REVIEWS

Heuristic Synthesis and Shortcut Design of Separation Processes Using Residue Curve Maps: A Review

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This paper presents a review and evaluation of a large body of the latest published literature, especially since 1989, on the use of ternary composition diagrams and residue curve maps (RCMs), in particular, for the heuristic synthesis and shortcut design of multicomponent separation processes, with emphasis on azeotropic systems. RCMs and analogous liquid/liquid and solid/liquid phase diagrams are significant design tools, because they can represent good approximations to actual equilibrium behavior and can be used to predict composition changes in separation processes involving vapor/liquid mixtures (e.g., azeotropic, extractive, and reactive distillations), liquid/liquid mixtures (e.g., extraction), and solid/liquid mixtures (e.g., extractive crystallization). We describe how to construct RCMs from minimal data, as well as how to represent separation operations on ternary diagrams. We illustrate the use of ternary diagrams including RCMs for the feasibility analysis, flowsheet development, and preliminary design of both homogeneous and heterogeneous separation processes, particularly involving azeotropic systems. Our discussion emphasizes the design applications of the published results, as well as the proper clarifications of some traditional misconceptions and contradicting recommendations reported in the literature. Given the fundamental and practical insights into various aspects of separation process synthesis that can be gained from ternary diagrams including RCMs, we suggest that they are of great value to practicing chemical engineers and in undergraduate design teaching.

1. Introduction

The objective of this work is to carry out a review and evaluation of a large body of the latest published literature, mostly since 1989, for the heuristic synthesis and shortcut design of separation processes, using ternary diagrams and especially so-called residue curve maps (RCMs). We shall emphasize the design applications of the published results, as well as the proper clarifications of some traditional misconceptions and contradicting recommendations.

When designing an equilibrium-stage separation process for multicomponent mixtures, engineers will be faced with overcoming or exploiting a limited set of significant features that are characteristic of the phase equilibrium of the given system. For ternary mixtures, we can represent most of these features in ternary diagrams (Figure 1), which makes ternary diagrams a particularly effective tool for the heuristic synthesis and shortcut design of separation processes. Residue curve maps are an important type of ternary diagrams, pertaining to vapor/liquid separations (Partin, 1993).

Residue curve maps, or RCMs, were first defined and used by Schreinemakers (1901). They are constructed of *residue curves* (RCs), which we can find through a simple experiment: we place a liquid mixture of known composition (the "feed composition") in a single-stage batch still and heat it up without any reflux (Figure 2). We continuously analyze the composition of the liquid remaining in the still (the residue liquid) over time, until the last drop is vaporized. We call the tracing of this change in residue liquid composition a residue curve (Figure 3).

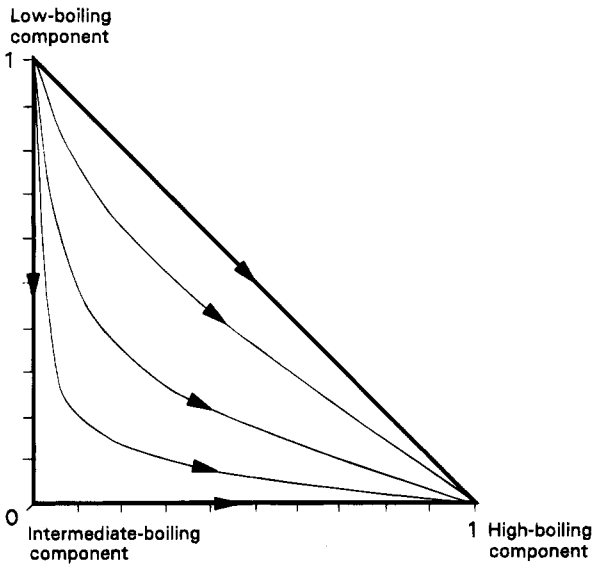

Figure 1. A simple residue curve map.

One important limitation: RCMs and analogous thermodynamic diagrams are only suitable for representing phase-equilibrium data (vapor/liquid, liquid/liquid, and solid/liquid equilibria) and are thus primarily useful for equilibrium-based separations. This excludes a whole class of separation methods based on kinetic behavior, such as adsorption, membrane permeation, etc. Equilibrium-based separations, however, are much more commonly used than kinetically-limited tech-

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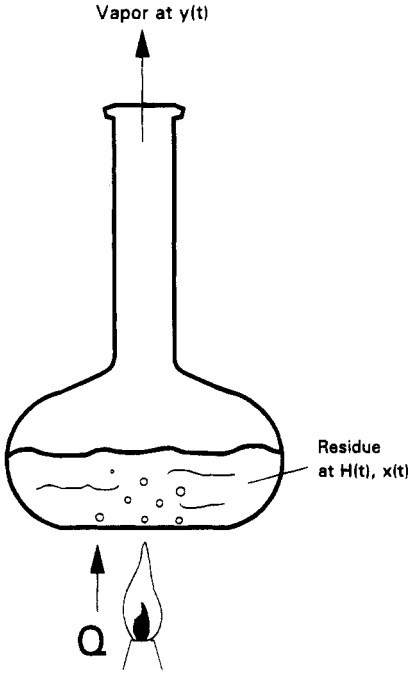

Figure 2. A simple batch still.

