Homogeneous Multicomponent Azeotropic Batch Distillation

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Mixed waste-solvent streams generated in pharmaceutical and specialty chemical manufacturing typically form multicomponent azeotropic mixtures. This highly nonideal behavior often prevents separation and recovery of the solvents. Batch distillation remains an important separation technology for these industries. The sequence of pure component and azeotropic cuts produced in batch distillation depends strongly on the feed composition. For ternary- and four-component mixtures the separation behavior can be studied graphically in residue-curve maps. For mixtures with more components, this approach is infeasible. Other tools are therefore required. Deficiencies in earlier work on ternary systems are demonstrated and addressed as well as a complete set of concepts to describe batch distillation of an azeotropic mixture with an arbitrary number of components. The body of theory is derived from the fields of nonlinear dynamics and topology.

Introduction

Pharmaceutical and specialty chemical products are typically required in small volumes and are subject to short product life cycles as well as fluctuating demand. Hence these industries are dominated by the use of multipurpose equipment in batch processes. In the past, economic incentives for the recovery and recycling of solvent have not been present in the manufacturing of these high value-added products. However, increasingly restrictive environmental regulations are forcing chemical manufacturers to reassess their use of solvents. The traditional use of end-of-pipe control alone is no longer acceptable, and pollution prevention has been adopted as a more forward-looking strategy. Our ultimate goal is to develop tools for analysis and design of batch processes with solvent recovery and recycling integrated in the process flowsheet. Ahmad and Barton (1994) present preliminary results on a *solvent-recovery targeting algorithm*.

Batch distillation remains an important separation technique in this mode of operation, and is also widely used for recovering fractions from mixed waste-solvent streams and in waste-treatment facilities. Typically, the components involved form multicomponent azeotropic mixtures. The sequence of pure component and azeotropic cuts generated by batch distillation of an azeotropic mixture, and the maximum feasible recovery in each cut, is highly dependent on the initial composition of the mixture. Any species that is recovered in azeotropic cuts that cannot be recycled is likely to leave the process and be treated as toxic waste. The ability to predict the feasibility of recovering components in pure form from a process stream is therefore essential to pollution prevention in these manufacturing systems. Several technologies are available to obtain such predictions, for example, test runs in pilot plants or detailed dynamic simulation models. However, these approaches are very elaborate and time-consuming. Our approach is based on extracting the necessary information from the residue-curve map of the mixture of interest. Most of the literature in this area has dealt with three- and four-component mixtures, and has relied on graphical representation to interpret the behavior of the system. Reviews of this work can be found in Fien and Liu (1994) and Widagdo and Seider (1996). With more than four components such an approach becomes infeasible. This article is devoted to generalizing the theory of residue-curve maps governing homogeneous azeotropic batch distillation of a mixture with an arbitrary number of components. The deficiencies in earlier work on ternary systems are demonstrated and addressed in the next two sections together with the new concepts needed to

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describe these systems. The theory is extended to multicomponent systems in the fourth section. The results will allow complete characterization of the structure of the composition space for a multicomponent system when using batch distillation based only on the information of the compositions, boiling temperatures, and the stability of the fixed points.

Ternary Systems

The least complicated of all distillation processes is the simple distillation (or open evaporation) process. Here a mixture is boiled in an open vessel such that the vapor is removed as soon as it is formed. The liquid (or residue) will become increasingly depleted in the more volatile component as the distillation progresses. The change in the composition of the residue during the distillation of an *nc* component mixture can be represented as curves that lie in an *nc*-1-dimensional composition hyperplane. Although ternary residue-curve maps are the most common, residue-curve maps can be derived for any number of components. However, graphical representation becomes increasingly difficult as the number of components increases. For systems with more than four components there is no straightforward way of studying the separation behavior of a mixture graphically. For ternary systems the residue curves may be represented either in a regular simplex or in a right simplex. The regular simplex is the well-known Gibbs composition triangle, and the right simplex is generated by projecting the composition plane onto a plane defined by $x_i = 0$, $i \in \{1,2,3\}$. x_i is the composition of component i in the liquid phase. The relationship between the two representations is shown in Figure 1. For the purposes of this article, it is most valuable to imagine the Gibbs composition simplex suspended in the host *nc* space.

The simple residue curves can be constructed experimentally using the distillation setup described earlier, or can be found numerically by solving a set of equations describing the composition path of the residue:

$$\frac{dx_i}{d\xi} = x_i - y_i \qquad \forall i = 1, \ldots, nc-1, \qquad (1)$$

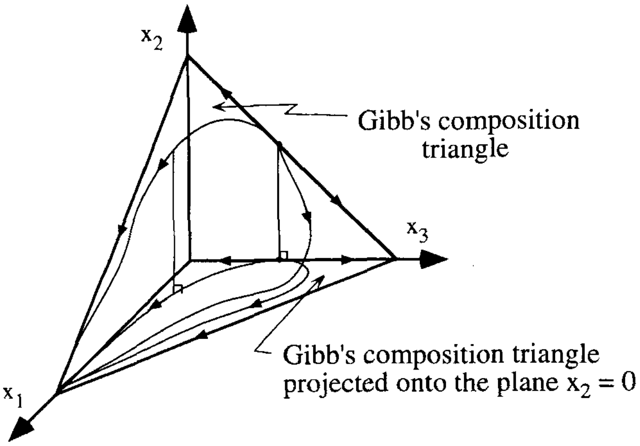

Figure 1. Relationship between regular and right-simplex representations of ternary residue-curve maps.

where y_i is the mole fraction of component i in the vapor phase. The relationship between x_i and y_i can be described by a suitable vapor–liquid equilibrium model. The independent variable ξ is a dimensionless measure of time. Residue curves (orbits) (the terminology describing the dynamic system $x(\xi)$ is adopted from Hale and Koçak (1991)) are projections of the trajectories defined by Eqs. 1 onto the plane $\xi = 0$ (i.e., the phase portrait of the dynamic system). Equations 1 can be analyzed, and a number of properties regarding the structure of the residue-curve map for the system of interest can be extracted. The mathematical basis for multicomponent simple distillation theory can be found in a series of articles by Doherty and Perkins (1978a,b, 1979). The residue curves also represent the column profile in a column that is operated at total reflux, indicating that the top and the bottom product composition in that case have to be located on the same residue curve (Van Dongen and Doherty, 1985a). The pure components and azeotropes are the fixed points (critical points) of Eqs. 1 with the properties of nodes or saddles (Doherty and Perkins, 1977, 1978a). The nature of the fixed points can be classified using topology theory (Doherty and Perkins, 1979; Fidkowski et al., 1993).

The presence of *distillation boundaries* in the composition space, and whether these boundaries can be crossed or not using continuous or batch distillation, have been the topic of considerable debate in the literature over the years. For example, see Reinders and De Minjer (1940), Ewell and Welch (1945), Van Dongen and Doherty (1984), and Doherty and Perkins (1978a). The separatrices play a central role, where a separatrix is defined in the following manner: if in each neighborhood there is a point q such that $\omega(q) \neq \omega(p)$, or $\alpha(q) \neq \alpha(p)$, then the orbit through p is called a separatrix (Hale and Koçak, 1991). The set $\alpha(\hat{x}) = \lim_{\xi \to -\infty} \varphi(\xi, \hat{x})$ is called the α-limit set of composition point $\hat{x}$. Similarly, the set $\omega(\hat{x}) = \lim_{\xi \to +\infty} \varphi(\xi, \hat{x})$ is called the ω-limit set of $\hat{x}$ (Hale and Koçak, 1991). $\varphi(\xi, \hat{x})$ refers to the trajectory through $\hat{x}$. It is important to understand the difference between stable and unstable separatrices. A stable separatrix is defined as a residue curve where the residue curves on each side are moving toward the same fixed point even at long time. Otherwise the separatrix is an unstable separatrix. Doherty and Perkins (1978a) conclude that unstable separatrices correspond to simple distillation boundaries.

Use of residue-curve maps in batch distillation

The use of residue curve maps for synthesis and design of continuous distillation systems have been explored in a number of papers (Doherty and Caldarola, 1985; Levy et al., 1985; Stichlmair and Herguijuela, 1992; Stichlmair et al., 1993; Van Dongen and Doherty, 1985a; Wahnschafft et al., 1992, 1993). Here we will focus on their properties when used for batch distillation systems.

Reinders and De Minjer (1940) studied the differences between residue curves (simple distillation lines) and distillation lines that describe rectification. They indicated that under certain conditions the lines of rectifying distillation will be almost straight. Figure 2 illustrates this behavior for a system with no azeotropes. Van Dongen and Doherty (1985b) reported that for batch distillation with very high reflux and a large number of equilibrium stages the rectifying distillation

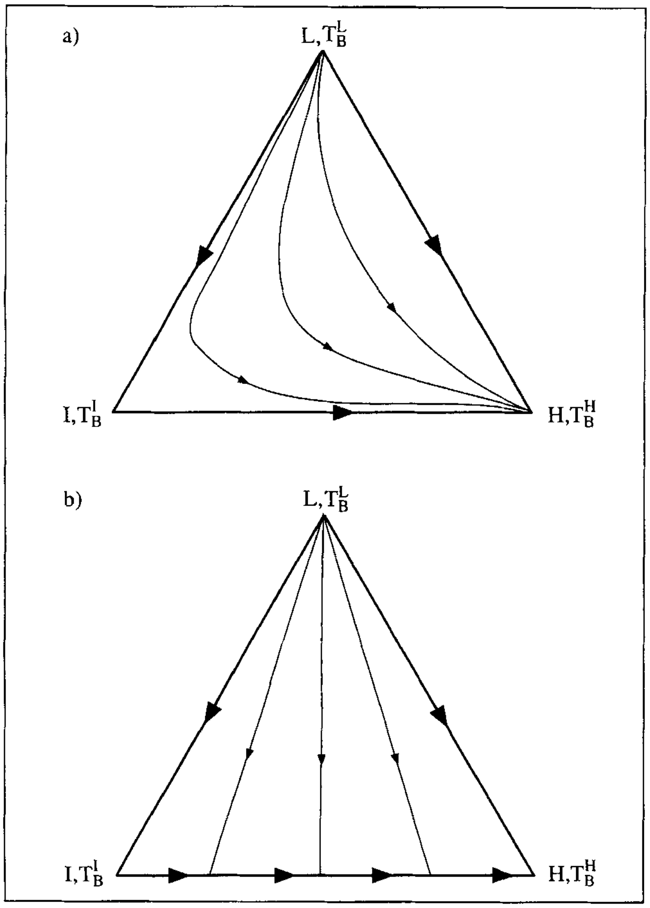

Figure 2. Residue curve map for a ternary system with no azeotropes: (a) simple residue curve map; (b) residue curve map with distillation lines that describe rectification.

