Effect of Mixing on Efficiencies for Reactive Tray Contactors

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The relationship between point efficiencies and Murphree tray efficiencies was studied for systems where reactions take place in the liquid within a tray column. For nonreactive systems, several well-known mixing models are available for predicting Murphree tray efficiency from point efficiencies. For reactive systems, the magnitude and nature of the effect of mixing on tray efficiency are different. An analytical representation is developed of the mixed-pool and plug-flow mixing models for reactive systems with first-order kinetics, and there are different regimes, depending on the reaction kinetics. For each of these regimes, the effect of mixing on tray efficiency differs in magnitude and arises from different mechanisms. The resulting tray efficiencies predicted for reactive systems using the methods may differ by an order of magnitude or more from the values predicted when standard methods for nonreactive trays are applied to reactive trays.

Introduction

Despite many decades of research and numerous published correlations and methods of approach, the prediction of mass-transfer performance for commercial columns from pilot-plant data or from published correlations is still subject to significant uncertainties. For applications where it is necessary to account for the effects of simultaneous chemical reaction and mass transfer, the analysis is complicated further. The approach for solving this problem has been either to model columns as equilibrium stages with an approach to equilibrium, that is, the Murphree tray efficiency, or to use a more rigorous rate-based model. While the rate-based models are arguably better grounded fundamentally, the equilibrium stage model (with application of a tray efficiency) is still widely used by industry and is of practical interest. In addition, the simplicity of the tray-efficiency approach may sometimes offer insights not easily gained from the more rigorous rate-based models. The subject of this article applies to the problems encountered when using the tray-efficiency model for reactive systems.

It has long been established that the tray efficiency for large diameter columns is different from that experienced in small diameter columns because of the effects of nonideal mixing on the tray (Lewis, 1936). For most processes, the tray efficiency is found to be higher for larger diameter columns, and the difference depends on the selection of the particular mixing model, the physical and chemical properties of the mixture to be processed, and the specific operating conditions for the column. In this article, the objective is to focus on one of the requirements common to all models for predicting tray efficiency, namely, to predict the overall tray efficiency based on the estimated point efficiency and application of a suitable mixing model.

For nonreactive systems, several methods are available for estimating the Murphree tray efficiency from point efficiency estimates made either from laboratory-scale measurements, such as using an Oldershaw column, or from published correlations (Dribika and Biddulph, 1986; Bennett and Grimm, 1991; AIChE, 1958). Klemola (1998) lists references for more than a dozen tray efficiency correlations. For each of these methods, the conversion of point efficiency to tray efficiency relies on the choice of the mixing model to be used.

The liquid mixing on the tray has been modeled using several approaches. Lewis (1936) analyzed the ideal case of plug flow across the tray, which may be approached for large diameter columns. Gautreaux and O'Connell (1955) treated the flow as a series of perfectly mixed pools across the tray. The

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primary difficulty in the utility of their method is in correctly estimating the number of mixed pools on the tray. The AIChE study used a more rigorous mixing model based on an eddy diffusivity for diffusive backmixing based on the dimensionless Peclet number (AIChE, 1958). Foss et al. (1958) developed a method for relating the Peclet number to the number of perfectly mixed pools across the tray. More recent work has included mixing models of increasing complexity (Prado and Fair, 1990; Garcia and Fair, 2000).

For the purpose of this article, the choice of mixing model is not paramount to the main points that are to be conveyed. Rather, it is the difference in results obtained between reactive and nonreactive systems that is to be emphasized. For this reason, the authors will address the mixed-pool model, including its reduction to plug flow for an infinite number of pools, to illustrate the differences between reactive and nonreactive systems.

For nonreactive systems with cross-flow trays, the concentration varies across the tray as a result of nonideal mixing. In the limit of perfect liquid mixing on the tray, the concentration is constant across the tray and the point efficiency and tray efficiency are the same. For nonideal mixing, concentration gradients develop across the tray that lead to differences in the tray and point efficiencies. In the extreme limit of plug flow across the tray, the concentration gradient is maximized and the difference is also at a maximum.

For reactive systems, the concentration gradient in the liquid is altered by the consumption or production of a species in the bulk liquid. This leads to a gradient in the driving force for mass transfer across the tray. For fast reactions with significant reaction occurring in the diffusion film, gradients in concentration of the reactants may also lead to gradients in the mass-transfer enhancement factor ϕ. The enhancement factor is defined as ($k_L = \phi k_L^o$), where k_L is the mass-transfer coefficient with chemical reaction and k_L^o is the mass-transfer coefficient for purely physical absorption.

