

Kinetic Azeotropy and Design of Reactive Distillation Columns

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The reactive fixed points in the distillation maps of a reactive distillation column (RDC) with kinetically controlled reactions are identified and their role in deciding the design feasibility has been elucidated. The fixed points at which both reaction and distillation vectors have zero magnitudes correspond to the equilibrium fixed point. It is known that the relative positions of these points for the rectifying and stripping sections determine the value of the minimum reflux ratio. However, apart from these fixed points, there are certain fixed points in the distillation map at which, though the reaction and distillation vectors have nonzero magnitudes, they nullify the effects of each other. These points correspond to the kinetic fixed points and have a special significance. Their positions have direct influence on the feasible product composition. A simple example of an ideal ternary system undergoing a reaction $2B \rightleftharpoons A + C$ has been illustrated to show the importance of kinetic azeotropy in the design aspects of RDC.

Introduction

The geometric theory based on the topological concept has been successfully used in the past for the design of nonreactive binary and multicomponent distillation columns.^{1–3} This method is based on the residue curve maps of the liquid-phase compositions of a c -component system, drawn in a $(c - 1)$ dimension Euclidean space. Barbosa and Doherty extended this concept for the first time to design the reactive distillation columns (RDC) with the equilibrium-controlled reactions.^{4–6} These reactions are very fast and the design procedure is simplified by deriving the model equations in the form of new transformed composition variables. However, for considerably slow reactions (i.e., for kinetically controlled reactions) such a simplification is not possible. The first step in a direction to design RDC with such reactions has been presented recently by Buzad and Doherty by illustrating an example of a three-component system.⁶ The model was based on the visualization of RDC as the series of back-mixed reactors. Their approach has been further extended by Mahajani and Kolah to a column in the absence of back-mixing for the same kind of reactive system.⁷

The design method is highly influenced by certain points, called “fixed points”, in the distillation maps. These are the points in the vicinity of which the composition profiles behave in a peculiar manner. In the case of a pinch node, the profiles merge into the fixed point for certain values of the design parameters, whereas if the fixed point is a saddle type, then the profiles approach the point very closely and change their course without actually passing through the fixed point. For a three-component system in RDC, there exists at least one such fixed point for each section at certain values of the design parameters such as the reflux ratio, reboil ratio, holdup, and reaction rate constants. The positions of such points decide the feasibility of a design for the desired operation. Hence, it is very important to identify such fixed points in the distillation maps and study the theory behind their existence.

A theory based on vector algebra to prove the existence of the fixed points in distillation maps has been

proposed by Hauan and Lein.⁸ The behavior of the reactive distillation process can be studied by evaluating three different vectors associated with reaction, separation, and mixing. The fixed point will exist when these three vectors nullify the effect of each other. In the most general case, if all the vectors have nonzero magnitudes and if they nullify the effect of each other, the fixed point corresponds to the kinetic fixed point. Whereas if the reaction and distillation vectors have zero magnitudes, then the point may be referred to as the equilibrium fixed point. In the present work, both the equilibrium and kinetic fixed points in the distillation map of a reactive distillation process in RDC are identified and it has been shown how these points influence the feasibility of a design.

A Design Problem

The system under consideration is a single-feed RDC with a reaction of the type shown in eq 1:



The order of volatility is $A > B > C$. The components A, B, and C are denoted by numbers 1, 2, and 3, respectively. The schematic representation of the problem is shown in Figure 1. In a design problem, the input and output compositions are known and it is required to determine the optimal column dimensions by fixing the various design parameters such as the reflux ratio, holdup, and so forth.

In all the computations performed in this exercise, the values of the relative volatilities of A, B, and C are 5, 3, and 1, respectively, and the equilibrium constant of the reaction (K) is 0.25.

Design Equations

The model equations for the design of a RDC can be formulated on the basis of either a discrete dynamic approach or a continuous dynamic approach. In the discrete dynamic approach, the column is viewed as a system of back-mixed reactors placed in a series.⁶ The equations based on the continuous dynamic approach

take into account the plug flow behavior of the packed columns, which have been formulated in our earlier work.⁷ The discussion in this article is mainly focused on the latter approach though the basic underlying theory is applicable to both the design methods. The model equations in the dimensionless form, based on the continuous dynamic approach, are presented below. The detailed derivation of these equations with the significance of the different parameters involved has been presented elsewhere.⁷

Vapor-side mass balance for the rectifying and stripping sections:

$$\frac{dy_i}{d\xi} = -\frac{\psi_i}{HTU^V} \quad i = 1, 3 \quad (2)$$

Liquid-side mass balance in the rectifying section:

$$\frac{dx_i}{d\xi} = -\frac{\psi_i}{HTU^V} \left(\frac{RF + 1}{RF} \right) - Da \frac{F}{V} \left(\frac{RF + 1}{RF} \right) \left(x_2^2 - \frac{x_1 x_3}{K} \right) \quad i = 1, 3 \quad (3)$$

$$RF = \frac{L}{D}, \quad \frac{D}{B} = \frac{(x_{F,1} - x_{F,3}) - (x_{B,1} - x_{B,3})}{(x_{D,1} - x_{D,3}) - (x_{F,1} - x_{F,3})}, \quad \frac{F}{V} = \frac{1 + B/D}{1 + RF} = \frac{1 + D/B}{SF} \quad (4)$$

Liquid-side mass balance in the stripping section:

$$\frac{dx_i}{d\xi} = -\frac{\psi_i}{HTU^V} \left(\frac{SF + 1}{SF} \right) - Da \frac{F}{L + F} \left(x_2^2 - \frac{x_1 x_3}{K} \right) \quad i = 1, 3 \quad (5)$$

$$SF = \frac{V}{B}, \quad \frac{F}{F + L} = \frac{1 + B/D}{1 + RF + B/D} = \frac{1 + D/B}{1 + SF} \quad (6)$$

Vapor-liquid equilibrium at the interface in terms of the bulk compositions:

$$y_i - \psi_i = f_i(\psi_i \beta + x_i) \quad i = 1, 3 \quad (7)$$

The dimensionless numbers are

$$Da = \frac{A_c H C_t^L I}{(1/k)F} \quad (8)$$

$$\frac{1}{HTU^V} = \frac{a A_c}{V} H k_v C_t^V \quad (9)$$

$$\psi_i = \frac{J_i^V}{C_t^V k_v} \quad (10)$$

$$\beta = \frac{C_t^V k_v}{C_t^L k_L} \quad (11)$$

where RF and SF are the reflux and reboil ratios, respectively. Da , the Damkohler number, decides the extent of the reaction and HTU^V is the parameter which determines the efficiency associated with the process of nonreactive distillation. ξ is the nondimensional axial coordinate given by $\xi = z/H$, where H is the length of the zone of the packed column for which concentration profiles are to be determined. ψ denotes the dimension-

