The Effect of Vapor Distribution on Distillation Plate Efficiencies

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The nonuniform distribution of vapor across a distillation plate causes a reduction in the Murphree plate efficiency. The magnitude of the reduction has been evaluated and the maximum effect occurs when the liquid mixing is intermediate between the perfectly mixed and the plug flow cases.

The AIChE bubble-tray design manual (1) provides a method for calculating the Murphree plate efficiency (E_{MV}) for binary systems for uniform vapor distribution across the plate. One of the causes given for the predicted efficiency being below the measured value is a poor vapor distribution. This can arise from a poor tray design, high liquid gradients, poor inlet arrangements and weir location. The numerous studies on the hydraulic gradient (2 to 6) all stress the reduction in vapor velocity through the plate near the liquid downcomer and higher vapor velocities near the discharge weir.

A simple vapor distribution function such as a linear function agrees well with Bolles calculations (2). Let v be a dimensionless vapor mass flow rate defined by

$$v = \frac{V_z}{V_{\rm ov}} \tag{1}$$

where V_z is the local or point vapor mass flow rate at point z and $V_{\rm av}$ is the average vapor mass flow rate which will occur at the midpoint of the plate. If w is a dimensionless distance defined by

$$w = \frac{z}{Z} \tag{2}$$

where z is the distance to a point on the plate and Z is the total length of the plate then

$$v = 1 + b(2w - 1) \tag{3}$$

where $b = BZ/2V_{\rm av}$ where 0 < b < 1 and B is the vapor velocity gradient across the plate. The value of b is restricted to the range 0 to 1 which allows for positive values of v throughout the plate, and a minimum positive velocity gradient of zero when the vapor is uniformly distributed.

MURPHREE PLATE EFFICIENCY

The Murphree plate efficiency is defined by

$$E_{mv} = \frac{y_{av} - y_{n+1}}{y^*_{n} - y_{n+1}} \tag{4}$$

where y_{av} is the average vapor composition leaving the plate, y_{n+1} is the vapor composition entering the plate, y_n^* is the vapor composition in equilibrium with x_n the liquid leaving the plate.

The average vapor composition leaving the plate is given by

$$y_{\rm av} = \frac{1}{V_T} \int_{0}^{z} V_z \, y \, dz$$

where V_T is the total vapor mass flow rate through the plate that is

$$V_T = V_{av} Z$$

Substituting from Equations (1) and (2)

$$y_{\rm av} = \int_0^1 v \, y \, dw \tag{5}$$

But the local or point overall gas phase plate efficiency E_{OG} is defined by

$$E_{OG} = \frac{y - y_{n+1}}{y^{\bullet} - y_{n+1}} \tag{6}$$

where y^* is the vapor composition in equilibrium with the liquid at the point z on the plate. Substituting y from Equation (6) into (5).

$$y_{av} = E_{OG} \int_{0}^{1} v(y^* - y_{n+1}) dw + y_{n+1} \int_{0}^{1} v dw$$

$$y_{av} = E_{OG} \int_{0}^{1} v(y^* - y_{n+1}) dw + y_{n+1}$$
 (7)

Substituting y_{av} from Equation (7) into (4)

$$E_{MV} = \frac{1}{y^*_{n} - y_{n+1}} \left[E_{OG} \int_0^1 v(y^* - y_{n+1}) \ dw \right]$$
 (8)

For a small change in composition across the plate the vapor liquid equilibrium relationship can be linearized as u = mx + c

$$\cdot \cdot \cdot E_{MV} = \frac{1}{m(x_n - x^{\bullet}_{n+1})} \left[E_{OG} \int_0^1 m \, v(x - x^{\bullet}_{n+1}) \, dw \right]$$

where x^{\bullet}_{n+1} is the liquid composition in equilibrium with the vapor y_{n+1} entering the plate. Defining a dimensionless liquid composition (X) by

$$X = \frac{x - x^{\circ}_{n+1}}{x_n - x^{\circ}_{n+1}} \cdot \frac{E_{MV}}{E_{OG}} = \int_0^1 v \, X \, dw \qquad (9)$$

For a uniform vapor distribution b = 0 then v = 1 and

$$\frac{E_{MV}}{E_{OG}} = \int_0^1 X \, dw \tag{10}$$

which is in agreement with (7). To evaluate the integral in Equation (10) the dimensionless composition distribution must be known, and this will depend on the degree of liquid mixing on the plate.