Overall, the behavior of these systems can be categorized into three regimes:

- Very slow reactions
- Moderate reactions
- Fast reactions

For the very slow reactions, the concentration gradients across the tray approach those for nonreactive systems; in this case the conventional methods apply for converting point efficiency to tray efficiency. For moderate reactions, the chemical reaction depresses the concentration gradient across the tray and reduces the difference in point efficiency and tray efficiency. For irreversible reactions, the point efficiency and tray efficiency become the same and are independent of the degree of mixing if the rate of reaction is sufficient to reduce concentrations in the bulk to near zero. For even faster reactions where enhancement of mass transfer occurs because of significant reaction in the diffusion film, gradients in the reactant concentration and enhancement factors may cause the tray efficiency and point efficiency to diverge again.

The primary conclusion of this work is that the widely used models for converting point efficiency to tray efficiency must be used with caution when dealing with reactive systems. Under certain conditions, application of conventional methods to reactive systems may result in serious errors in determining the number of required trays. In the case of multicomponent distillation or absorption with reversible reactions and reactions occurring in the diffusion film, the effect of mixing quickly becomes too complex to allow accurate predictions of tray efficiency from point efficiency correlations, necessitating the use of a more rigorous rate-based approach.

Murphree and Point Efficiencies

The Murphree vapor efficiency for a tray is defined as the ratio of the actual change in vapor mole fraction for a component divided by the change in mole fraction that would be experienced if the vapor leaving the tray were in equilibrium with the liquid leaving the tray

$$E_{MV} = \left(\frac{y_{\text{in}} - y_{\text{out}}}{y_{\text{in}} - y^*} \right)_{\text{TRAY}} \tag{1}$$

where E_{MV} is Murphree vapor efficiency, y_{in} is average mole fraction in the vapor entering the tray, y_{out} is average mole fraction in the vapor leaving the tray, and y^* is the mole fraction that would be in equilibrium with the liquid leaving the tray.

The point efficiency E_P is defined similarly, but applies to a particular point on the tray, with a particular liquid-phase composition

$$E_P = \left(\frac{y_{\text{in}} - y_{\text{out}}}{y_{\text{in}} - y^*} \right)_{\text{POINT}} \tag{2}$$

The point efficiency follows from application of the two-film mass-transfer model for point of vapor as it travels upward through the liquid phase and engages in mass-transfer exchange with the liquid. The liquid composition is assumed to be constant in the vertical direction; the composition of the vapor changes in the vertical direction. The basic derivation of the point efficiency has been reported many times elsewhere and therefore will not be described further in this article (AIChE, 1958).

The key point in introducing the above equations is to realize that the difference between point efficiency and Murphree vapor efficiency arises as a result of the variation in y^* that occurs across the tray as the liquid-phase composition changes. These changes result from mass balance considerations (as components are absorbed or desorbed) for nonreactive systems, and from both mass balance and chemical reaction considerations for reactive systems. Thus, it is necessary to perform some type of integration across the tray, that is, to invoke a mixing model, to account for these changes. In addition, for fast reactions where local mass-transfer coefficients are enhanced depending on the local concentration of reactants, the resulting gradient in mass-transfer enhancement factor must also be accounted for.

Effect of Liquid Mixing for Nonreactive Systems

Numerous models appear in the literature that describe methods for analyzing the effect of liquid mixing on distillation trays (Lewis, 1936; Gautreaux and O'Connell, 1955;

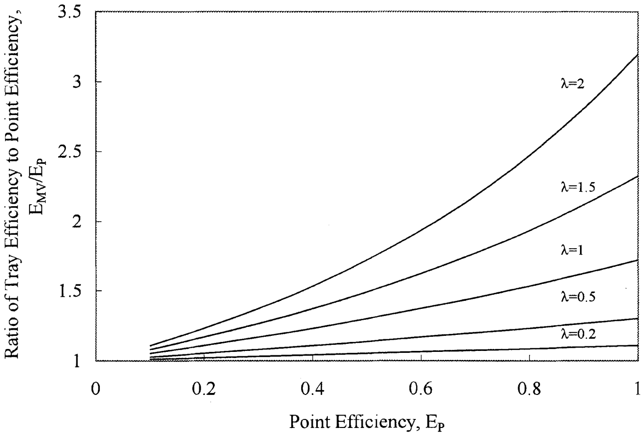

Figure 1. Effect of mixing without chemical reaction for plug flow (Lewis, 1936).

AIChE, 1958; Shore and Haselden, 1969; Lockett and Safekourdi, 1976). For the purpose of illustrating the interaction of chemical reaction with these mixing models, this article will focus on the idealized models of perfectly mixed, plug flow, and the "mixed-pool" model. The more rigorous eddy diffusivity models, and even more recent models utilizing sophisticated spray droplet trajectory analysis, while applicable, are not required to develop the main conclusions of this article.