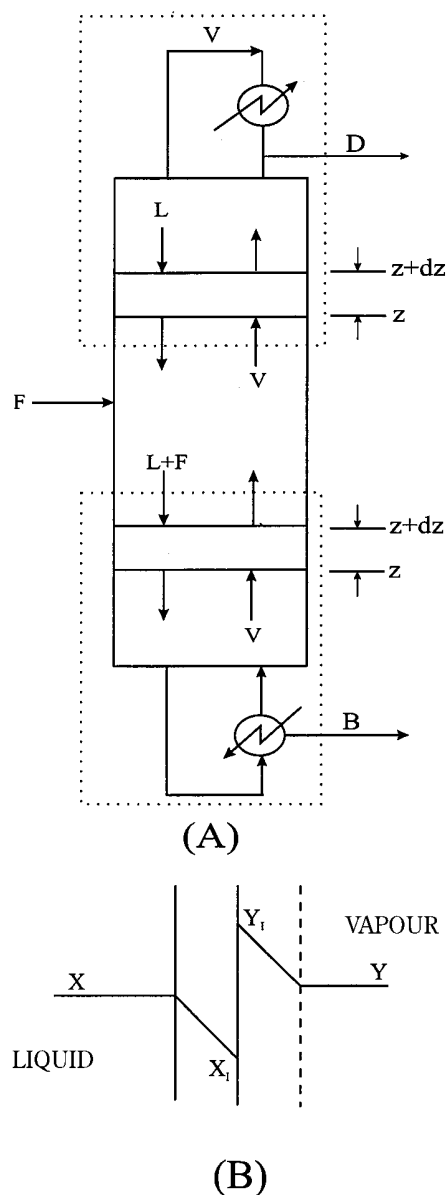


Figure 1. (A) Schematic representation of a reactive distillation column. (B) Gas-liquid diffusion film.

less flux of the component in the vapor phase and may be related to the liquid- and vapor-phase compositions by the following equation:

$$\psi_i = (y_i - y_i^J) = \left(\frac{(x_i^J - x_i)}{\beta} \right) \quad i = 1, 3 \quad (12)$$

In comparison to the discrete dynamic approach, the above method needs two additional equations of operating curves to be solved for the vapor phase, apart from those for the liquid phase wherein the actual reaction takes place. The main underlying assumptions are that the internal reflux and reboil ratios remain unchanged along the height of the column, the enthalpy associated with the reaction, mixing, and loss through the column wall is negligible, and the feed enters into the column at its bubble point.

In a design problem, the first step is to choose the set of end compositions, which is followed by the determination of the minimum reflux ratio and compu-

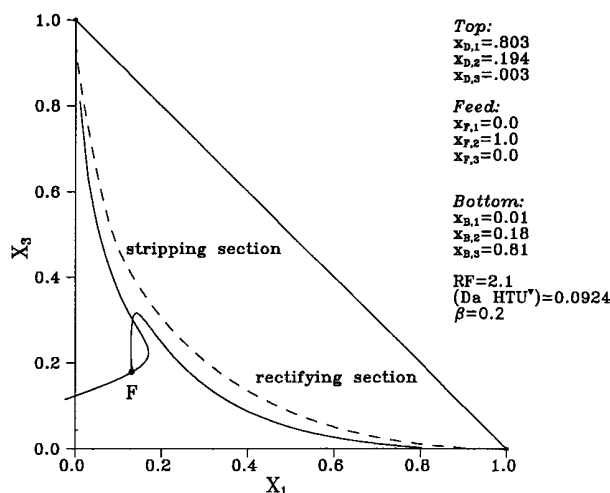


Figure 2. Composition profiles for rectifying and stripping sections for the specified conditions (feasible design).

tations for the column dimensions for the known values of liquid holdup and mass-transfer parameters. The convenient way to deal with the choice of end compositions for the present system has been described elsewhere.⁶ Out of the six output compositions, two top and two bottom compositions have to be fixed independently. Since the ratio of the distillate to bottoms molar flow rate (D/B) is directly related to the quantities such as ($x_{D,1} - x_{D,3}$) and ($x_{B,3} - x_{B,1}$) (see eq 4) and since these quantities decide the value of the minimum reflux ratio through the positions of the equilibrium fixed points, it is advisable to fix the values of these quantities. Once the desired values are assigned to ($x_{D,3} - x_{D,1}$) and ($x_{B,3} - x_{B,1}$), one is left with the choice of only one individual composition of distillate stream (e.g., $x_{D,3}$) and one individual composition of the bottom stream (e.g., $x_{B,1}$). It will be shown in the latter part of this article how the choice of these individual compositions is again governed by the positions of the fixed points in the distillation maps of the liquid compositions.

The design procedure involves the simultaneous solution of eqs 2–5 for the rectifying and stripping sections at the desired values of the end compositions (as the boundary conditions) and the known values of design and operating parameters such as the reflux ratio, Da , HTU^V , and β . A design is said to be feasible when the profiles determined by the above procedure intersect in the positive reaction zone of the distillation map. The typical composition profiles of both the sections corresponding to a feasible design are shown in Figure 2. Point F corresponds to the composition of the feed position. Once the feasibility criterion is fulfilled, a sufficient condition obtained by the overall material balance is required to be satisfied. From the overall material balance, we get

$$RXN_i = \frac{D/B}{D/B + 1} x_{D,i} + \frac{1}{D/B + 1} x_{B,i} - x_{F,i} \quad i = 1, 3 \quad (13)$$

The value of the total reaction term (RXN_i) from the overall material balance should match the value calculated by integration of the reaction term over the entire column as follows:

$$RXN_i^M = \int_0^{\xi_r} r_i^r d\xi + \int_0^{\xi_s} r_i^s d\xi \quad i = 1, 3 \quad (14)$$

where

$$r_i = Da \left(x_2^2 - \frac{x_1 x_3}{K} \right) \quad i = 1, 3 \quad (15)$$

Fixed Points

The fixed points are those points in the distillation map at the vicinity of which the liquid compositions along the column height change infinitesimally and, as mentioned by Haun and Lien,⁸ the vectors associated with different processes such as distillation, reaction, and mixing nullify the effect of each other. In other words, at the fixed-point composition, the right-hand sides of eqs 3 and 5 are equal to zero. That is,

$$-\frac{\psi_i}{HTU^V} \left(\frac{RF + 1}{RF} \right) - Da \frac{F}{V} \left(\frac{RF + 1}{RF} \right) \left(x_2^2 - \frac{x_1 x_3}{K} \right) = 0 \quad i = 1, 3 \quad (16)$$

$$-\frac{\psi_i}{HTU^V} \left(\frac{SF + 1}{SF} \right) - Da \frac{F}{L + F} \left(x_2^2 - \frac{x_1 x_3}{K} \right) = 0 \quad i = 1, 3 \quad (17)$$

In the above equations, the first term on the left-hand side corresponds to a change in the composition due to mass transfer occurred by distillation and the second term arises as a result of the reaction. It has been shown in our earlier work⁷ that when the equation for the composition profile of either the rectifying or stripping section (eq 3 or 5) is solved for the different values of the product ($Da \times HTU^V$), there exists a singular critical value of this product for which the composition profile of that particular section nearly touches the fixed point. The stability and nature of such a fixed point in the residue curve or distillation maps is normally determined by evaluating the eigenvalues of the Jacobin of the functions that appear on the left-hand side of the differential equation. In the present problem (see eqs 16 and 17), it is not possible to derive a general expression for the corresponding eigenvalues. Hence, the nature of the fixed point cannot be determined without solving the differential equations of the composition profiles. In all the cases, for the present reactive system, it has been observed that the fixed points are of the saddle type.