EDDY DIFFUSION MODEL

The liquid mixing by an eddy dispersion model which assumes that the rate of back mixing is proportional to the concentration gradient on the plate is described in the manual (1). A mass balance for the more volatile component over a vertical element of width dz has been given for constant plate width and constant point efficiency by

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$$\frac{1}{N}\frac{d^2x}{dw^2} - \frac{dx}{dw} - \lambda E_{OG}(x - x^*_{n+1}) = 0$$
 (11)

while N is the Peclet number defined by

$$N = \frac{UZ}{D_E}$$

where U is the froth velocity across the plate and D_E is the eddy diffusion or eddy dispersion coefficient. And λ is defined by

$$\lambda = \frac{m(VZ)}{L}$$

A mass balance including the vapor distribution can be expressed in dimensionless terms giving

$$\frac{1}{N} \frac{d^2 X}{dw^2} - \frac{dX}{dw} - v \lambda E_{OG} X = 0$$
 (12)

where λ is defined as

$$\lambda = \frac{m(V_{av}Z)}{T_{e}}$$

Substituting for v

$$\frac{1}{N}\frac{d^2X}{dw^2} - \frac{dX}{dw} - \lambda E_{OG} [1 + b(2w - 1] X = 0 (13)$$

With the boundary conditions as given (1)

$$X=1$$
 $w=1$

$$\frac{dX}{dw} = 0 \quad w = 1$$

So the problem of evaluating the Murphree plate efficiency requires a solution of the differential Equation (13) with the corresponding boundary conditions and then evaluating the integral (9). The solution will be of the form

$$\frac{E_{MV}}{E_{OG}} = f_1(N, \lambda E_{OG}, b)$$

So with three parameters a series of graphs will be required to express E_{MV}/E_{OG} over wide ranges of N, E_{OG} , and b.

PLUG-FLOW MODEL

The plug-flow model can be considered as an eddy dispersion model with an infinite Peclet number. Equation (13) becomes

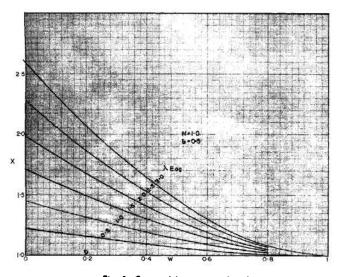


Fig. 1. Composition across the plate.

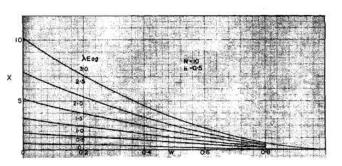


Fig. 2. Composition across the plate.

$$\frac{dX}{dw} + \lambda E_{OG} [1 + b(2w - 1)] X = 0$$

with the boundary condition

$$X = 1$$
 $w = 1$

The variables can be separated in this differential equation and integrated as

$$\int_{1}^{X} \frac{dX}{X} = -\lambda E_{OG} \int_{1}^{w} [1 + b(2w - 1)] dw$$

the solution is

$$X = \exp(-\lambda E_{OG})[w(1-b) + bw^2 - 1] \quad (14)$$

From Equation (9)

$$\frac{E_{MV}}{E_{GG}} = \int_0^1 \left[1 + b(2w - 1) \right] X \, dw \tag{15}$$

Substitution of X in these integrals will lead to a solution of the form

$$\frac{E_{MV}}{E_{OG}} = f_2(\lambda E_{OG}, b)$$

Uniform Vapor Distribution b = 0

$$\cdot \cdot \cdot \frac{E_{MV}}{E_{OG}} = \int_0^1 X \, dw$$

where $X = \exp(-\lambda E_{OG})(w-1)$

$$\frac{E_{MV}}{E_{OG}} = \int_0^1 \exp\left(-\lambda E_{OG}\right) (w-1) dw$$

$$\cdot \cdot \frac{E_{MV}}{E_{OG}} = \frac{1}{\lambda E_{OG}} \left[e^{\lambda E_{OG}} - 1 \right]$$