Lewis (1936) integrated the mass balance equations across the tray for the case of plug flow. His result is given below

$$\frac{E_{MV}}{E_P} = \left(\frac{1}{\lambda E_P}\right)\left[\exp\left(\lambda E_P - 1\right)\right] \qquad (3)$$

where λ is the stripping factor, mV/L, m is the slope of equilibrium line ($y = mx + b$), V is the vapor molar flow rate, and L is the liquid molar flow rate.

Figure 1 illustrates the relationship between Murphree vapor efficiency and point efficiency for nonreactive systems, based on the Lewis's plug-flow model given by Eq. 3. Figure 1 shows that the ratio of Murphree efficiency to point efficiency is strongly dependent on the "stripping factor" λ. The ratio of the Murphree vapor efficiency for plug flow to the point efficiency (complete mixing) (E_{MV}/E_P) is a measure of the influence of mixing. In the case of absorption of a gas with low solubility where the stripping factor is large, the effect of liquid nonmixing is increased. Secondly, Figure 1 shows that the effect of mixing increases as the point efficiency increases.

Gautreaux and O'Connell (1955) proposed that the liquid mixing could be represented as a series of perfectly mixed pools across the tray. Their derivation resulted in the following equation

$$\frac{E_{MV}}{E_P} = \frac{1}{\lambda E_P}\left[\left(1 + \frac{\lambda E_P}{n}\right)^n - 1\right] \qquad (4)$$

where n is the number of mixed pools on the tray.

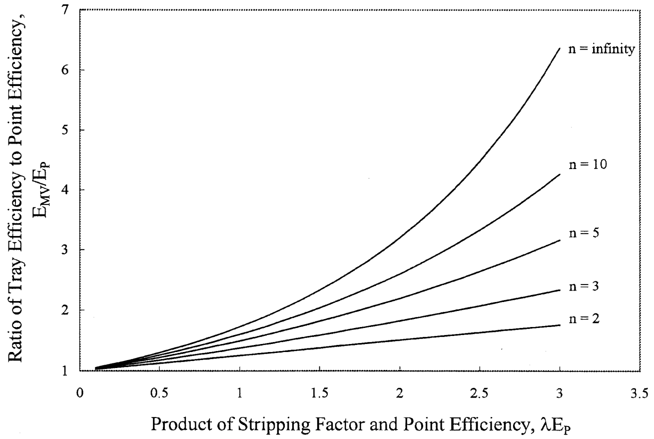

Figure 2. Effect of mixing without chemical reaction, with *n* well-mixed pools (Gautreaux and O'Connell, 1955).

This model covers the entire range of mixing from perfectly mixed ($n = 1$) to plug flow ($n = \infty$). By comparing Eqs. 3 and 4, one can see that the mixed pool model reduces to the plug-flow model in the limit as the number of pools n goes to infinity.

Figure 2 shows the relationship between Murphree vapor efficiency and point efficiency for nonreactive systems, based on Gautreaux and O'Connell's mixed-pool model (Eq. 4). The Murphree efficiency increases with increasing values of the dimensionless parameters λE_P and the number of pools n. The Murphree efficiency continues to increase as the number of pools increases until plug-flow conditions are achieved with $n = \infty$. Figure 2 shows that significant differences between point efficiency and tray efficiency can arise under certain conditions, underscoring the need to account for the effects of liquid mixing during design and scale-up of new processes.

Effect of Liquid Mixing for Reactive Systems

The effect of liquid mixing on the tray efficiency for reactive systems depends on the reaction kinetics and whether or not the reaction can be treated as irreversible or reversible. Each of these possibilities is discussed in the following subsections.

Slow irreversible reactions

The slow irreversible reaction may be represented by a simple case of absorption of component A from the gas stream, followed by a reaction in the liquid phase with a component B to form products

$$\mathrm{A} + \mathrm{B} \rightarrow \text{Products} \qquad (5)$$

For the purpose of this analysis, a slow reaction is one that occurs primarily in the bulk liquid phase and not in the diffusion film. More precisely, the enhancement factor must be near unity.

The enhancement factor using film theory for a first-order irreversible reaction is given by the following equation

(Sherwood et al. (1975), p. 313)

$$\phi = \left(\frac{k_1}{D}\right)^{1/2} \delta \coth\left[\left(\frac{k_1}{D}\right)^{1/2} \delta\right] \tag{6}$$

where ϕ is the mass transfer enhancement factor, $= k_L/k_L^o$, k is the first-order rate constant, D is the diffusivity of component A, and δ is the thickness of liquid diffusion film.