The earlier work on the design of a RDC illustrated with the three-component kinetically controlled reaction is mainly concerned about the existence and significance of only one type of fixed saddles at which magnitudes of both, reaction and distillation, vectors approach zero.^{6,7} This point is referred to, in the current discussion, as the equilibrium fixed point (EFP). The position of the EFP, irrespective of the approach followed (discrete or continuous), remains the same for the given values of the reflux ratio, ($x_{D,1} - x_{D,3}$) and ($x_{B,3} - x_{B,1}$). Apart from EFPs there exist fixed saddles at which the distillation and reaction vectors having nonzero magnitudes nullify the effect of each other. It will be shown in the subsequent sections of the article how these saddles, referred to as the kinetic fixed points (KFP), affect the positions of the separating manifolds of both stripping and rectifying sections and, in turn, influence a possible feasible design.

An azeotropic composition for a system results from the physicochemical properties of the system compo-

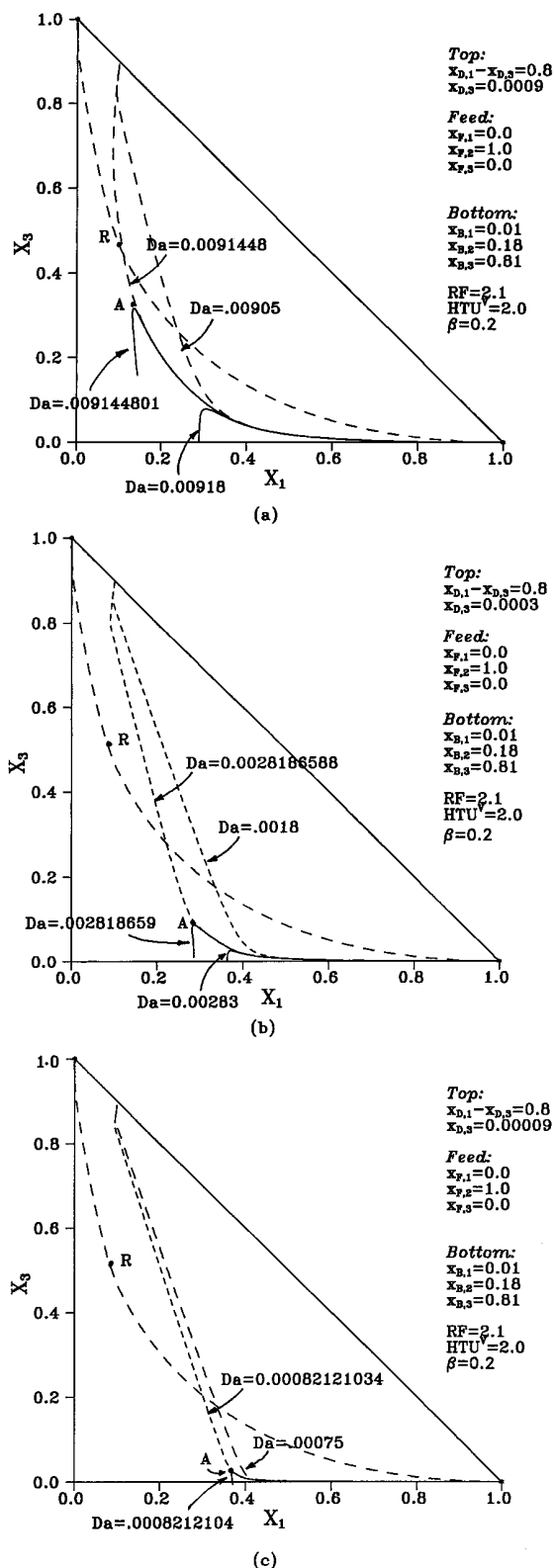


Figure 3. Residue curve maps showing composition profiles of a rectifying and stripping section at different values of $(Da \times HTU^V)$ to identify the fixed points with varying top compositions. A: Fixed saddle.

nents. The fixed points in the present exercise are the functions of not only the physicochemical properties of the components but also the design parameters such as the reflux ratio, hold up, and the end compositions.

Hence, instead of calling these points *azeotropes*, they are referred to as either the equilibrium or kinetic fixed points.

Figure 3, parts a–c, shows the composition profiles of the rectifying section for different values of the distillate composition under otherwise identical values of the reflux ratio and bottom composition. In every case, the composition profiles are plotted for different values of $(Da \times HTU^V)$. It must be noted here that, only for the computational convenience, the values of Da are varied by keeping HTU^V constant in each case though it is the product $(Da \times HTU^V)$ which determines the nature of the composition profiles.⁷ As mentioned earlier, it is clear from these figures that, at a certain critical value of the product $(Da \times HTU^V)$, the composition profile travels down very close toward the fixed saddle and changes its course thereafter. If the value of $(Da \times HTU^V)$ is less than the critical value, then the profile escapes out of the composition triangle through the upper part of the composition triangle (i.e., the negative reaction zone in which the reaction takes place in the reverse direction). If the value of $(Da \times HTU^V)$ is greater than the critical value, the profile remains in the positive reaction zone before leaving the composition triangle. One should manipulate the design parameters in such a way that the profiles strictly remain in the positive reaction zone. Hence, for a feasible design, the values of $(Da \times HTU^V)$ for both the sections should always be greater than or equal to their critical values. It can be seen from Figure 3, parts a–c, that with a reduction in the value of the distillate composition of the least volatile component ($x_{D,3}$) a shift in the fixed saddle takes place. The fixed saddle (A) moves away from the position of the EFP (R in Figure 3). For the considerably large values of $x_{D,3}$, the fixed saddle is very close to the reaction equilibrium curve and is insensitive of the value of $x_{D,3}$. In other words, at higher values of $x_{D,3}$, the fixed saddle tends to coincide with the EFP on the reaction equilibrium curve. This fixed saddle is nothing but the kinetic fixed point (KFP).

As defined by Rev,⁹ for batch reactive distillation, the reactive and kinetic azeotropes are the fixed stable points at which the composition does not change with time. Since, in the case of the RDC, the fixed points are of the saddle type, the compositions corresponding to these points are never realized anywhere in the RDC. However, their positions certainly help in deciding the end compositions and the values of the design parameters.

In our earlier work,⁷ it has been shown how the values of ψ , which represent the extent of mass transfer due to distillation, approach zero near the vicinity of the EFP. Now let us examine the values of ψ in the vicinity of the KFP of the rectifying section. According to the condition of kinetic azeotropy, the distillation vector should nullify the reaction vector, that is,

$$-\frac{1}{HTU^V} \left(\frac{RF+1}{RF} \right) [\psi_i] = Da \frac{F}{V} \left(\frac{RF+1}{RF} \right) \left(x_2^2 - \frac{x_1 x_3}{K} \right) [v_i] \quad i = 1-3 \quad (18)$$

Hence,

$$P[\psi]^T = [1 \quad -2 \quad 1] \quad i = 1-3 \quad (19)$$

where P is a scalar. The right-hand side of eq 19 is the matrix of the stoichiometric coefficients (see eq 1).