This result for a uniform vapor distribution and plug flow of liquid across the plate was given by Lewis (1)

Linear Vapor Distribution $b \neq 0$

$$\frac{E_{MV}}{E_{OG}} = \int_{0}^{1} [1 + b(2w - 1) \exp(-\lambda E_{OG})[w(1 - b) + bw^{2} - 1]dw$$

Evaluating the integral by substitution.

$$\frac{E_{MV}}{E_{OG}} = \frac{1}{\lambda E_{OG}} \left[e^{\lambda E_{OG}} - 1 \right]$$

This result is identical with the value for b=0 so we can make a general statement that the Murphree plate efficiency is independent of the vapor distribution for the plug flow of liquid across the plate

$$\cdot \cdot \frac{E_{MV}}{E_{OG}} = f_2 \; (\lambda \; E_{OG})$$

GENERAL CASE

Uniform Vapor Distribution b = 0

Equation (13) becomes

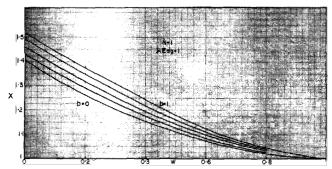


Fig. 3. Effect of b.

$$\frac{1}{N}\frac{d^2X}{dw^2} - \frac{dx}{dw} - \lambda E_{\rm OG} X = 0$$

and solution of this differential equation with the appropriate boundary conditions has the form,

$$X = f_1(N, \lambda E_{OG})$$

The Murphree plate efficiency is obtained by substituting this value of X in Equation (10) and evaluating the integral. The solution is given as

$$\frac{E_{MV}}{E_{OG}} = f_3 \ (N, \lambda \ E_{OG})$$

This function is given numerically and graphically in the manual (1).

Linear Vapor Distribution $b \neq 0$

Solution of the differential Equation (13) with finite values for the Peclet number and for a linear vapor distribution can be obtained by evaluating the coefficients in a solution expressed as an infinite series. A solution can also be obtained by numerical methods which will be an approximation to the exact solution. The Runge-Kutta-Nystrom method has been used as outlined:

In the (n + 1)th step of the method, the following quantities are computed.

$$A_n = \frac{h}{2} f(w_n, X_n, X_{n'})$$

$$h$$

$$B_n = \frac{h}{2} f(w_n + \frac{h}{2}, X_n + \beta_n, X_n' + A_n)$$

where

$$\beta_{n} = \frac{h}{2} \left(X_{n'} + \frac{A_{n}}{2} \right)$$

$$C_{n} = \frac{h}{2} f \left(w_{n} + \frac{h}{2}, X_{n} + \beta_{n}, X_{n'} + B_{n} \right)$$

$$D_{n} = \frac{h}{2} f(w_{n} + h, X_{n} + \delta_{n}, X_{n'} + 2C_{n})$$

where $\delta_n = h(X_n' + C_n)$. The new values for X_{n+1} and X'_{n+1} are obtained from

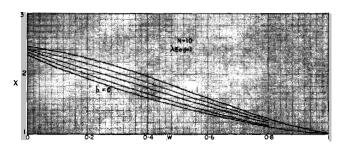


Fig. 4. Effect of b.

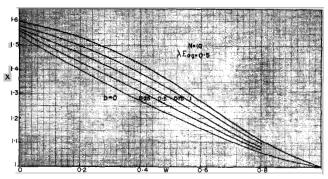


Fig. 5. Effect of b.

the following

$$X_{n+1} = X_n + h(X_n' + K_n)$$

$$K_n = 1/3 (A_n + B_n C_n)$$

 $X'_{n+1} = X_n' + K_n^*$

where

$$K_n^* = 1/3 (A_n + 2B_n + 2C_n + D_n)$$

where h is increment size.