For example, with typical values of 1.0e−09 m^2/s for D, and 5.0e−06 m for δ, Eq. 6 shows that the first-order rate constant k_1 may be as large as 12 s^{-1} before the enhancement factor exceeds 1.1.

In order to proceed further with the analysis of Murphree and point efficiency for irreversible reactive systems, it becomes necessary to define what is meant by the equilibrium vapor-phase concentration y^*. There are two somewhat arbitrary points of view. First, one may consider the long-term equilibrium value which is zero for irreversible reactions. This is the view described by King (1980). From this definition, the tray efficiency would be affected by the "resistance" offered by the finite chemical reaction in the bulk liquid phase. Levenspiel (1999) has also adopted this approach in the kinetic analysis of fluid-fluid reactors. The second interpretation is to consider the phase equilibrium separate from the reaction. In this view, y^* is based on the true nonzero bulk concentration of the component in the liquid. This second view is the approach taken in this article and is commonly employed in most commercial simulation packages that offer an equilibrium stage model with Murphree efficiency for simulating reactive absorption and distillation.

For the case of a perfectly mixed tray, the Murphree and point efficiency are the same when a slow irreversible reaction is occurring on the tray. However, the actual absorption efficiency across the tray for reactive absorbers may be significantly higher for the reactive system, simply because the reaction has lowered the bulk concentration in the liquid and increased the driving force for mass transfer. For example, a perfectly-mixed absorber tray having a point efficiency of 40% would remove 40% of component A from the vapor phase if the reaction reduced the bulk concentration of component A in the liquid to zero. However, in the absence of chemical reaction, the actual absorption would be less than 40% and would depend on the stripping factor and the inlet liquid concentration of component A.

For partially mixed trays, an equation analogous to Eq. 4 for nonreactive systems may be derived using the mixed-pool model with the assumption of simple first-order or pseudo-first-order kinetics, as given by the following rate equation

$$r = kC \tag{7}$$

where r is the rate of reaction of component A and C is the molar concentration of component A.

The equivalent expression for the rate of reaction on pool i is

$$r_i = k_1 \frac{H}{n} x_i \tag{8}$$

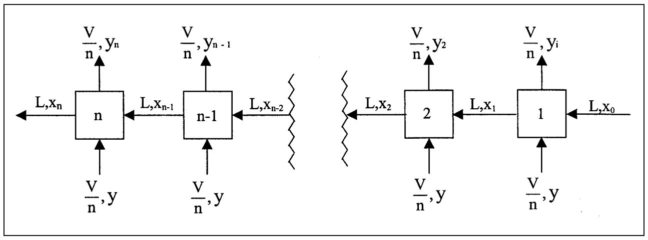

Figure 3. Perfectly mixed stages on a tray.

where H is the molar holdup of liquid on the tray, and x_i is the liquid mole fraction of component A on pool i.

The derivation of an equation analogous to Eq. 4 is based on Figure 3. The derivation begins with the mass balance equation for pool one

$$Lx_o + \frac{V}{n} y = Lx_1 + \frac{V}{n} y_1 + \frac{k_1 H}{n} x_1 \tag{9}$$

This equation is the same as Gautreaux and O'Connell's Eq. 1, except for the reaction term that has been added. From this point on, the derivation essentially follows the same method as the derivation published by Gautreaux and O'Connell (1955) for the nonreactive system, with the exception that the reaction term in Eq. 9 is carried throughout. The detailed derivation is quite lengthy involving many algebraic manipulations and is therefore not shown here. The final result is given below

$$\frac{E_{MV}}{E_P} = \frac{\left[N + \frac{\lambda E_P}{\lambda E_P + N} - \frac{m x_o}{y'}\right]\left[\left(1 + \frac{\lambda E_P + N}{n}\right)^n - 1\right] + N}{\left(1 + \frac{\lambda E_P + N}{n}\right)^n N + \lambda E_P - \left(\frac{m x_o}{y'}\right)(\lambda E_P + N)} \tag{10}$$

where N is the dimensionless Reaction Number $= (k_1 H/L)$, y' is $y_{\text{in}} - b$, b is the intercept of equilibrium line $y = mx + b$, x_o is the inlet liquid mole fraction, and y_{in} is the inlet vapor mole fraction.

Equation 10 is analogous to the Gautreaux and O'Connell's result for the mixed-pool model for nonreactive systems. Equation 10 shows that the Murphree tray efficiency depends on four dimensionless parameters

$$\frac{E_{MV}}{E_P} = f\left(n, \lambda E_P, N, \frac{m x_o}{y'}\right) \tag{11}$$

Two additional parameters have appeared with the introduction of chemical reaction. The dimensionless reaction number N characterizes the relative importance of chemical reaction on the tray. It is equal to the ratio of the liquid holdup time to the approximate time-scale for chemical reaction as given by the reciprocal of the first-order rate constant. The fourth parameter mx_o/y' shows that the Murphree tray efficiency for reactive systems depends additionally on the inlet liquid and vapor compositions.