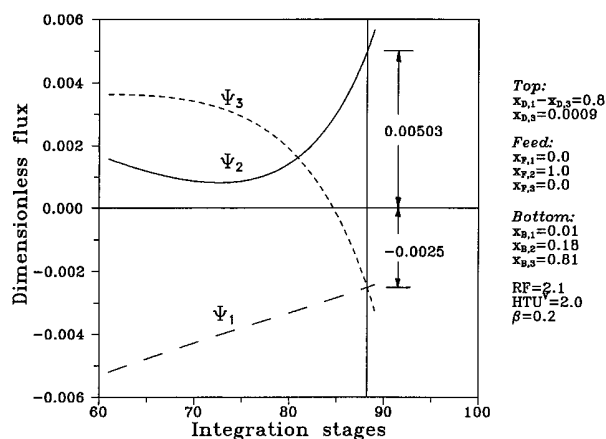


Figure 4. Dimensionless flux vs integration stages.

Figure 4 shows the profile of the dimensionless flux along the column height. The abscissa of the plot in Figure 4 represents the number of integration stages (n) which is proportional to the actual column height. The column height in terms of integration stages may be expressed as $n[V/(HTU^V a A_c k_v C_t^V)]$. These profiles correspond to the distillation map shown in Figure 3a. The KFP is realized very close to the 87th stage in the column. At this stage, $[\psi]^T = [-0.0025 \ 0.00503 \ -0.0025]$. Hence, the condition mentioned in eq 19 is nearly satisfied. Similarly, one can prove the existence of the KFP on the basis of the profiles of ψ corresponding to the distillation maps in Figure 3, parts b and c, and at the conditions mentioned therein.

Though the earlier work on the design of the RDC explains the importance and significance of the position of the EFP, the existence of the KFP with its implications has not been discussed in detail.

Kinetic Azeotropy

The kinetic fixed points (KFP) are realized in a vapor-liquid kinetically controlled reactive system. At the composition of KFP, the vectors associated with the different processes such as the reaction, distillation, and mixing have nonzero magnitudes but result in a null vector upon their addition. In the present system, unlike the position of the EFP, the exact position of the KFP cannot be determined until all the equations for the composition profiles are solved for the known values of the end compositions and the other parameters. In the case of EFP, the fixed point always satisfies an additional constraint of reaction equilibrium, and hence it can be determined a priori (i.e., without solving actual equations for the composition profiles). The position of the EFP is influenced only by the reflux ratio and the quantities such as $(x_{D,1} - x_{D,3})$ and $(x_{B,3} - x_{B,1})$. However, the position of the KFP, resulting from the nonzero magnitudes of the reaction and distillation vectors, is also related to the parameters which contribute substantially toward the magnitudes of these vectors. These parameters are HTU^V and Da .

As we know, the condition of kinetic azeotropy (i.e., eqs 16 and 17) has to be satisfied by the composition corresponding to the KFP of that section. Along with these equations, the composition at the KFP should also satisfy the following equations of material balance taken

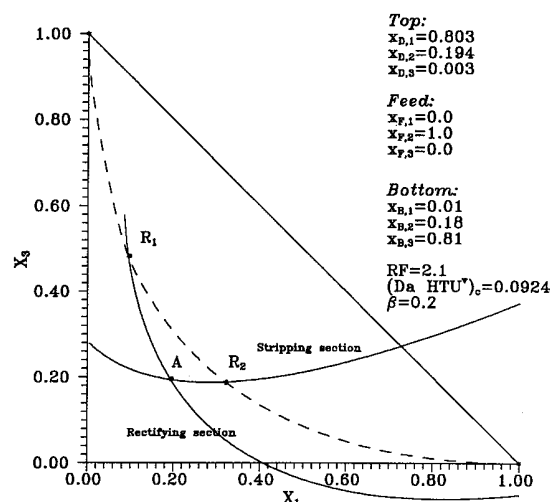


Figure 5. Kinetic azeotropy curves for rectifying and stripping sections.

across the boundaries shown in Figure 1. These are as follows:

rectifying section

$$y_i - \left(\frac{RF}{RF+1} \right) x_i - \left(\frac{1}{RF+1} \right) x_{D,i} + \int_0^{\xi_r} r_i^r d\xi = 0 \quad i = 1, 3 \quad (20)$$

stripping section

$$y_i - \left(\frac{SF+1}{SF} \right) x_i + \left(\frac{1}{SF} \right) x_{D,i} - \int_0^{\xi_s} r_i^s d\xi = 0 \quad i = 1, 3 \quad (21)$$

The reaction term in the above equations can be eliminated by subtracting eqs 20 and 21 for $i=1$ from eqs 20 and 21 for $i=3$, respectively.

$$(y_1 - y_3) - \left(\frac{RF}{RF+1} \right) (x_1 - x_3) - \left(\frac{1}{RF+1} \right) (x_{D,1} - x_{D,3}) = 0 \quad (22)$$

$$(y_1 - y_3) - \left(\frac{SF+1}{SF} \right) (x_1 - x_3) + \left(\frac{1}{SF} \right) (x_{B,1} - x_{B,3}) = 0 \quad (23)$$

Hence, eqs 7, 16, and 22 together form a locus of points in the composition triangle, which satisfy the necessary condition of the kinetic azeotropy for the rectifying section. Similarly, eqs 7, 17, and 23 represent the corresponding locus for the stripping section. A simultaneous solution of these equations leads to the azeotropy curves for both the sections, shown in Figure 5. It can be seen from the figure that the curves of kinetic azeotropy pass through the EFPs (R_1 and R_2) of the respective sections. Hence, the EFP is a special case of kinetic azeotropy. For the given end compositions and reflux ratio, the KFPs of the rectifying and stripping sections lie on the respective curves shown in Figure 5. The sufficient condition for the KFP is that the composition of this point should satisfy eq 20 ($i=1$ or 3) for the rectifying section and eq 21 ($i=1$ or 3) for the stripping section. The reaction term in these equations is obtained only by solving the equations for the composition profiles (eqs 2, 3, and 5) of these sections. Hence, as mentioned

earlier, a priori prediction of such fixed points is not possible and the differential equations associated with the sections have to be solved.

It must be noted here that the positions of the curves of kinetic azeotropy in the distillation map are determined at the critical values of the parameter $(Da \times HTU^V)$ for the respective sections. The value of $(Da \times HTU^V)_c$, in turn, is strongly influenced by the individual end compositions ($x_{D,3}$ and $x_{B,1}$) once the reflux ratios, $(x_{D,3} - x_{D,1})$ and $(x_{B,1} - x_{B,3})$, are fixed.