A computer program written in Fortran IID followed the procedure above to solve the differential equation. Ten iterations were used for Peclet numbers of 1 and 2 and twenty for higher Peclet numbers. The range of variables covered is Peclet number = 1, 2, 4, 7, 10; $E_{OG} = 0, 0.5, 1, 1.5, 2, 2.5, 3.0; b \text{ values} = 0, 0.25, 0.5,$ 0.75, 1.0;

A print out of the result gives X at values of w from 0 (0.1) 1.0, which have been presented graphically in

The next procedure is to evaluate the integral (9) so a polynominal was used to fit a curve through the points X, w as given above. The coefficients of the polynominal were evaluated by Gaussian elimination in the following set of linear equations, by a computer program.

$$X_1 = a_0 + a_1 w_1 + a_2 w_1^2 + \dots \qquad a_9 w_1^9$$

 $X_2 = a_0 + a_1 w_2 + a_2 w_2^2 + \dots \qquad a_9 w_2^9$

$$X_{10} = a_0 + a_1 w_{10} + a_2 w_{10}^2 + a_9 w_{10}^9$$

The integral

$$\frac{E_{MV}}{E_{OG}} = \int_0^1 [1 + b(2w - 1)] X dw$$

was evaluated numerically, by a computer program, using Simpsons rule.

The value of E_{MV}/E_{OG} when b=0 was checked against the values given in Table 6 of the manual (1)

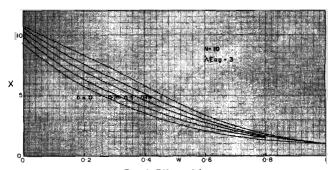
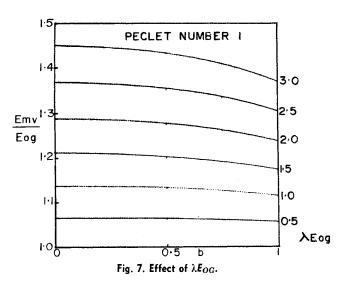


Fig. 6. Effect of b.



and identical results were obtained. The results have been presented graphically in Figure 7.

DISCUSSION

It can be seen from Figure 7 that there is a reduction in the Murphree plate efficiency when there is a nonuniform vapor distribution. The effect can be seen clearly in Figure 8 when E_{MV}/E_{OG} has been plotted against the Peclet number for various values of \vec{b} . There is only a small difference between the b = 0 and b = 0.25 lines, but a larger difference between the b=0.75 and b=1lines. The difference between $(E_{MV})/(E_{OG})_{b=0}$ at b=0and the value at b = 1, $(E_{MV})/(E_{OG})_{b=1}$ has been plotted against the Peclet number with λE_{OG} as a parameter in Figures 9 and 10. These curves must pass through the origin for a perfectly mixed plate and it has been shown previously that $E_{MV}/E_{OG} = 1$ for an infinite Peclet number, so there must be a maximum in the curves on Figures 9 and 10. The maximum is not well defined and to assist in its location some additional calculations were completed for Peclet numbers of 20 and 50. These cal-

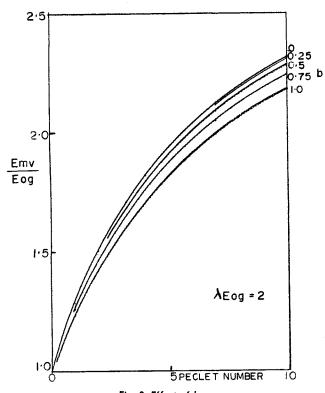


Fig. 8. Effect of b.

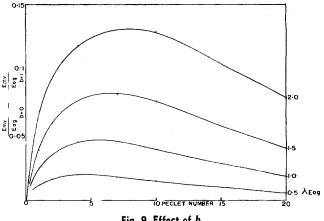


Fig. 9. Effect of b.

0.3

0.2

\$\frac{2}{5} \frac{2}{5} \frac{2}{5} \frac{1}{5} \frac{1}{

Fig. 10. Effect of b.

Emv Eog

culations required a large number of iterations and no attempt was made to explore the region from 50 to infinity. Figures 9 and 10 show that the maximum in the curve increases with increasing values of λE_{OG} . These figures can be used to obtain the value of $(E_{MV})/(E_{OG})_{b=1}$ by selecting a value of the Peclet number and λE_{OG} and obtaining $(E_{MV})/(E_{OG})_{b=0}$ from either Figure 11-2 or Table 11-1 in the AIChE bubble-tray design manual (1).

| λEog 2 Fig. 11. Maximum difference curves.