As expected, the model given by Eq. 10 reduces to the nonreactive model (Eq. 4), as the reaction number N approaches zero. Also, as the number of pools on the tray increases, plug flow is approached on the tray. The equation for the case of plug flow is obtained by taking the limit as n approaches infinity

$$\frac{E_{MV}}{E_P} = \frac{\left[N + \frac{\lambda E_P}{\lambda E_P + N} - \frac{mx_o}{y'}\right]\left[\exp\left(\lambda E_P + N\right) - 1\right] + N}{\exp\left(\lambda E_P + N\right)N + \lambda E_P - \left(\frac{mx_o}{y'}\right)\left(\lambda E_P + N\right)} \tag{12}$$

This equation is analogous to Eq. 3 derived by Lewis for plug flow of nonreactive systems. Inspection of Eq. 12 shows that Eq. 3 is recovered in the limit as the reaction number goes to zero.

Equations 10 and 12 also show that E_{MV}/E_P approaches one for slow reactions as the reaction number grows large (ignoring, for the moment, any enhancement of mass transfer that would occur as the chemical reaction eventually shifts from the bulk liquid to the diffusion film). As a result, there is an intermediate regime of reaction rates for both reversible and irreversible reactions where there is no effect of mixing on the tray, even for plug flow across the tray. If a standard mixing model (such as the AIChE model) for nonreactive systems were applied to a reactive system in this regime to calculate the Murphree tray efficiency from point efficiency data, significant errors would result.

Figure 4 shows how E_{MV}/E_P varies with λE_P and the reaction number N for an example case for two mixed pools on the tray, with the inlet concentration of component A in the liquid equal to zero. Figure 4 shows that E_{MV}/E_P increases with λE_P, as did the example for the nonreactive case given in Figure 2. More importantly, the tray efficiency declines as the reaction number N increases until $E_{MV}/E_P = 1$ and the tray efficiency and point efficiency become equal. Figure 5 shows the same case for plug-flow conditions on the tray. The resulting trends are very similar, with the primary difference being that the magnitude of E_{MV}/E_P is larger.

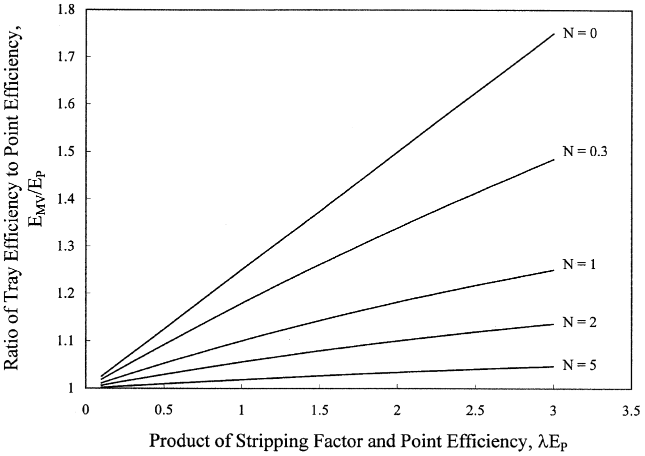

Figure 4. Effect of slow irreversible reaction: two mixed stages ($n = 2$) with $mx_o/y' = 0$.

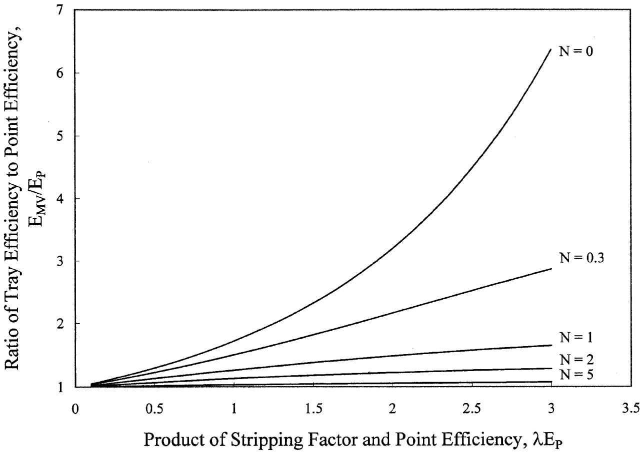

Figure 5. Effect of slow irreversible reaction: plug flow with $mx_o/y' = 0$.