The discrete dynamic approach can also be used to determine the locus of the points which satisfy the necessary condition of kinetic azeotropy. The determination of the curve of kinetic azeotropy based on this approach is comparatively easy. Since the discrete dynamic approach imposes an additional constraint on the system that the vapor and liquid streams leaving any stage are always in phase equilibrium, the kinetic azeotropy curve is independent of the parameters such as Da and the individual end compositions ($x_{D,3}$ and $x_{B,1}$). In a distillation column, following is the equation for the composition of component i on plate n for the rectifying section:

$$\left(\frac{RF}{RF+1}\right)x_{n,i} = y_{n+1,i} - \left(\frac{1}{RF+1}\right)x_{D,i} + \left(\frac{F}{V}\right)Da \sum_j^n \left(x_{j,2}^2 - \frac{x_{j,1}x_{j,3}}{K}\right) \quad i = 1, 3 \quad (24)$$

By subtracting $[RF/(RF+1)]x_{n+1,i}$ from both sides and applying the fixed point condition, eq 24 can be reduced to the following form:

$$\left(\frac{RF}{RF+1}\right)(x_1 - x_3) = (y_1 - y_3) - \left(\frac{1}{RF+1}\right)(x_{D,1} - x_{D,3}) \quad (25)$$

This is an equation for the curve of kinetic azeotropy of the rectifying section. The vapor compositions (y_i) are in equilibrium with the liquid compositions, which is the main underlying assumption of this approach. Similarly, the expression for the curve of kinetic azeotropy of the stripping section can be derived as

$$(x_1 - x_3) = \left(\frac{SF}{SF+1}\right)(y_1 - y_3) + \left(\frac{1}{SF+1}\right)(x_{B,1} - x_{B,3}) \quad (26)$$

Equations 25 and 26 prove that the position of the curve of kinetic azeotropy in the distillation map is independent of the value of Da , $x_{D,3}$ and $x_{B,1}$, and is only dictated by the values of RF , $(x_{D,3} - x_{D,1})$ and $(x_{B,3} - x_{B,1})$.

Influence of Kinetic Azeotropy on the Design Method

A design is said to be feasible if the composition profiles of both the sections intersect each other in the positive reaction zone. A general step-by-step design procedure for this reactive system has been first outlined by Buzad and Doherty.⁶ In any design method, it is always necessary to determine the value of the minimum reflux ratio before we proceed further to determine the actual dimensions of the column. The value of the reflux ratio decides the position of the separating manifolds (or lines) of each section in the distillation map. The separating manifold is the boundary of the composition domain in which a composition

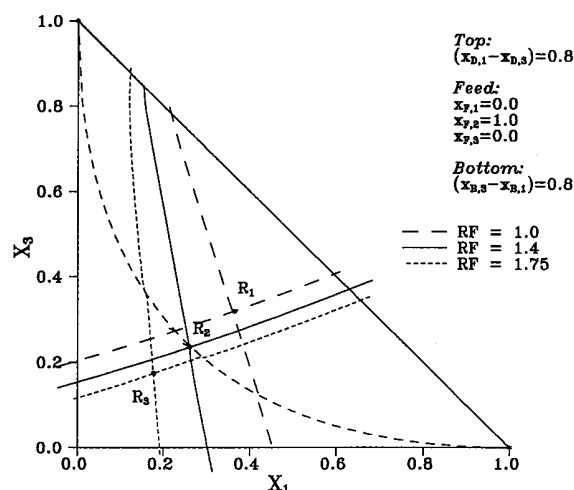


Figure 6. Separating manifolds of the rectifying and stripping sections as a function of the reflux ratio.

profile of that particular section lies. The position of the separating manifold can be determined on the basis of the composition profiles obtained at $(Da \times HTU^V)_c + \epsilon$ and $(Da \times HTU^V)_c - \epsilon$ where ϵ is a very small number. The separating line moves and the composition domain expands with an increase in the value of the reflux ratio, as shown in Figure 6 for both the sections. At the low values of the reflux ratio, the separating lines of both the sections intersect in the negative reaction zone (R_1) and there is no common space in the positive reaction zone for the composition spaces of the two sections in which the corresponding profiles may intersect. As the value of the reflux ratio is increased further, the point of intersection of separating lines moves toward the positive reaction zone. At a particular value of the reflux ratio, the separating lines of both the sections intersect each other on the reaction equilibrium curve (R_2). This point of intersection R_2 is nothing but the EFP of both the sections at that reflux ratio ($RF = 1.4$). Hence, it has been concluded that the minimum reflux ratio is the value of the reflux ratio at which the EFPs of both the sections overlap each other.^{6,7} It only means that, below the value of the minimum reflux ratio, the profiles will never intersect in the positive reaction zone and the design is not feasible. The profiles may have multiple intersections as shown in Figure 2. It may be concluded, on the basis of the results obtained in the earlier work, that the sufficient condition given by eqs 14 and 15 is more likely to be satisfied if

$$\left[\frac{d(r_i)}{d\xi}\right]_{\text{intersection}} > 0 \quad i = 1, 3 \quad (27)$$

for both rectifying and stripping sections. Hence, the intersection satisfying the above condition corresponds to the feed point. It is that intersection which takes place just before the profiles leave the composition triangle through the positive reaction zone.

Now an important question is the following: *Are the composition profiles always likely to intersect for the reflux ratios higher than the minimum reflux ratio?* To examine this, let us consider an example wherein the end compositions $x_{D,3}$ ($=0.000239$) and $x_{B,1}$ ($=0.0008$) have considerably low values in distillate and bottom streams, respectively. Figure 7 shows the results obtained by solving the design equations for the conditions

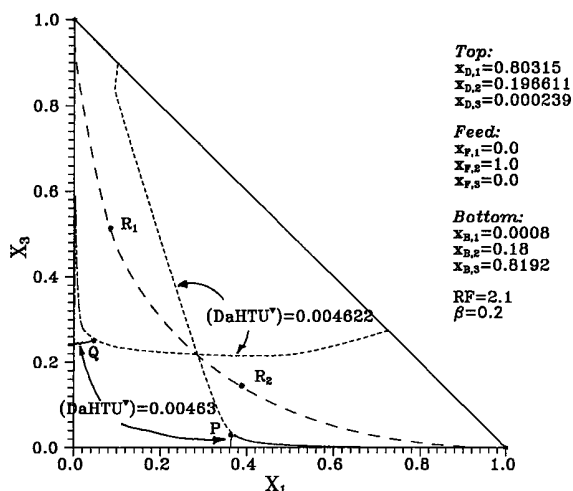


Figure 7. Composition profiles for rectifying and stripping sections. The profiles intersect to satisfy the sufficient condition.