lines will move in such a manner. They demonstrated that when distilling a ternary mixture under these limiting conditions it is possible to draw the exact orbits following the composition of the liquid in the still, and to predict the sequence of constant-boiling vapor distillates overhead, provided that the structure of the residue curve map for the system of interest is known. This is particularly important for azeotropic mixtures, as the sequence of products will typically change with feed composition. A simple batch distillation model was developed describing the time evolution of the composition in the still pot:

$$\frac{dx_i^p}{d\xi} = x_i^p - x_i^d \qquad \forall i = 1,\ldots,nc-1, \qquad (2)$$

where x_i^p is the mole fraction of component i in the still pot and x_i^d is the fraction in the distillate. It is important to note that these equations are different from the simple distillation Eqs. 1, as x_i^d is not in equilibrium with x_i^p. Rather, x_i^d is calculated (given x_i^p) using the design equations for the column. $x^p(\xi)$ denotes the pot composition trajectory ($\varphi^p(\xi)$) projected onto the plane $\xi = 0$. The set of equations used was based on the assumption of high reflux ratio ($r \geq 7$). With few theoretical stages (small N), the batch distillation residue curves [$x^p(\xi)$] calculated look similar to the residue curves from simple distillation, as expected. When N is increased to a high value ($N \geq 10$–20), the batch distillation residue curves appear to move directly away from the initial composition point $x^{p,0}$ in a direction opposite from the position of the low-boiling species (pure component or azeotrope) in the region where $x^{p,0}$ was located. The change in the pot composition $x^p(\xi)$ is almost linear because a large number of trays and high reflux ratio cause the composition of the distillate $x^d(\xi)$ to be approximately constant at a value near the low-boiling point. The composition of the pot will move along this straight line until it hits a *pot composition barrier* (discussed later), then it will turn and follow the limiting boundary toward the higher boiling point. For each batch distillation residue curve there will be a corresponding distillate curve that denotes the locus of distillate compositions $x^d(\xi)$ as they change with time during the course of distillation. The relationship between these curves is precisely the same as the relationship between a simple distillation residue curve and its vapor boil-off curve. Hence, the distillate composition $x^d(\xi')$ corresponding to any particular instantaneous still pot liquid composition $x^p(\xi')$ will lie on the tangent line to the batch distillation residue curve through $x^p(\xi')$. The two instantaneous compositions also have to lie on the same simple distillation residue curve due to the assumption of close to total reflux in the column. In Figure 3 the relationship between the pot liquid composition $x^p(\xi)$ and the distillate composition $x^d(\xi)$ during the course of distillation is shown for a ternary mixture. $x^{p,0}$ is the initial composition in the reboiler. The white arrow indicates the orbit $x^p(\xi)$. The set of points $x^{d,1}$, $x^{d,2}$, and $x^{d,3}$ represents the distillate curve, that is, the sequence of distillate compositions that will appear overhead if the column is run until the reboiler is dry.

It has been demonstrated that this behavior also applies to mixtures with more than three components. For example, Bernot et al. (1991) present an example with four components. However, no attempt has been reported at extending and generalizing the theory to mixtures with an arbitrary number of components.

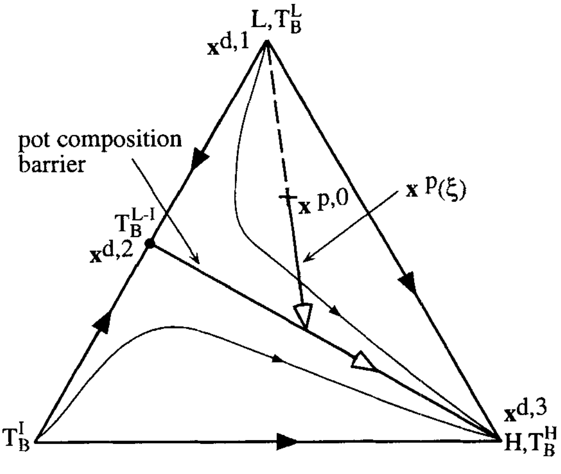

Figure 3. Relationship between pot composition $x^p(\xi)$ and the distillate composition $x^d(\xi)$ when distilling a ternary mixture.

Batch distillation boundaries and regions

The definitions of distillation boundaries and regions are closely related. Doherty and Perkins (1978a) state that two residue curves that are initially close together and are still close at long time belong to the same simple distillation region. In batch distillation the situation is different. At this point it is necessary to define a *batch distillation region*, and we adopt a modification of the definition due to Ewell and Welch (1945):

Definition 1. A batch distillation (rectification or stripping; the theory is derived for a rectifier configuration) region $B(\boldsymbol{P})$ is the set of compositions that lead to the same sequence of product cuts $\boldsymbol{P} = \{\boldsymbol{p}_0, \boldsymbol{p}_1, \dots\}$ upon distillation (rectification or stripping) under the limiting conditions of very high reflux ratio and large number of equilibrium stages.

Under the limiting conditions, a product cut sequence is defined as the sequence of pure-component and azeotropic compositions ($\boldsymbol{p}_k\ \forall k = 0, 1, \dots$) drawn overhead when distilling a multicomponent mixture using batch distillation. The element p_{ki} in the nc vector $\boldsymbol{p}_k$ is the mole fraction of pure component i in product cut k. For an azeotropic mixture the product cut sequence depends on the location of the feed stream, and by definition any initial composition that is taken interior to a given batch distillation region will always result in the *same* sequence of cuts. Hence, once the batch-distillation regions are defined, the set of products can be predicted from the distillate path. See Figure 4 for an example. Components L and I form a minimum boiling azeotrope, and so do components I and H. The composition space is divided into three batch distillation regions, B^1, B^2, and B^3. The feed composition $\boldsymbol{x}^{p,0}$ is located in batch distillation region B^3. The resulting product cuts are therefore: (1) the binary azeotrope L-I with composition $\boldsymbol{x}^{d,1}$; (2) the pure component L with composition $\boldsymbol{x}^{d,2}$; and (3) the pure component H with composition $\boldsymbol{x}^{d,3}$.

The boundaries Ewell and Welch (1945) observed have later been termed *batch-distillation boundaries* (see Figure 4). Bernot et al. (1990, 1991) propose how the batch distillation boundaries can be found for a ternary system:

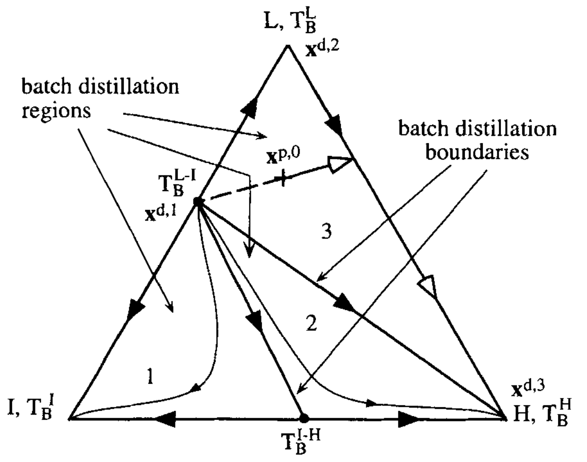

Figure 4. Ternary residue curve map with pot composition path and batch distillation boundaries.

The order of the boiling temperatures is $T_B^{L\text{-}I} < T_B^L < T_B^{I\text{-}H} < T_B^I < T_B^H$.

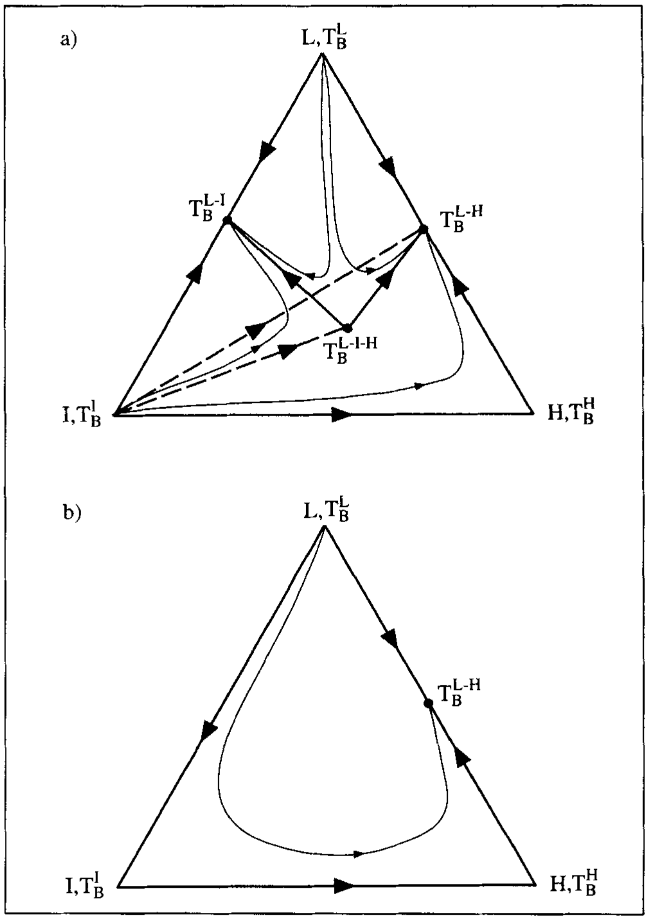

Figure 5. Residue curve maps where some batch distillation boundaries are discarded.

The order of boiling temperatures: (a) $T_B^L < T_B^I < T_B^H < T_B^{L\text{-}I\text{-}H} < T_B^{L\text{-}I} < T_B^{L\text{-}H}$, and (b) $T_B^L < T_B^I < T_B^H < T_B^{L\text{-}H}$.

1. The stable separatrices dividing the simplex into subdomains each containing an unstable node constitute batch distillation boundaries.
2. Within each of these subdomains (or the entire simplex in the case of only one domain) connections between the unstable node and all the other species in the domain may be introduced as straight-line batch distillation boundaries.

A straight-line boundary should not intersect a stable separatrix, and if a stable separatrix is highly curved, the straight-line boundary is tangent to the separatrix. For example, in the ternary residue curve map in Figure 5a the boundary connecting component I and the binary azeotrope L-H will intersect the stable separatrix between L-I-H and L-I and should therefore be discarded. Figure 5b illustrates another example. When placing batch distillation boundaries according to the preceding rules a boundary connecting L and H will be introduced. However, as this boundary will intersect the binary edge (L, H), it should be discarded. Another interesting feature of the latter system is that any initial pot composition $\boldsymbol{x}^{p,0}$, $x_i > 0$ will yield the product sequence $\boldsymbol{P} = \{L, I, H\}$. Compositions on the (L, I) edge, or the (I, H) edge will yield a subset of $\boldsymbol{P}$, $\{L, I\}$, or $\{I, H\}$, respectively. In contrast, compositions on the binary edge (L, H) will yield $\{L, L\text{-}H\}$ or $\{H, L\text{-}H\}$, depending on which side of the L-H

azeotrope the initial composition is located. This irregular behavior will only be apparent if the initial composition is located on the edge.

Pot Composition Boundaries

The results presented by Bernot et al. (1990, 1991) assume that if stable separatrices are present, they will divide the composition space. However, that is not necessarily the case. Figure 6a shows a residue curve map with a simple distillation region where a stable ternary node is connected to a binary saddle azeotrope with a stable separatrix. There is only one unstable node (L) in the composition space. However, when the pot orbit hits the stable separatrix, it will be constrained to stay on this boundary. Three batch distillation regions can therefore be constructed, as indicated in Figure 6b.

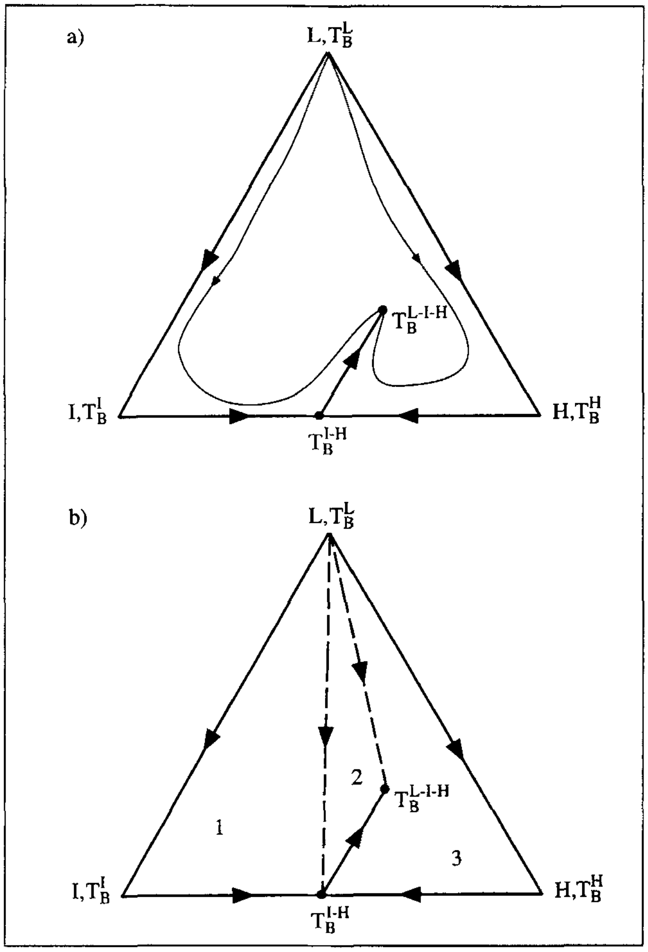

Figure 6. Ternary residue curve map where stable separatrix does not divide the composition space.