The trends shown in Figures 4 and 5 are rather well behaved as a result of the inlet liquid concentration being zero. For real systems, however, the inlet concentration of component A on a given tray in the column would not be zero. If the quantity mx_o/y' is small compared to unity, then the model predictions are similar to that predicted for zero inlet concentration. This condition is likely to be met in reactive absorbers if the preceding tray allows the reaction to near completion before the liquid is fed to the next tray. [The quantity mx_o/y' is unity if the inlet vapor is in equilibrium with the inlet liquid, because $y' = y - b$ and, by definition, y and x_o are in equilibrium if $y = mx_o + b$.]

If the quantity mx_o/y' becomes larger, however, the relationship between tray efficiency and point efficiency becomes more difficult to interpret. The tray efficiency may become less than the point efficiency, and may even be a *negative* number. The reason for this seemingly anomolous behavior becomes clear upon inspection of the concentration gradients and mass-transfer driving forces along the liquid flow path across the tray. For large inlet concentrations coupled with high reaction numbers, it is possible to have both stripping and absorption taking place on the same tray. If the quantity mx_o/y' is large enough, component A will be stripped near the liquid inlet. At the same time, the reaction may reduce the concentration to extremely low levels near the liquid outlet such that absorption may be occurring. In this case, it is possible for the tray efficiency to be negative. Klemola (1998) also noted this phenomenon for tray efficiencies with reactive systems. This type of behavior suggests that the tray efficiency model is severely limited for many reactive systems and underscores the need for more rigorous rate-based models to approach the general problem of reactive distillation or absorption.

Slow reversible reactions

For slow reversible reactions, the analysis of the effect of mixing on the tray efficiency becomes considerably more complex. The need to model these systems appears to be increasing as industrial applications, such as reactive distillation for production of ethyl acetate, become more common (Lee and Dudukovic, 1998). As in the case of slow irreversible reaction, the chemical reaction dampens the gradients in composition across the tray causing the Murphree efficiency and point efficiency to become more nearly equal. However, the effect is lessened since the concentration of the absorbed component is not reduced to essentially negligible levels as in the case of an irreversible reaction.

For the general case of reversible reactions involving several components participating in both vapor-liquid mass-transfer and chemical reaction, the analysis of mixing effects on trays is not amenable to the techniques used for the simple irreversible reactions previously described. However, for the simplest case of reversible reaction, tray efficiency expressions analogous to Eqs. 10 and 12 can be derived if certain simplifying assumptions are used. The derivation begins by considering the following model for reversible reaction on a tray

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{C} \tag{13}$$

The elementary kinetic rate expressions are assumed to be of the form

$$r_f = k_f C_A C_B \tag{14}$$

$$r_b = k_b C_C \tag{15}$$

where r_f and r_b are the forward and backward reaction rates, respectively, and k_f and k_b are the forward and backward rate coefficients.

It can be shown that if the concentrations of B and C are constant, then the rate of reaction of component A can be expressed in terms of a driving force between the concentration of A, C_A, and the equilibrium concentration of A, $C_{A\mathrm{eq}}$

$$r = k_f (C_A - C_{A\mathrm{eq}}) \tag{16}$$

With these simplifying assumptions, it is possible to proceed with the derivation as with the case of irreversible reaction. The analogous expression for the mass balance on the first pool is, therefore

$$Lx_o + \frac{V}{n} y = Lx_1 + \frac{V}{n} y_1 + \frac{k_1 H}{n}(x_1 - x_{\mathrm{eq}}) \tag{17}$$

where the mole fraction corresponding to chemical equilibrium is x_{eq}.

The derivation is essentially the same as that employed previously and leads to the following expression for slow reversible reactions using the mixed-pool model

$$\frac{E_{MV}}{E_P} = \frac{\left(1+\frac{\alpha}{n}\right)^n (\beta - \alpha) + \left[\left(1+\frac{\alpha}{n}\right)^n - 1\right]\gamma}{\left(1+\frac{\alpha}{n}\right)^n (\beta - \alpha) + \alpha\gamma} \tag{18}$$

where

$$\alpha = \lambda E_P + N \tag{19}$$

$$\beta = \lambda E_P + N\left(\frac{mx_{\mathrm{eq}}}{y'}\right) \tag{20}$$

$$\gamma = \left(\frac{mx_o}{y'}\right) - \frac{\beta}{\alpha} \tag{21}$$

Equation 18 for the simplified reversible reaction case is analogous to the Gautreaux and O'Connell result for the mixed-pool model for nonreactive systems. Equation 18 shows that the Murphree tray efficiency for this case depends on five dimensionless parameters

$$\frac{E_{MV}}{E_P} = f\left(n, \lambda E_P, N, \frac{mx_o}{y'}, \frac{mx_{\mathrm{eq}}}{y'}\right) \tag{22}$$

The fourth and fifth parameters mx_o/y' and mx_{eq}/y' show that the Murphree tray efficiency for reversible reactive systems depends additionally on the inlet liquid and vapor compositions, as well as the equilibrium value of x_{eq}.