specified therein. Points *P* and *Q* are the kinetic fixed points of the rectifying and stripping sections, respectively. The design, of course, is not feasible, though the EFPs (R_1 and R_2) of both the sections cross each other on the reaction equilibrium curve. Even though the profiles intersect in the positive reaction zone, the sufficient condition (i.e., eqs 14 and 15) is not fulfilled as $dr/d\xi < 0$, at the point of intersection of the profiles. The extent of reaction obtained by the integration over the entire column length (eq 15) is much less than that calculated by the overall material balance (eq 14). The only way to increase the extent of reaction occurring in the column, once the profiles intersect, is to increase the value of Da . However, in this case, since the profiles pass very close to the KFP of the corresponding section (points *P* and *Q*), an increase in the value of Da will cause the profiles to change their course in such a way (shown by dotted lines) that they do not intersect each other in the composition triangle. This is because the KFPs of both the sections are far away from the point of intersection of their kinetic azeotropy curves. That leads us to the conclusion that as the KFP moves away from the EFP, the probability of intersection of the profiles decreases. The point of intersection of kinetic azeotropy curves of both the sections, carries a special significance here. *The profiles will intersect if and only if the kinetic fixed point of any of the sections lies between the equilibrium fixed point of that section and the point of intersection of the kinetic azeotropy curves of both the sections.*

We have seen that the KFP moves on the curve of kinetic azeotropy with a change in the value of the end composition of the least volatile component for the given values of the reflux ratio and $(x_{D,3} - x_{D,1})$. The boundary of the composition space or the separating line of the rectifying section can be determined on the basis of the composition profiles determined at $(Da \times HTU^V)_c + \epsilon$ and $(Da \times HTU^V)_c - \epsilon$. The separating line moves to expand the composition space with an increase in the value of $x_{D,3}$ as shown in Figure 8. Beyond a certain limiting value of $x_{D,3}$, it was observed that the position of the separating line of the rectifying section becomes insensitive to the value of $x_{D,3}$. Hence, the continuous line represents the boundary of the maximum allowable space for the profile of the rectifying section in the positive reaction zone, irrespective of the value of $x_{D,3}$.

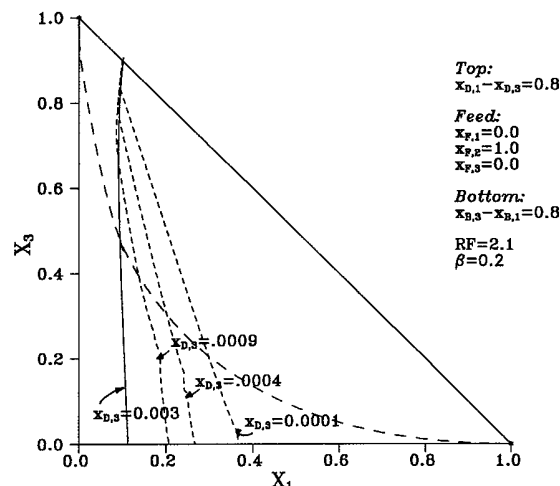


Figure 8. The boundaries of the composition space of the rectifying section as a function of $x_{D,3}$.

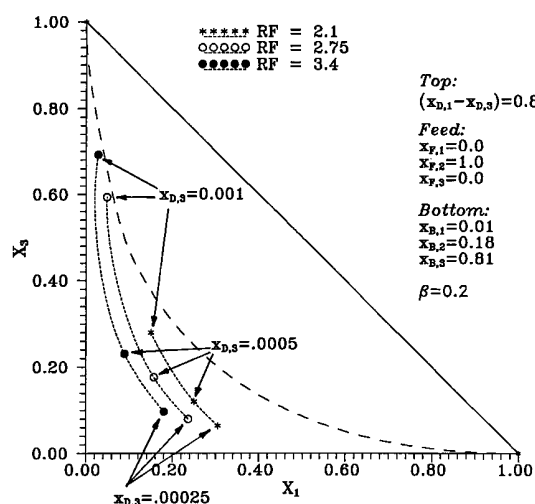


Figure 9. Effect of the reflux ratio and $x_{D,3}$ on the fixed saddle of the rectifying section.

One such separating line also exists for the stripping section. *The profiles will never intersect to give a feasible design for any value of $x_{D,3}$ and $x_{B,1}$, if the kinetic fixed point of a section does not lie between the equilibrium fixed point of that section and the point of intersection of the kinetic azeotropy curve of that section and the separating line of the other section.* Hence, apart from the reflux ratio, the end composition of one of the components also has the minimum value below that for which the design is not feasible. In other words, for a given reflux ratio, there exists a value of the composition of the least volatile component in the rectifying section and that of the most volatile component in the stripping section below which the design is not feasible.

The influence of the value of $x_{D,3}$ on the position of the KFP of the rectifying section under otherwise identical values of the reflux ratio and $(x_{D,1} - x_{D,3})$ is shown in Figure 9. Every different position of the fixed point corresponds to a certain critical value of $(Da \times HTU^V)_c$. Figure 10 gives the relationship between $x_{D,3}$ and $(Da \times HTU^V)_c$ and shows the region for feasible composition profiles. $x_{D,3}^U$ is the upper limit of the end composition at which $(Da \times HTU^V)_c$ approaches infinity. $x_{D,3}^L$ is the value of $x_{D,3}$ at which the KFP of the

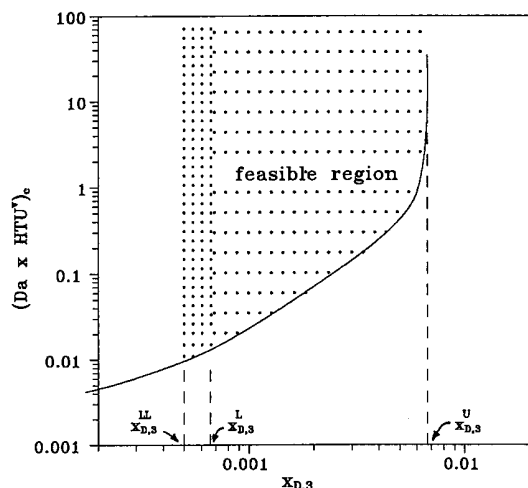


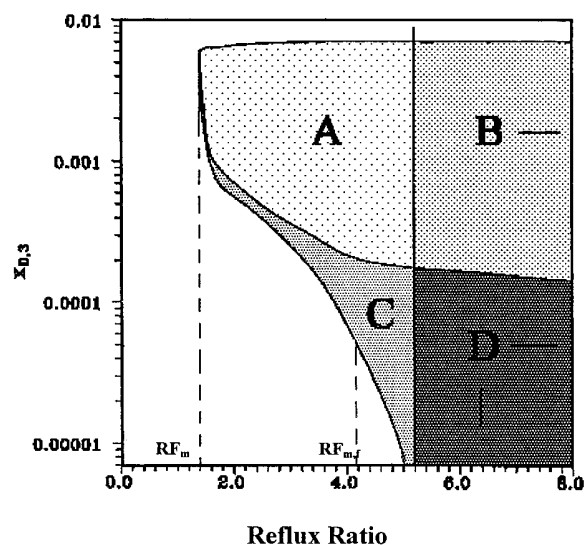
Figure 10. A plot of $(Da \times HTU^V)_c$ vs $x_{D,3}$ and the region of feasible distillate composition.