The order of boiling temperatures: $T_B^L < T_B^I < T_B^H < T_B^{L\text{-}I} < T_B^{L\text{-}I\text{-}H}$.

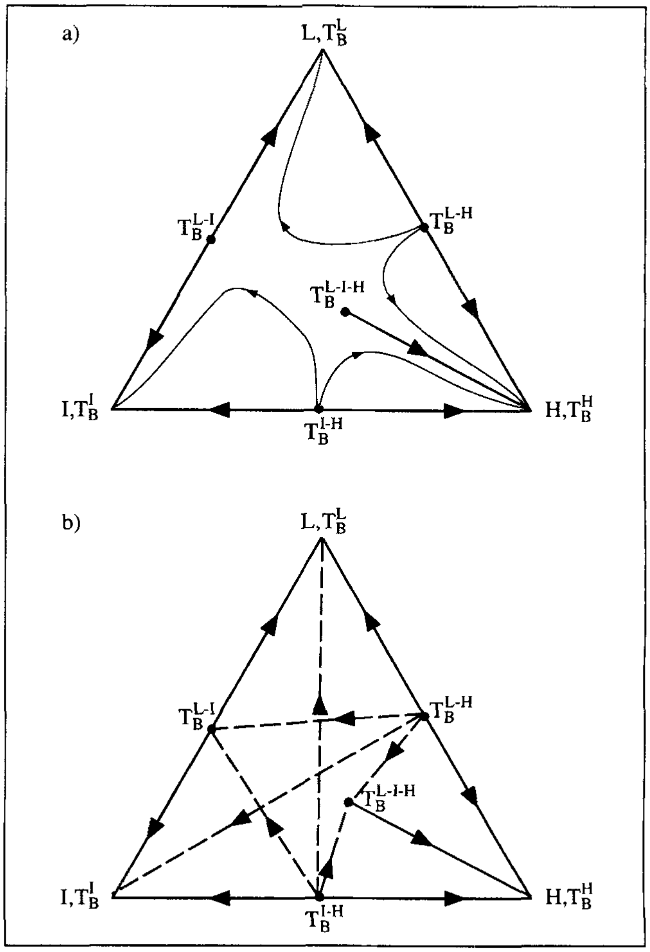

Figure 7. Ternary residue curve map where stable separatrix does not divide the composition space, but which has two unstable nodes.

The order of boiling temperatures: $T_B^{L\text{-}H} < T_B^{I\text{-}H} < T_B^{L\text{-}I\text{-}H} < T_B^{L\text{-}I} < T_B^L < T_B^I < T_B^H$.

It is now evident that all stable separatrices will constrain the movement of the pot orbit. Residue curves are approaching from either side. Hence, the pot orbit is restricted to move ever closer to the stable separatrix, and finally, to follow the same path as the separatrix. Here we present the less obvious result that certain unstable separatrices also play the role of impassable boundaries. Figure 7a shows a residue curve map containing a saddle ternary connected to three binary azeotropes and pure component H by separatrices. Only stable separatrices are shown. Note that the trajectory connecting L-I-H and L-I is an unstable separatrix. Two of the binaries are unstable nodes, while the third binary is a saddle point. The stable separatrix connecting L-I-H and H does not divide the composition space, but there are two unstable nodes (I-H and L-H) present indicating that two subdomains exist. In this case the previous rules will lead to intersecting batch distillation boundaries (see Figure 7b), and no guidelines are provided in the existing literature to deal with this situation. In fact, there is a boundary constraining the movement of the pot composition path between the ternary azeotrope and the binary L-I, as illustrated in Figure 8. Initial composition $x^{p,0}$ will produce the binary azeotrope L-H as the first product cut, while the pot composition is moving toward the unstable separatrix connecting the ternary azeotrope L-I-H and the binary azeotrope L-I. When $x^p(\xi)$ hits the unstable separatrix, there is apparently nothing preventing it from crossing the separatrix. However, at that point it will switch to a different family of residue curves where the unstable node is the binary azeotrope I-H. Hence, the com-

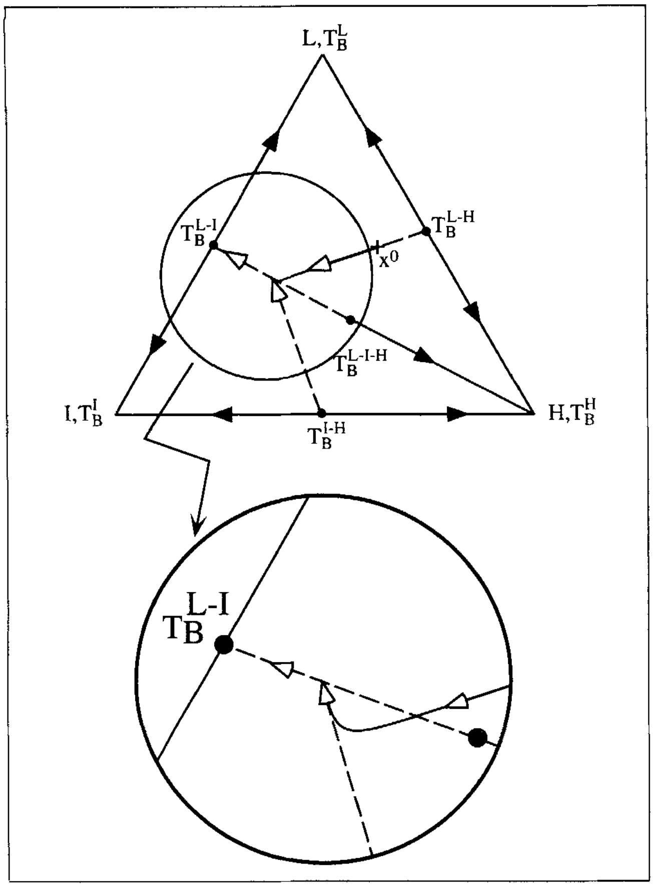

Figure 8. Ternary residue curve map with unstable separatrix constraining the movement of the pot composition.

position path will turn and move in a straight line away from *I-H*, and as $x^p(\xi)$ tries to cross the unstable separatrix in the opposite direction it will again be forced back to the separatrix, this time by *L-H*. The two opposing unstable nodes *L-H* and *I-H* will in fact constrain the pot composition to stay on the unstable separatrix. If the unstable separatrix is highly curved, a similar behavior to the one encountered for stable separatrices in the acetone, chloroform, and methanol system discussed by Bernot et al. (1990) will be observed. Following the analogy with stable separatrices this type of unstable separatrix can be defined as a residue curve where the residue curves on each side *at least locally* are moving toward the same equilibrium point.

Note that most unstable separatrices will not behave in this manner. The type of unstable separatrix shown in Figure 8 is a consequence of the presence of three stable nodes, and was only found in six of the 113 possible ternary residue maps presented by Matsuyama and Nishimura (1977). For example, an unstable separatrix that is connected to an unstable node (e.g., the unstable separatrix between *L-H* and *L-I-H* in Figure 7) will not constrain the movement of the residue path. On the other hand, the path will not cross it either, but that is due to the fact that the path under the limiting assumptions above is composed of segments of straight lines. Therefore, we cannot achieve distillate compositions on the other side. Consequently, a new term may be introduced:

Definition 2. A pot composition barrier is a barrier that will constrain the movement of the pot composition during the course of batch distillation. When the pot composition orbit $x^p(\xi)$ intersects a pot composition barrier, it is restricted to stay on or close to that barrier. $x^p(\xi)$ moving on a pot composition barrier may be further constrained by lower dimensional pot composition barriers.

If the boundaries forming this barrier are curved $x^p(\xi)$ may move slightly away from the barrier. However, as the temperature in the reboiler must increase monotonically, and the simple residue curves are approaching on either side of such a barrier, the pot composition orbit must remain relatively close. The geometric and algebraic definitions will be introduced later. At the moment we are only interested in knowing that such a barrier might be present. A pot composition $x^{p,0}$ initially located in batch distillation region *B* of dimension $nc-1$ will first encounter a pot composition barrier $\mathrm{PCB}^{(nc-2)}$ of dimension $nc-2$. The subsequent pot composition orbit will be constrained to move on or close to $\mathrm{PCB}^{(nc-2)}$ until a pot-composition barrier of dimension $nc-3$ is encountered, etc.

Obviously, if the pot orbit hits one of the edges or vertices of the ternary composition simplex, it will be constrained to stay on this edge or vertex, as one or more of the species are exhausted, and, following the definition of a separatrix, any segment of an edge connecting two fixed points is also a separatrix. However, as with separatrices internal to the composition space, not all the edges may be pot composition barriers. For example, in the ideal system shown in Figure 2 the binary edge between the pure components *I* and *H* will constrain the pot orbit during the first product cut (when *L* is boiled off). During the second product cut (when *I* is boiled off), the pot orbit is constrained by the vertex *H*. The edge $[L, I]$ is not a pot composition barrier.

To summarize, we argue that the following types of pot-composition barriers of dimension 1 are observed in ternary systems:

- Stable separatrices
- Certain unstable separatrices
- Some of the edges.

In ternary residue curve maps all pot composition barriers will be composed of straight lines except the ones resulting from curved separatrices. Accounting for the curvature of the separatrices will require integration of Eqs. 1. Although a separatrix will almost always have some curvature (Reinders and Minjer, 1940), for many systems assuming that the separatrices are straight will suffice. The consequence and desired outcome of this assumption is that the composition path $x^p(\xi)$ will be composed of segments of straight lines. Therefore, all distillation cuts will have compositions equal to fixed points, and no other distillation cuts may be achieved. In the next section the extension of this assumption to multicomponent systems will be discussed.

Multicomponent Batch Distillation

The theory is derived for a homogeneous system with *nc* components based on the limiting assumptions of very high reflux ratio and large number of trays. First pot composition barriers and batch distillation regions in multicomponent systems will be discussed, and then the theory governing prediction of the number of product cuts and their sequence will be introduced. The exceptions for ternary systems are used throughout to motivate the derivation of the theory. A rectifier configuration is assumed, but it should be noted that the same arguments will apply for a stripper configuration. Appendix A demonstrates how our approach can be extended to such a column configuration.

Simple distillation

The concept of separatrices as distillation boundaries is only useful in ternary systems. A separatrix is an orbit and will form an infinitely thin barrier in higher dimensions. In order to extend the notion of distillation boundaries for ternary systems to systems with an arbitrary number of components it is advantageous to introduce the concept of *global unstable and stable manifolds* of a fixed point x^*, $W^u(x^*)$, and $W^s(x^*)$, respectively (Hale and Koçak, 1991):

$$W^u(x^*) \equiv \{\hat{x} \in R^{nc}: \varphi(\xi, \hat{x}) \rightarrow x^* \quad \text{as} \quad \xi \rightarrow -\infty\} \tag{3}$$

$$W^s(x^*) \equiv \{\hat{x} \in R^{nc}: \varphi(\xi, \hat{x}) \rightarrow x^* \quad \text{as} \quad \xi \rightarrow +\infty\}, \tag{4}$$

where $\varphi(\xi, \hat{x})$, defined by Eqs. 1, refers to the simple distillation trajectory through the composition point $\hat{x}$. $W^u(x^*)$ can also be defined as all compositions that have x^* as their α-limit set, and similarly, $W^s(x^*)$ as all compositions that have x^* as their ω-limit set. The trajectory $\varphi(\xi, x^*)$ is x^* itself, and x^* therefore belongs to both $W^u(x^*)$ and $W^s(x^*)$. For convenience a fixed point is allocated to its unstable manifold, and the notation $\overline{W}^w(x^*)\ \forall w \in \{u, s\}$ will in the following refer to $W^u(x^*)$ and $W^s(x^*) \backslash \{x^*\}$ projected onto the plane $\xi = 0$. For consistency, $\alpha(x^*) \equiv \{x^*\}$, and $\omega(x^*) \equiv \emptyset$.