The model given by Eq. 18 reduces to the irreversible reaction model given by Eq. 10 when x_{eq} approaches zero. Equation 18 further reduces to the nonreactive model (Eq. 4) as the reaction number N approaches zero. As with the case for irreversible reaction, $E_{MV}/E_P = 1$ in the limit as N becomes large.

Also, as the number of pools on the tray increases, plug flow is approached on the tray. The equation for the case of plug flow with slow reversible reaction is obtained by taking the limit as n approaches infinity

$$\frac{E_{MV}}{E_P} = \frac{\exp(\alpha)(\beta - \alpha) + [\exp(\alpha) - 1]\gamma}{\exp(\alpha)(\beta - \alpha) + \alpha\gamma} \tag{23}$$

This equation is also analogous to Eq. 3 derived by Lewis for plug flow of nonreactive systems. Inspection of Eq. 23 shows that Lewis's equation (Eq. 3) is recovered in the limit as the reaction number goes to zero.

Figures 6 and 7 show the dependence of E_{MV}/E_P on λE_P and the reaction number N for the case of two mixed pools and plug flow conditions, respectively. The figures were based on an example case with the quantity $mx_{\mathrm{eq}}/y' = 0.5$. As with the case for irreversible reaction, E_{MV}/E_P increases as the flow conditions approach plug flow.

Compared to Figures 4 and 5 for the irreversible reaction case, the variation in E_{MV}/E_P is more complex. For low values of λE_P, E_{MV}/E_P increases as the reaction number increases, and then eventually approaches one as N becomes large. For larger values of λE_P, the behavior is more like the irreversible case where E_{MV}/E_P declines monotonically with the increase in reaction number. Again, the more complicated behavior is derived from the possibility of opposing driving forces for mass transfer. An additional complexity is introduced with the possibility of reversible reactions since the reaction may proceed in both directions, either opposing or increasing the driving force for mass transfer depending

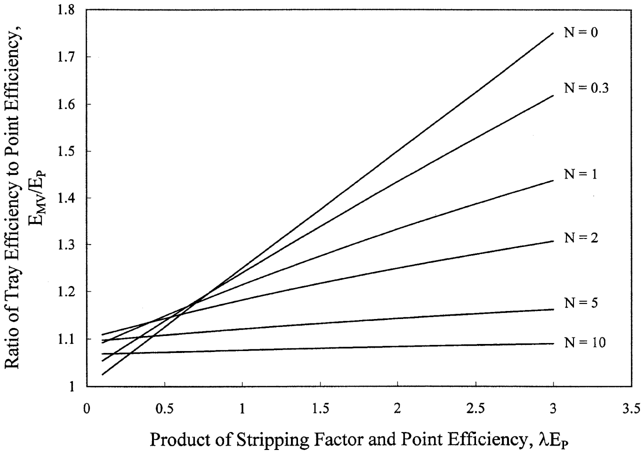

Figure 6. Effect of slow reversible reaction: two mixed stages ($n=2$) with $mx_0/y'=0$ and $mx_{eq}/y'=0.5$.

on the local concentrations in the liquid as it flows across the tray.

Fast reactions occurring in the diffusion film

As shown in Figure 5, the Murphree Efficiency and point efficiency become equal as the dimensionless reaction number becomes large. Eventually, the reaction will begin to enhance mass transfer in the diffusion film, causing the point efficiency to increase. For the simple first-order kinetic model given by Eq. 7, the enhancement factor given by Eq. 6 is independent of the liquid composition. (This result is correct provided that the first-order rate coefficient, liquid diffusivity, and liquid-film mass-transfer coefficient can be treated as independent of liquid composition.) In this case, the Murphree efficiency and point efficiency will continue to be equal and independent of the degree of mixing. However, both quantities will continue to increase with the first-order rate coefficient as the enhancement factor increases.

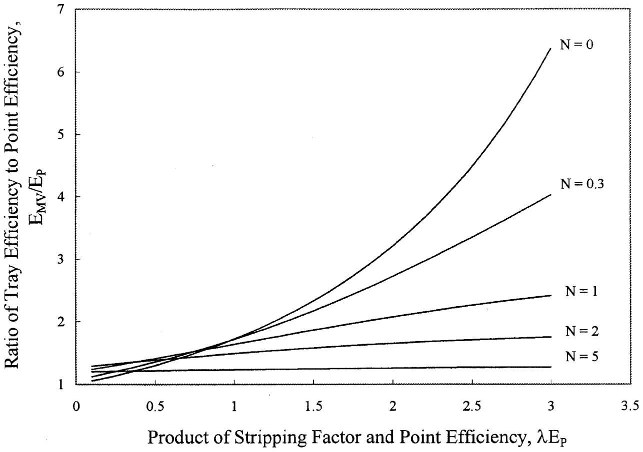

Figure 7. Effect of slow reversible reaction: plug flow with $mx_0/y'=0$ and $mx_{eq}/y'=0.5$.