rectifying section coincides with the intersection of kinetic azeotropy curves. In other words, $x_{D,3}^L$ is the limit of $x_{D,3}$ above which the design is feasible at any value of the individual end composition of the bottom stream (i.e., $x_{B,1}$), for the given value of $(x_{B,3} - x_{B,1})$. It must be noted that the value of $x_{D,3}^L$ calculated by the continuous dynamic approach depends on the value of $x_{B,1}$. The value of $x_{D,3}^L$ is evaluated at $x_{B,1} = 0.001$ for which most of the calculations are performed in this exercise. However, the value of $x_{D,3}^L$, calculated on the basis of the discrete dynamic approach, does not depend on $x_{B,1}$ because, as discussed earlier, the position of the curve of kinetic azeotropy of the rectifying section is independent of $x_{B,1}$ in this case. The feasible composition profiles can also be obtained for $x_{D,3} < x_{D,3}^L$ and $x_{B,1} > x_{B,1}^L$ where $x_{B,1}^L$ is the limit on the value of $x_{B,1}$ and may be calculated by a similar procedure followed for the calculation of $x_{D,3}^L$. $x_{D,3}^{LL}$ in Figure 10 represents the minimum value of $x_{D,3}$ below which the design is not feasible at any value of $x_{B,1}$. $x_{D,3}^{LL}$ is independent of the value of $x_{B,1}$. This is the value of $x_{D,3}$ at which the KFP of the rectifying section is the point of intersection of the kinetic azeotropy curve of the rectifying section and the separating line of the stripping section.

Effect of the Reflux Ratio

As the reflux ratio increases, the KFP shifts its position as shown in Figure 9. This shift is favorable for a feasible design because the KFP moves toward the EFP and further enhances the possibility of intersection of the profiles. It is evident from the equations of kinetic azeotropy (eqs 22 and 23) that the positions of the kinetic azeotropy curves are strongly influenced by the values of the reflux and reboil ratios. With an increase in the value of the reflux ratio, the intersection of the curves of kinetic azeotropy moves away from the EFP, allowing more space for the profiles to intersect. Hence, at higher values of the reflux ratio, the profiles may even intersect at still lower values of $x_{D,3}$ or $x_{B,1}$.

Figure 11 shows how the range of feasible values of $x_{D,3}$ expands as the reflux ratio increases. The maximum value of $x_{D,3}$ is that value at which $(Da \times HTU^V)_c$ approaches infinity. RF_m is the minimum reflux ratio at which the EFP of both the sections overlap on each



- All $(Da \times HTU^V) > (Da \times HTU^V)_c$ and All $x_{B,1}$
- High values of $(Da \times HTU^V)$ and All $x_{B,1}$
- All $(Da \times HTU^V) > (Da \times HTU^V)_c$ and $x_{B,1}^L > x_{B,1} > x_{B,1}^{LL}$
- High values of $(Da \times HTU^V)$ and $x_{B,1}^L > x_{B,1} > x_{B,1}^{LL}$

Figure 11. Feasible regions $x_{D,3}$ as a function of the reflux ratio ($x_{D,1} - x_{D,3}$) = ($x_{B,3} - x_{B,1}$) = 0.8.

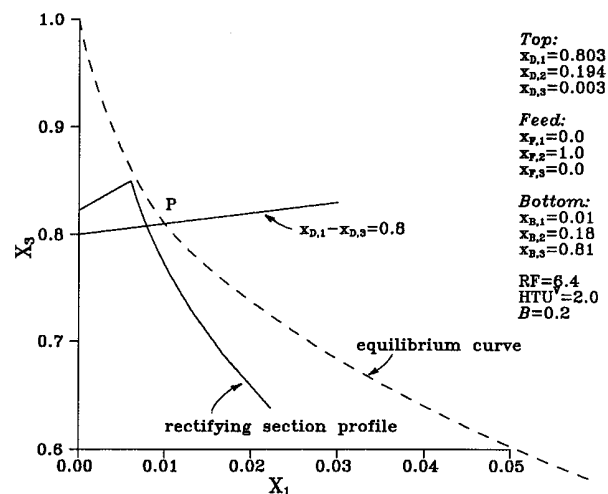


Figure 12. Composition profile of a rectifying section at large values of the reflux ratio.

other. Hence, for $RF < RF_m$ the profiles will never intersect. In the regions C and D, $x_{D,3} < x_{D,3}^L$ and hence, as explained earlier, a feasible design is obtained only for $x_{B,1} > x_{B,1}^L$. Any point in the regions A and B satisfies the feasibility criterion for all values of $x_{B,1}$. However, as the reflux ratio increases, the EFP of the rectifying section moves on the reaction equilibrium curve toward the composition of the least volatile component. At one stage it crosses the intersection (point P in Figure 12) of the line formed by the condition $(x_{B,3} - x_{B,1}) = 0.8$ and the reaction equilibrium curve. The profile corresponding to this reflux ratio escapes out of the composition triangle in a manner shown in Figure 12. The profiles of the rectifying section obtained at such a high reflux ratio are unlikely to intersect with

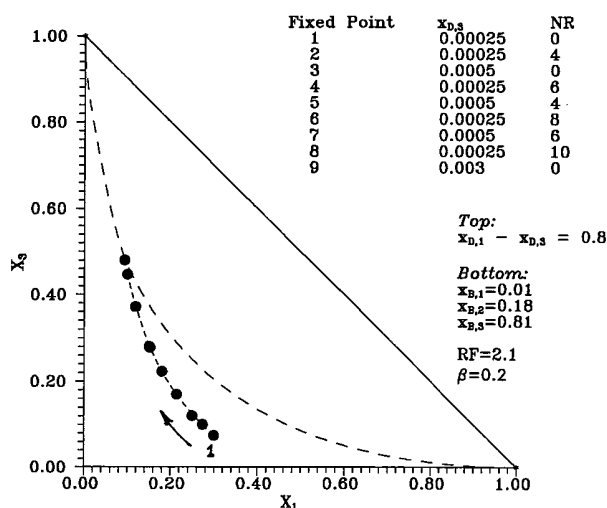


Figure 13. Position of a fixed point as a function of $x_{D,3}$ and the height of the nonreactive zone in the rectifying section.

the profile of the stripping section unless the values of $(Da \times HTU^V)$ are significantly high. Hence, above a certain value of the reflux ratio, a feasible design is obtained only for considerably high values of $(Da \times HTU^V)$. The regions B and D could thus be distinguished from the regions A and C in which the design is feasible for any value of $(Da \times HTU^V) > (Da \times HTU^V)_c$. It is evident from Figure 11 that, for each value of $x_{D,3}$, there exists a minimum feasible value of the reflux ratio ($RF_{m,f}$), which is either equal to or greater than the minimum reflux ratio (RF_m). If the operating reflux ratio is less than $RF_{m,f}$, then the profiles will never intersect. The arrows in the regions B, C, and D show that the regions extend in those directions beyond the limits of the graph.

While determining the regions of feasibility, the author has not considered a link between the $(Da \times HTU^V)$ value of the rectifying section and that of the stripping section. In a normal practice, the $(Da \times HTU^V)$ values for both the sections are very close to each other. Hence, even if the end compositions lie in the regions of feasibility, the profiles may not intersect if the $(Da \times HTU^V)_c$ values of both the sections are wide apart. This fact puts an additional constraint on the feasibility of a design and the respective area of the feasible regions shown in Figure 10 may attenuate further. An elaborate discussion on the design feasibility for equal values of $(Da \times HTU^V)$ of both the sections may be found elsewhere.⁷ The practical limitations on the values of the reflux ratio, Da , and so forth, imposed by factors such as the hydrodynamic condition of the column, have also not been considered here and are out of the scope of this work.