If x^* is an unstable node (the definitions are based on systems with at least two components, as it makes little sense to define the nature of the fixed point of a pure component system) $\{x^*\} \subset \overline{W}^u(x^*) \subset Q$, while $\overline{W}^s(x^*) = \emptyset$, where Q defines the whole composition simplex. $\subset$ denotes a proper subset. If x^* is a stable node $\overline{W}^u(x^*) = \{x^*\}$, and $\emptyset \subset \overline{W}^s(x^*) \subset Q$. If x^* is a saddle point $\{x^*\} \subset \overline{W}^u(x^*) \subset Q$ and $\emptyset \subset \overline{W}^s(x^*) \subset Q$. From the definition given earlier it follows that $\overline{W}^u(x^*) \cap \overline{W}^s(x^*)$ does not contain the fixed point itself. Furthermore, the absence of homoclinic orbits [a homoclinic orbit is an orbit that will approach the same fixed point for $\xi \rightarrow -\infty$ and $\xi \rightarrow +\infty$ (Hale and Koçak, 1991)] (Doherty and Perkins, 1978a) (except the fixed points themselves) indicates that $\overline{W}^u(x^*) \cap \overline{W}^s(x^*) = \emptyset$. In addition, because orbits do not intersect $\overline{W}^w(x_a^*) \cap \overline{W}^w(x_b^*) = \emptyset\ \forall w \in \{u, s\}$ unless x_a^* and x_b^* are the same fixed point. The composition space Q can therefore be expressed as the following union of disjoint sets:

$$\begin{aligned} Q &= \bigcup_{e=1}^{ep} \overline{W}^u(x_e^*) \\ &= \bigcup_{m=1}^{un} \overline{W}^u(x_m^*) \cup \bigcup_{n=1}^{s} \overline{W}^u(x_n^*) \cup \bigcup_{q=1}^{sn} \overline{W}^u(x_q^*), \end{aligned} \tag{5}$$

where x_m^*, x_q^*, and x_n^* refer to unstable nodes, stable nodes, and saddle points, respectively; *ep* is the number of fixed points in the system; and *un*, *s*, and *sn* are the number of unstable nodes, saddle points, and stable nodes in the system.

Definition 3. *$\overline{\omega}^u(x^*)$ is the set of fixed points that are also* limit points (a point p is a limit of the set E if every neighborhood of p contains a point $q \neq p$ such that $q \in E$) of $\overline{W}^u(x^*)$ excluding x^*. Likewise, $\overline{\omega}^s(x^*)$ is the set of fixed points that are also limit points of $\overline{W}^s(x^*)$ excluding x^*. $\overline{\omega}^u(x^*)$ and $\overline{\omega}^s(x^*)$ are termed the unstable and stable boundary limit sets of x^*, respectively.

Alternatively, the boundary limit sets can be defined as

$$\overline{\omega}^u(x^*) \equiv \bigcup_{\hat{x} \in \overline{W}^u(x^*)} \omega(\hat{x}) \cup \{x_{n'}^*\} \tag{6}$$

$$\overline{\omega}^s(x^*) \equiv \bigcup_{\hat{x} \in \overline{W}^s(x^*)} \alpha(\hat{x}) \cup \{x_{n''}^*\}, \tag{7}$$

where $\{x_{n'}^*\}$ represents the set of saddle points that are passed infinitesimally close but not entered by any of the orbits in $\overline{W}^u(x^*)$, and $\{x_{n''}^*\}$ represents the set of saddle points that are passed infinitesimally close but not entered by any of the orbits in $\overline{W}^s(x^*)$. As defined, $\overline{\omega}^w(x^*) \not\subset \overline{W}^w(x^*)\ \forall w \in \{u, s\}$. It is evident that $\overline{\omega}^u(x^*)$ does not contain unstable nodes. Similarly, $\overline{\omega}^s(x^*)$ does not contain stable nodes. The term *boundary limit set* of x^* refers to $\overline{\omega}(x^*) = \overline{\omega}^u(x^*) \cup \overline{\omega}^s(x^*) \cup \{x^*\}$.

The closure of $\overline{W}^u(x^*)$, denoted by $\overline{\overline{W}}^u(x^*)$, can be expressed as

$$\overline{\overline{W}}^u(x^*) = \overline{W}^u(x^*) \cup \{\hat{x} \in R^{nc}: \gamma(\xi, \hat{x}) \rightarrow x_j^* \in \overline{\omega}(x^*) \quad \text{as} \quad \xi \rightarrow \pm\infty\}, \tag{8}$$

where $\gamma(\xi, \hat{x})$ represents the residue curve through $\hat{x}$. For example, this can be illustrated by Figure 5b. There $\overline{W}^u(L)$ includes the whole composition simplex except the binary compositions between I and H and between H and L-H. $\overline{\omega}^u(L) = \{I, H, L\text{-}H\}$. Therefore, $\overline{\overline{W}}^u(L) = \overline{W}^u(L) \cup \{\hat{x} \in R^3: \gamma(\xi, \hat{x}) \rightarrow x_j^* \in \{I, H, L\text{-}H\}$ as $\xi \rightarrow \pm\infty\} = Q$, the whole composition simplex.

The closure of $\overline{W}^s(x^*)$, $\overline{\overline{W}}^s(x^*)$, can be expressed in a similar manner.

Pot composition barriers and batch distillation regions

Theorem 1. Distillation cut 1 starting with pot composition $x^{p,0} \in \overline{W}^u(x_m^*)$, where x_m^* is an unstable node, will at limiting conditions of very high reflux ratio and large number of trays have a distillate composition $x^{d,1}$ close to x_m^* as long as pot composition $x^p(\xi) \in \overline{W}^u(x_m^*)$.

Proof. At very high reflux $x^p(\xi')$ and $x^d(\xi')$ are located on the same simple residue curve, where $x^p(\xi')$ and $x^d(\xi')$ refer to the instantaneous reboiler composition and distillate composition, respectively. Thus, $x^d(\xi') \in \overline{W}^u(x_m^*)$. The assumption of a large number of trays ensures that $x^d(\xi')$ stays constant at the α-limit set of $x^p(\xi')$, that is, x_m^*.

Corollary 1. Equations 2 state that $x^d(\xi')$ lies on the tangent to the pot composition path $x^p(\xi)$ through $x^p(\xi')$. Hence, since $x^d(\xi') = x_m^*$, $x^p(\xi)$ will move in a straight line away from x_m^*. This can also be confirmed by an overall material balance.

Theorem 1 is a more formal statement of the results discussed in Van Dongen and Doherty (1985b).

At the limit, $\boldsymbol{x}^p(\xi)$ will intersect PCB($\boldsymbol{x}_m^*$), the pot composition barrier for any pot composition orbit with initial condition $\boldsymbol{x}^{p,0} \in \overline{W}^u(\boldsymbol{x}_m^*)$. The intersection, $\boldsymbol{x}^{p,1}$, has to be a limit point of $\overline{W}^u(\boldsymbol{x}_m^*)$. However, $\boldsymbol{x}^{p,1} \notin \overline{W}^u(\boldsymbol{x}_m^*)$. It therefore follows from Eq. 9 that the pot-composition barrier can be defined as

$$\begin{aligned}\mathrm{PCB}(\boldsymbol{x}_m^*) &= \overline{\overline{W}}^u(\boldsymbol{x}_m^*) \setminus \overline{W}^u(\boldsymbol{x}_m^*)\\ &= \{\hat{\boldsymbol{x}} \in \boldsymbol{R}^{nc}: \gamma(\xi, \hat{\boldsymbol{x}}) \to \boldsymbol{x}_j^* \in \overline{\omega}^u(\boldsymbol{x}_m^*) \quad \text{as} \quad \xi \to \pm\infty\}. \quad (9)\end{aligned}$$

$\boldsymbol{x}^{p,1} \in \overline{W}^u(\boldsymbol{x}_j^*)$ for some $\boldsymbol{x}_j^* \in \overline{\omega}^u(\boldsymbol{x}_m^*)$ will be the starting point of distillation cut 2. The relationship between the instantaneous distillate composition $\boldsymbol{x}^d(\xi')$ and the instantaneous pot composition $\boldsymbol{x}^p(\xi')$ is still governed by Eqs. 2. However, if $\overline{W}^u(\boldsymbol{x}_j^*)$ is curved, the tangent to $\boldsymbol{x}^p(\xi)$ through $\boldsymbol{x}^p(\xi')$ may not lie within $\overline{W}^u(\boldsymbol{x}_j^*)$, and hence $\boldsymbol{x}^d(\xi')$ may not equal $\boldsymbol{x}_j^*$. Moreover, as $\boldsymbol{x}^p(\xi)$ is forced to move relatively close to this curved surface (Definition 2), the slope of the tangent will vary, and hence the distillate composition $\boldsymbol{x}^d(\xi')$ will not stay constant. However, if we could ensure that $\boldsymbol{x}^p(\xi)$ will always move in a straight line during a certain distillation cut, Theorem 1 could be generalized to apply for all subsequent distillation cuts. Assuming that $\overline{W}^u(\boldsymbol{x}_e^*)\ \forall e = 1, \ldots, ep$ are linear would lead to the desired outcome. As will be demonstrated, this is too restrictive, and may introduce large inaccuracy in the analysis. For example, consider the ternary system in Figure 9a. The unstable manifolds of *L* and *I-H* are inherently linear, as they have dimension $nc - 1 = 2$. Likewise, $\overline{W}^u(I)$, $\overline{W}^u(L\text{-}I)$, and $\overline{W}^u(H)$ are linear because they are located on the binary edges. However, $\overline{W}^u(L\text{-}I\text{-}H)$ is not linear, as it is composed of the two line segments connecting the ternary saddle point *L-I-H* to *L-I* and *H* including *L-I-H*, but excluding *L-I* and *H*. The dashed lines in Figure 9b labeled *a* and *b* show two possible linearizations of $\overline{W}^u(L\text{-}I\text{-}H)$. Both of them will require a shift in the position of a fixed point [either *L-I* (a) or *L-I-H* (b)]. A closer look at Figure 9a reveals that the composition space can be divided into five batch distillation regions, as indicated by the dashed lines. The composition paths in regions 2, 3, 4 and 5 will all approach and intersect $\overline{W}^u(L\text{-}I\text{-}H)$. The composition paths starting in 2 and 4 will intersect to the left of *L-I-H* and then turn and move toward *L-I*, and the composition paths starting in 3 and 5 will intersect to the right of *L-I-H* and then turn and move toward *H*. Hence, both linearization *a* and *b* will serve to satisfy the requirement that $\boldsymbol{x}^p(\xi)$ should move in a straight line during a certain distillation cut; in this case, while *L-I-H* is boiling off. However, nonlinearity in the line segment between *L-I-H* and *L-I* will not effect the path of the orbit with initial composition in regions 3 and 5, in the same way as nonlinearity in the line segment between *L-I-H* and *H* will not effect the orbit with initial composition in regions 2 and 4. A third linearization of $\overline{W}^u(L\text{-}I\text{-}H)$ may therefore be considered where the two line segments between *L-I-H* and *L-I*, and *L-I-H* and *H* are linearized separately (labeled *c* in Figure 9b).