However, if a more realistic pseudo-first-order model is used, the enhancement factor will depend on the concentration of the component B

$$r = k_2 c_B c_A \tag{24}$$

As liquid flows across the tray, the concentration of species B will decrease, causing the enhancement factor and point efficiency to decrease. Pohorecki and Szewczyk (1978) studied the case of pseudo-first-order reaction kinetics on a tray for fast irreversible reactions and showed that the point efficiency is given by the following equation

$$E_P = 1 - \exp\left(-K\sqrt{c_B}\right) \tag{25}$$

where

$$K = \frac{\sqrt{Dk_2}\, h_f a}{mG_M} \tag{26}$$

h_f is the height of froth on tray, a is the interfacial area per unit volume of froth, and G_M is the molar gas flow rate per unit of tray area.

To calculate the tray efficiency from the above point efficiency model, it is necessary to integrate the mass balance equation for component B over the length of the tray. The resulting concentration gradient for component B is then used to calculate the local point efficiencies and outlet vapor composition, which finally allows calculation of the tray efficiency. Pohorecki and Moniuk (1983a,b) were unable to solve the mass balance equations analytically, but did provide a numerical solution for the plug-flow case and for a longitudinal dispersion coefficient model for both reversible and irreversible reactions.

Conclusions

In conclusion, it has been shown that the conversion of point efficiency to tray efficiency for design and scale-up must be executed with caution when dealing with reactive systems. An analytical representation of simple first-order kinetics has been developed for both irreversible and reversible slow reactions, showing how the tray efficiency can be related to the point efficiency for these systems. Conventional methods of estimating point efficiency can be used with these equations to predict tray efficiencies for nonideal mixing using the mixed pool models. The same method could be extended to other mixing models such as the eddy diffusivity model. In certain applications, this correction could dominate the scale-up calculations and subsequent sizing of columns.

For slow reversible reactions and fast reversible or irreversible reactions, the effect of coupling the chemical reaction with mixing again appears to be important in converting point efficiency to tray efficiency. However, by their nature, these systems are much more complex and should probably be modeled using more rigorous rate-based approaches. Seemingly anomolous behavior, such as negative tray efficiency, may arise under certain conditions as shown in this analysis. Nevertheless, the analysis given in this article shows some of the insights into how the effects of reaction impact the relationship of point and tray efficiencies, even for the more complex reversible and fast-reaction systems.

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Notation

a = interfacial area per unit volume of froth
b = intercept of equilibrium line $y = mx + b$
C = molar concentration of component, mol/vol.
D = diffusivity of component A
E_P = Murphree vapor point efficiency
E_{MV} = Murphree vapor tray efficiency
G_M = molar gas-flow rate per unit of tray area
H = molar holdup on tray, moles
i = index for the ith mixed pool on the tray
h_f = height of froth on tray
k_1 = first-order rate coefficient, defined by Eq. 7
k_2 = second-order rate coefficient, defined by Eq. 24
k_b = backward rate coefficient defined by Eq. 15
k_f = forward rate coefficient defined by Eq. 14
k_L = mass-transfer coefficient with chemical reaction
k_L^o = mass-transfer coefficient for purely physical absorption
K = quantity defined by Eq. 26
L = liquid phase molar flow rate
m = slope of equilibrium line $y = mx + b$
n = number of mixed pools on a tray
N = reaction number, defined as $k_1 H/L$
r = rate of reaction, mol/vol./time
V = vapor phase molar flow rate
x = liquid phase mole fraction
x_o = liquid phase mole fraction at tray inlet
x_{eq} = liquid phase mole fraction at chemical equilibrium
y_{in} = inlet vapor phase mole fraction
y_{out} = outlet vapor phase mole fraction
y^* = equilibrium vapor phase mole fraction
y = vapor phase mole fraction
y' = defined as the inlet vapor phase mole fraction y minus b
α = quantity defined by Eq. 19
β = quantity defined by Eq. 20
γ = quantity defined by Eq. 21
δ = thickness of mass-transfer diffusion film
λ = stripping factor, mV/L
ϕ = enhancement factor, $= k_L/k_L^o$ and defined by Eq. 6

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