Nonreactive Stages

It is interesting to see the consequences of introducing nonreactive zones at the end of either the rectifying or the stripping section. Figure 13 shows that as we increase the number of nonreactive stages in the rectifying section (NR), the KFP moves toward the EFP. This figure also indicates that all the KFPs, determined for different combinations of $x_{D,3}$ and the number of nonreactive stages in the rectifying section, lie on a single curve, under otherwise identical values of the

reflux ratio, $(x_{D,1} - x_{D,3})$ and $(x_{B,3} - x_{B,1})$. That means introducing nonreactive stages is equivalent to changing the boundary conditions of the differential equations of the composition profiles of reactive sections. Hence, in context of the position of the fixed point, introducing a nonreactive zone and increasing the value of $x_{D,3}$ without introducing a nonreactive zone have similar consequences. The lower limit on $x_{D,3}$ (i.e., $x_{D,3}^{LL}$) for the RDC with nonreactive zones thus decreases with an increase in the height of the nonreactive zone of the rectifying section. However, the upper limit on $x_{D,3}$ (i.e., $x_{D,3}^U$) decreases with an increase in the height of nonreactive zone in the rectifying section. Hence, sometimes the introduction of nonreactive stages in either of the sections helps in overcoming the restrictions imposed by the kinetic azeotropy of that section. A similar exercise can be performed for the stripping section to work out the dependence of limits of $x_{B,1}$ on the height of a nonreactive zone in the stripping section.

Feasible Product Compositions

From the above discussion, it can be summarized that the end compositions of the RDC should always satisfy the following constraints so that the composition profiles of the two sections may intersect to satisfy the necessary condition of a feasible design:

1. The values of $(x_{D,1} - x_{D,3})$ and $(x_{B,3} - x_{B,1})$ should be such that, over a desired range of the values of the operating reflux ratio, the EFPs of the rectifying and stripping sections should cross each other on the reaction equilibrium curve. The quantities $(x_{D,1} - x_{D,3})$ and $(x_{B,3} - x_{B,1})$ also decide the relative flow rates (D/B) of the distillate and bottom streams.

2. The minimum feasible values of $x_{D,3}$ and $x_{B,1}$ are determined on the basis of kinetic azeotropy. These values should be such that the KFP of either the rectifying section or the stripping section should lie between the EFP and the intersection of kinetic azeotropy curves of the two sections. The plot for regions of feasible end compositions based on the condition of kinetic azeotropy (as shown in Figure 10 for the rectifying section) may help in deciding the individual end compositions.

3. The maximum feasible values of $x_{D,3}$ and $x_{B,1}$ are those compositions at which the respective values of $(Da \times HTU^V)_c$ tend toward infinity. As we increase the values of $x_{D,3}$ and $x_{B,1}$, the points corresponding to the distillate or bottom compositions in the distillation map move on the straight lines formed by the given values of $(x_{D,1} - x_{D,3})$ and $(x_{B,3} - x_{B,1})$ and enter into the negative reaction zone. It should be noted here that, unless nonreactive stages have been introduced, the values of $x_{D,3}$ and $x_{B,1}$ should be such that the distillate and bottom compositions lie in the positive reaction zone. In all the cases we have studied for this reactive system, it was observed that with an increase in the value of $x_{D,3}$ and $x_{B,1}$, the value of $(Da \times HTU^V)_c$ of the corresponding section approaches infinity well before the end compositions enter into the negative reaction zone. Hence, the maximum limit on $x_{D,3}$ and $x_{B,1}$ for the present system is imposed by the infinite value of $(Da \times HTU^V)_c$.

Conclusions

The design method of the RDC based on the distillation maps not only should consider the fixed points on

the equilibrium curve but also needs to identify the position of the kinetic fixed points (KFPs). These fixed points are the points in the positive reaction zone where the shift in compositions that resulted from the chemical reaction in the liquid phase is compensated by the composition change due to mass transfer or distillation. These points have a direct relationship with the feasible product composition. The output compositions for which the KFP of the corresponding section lies between the equilibrium fixed point of that section and the point of intersection of the kinetic azeotropy curves of the two sections is a feasible product composition for which the profiles of the two sections may intersect to make the design feasible. One can study the influence of the reflux ratio and nonreactive zones on the range of feasible top and bottom product compositions on the basis of the positions of the KFP. The understanding of the theory behind the existence of the kinetic and equilibrium fixed points is essential while making a proper choice of end compositions in a design problem.

Nomenclature

A,B,C = chemical species
 A_c = cross-sectional area of the column, m^2
 a = interfacial area per unit volume of dispersion, m^2/m^3
 B = bottom product molar flow rate, $kmol/s$
 C_t = mixture molar density, $kmol/m^3$
 D = distillate molar flow rate, $kmol/s$
 Da = Damkohler number given by eq 18
 Da_c = critical value of Damkohler number
 D_{GL} = diffusivity of components in G–L film, m^2/s
 F = feed molar flow rate
 H = height of the column zone, m
 HTU^V = height of transfer unit defined by eq 9
 J^V = molar diffusion flux for vapor side, $mol/m^2 \cdot s$
 J^L = molar diffusion flux for liquid side, $mol/m^2 \cdot s$
 K = chemical equilibrium constant
 k = forward reaction rate constant
 k_L = liquid-side mass-transfer coefficient, m/s
 k_{OV} = overall mass-transfer coefficient, m/s
 k_V = gas-side mass-transfer coefficient, m/s
 I = fractional liquid holdup
 L = liquid molar flow rate
 N = number of integration stages
 NR = number of nonreactive integration stages
 RF = reflux ratio
 RXN_i = extent of reaction in RDC given by eq 7
 r_i = reaction rate of component i , per unit volume
 s = coordinate in the direction across the G–L diffusional film
 SF = reboil ratio
 V = vapor molar flow rate, $kmol/s$
 x_i = mole fraction of component i in the liquid phase (bulk)
 y_i = mole fraction of component i in the vapor phase (bulk)
 z = differential height of the column, m

Greek Letters

α = relative volatility

$$\beta = \frac{C_t^V k_V}{C_t^L k_L} = \frac{\text{characteristic time for mass transfer in the liquid phase}}{\text{characteristic time for mass transfer in the vapor phase}}$$

ν_i = stoichiometric coefficient of component i

ξ = dimensionless height of the column section

$$\psi_i = \frac{J_i^V}{C_t^V k_V} = \text{dimensionless flux}$$

Subscripts

B = bottom product

D = distillate

f = composition or reaction in the G–L film

F = feed

i = component

j = component

n = stage number

r, s = rectifying and stripping sections

1,2,3 = 1: reactant A; 2: reactant B; 3: reactant C

Superscripts

I = gas–liquid interface

D = distillate

L = liquid

M = model

r, s = rectifying and stripping sections

V = vapor

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