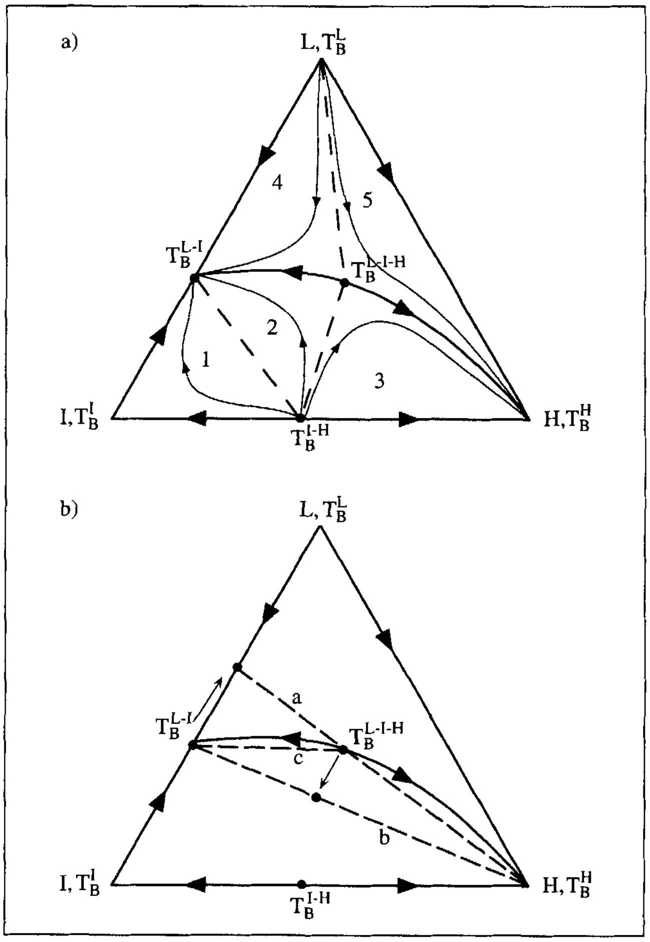

Figure 9. Linearization of $\overline{W}^u(x^*)$ to ensure that the pot composition will move in a straight line during a certain distillation cut.

In conclusion, it has been found that PCB($\boldsymbol{x}_j^*$) can be divided into one or more domains, termed *pot composition boundaries*:

Definition 4. A pot composition boundary is the set of compositions that lead to the same sequence of product cuts $\hat{\boldsymbol{P}} = \{\boldsymbol{p}_{k+1}, \boldsymbol{p}_{k+2}, \ldots\}$ upon distillation under the limiting conditions of very high reflux ratio and large number of trays. The pot composition boundaries are subsets of the respective unstable manifolds of PCB($\boldsymbol{p}_k$) where $\boldsymbol{p}_k$ represents the composition of cut *k*.

We can now proceed to generalize Theorem 1.

Theorem 2. Distillation cut *k* starting with pot composition $\boldsymbol{x}^{p,k-1} \in \overline{W}^u(\boldsymbol{x}_j^*)$ will at limiting conditions of very high reflux and large number of trays, and with linear pot composition boundaries, have a distillate composition $\boldsymbol{x}^{d,k}$ close to $\boldsymbol{x}_j^*$ as long as pot composition $\boldsymbol{x}^p(\xi) \in \overline{W}^u(\boldsymbol{x}_j^*)$.

Proof. At very high reflux, $\boldsymbol{x}^p(\xi')$ and $\boldsymbol{x}^d(\xi')$ are located on the same residue curve. Thus, $\boldsymbol{x}^d(\xi') \in \overline{W}^u(\boldsymbol{x}_j^*)$. Furthermore, $\boldsymbol{x}^d(\xi')$ lies on the tangent to $\boldsymbol{x}^p(\xi)$ through $\boldsymbol{x}^p(\xi')$. The assumption of linear pot composition boundaries ensures that the tangent lies within $\overline{W}^u(\boldsymbol{x}_j^*)$. Combined with the assumption of a large number of trays this ensures that $\boldsymbol{x}^d(\xi')$ stays constant at the α-limit set of $\boldsymbol{x}^p(\xi')$, that is, $\boldsymbol{x}_j^*$.

Of course, if $\boldsymbol{x}^{p,k-1} = \boldsymbol{x}_j^*$, then $\boldsymbol{x}^p(\xi) = \boldsymbol{x}^{d,k} = \boldsymbol{x}_j^*$ as $\xi \to +\infty$.

Corollary 2. If batch distillation region $B(\boldsymbol{P})$ gives rise to the product sequence $\boldsymbol{P} = \{\boldsymbol{p}_0, \boldsymbol{p}_1, \ldots\}$, then at limiting conditions $B(\boldsymbol{P})$ is the set of composition points $\hat{\boldsymbol{x}} \in \overline{W}^u(\boldsymbol{p}_0)$ such that the resulting pot composition path $\boldsymbol{x}^p(\xi)$ will intersect $\overline{W}^u(\boldsymbol{p}_k)$ $\forall \boldsymbol{p}_k \in \boldsymbol{P}$ as $\xi \rightarrow +\infty$. Composition points that give rise to a subset of $\boldsymbol{P}$ form the batch distillation boundaries of $B(\boldsymbol{P})$.

Corollary 3. The pot composition boundary for product cut k is at limiting conditions the set of composition points $\hat{\boldsymbol{x}} \in \mathrm{PCB}(\boldsymbol{p}_k)$ such that the subsequent pot composition path will intersect $\overline{W}^u(\boldsymbol{p}_l)$ $\forall \boldsymbol{p}_l \in \hat{\boldsymbol{P}} = \{\boldsymbol{p}_{k+1}, \boldsymbol{p}_{k+2}, \ldots,\} \subset \boldsymbol{P}$ as $\xi \rightarrow +\infty$, where $\boldsymbol{P}$ is the product sequence for a particular batch-distillation region. Thus, assuming linear pot composition boundaries is equivalent to assuming that the boundaries of a batch-distillation region are linear.

Figure 10 illustrates what would happen if a pot composition boundary was curved. The initial reboiler composition, $\boldsymbol{x}^{p,0} \in \overline{W}^u(L)$, and the first distillate composition therefore will be equal to L according to Theorem 1. PCB(L) is equal to the separatrix connecting L-I and H including the endpoints, and in this case the pot composition boundary coincides with PCB(L). At the end of the first cut $\boldsymbol{x}^p(\xi)$ will intersect $\overline{W}^u(L\text{-}I)$, or so it appears. However, the conditions that $\boldsymbol{x}^p(\xi')$ and $\boldsymbol{x}^d(\xi')$ lie on the same residue curve, and $\boldsymbol{x}^d(\xi')$ lies on the tangent to $\boldsymbol{x}^p(\xi)$ through $\boldsymbol{x}^p(\xi')$, can only be satisfied if $\boldsymbol{x}^p(\xi)$ remains in $\overline{W}^u(L)$. The distillate will therefore take on compositions as indicated in Figure 10. $\boldsymbol{x}^p(\xi)$ may move ever closer to $\overline{W}^u(L\text{-}I)$, but it will not intersect it. On the other hand, if $\boldsymbol{x}^{p,0} \in \overline{W}^u(I)$, $\boldsymbol{x}^p(\xi)$ will necessarily have to intersect and cross $\overline{W}^u(L\text{-}I)$ in order to satisfy the same conditions. Note that this does not result in crossing trajectories, as $\boldsymbol{x}^p(\xi)$ is governed by Eqs. 2, while $\overline{W}^u(L\text{-}I)$ is governed by Eqs. 1. At that point $\boldsymbol{x}^p(\xi)$ will follow the same path as the orbits, starting on the convex side. As the temperature in the reboiler must increase monotonically, $\boldsymbol{x}^p(\xi)$ must remain relatively close to $\overline{W}^u(L\text{-}I)$ in both cases. This behavior has been observed and discussed by several other authors (Ewell and Welch, 1945; Van Dongen and Doherty, 1985b; Bernot et al., 1990).

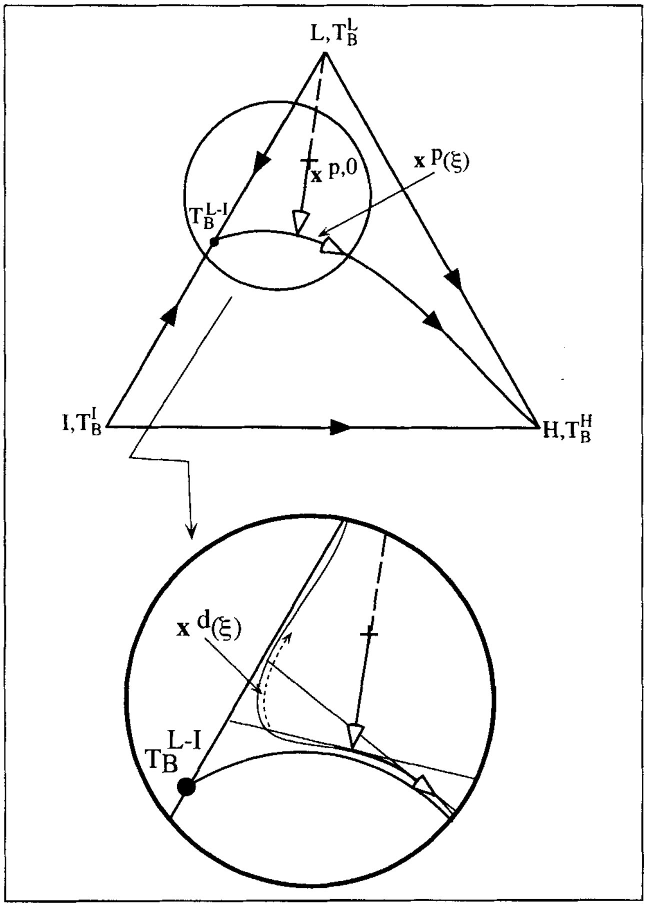

Figure 10. Ternary system with curved pot composition boundary.

Product sequence

As stated in Definition 1, any composition taken interior to a specific batch distillation region will always result in the same sequence of product cuts. It is demonstrated here that, subject to the assumptions at the beginning of this section, the number of cuts can be predicted *a priori*.

Theorem 3. At very high reflux, large number of trays, and with linear pot composition boundaries, an nc component mixture located interior to a batch-distillation region will produce exactly nc product cuts.

Proof. Initial composition $\boldsymbol{x}^{p,0}$ interior to $B(\boldsymbol{P})$ will always result in the same sequence of cuts $\boldsymbol{P} = \{\boldsymbol{p}_0, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots\}$. Following Theorem 1 the pot composition path $\boldsymbol{x}^p(\xi)$ will move in $\overline{W}^u(\boldsymbol{p}_0)$ until it intersects $\overline{W}^u(\boldsymbol{p}_1) \subseteq \mathrm{PCB}(\boldsymbol{p}_0)$, then it will continue in $\overline{W}^u(\boldsymbol{p}_1)$ until it intersects $\overline{W}^u(\boldsymbol{p}_2) \subseteq \mathrm{PCB}(\boldsymbol{p}_1) \subseteq \mathrm{PCB}(\boldsymbol{p}_0)$, and so on. Initially, $\boldsymbol{x}^p(\xi)$ is free to move in the hyperplane defined by $\sum_{i=1}^{nc} x_i = 1$. However, the number of degrees of freedom is reduced by one each time a pot-composition barrier is encountered, until $\boldsymbol{x}^p(\xi)$ moves in a fixed point in the composition space. Thus, this point (azeotrope or pure component) is the final value of the pot composition. Hence, the number of product cuts including the final composition left in the pot is equal to the number of pure components in the initial mixture. We can conclude from this exercise that the distillate path consists of exactly nc vertices.

