Eq. 14 was derived for the former case.

Equations 14 and 17 can also be applied to binary systems for which the equilibrium is not described exactly by a constant relative volatility. In this case the equilibrium data should be fitted to a constant relative volatility over the range of compositions that would exist in the still for the specified separation.

Notation

D = moles of distillate, kmol
L = moles of liquid overflow, kmol
R = reflux ratio
V = mole of vapor, kmol
W = moles of liquid in still, kmol
x = mole fraction of light component in liquid
x_w = mole fraction in still
x_D = mole fraction in distillate
y_w = mole fraction in vapor in equilibrium with still composition
α = relative volatility

Subscripts

1 = initial condition
2 = final condition

Literature cited

Perry, R. C., and C. H. Chilton, eds., *Chemical Engineer's Handbook*, 5th ed., McGraw-Hill, New York, ch. 13 (1973).

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