The difference between $(E_{MV})/(E_{OG})_{b=0}$ and $(E_{MV})/(E_{OG})_{b=0}$ $(E_{OG})_{b=1}$ can then be obtained from Figures 9 and 10 and the value of $(E_{MV})/(E_{OG})_{b=1}$ evaluated. Figure 11 shows a plot of E_{MV}/E_{OG} against λE_{OG} showing where the maximum difference occurs. Figure 8 shows a plot of E_{MV}/E_{OG} against the Peclet number for various values of b. For constant values of E_{OG} , the froth velocity and the dispersion coefficient then Figure 8 is effectively a plot of E_{MV} against Z the plate length. Increases in Z would be expected to cause an increase in E_{MV} but increasing Z would also increase the hydraulic gradient across the plate causing a non-uniform vapor distribution. The effect of the non-uniform vapor distribution would increase b from zero towards 1 as Z increased. A curve could be drawn on Figure 8 starting at b = 0 for small values of Z then moving towards b = 1 for large values of Z. It could be possible for a maximum to occur in this curve.

CONCLUSION

The ratio of the Murphree plate efficiency to the point or local efficiency has been extended from the uniform vapor distribution as described in the AIChE bubble-tray design manual to a linear vapor distribution. Except for the perfectly mixed plate and the plug flow of liquid there is a reduction in the Murphree plate efficiency. The magnitude of the reduction can be readily evaluated by the use of Figures 7 to 10. The maximum reduction occurs when the liquid mixing is intermediate between the extreme cases of plug flow and perfectly mixed.

NOTATION

= constant

= dimensionless vapor gradient

= vapor gradient E_{OG} = point plate efficiency

= Murphree vapor plate efficiency

= liquid flow rate N = Peclet number

= dimensionless vapor flow rate

V = vapor flow rate

w = dimensionless distance = liquid composition

= equilibrium liquid composition \boldsymbol{X} = dimensionless liquid composition

= vapor composition

= equilibrium vapor composition

= distance along the plate = distance to the weir

= defined by $m(V_{av}Z)/L$

Subscripts

= average aυ

= plate or step nn

T = total

= at point

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Manuscript received August 18, 1967; revision received January 30, 1968; paper accepted February 5, 1968.

The Fluid Hydrates of Methylene Chloride and Chloroform: Their Phase Equilibria and Behavior as Influenced by Hexane

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Thermodynamic properties pertaining to phase equilibria in the binary-fluid hydrate systems, methylene chloride-water and chloroform-water, and the ternary hydrate system, methylene chloride-chloroform-water, were measured. Total vapor pressure data were recorded as a function of temperature over a range of -3 to $+10^{\circ}$ C. Quadruple locus measurements of the ternary four-phase equilibrium, L_1 - L_2 -H-G, and isobaric studies of the ternary system chloroform-methylene chloride-water, support the existence of a solid solution hydrate between methylene chloride and chloroform. The addition of the nonhydrate former, hexane, to the methylene chloride-water system lowered the isobaric critical decomposition temperature of the hydrate.

Gas or fluid hydrates are a specific type of crystalline clathrate or cage-like compound wherein the hydrated molecules are enclosed in a rigid lattice of water molecules. The water molecules are usually referred to as the host and the hydrated molecule as the guest. Hydrated molecules are most commonly either gases such as methane or argon, or volatile liquids such as methylene chloride or chloroform. The entrapped guest molecules stabilize the otherwise metastable host lattice. There are no chemical bonds between the water molecules and the hydrated molecules; stabilization occurs by forces similar to intermolecular forces in dense gases and liquids.

By using X-ray techniques Von Stackelberg (25) and Claussen (6) characterized hydrates into two major crystalline structures which they labelled I and II. A specific framework will retain only those molecules that fit the dimensions of the void spaces available. In a structure II hydrate, slightly distorted regular pentagonal dodecahedrons composed of water molecules assemble to form a modified cubic lattice with a lattice constant of approximately 17.3Å. The unit cell consists of 136 water molecules having two characteristic types of void spaces:

16 small voids of 4.8 A.diameter.