Corollary 4. Following Corollary 2, an nc component mixture located on the boundary of a batch distillation region will at very high reflux, large number of trays, and with linear pot composition boundaries produce at most $nc-1$ product cuts.

The nc product cuts form a string of nc fixed points where each consecutive fixed point has a higher boiling temperature then the previous fixed point. The first fixed point is the unstable node $\boldsymbol{p}_0$, and the last fixed point is the stable node. The rest are saddle points. It should be noted that some fixed points that have the properties of saddle points in the simple residue curve map will appear to be stable nodes (end nodes) in batch distillation. The distillate curve for the separation is the set of these points.

Definition 5 (Hocking and Young, 1961). Let $A = \{a_0, a_1, \ldots, a_k\}$ be a set of $k+1$ pointwise-independent points in $\boldsymbol{R}^{nc}$. The geometric k-simplex in $\boldsymbol{R}^{nc}$ determined by A is the set of all points of the hyperplane H^k containing A for which the barycentric coordinates with respect to A are all nonnegative. The barycentric coordinates of a vector $\boldsymbol{h}$ with respect to A are the real numbers $f_0, f_1, \ldots, f_k$ if and only if (i) $\boldsymbol{h} = \sum_{i=0}^{k} f_i \boldsymbol{a}_i$ and (ii) $\sum_{i=0}^{k} f_i = 1$. $\boldsymbol{a}_i$ is the vector from the origin to the point a_i.

Theorem 4. The *nc* vertices representing product cuts bound an $(nc-1)$-simplex.

Proof. The composition simplex for an *nc* component system is an $(nc-1)$-simplex defined by the *nc* pure component fixed points on the hyperplane H^{nc-1} described by $\Sigma_{i=1}^{nc} x_i = 1$. Any composition $x^{p,0}$ located in batch distillation region $B(\boldsymbol{P})$ will produce the set of product cuts $\boldsymbol{P} = \{\boldsymbol{p}_0, \ldots, \boldsymbol{p}_{nc-1}\}$. The vertices are necessarily pointwise independent, as the dimensionality is reduced by one every time a new pot composition boundary is encountered and a new product cut is produced. (A set of vertices would be pointwise dependent if and only if the dimensionality remained the same even after a vertex has been exhausted.) A vector $\boldsymbol{h}$ through any composition $\hat{x}$ lying in the interior of $\boldsymbol{P}$ will have positive barycentric coordinates that sum to unity, as they would represent the fractions of a mixture with composition $\hat{x}$ that would be recovered in each product cut. Hence, $\boldsymbol{P}$ bounds an $(nc-1)$-simplex, which we will term the *product simplex.*

It is evident that any point in $B(\boldsymbol{P})$ must be a point in $\boldsymbol{P}$. However, the converse is not necessarily true. The residue curve map in Figure 6 has three batch distillation regions, and hence three product simplices. Product simplex $\boldsymbol{P}^1$ is bounded by the pure components *L*, *I*, and maximum boiling binary azeotrope *I-H*, product simplex $\boldsymbol{P}^2$ is bounded by *L*, *I-H*, and ternary azeotrope *L-I-H*, and product simplex $\boldsymbol{P}^3$ is bounded by *L*, *H*, and *I-H*. $\boldsymbol{P}^2$ and $\boldsymbol{P}^3$ intersect, and hence a reboiler composition $x^{p,0}$ interior to $\boldsymbol{P}^2$ will in fact produce positive barycentric coordinates for both product sets. However, the correct product sequence is {*L*, *I-H*, *L-I-H*}. Therefore, $x^{p,0}$ is truly located in batch distillation region B^2. On the other hand, a composition located in batch distillation region B^3 (bounded by the straight lines connecting *L*, *I*, *I-H*, and *L-I-H*) will only produce positive barycentric coordinates for this region. The product sequence will be {*L*, *I*, *I-H*}. Hence, region B^3 is an exception where the simplex bounded by the product compositions does not coincide with the batch distillation region itself. Therefore, a batch-distillation region may not be a simplex. However, from the preceding properties, each batch distillation region can be characterized by a product simplex.

From the properties of simplices the result implies that any subset of the vertices of $\boldsymbol{P}$ is itself the set of vertices for a geometric simplex (Hocking and Young, 1961). Each such subsimplex is called a *face* of the product simplex. In particular, the subsets of $nc-1$ vertices are the highest order faces (facets). There exist $nc-1$ such facets. These will be termed *product simplex facets* and are $(nc-2)$-simplices. The product simplex facet defined by the points $\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_{nc-1}$ will be termed a *product simplex boundary*. A product simplex boundary does not necessarily coincide with a pot composition boundary, in the same way product simplices and batch-distillation regions do not necessarily coincide. A product simplex boundary can be found by removing the unstable node from the set describing the product simplex. Conversely, a product simplex is an $(nc-1)$-simplex defined by a set of *nc* fixed points, where $nc-1$ points form a product-simplex boundary and the remaining point is the unstable node in the set.

Example: four-component system

To demonstrate the applications of the results just derived, the four-component system acetone (*A*), chloroform (*C*), ethanol (*E*), and benzene (*B*) has been characterized using the new concepts. The fixed points of this system at 1 atm were found by Fidkowski et al. (1993) and are shown in Table 1. The system features four azeotropes, and its composition simplex is shown in Figure 11.

Table 1. Compositions, Boiling Temperatures, and Stability of Fixed Points for the System Acetone (*A*), Chloroform (*C*), Ethanol (*E*), and Benzene (*B*) at 1 atm

e	*A*	*C*	*E*	*B*	T_B [K]	Type
A	1	0	0	0	329.22	un
CE	0	0.8536	0.1464	0	333.08	un
C	0	1	0	0	334.94	s
ACE	0.3383	0.4642	0.1967	0	337.04	s
AC	0.3437	0.6563	0	0	338.62	s
EB	0	0	0.4514	0.5486	340.98	s
E	0	0	1	0	351.44	sn
B	0	0	0	1	353.25	sn

A and the binary azeotrope *CE* are both unstable nodes, and their unstable manifolds fill most of the composition space. $\bar{W}^u(A)$ includes all the compositions above the shaded area in Figure 11a, including point *A* itself, but excluding the shaded area and the fixed points located on it. Similarly, $\bar{W}^u(CE)$ includes the compositions below the shaded area, including *CE*, but excluding the shaded area and all the compositions not involving *E*, while $\bar{W}^s(A) = \bar{W}^s(CE) = \emptyset$. $\bar{W}^u(C)$ includes all the compositions not involving *E* below the unstable separatrix connecting *AC* and *B*, while $\bar{W}^s(C)$ includes the binary compositions between *CE* and *C*, excluding *CE* and *C*. $\bar{W}^u(AC)$ includes the compositions along the stable separatrix connecting *AC* and *B*, excluding *B*, while $\bar{W}^s(AC)$ includes all the compositions not involving *B* to the left of the unstable separatrices between *A* and *ACE*, and *CE* and *ACE*, excluding the fixed points and the binary edge between *CE* and *C*. $\bar{W}^u(ACE)$ includes all the compositions on the shaded area in Figure 11a, excluding the edges between *AC* and *B*, and *E* and *B*. $\bar{W}^s(ACE)$ includes the compositions along the two unstable separatrices connecting the ternary azeotrope to *A* and *CE*, excluding the fixed points. $\bar{W}^u(EB)$ includes the entire binary edge between *E* and *B*, excluding the pure components, while $\bar{W}^s(EB)$ includes the entire shaded area in Figure 11b, excluding the fixed points and the unstable separatrices between *A* and *ACE*, and *CE* and *ACE*. Finally, $\bar{W}^u(E) = \{E\}$, and $\bar{W}^u(B) = \{B\}$. $\bar{W}^s(E)$ includes all the compositions to the right of the shaded area in Figure 11b, excluding the fixed points, while $\bar{W}^s(B)$ includes all the compositions to the left of the shaded area in Figure 11b, excluding all compositions not involving *B* and the fixed points.

When the unstable and stable manifolds are established, we can determine the boundary limit sets from Definition 3. $\bar{\omega}^u$ and $\bar{\omega}^s$ are presented in Table 2.

We now proceed to determine the pot composition boundaries for the two unstable nodes. Application of Eq. 9 leads to Eqs. 10 and 11. Hence PCB(*A*) is equal to the shaded area in Figure 11a, including the fixed points, while PCB(*CE*) is equal to PCB(*A*) plus the compositions below the stable separatrix between *AC* and *B* in the ternary subsystem *A*, *C*, and *B*:

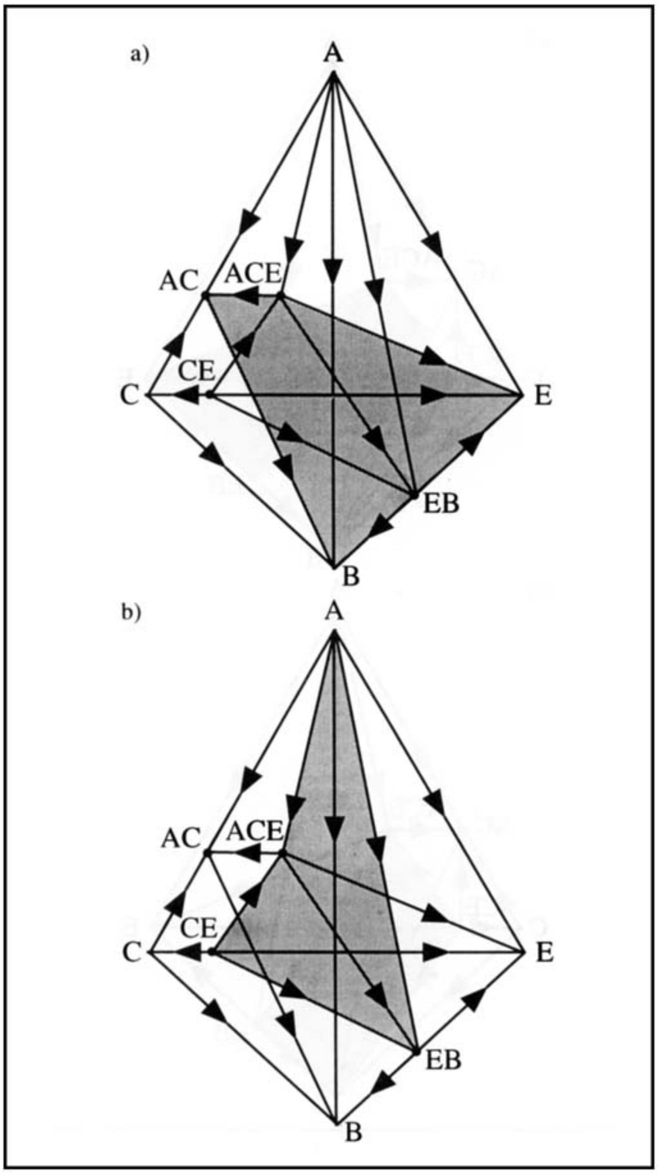

Figure 11. Composition simplex for acetone, chloroform, ethanol, and benzene.

(a) Shaded area separates $\overline{W}^u(A)$ and $\overline{W}^u(CE)$. (b) Shaded area separates $\overline{W}^s(E)$ and $\overline{W}^s(B)$.

$$\mathrm{PCB}(A) = Q \cap \bigcup_{x_j^* \in \{ACE, AC, EB, E, B\}} \overline{W}^u(x_j^*) \tag{10}$$

$$\mathrm{PCB}(CE) = Q \cap \bigcup_{x_j^* \in \{C, ACE, AC, EB, E, B\}} \overline{W}^u(x_j^*). \tag{11}$$

PCB(A) can be divided into three pot composition boundaries, the 3-simplices $\{ACE, EB, E\}$, $\{ACE, EB, B\}$, and $\{ACE, AC, B\}$, as illustrated in Figure 12. Hence, an initial composition $x^{p,0} \in \overline{W}^u(A)$ may give rise to three different product sequences starting with A: $\boldsymbol{P}^1 = \{A, ACE, EB, E\}$, $\boldsymbol{P}^2 = \{A, ACE, EB, B\}$, and $\boldsymbol{P}^3 = \{A, ACE, AC, B\}$ (see Figure 13). PCB(CE) can be divided into four pot composition boundaries, the same three 3-simplices as before plus $\{C, AC, B\}$. Therefore, $x^{p,0} \in \overline{W}^u(CE)$ may give rise to four different product sequences, starting with CE: $\boldsymbol{P}^4 = \{CE, ACE, EB, E\}$, $\boldsymbol{P}^5 = \{CE, ACE, EB, B\}$, $\boldsymbol{P}^6 = \{CE, ACE, AC, B\}$, and $\boldsymbol{P}^7 = \{CE, C, AC, B\}$ (see Figures 14 and 15). Note that in this system the batch distillation regions coincide with their corresponding product simplices.

Table 2. Unstable and Stable Boundary Limit Sets for the System Acetone, Chloroform, Ethanol, and Benzene

e	$\overline{\omega}^u$	$\overline{\omega}^s$
A	ACE, AC, EB, E, B	ϕ
CE	C, ACE, AC, EB, E, B	ϕ
C	AC, B	CE
ACE	AC, EB, E, B	A, CE
AC	B	A, CE, C, ACE
EB	E, B	A, CE, ACE
E	E	A, CE, ACE, EB
B	B	A, CE, C, ACE, AC, EB

Relaxing limiting assumptions

The theory for multicomponent homogeneous batch distillation is derived based on the assumptions of very high reflux ratio, large number of theoretical stages, and linear pot composition boundaries. If any of these limiting conditions are relaxed, a slight deviation from the predicted behavior may be observed.

Finite Number of Stages and Reflux Ratio. If the assumptions of very high reflux ratio and large number of theoretical stages are relaxed, the column profile will no longer follow a simple residue curve and the pot composition path will not move in a straight line, but will take on some curvature. Bernot et al. (1991) demonstrated that the pot and distillate paths can move slightly into another batch distillation region,

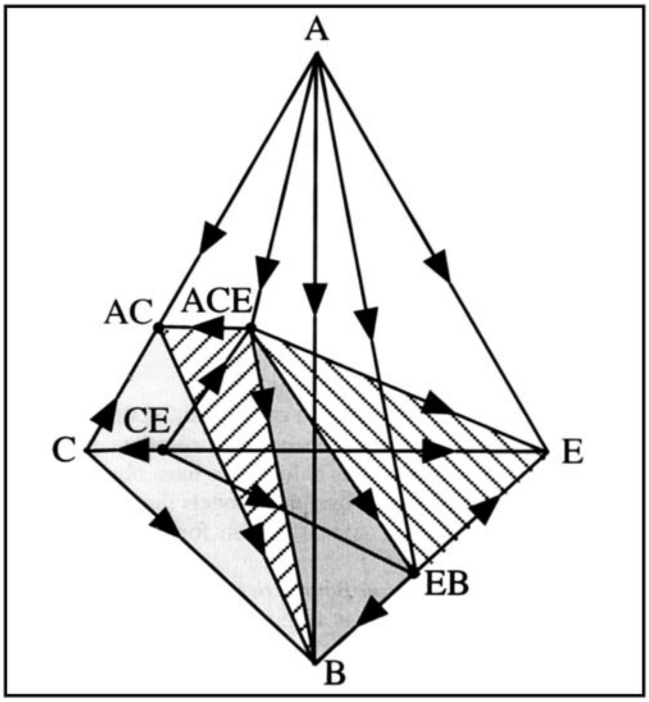

Figure 12. Pot composition boundaries.

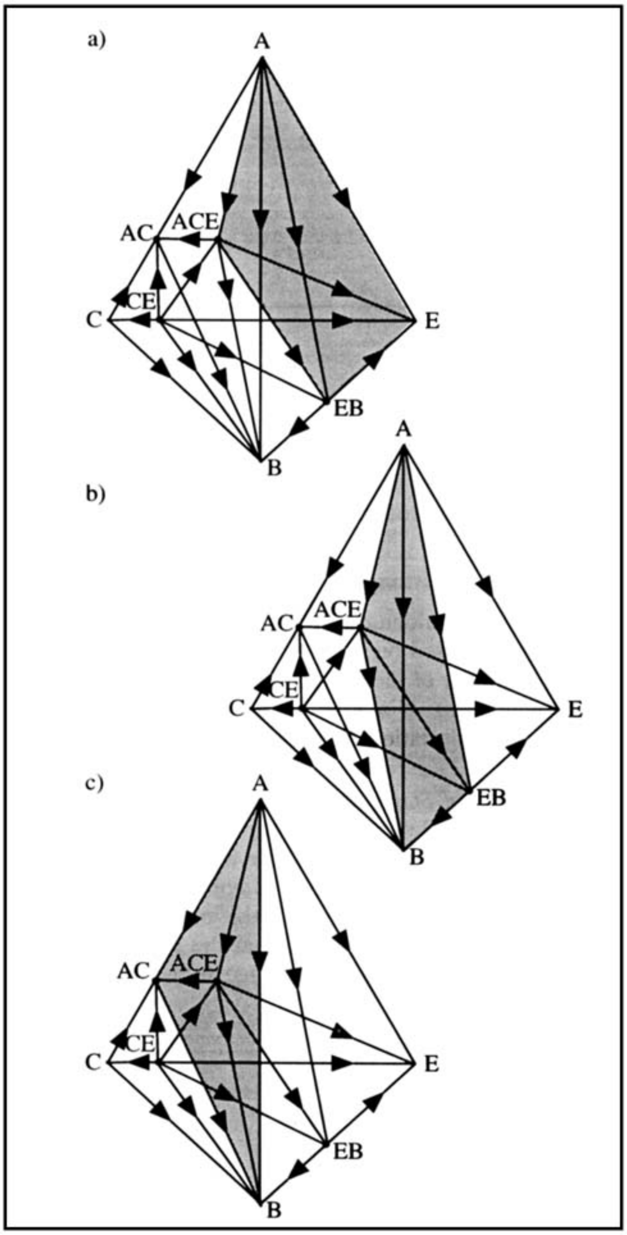

Figure 13. Composition simplex divided into batch distillation regions: (a) $B(P^1) \rightarrow P^1 = \{A, ACE, EB, E\}$; (b) $B(P^2) \rightarrow P^2 = \{A, ACE, EB, B\}$; and (c) $B(P^3) \rightarrow P^3 = \{A, ACE, AC, B\}$.

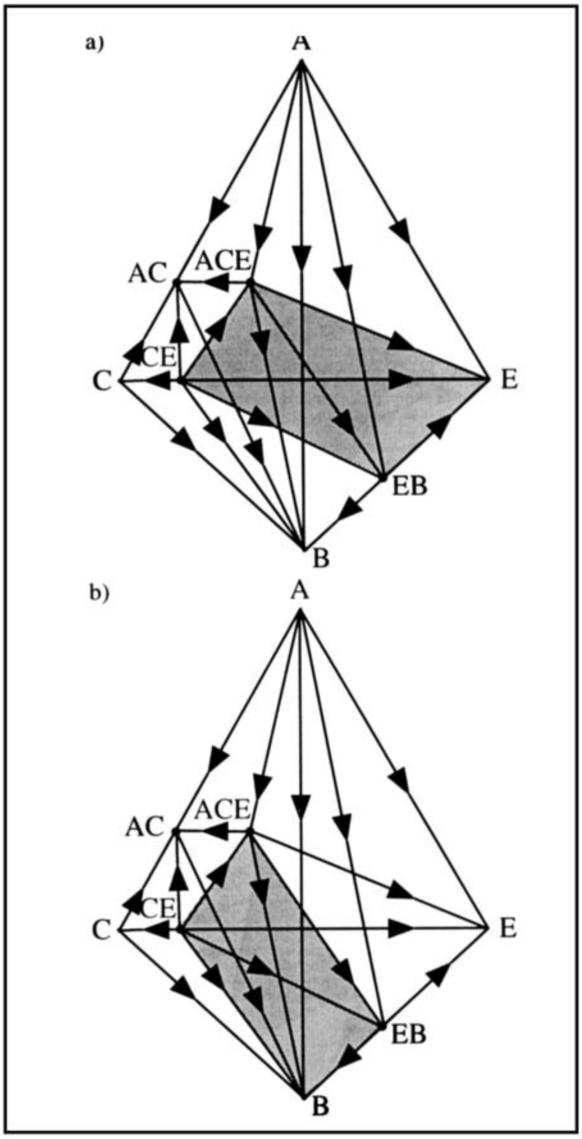

Figure 14. Composition simplex divided into batch distillation regions: (a) $B(P^4) \rightarrow P^4 = \{CE, ACE, EB, E\}$; and (b) $B(P^5) \rightarrow P^5 = \{CE, ACE, EB, B\}$.

and one may get a small fraction of an additional product cut ($nc+1$ cuts). Nevertheless, the pot and distillate paths will have the same basic shape as before. We have observed from studies with more detailed dynamic models that the theory is an accurate engineering approximation for columns with as few as 6–8 trays.

Curved Pot Composition Boundaries. As demonstrated by Ewell and Welch (1945), it is possible to obtain distillate compositions on the other side of a stable separatrix when running a rectifier under the limiting conditions of very high reflux ratio and large number of trays. When distilling mixtures of acetone, chloroform, and methanol, the researchers observed a nonmonotonic variation in the distillate temperature for certain initial reboiler compositions. Ewell and Welch could not explain their findings, and concluded that the temperature drop was an anomaly. Van Dongen and Doherty (1985b) showed that this "anomaly" has a logical explanation related to the curvature of stable separatrices. Figure 16 shows the residue curve map for the system acetone, methanol, and chloroform with batch-distillation boundaries. Stable separatrices are indicated with solid lines, while the other boundaries are dashed (long dash segments). Unstable separatrices are shown for clarity (short dash segments). When the pot orbit starting in $x_1^{p,0}$ hits the stable separatrix connecting the binary acetone–chloroform azeotrope and the ternary azeotrope, it is forced to stay close to this boundary, and the pot composition $x^p(\xi)$ will therefore follow the curvature of the separatrix. The instantaneous distillate compo-

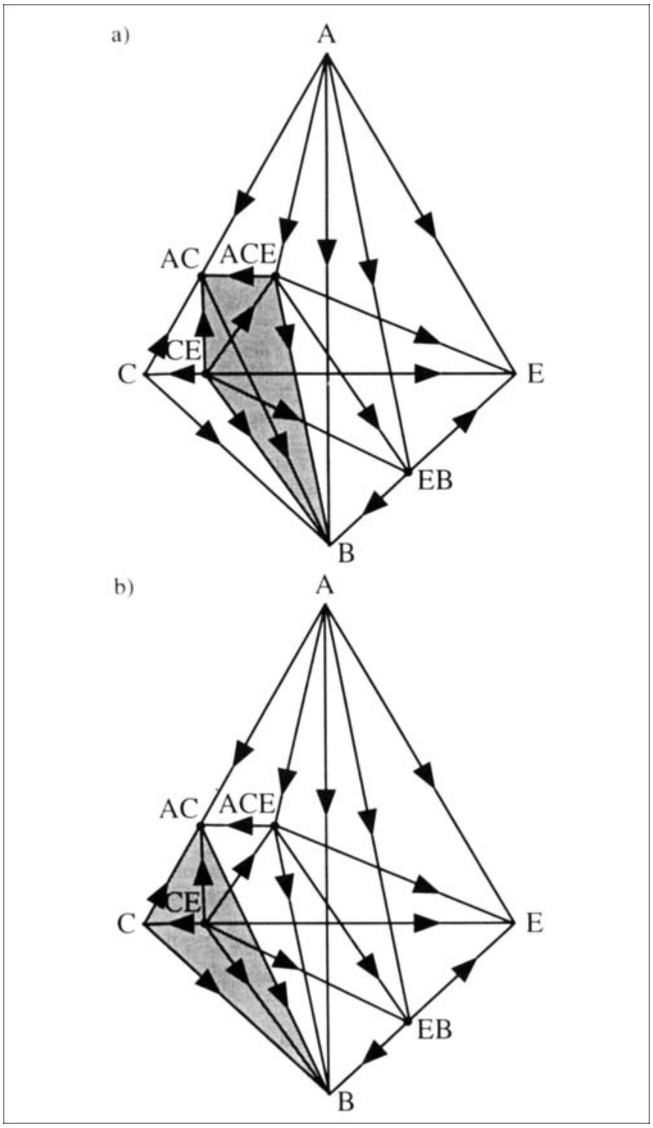

Figure 15. The composition simplex divided into batch distillation regions: (a) $B(P^6) \rightarrow P^6 = \{CE, ACE, AC, B\}$; and (b) $B(P^7) \rightarrow P^7 = \{CE, C, AC, B\}$.

sition $x^d(\xi')$ will lie on the tangent line to the pot orbit through the instantaneous pot composition $x^p(\xi')$. Hence, the distillate composition will not be equal to the ternary saddle azeotrope, but will have a composition that will vary along the unstable separatrix connecting the binary azeotrope acetone–methanol and the ternary azeotrope. A decrease in the distillate temperature may therefore be detected, before the temperature eventually increases again as the distillate composition path reaches the binary acetone–methanol azeotrope. The deviation from the ternary saddle azeotrope composition will depend on the curvature of the stable separatrix. Distillation of an initial reboiler composition located in batch distillation region B^2 will result in a similar outcome, with some distillate compositions located on the other side of the stable separatrix. On the other hand, initial compositions taken within regions B^3 and B^4 will not result in distillate compositions located on the other side of the stable separatrices. For example, when the pot orbit starting with $x_3^{p,0}$ hits the stable separatrix connecting the ternary azeotrope and the binary acetone–chloroform azeotrope, the corresponding distillate orbit will follow the same path as the distillate orbit resulting from $x_1^{p,0}$ (i.e., at that point the distillate composition will vary along the unstable separatrix connecting the binary azeotrope acetone–methanol and the ternary azeotrope). Hence, the distillate orbit will not cross the stable separatrix. A detailed discussion of the other possible product sequences can be found in Bernot et al. (1990).

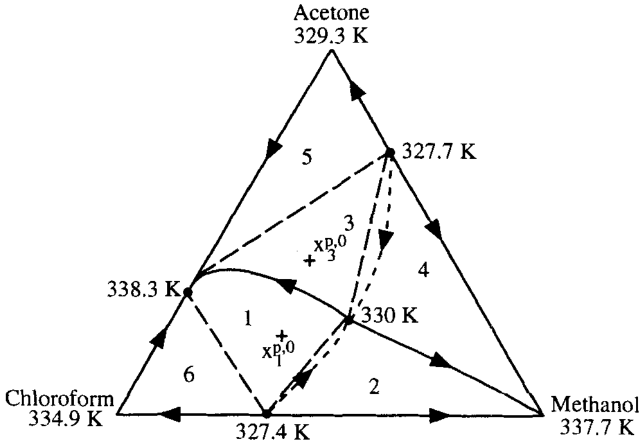

Figure 16. Residue curve map (qualitative) for the system acetone, chloroform, and methanol.

In conclusion, in the case of a highly curved pot composition boundary the pot composition path will move along the boundary, while the distillate path may move into another batch distillation region, resulting in additional product cuts. However, our experience indicates that the amount of material recovered in these additional cuts is small in comparison to the overall charge.

Conclusion

In this article work on the use of residue curve maps for the analysis of batch distillation of homogeneous mixtures has been reviewed, and the deficiencies in earlier work on ternary systems have been demonstrated and addressed. Furthermore, the theory has been generalized and extended to homogeneous systems with an arbitrary number of components. The following properties for simple distillation have been demonstrated:

- The whole composition simplex can be defined in terms of the respective disjoint unstable manifolds of the fixed points: $\underline{Q} = \bigcup_{e=1}^{ep} \overline{W}^u(x_e^*) = \bigcup_{m=1}^{un} \overline{W}^u(x_m^*) \cup \bigcup_{n=1}^{s} \overline{W}^u(x_n^*) \cup \bigcup_{q=1}^{sn} \overline{W}^u(x_q^*)$.
- Each fixed point can be characterized by its *unstable* and *stable boundary limit sets*, $\overline{\omega}^u(x^*)$ and $\overline{\omega}^s(x^*)$, respectively.

Moreover, based on the limiting assumptions of very high reflux ratio, large numbers of trays, linear pot composition boundaries, and a rectifier configuration, properties of the batch distillation composition simplex have been introduced:

- The movement of the pot composition orbit will be constrained by *pot composition barriers* present in the composition simplex. If $\boldsymbol{x}^p(\xi) \in \overline{W}^u(\boldsymbol{x}^*)$, the unstable manifold of fixed point $\boldsymbol{x}^*$, the constraining barrier is defined as $\mathrm{PCB}(\boldsymbol{x}^*) = \{\hat{\boldsymbol{x}} \in \boldsymbol{R}^{nc}: \gamma(\xi, \boldsymbol{x}) \to \boldsymbol{x}_j \in \overline{\omega}^u(\boldsymbol{x}^*) \text{ as } \xi \to \pm\infty\}$. *Pot composition boundaries* are subsets of the pot-composition barriers.

- If batch distillation region $B(\boldsymbol{P})$ gives rise to the product sequence $\boldsymbol{P} = \{\boldsymbol{p}_0, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots\}$, then at limiting conditions $B(\boldsymbol{P})$ is the set of composition points $\hat{\boldsymbol{x}} \in \overline{W}^u(\boldsymbol{p}_0)$ such that the resulting pot composition path $\boldsymbol{x}^p(\xi)$ will intersect the unstable manifolds of $\boldsymbol{p}_k$, $\overline{W}^u(\boldsymbol{p}_k)\ \forall \boldsymbol{p}_k \in \boldsymbol{P}$ as $\xi \to +\infty$. Composition points that give rise to a subset of $\boldsymbol{P}$ form the batch distillation boundaries of $B(\boldsymbol{P})$.
- An initial composition $\boldsymbol{x}^{p,0}$ located interior to batch distillation region B at limiting conditions will give rise to exactly *nc* product cuts, and these *nc* cuts form an *nc product simplex*.
- A batch distillation region and its corresponding product simplex defined by the *nc* fixed points in $\boldsymbol{P} = \{p_0, \ldots, p_{nc-1}\}$ do not necessarily coincide.

These results will allow complete characterization of the structure of the composition space for a multicomponent system when using batch distillation based only on the information of the compositions, boiling temperatures, and the stability of the fixed points. To demonstrate the applications of the derived results, a four-components system has been characterized using the new concepts.

Acknowledgments

This research was supported by the Emission Reduction Research Center under grant E12 9/96760, and the Chlorine Project of the MIT Initiative in Environmental Leadership. One of the authors (B.S.A.) acknowledges funds from the Norwegian Research Council.

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Appendix: Theory Applied to a Batch Stripper

A batch stripper is configured in a similar manner to a batch rectifier. However, the material is fed to the column from a holding tank where the mixture is held at its boiling temperature by a condenser. The product is taken out at the bottom of the column, and the recycled material is evaporated in a reboiler. Hence, the heaviest species is separated off first. When constructing the residue curve map for the mixture of interest, the arrows indicating direction of residue path should be reversed, as we now will be moving from heavier to lighter species in the holding tank. Therefore, all residue curves will reverse direction. As a result, the unstable nodes when a rectifier is assumed will become stable, and vice versa for the stable nodes. From there the analysis is analogous to the analysis when a rectifier configuration is used, based on the same limiting assumptions of high reflux ratio, large number of trays, and linear pot composition boundaries.

Example. The residue curve map when using a batch stripper has been derived for the ternary system in Figure 6a. The resulting batch distillation regions are shown in Figure 17. Observe that the batch distillation regions and their corresponding product simplices coincide. An initial composition located in batch distillation region B^1 will produce $\boldsymbol{P}^1 = \{L\text{-}I\text{-}H,\ I\text{-}H,\ I\}$, any composition in B^2 will produce $\boldsymbol{P}^2 = \{L\text{-}I\text{-}H,\ I\text{-}H,\ H\}$, B^3 will result in the product sequence $\boldsymbol{P}^3$

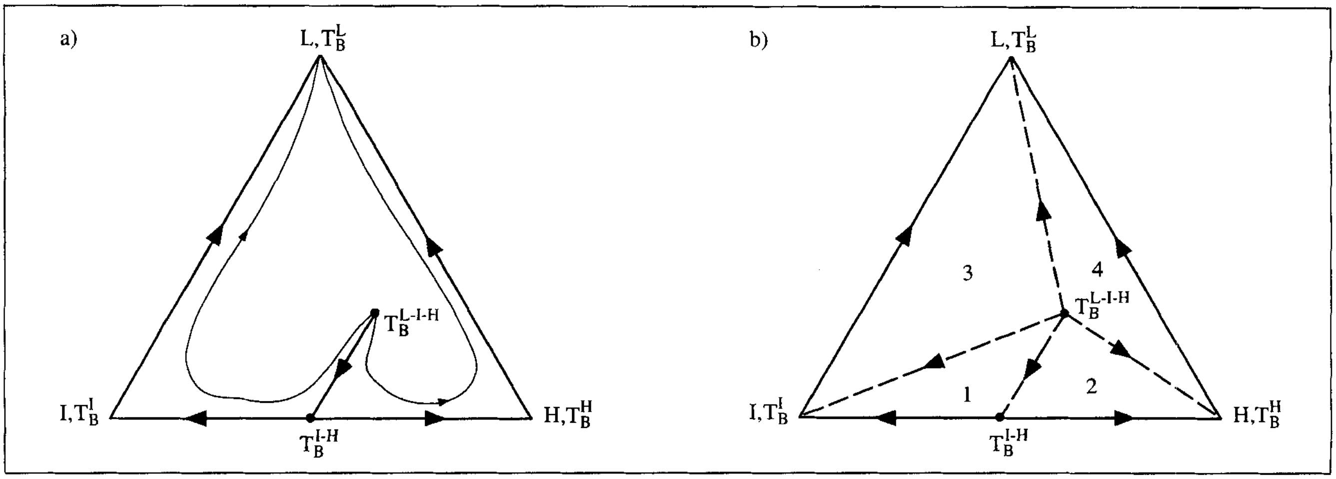

Figure 17. Residue curve map with batch distillation regions and product simplices for a stripper configuration.

$=\{L\text{-}I\text{-}H, I, L\}$, and B^4 will result in $P^4=\{L\text{-}I\text{-}H, H, L\}$. Because ternary azeotrope *L-I-H* is the unstable node in all batch distillation regions, it will always appear as the first product when a stripper configuration is used. In contrast, only initial compositions located in B^2 in Figure 6b have the ternary azeotrope as a product cut. Since it is always desirable to achieve products involving fewer components, this simple analysis implies that for distilling such a mixture the rectifier configuration should be chosen.

For mixtures with highly curved separatrices Bernot et al. (1991) demonstrated that using the stripper configuration may reduce the number of cuts necessary to achieve the desired products. It should be noted, however, that the stripper configuration is less likely to be adopted, as any solids (e.g., catalysts, crystals) in the process stream will complicate such an operation.

Manuscript received Feb. 26, 1996, and revision received June 11, 1996.