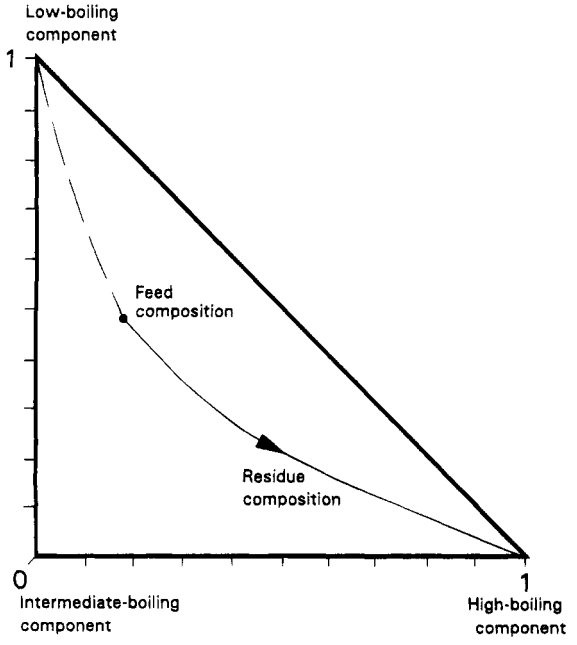

Figure 3. Tracing the residue composition.

niques. We shall confine ourselves here to separation of ternary mixtures for the ease of graphical representation and because most of the (topological) techniques involved apply only to ternary mixtures.

The overall design problem of separation sequencing may consist of three steps: (1) if necessary, selecting an appropriate *entrainer* (that is, an additional component that facilitates separation by changing the relative volatilities in the mixture through physical or chemical interaction with the original components); (2) finding feasible sequences; and (3) design and optimization of each sequence, using shortcut methods and rigorous simulation to allow selection of the best option. Ternary diagrams containing RCMs can be used in the first two steps.

2. Azeotropic Distillation

For a long time, distillation has been the most widely used and most energy-consuming, equilibrium-based separation method around. This fact makes it worthwhile to gain a good understanding of distillation processes and of the possibilities for energy- and materials-efficiency improvement.

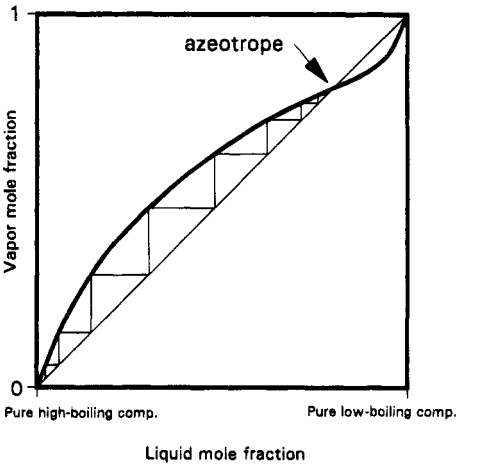

Figure 4. A generic binary McCabe–Thiele diagram. Stages are drawn in for total reflux conditions.

In many multicomponent mixtures, nonideal interactions between molecules of two or more species can cause azeotropic behavior. We may visualize this fairly common phenomenon in a binary McCabe–Thiele diagram (Figure 4), where it is obvious that, no matter how many stages we stack in a simple distillation column, we will not be able to pass the point (or "azeotrope") where the compositions of the vapor and liquid phases are identical. Ternary, quaternary, and higher-order azeotropes can occur, when three or more components are involved in an azeotropic composition. The existence of such binary and higher-order azeotropes greatly complicates the problem of distillative separation. Doherty (1985) goes as far as stating that "there are many ternary azeotropic mixtures for which there is no feasible sequence of columns" for obtaining certain desired product specifications. We shall discuss the use of ternary diagrams containing RCMs as a valuable tool for designing feasible sequences for the distillation of nonideal, azeotropic mixtures. As mentioned previously, thermodynamical diagrams analogous to RCMs are also useful for sequencing liquid/liquid separations (e.g., extraction) and solid/liquid separations (e.g., extractive crystallization; Cisternas and Rudd, 1993; Rajagopal et al., 1991).

When attempting to separate a binary azeotropic mixture, we should first investigate the possibility of using a two-tower system at different pressures, since this technique does not require any extra components to be added and may therefore save us at least one complete separation step. When such a "pressure-swing distillation" is not an option, due to insensitivity of the azeotrope(s) to pressure, a risk of product degradation, or (oftentimes) economic reasons, we are left with basically four well-established alternatives for separation through distillation (Laroche et al., 1992b): (1) *homogeneous azeotropic distillation*, where the entrainer changes the relative volatility of the azeotropic constituents without causing liquid–liquid immiscibility; (2) *heterogeneous azeotropic distillation*, where the entrainer alters the relative volatility and induces liquid-phase separation; (3) *reactive distillation*, where the entrainer reacts preferentially with one of the azeotropic constituents; and (4) *"salted" distillation*, in which the entrainer dissociates ionically, thereby changing the azeotropic composition.

According to Van Dongen (1983), we should distinguish between (1) *azeotropic distillation*, using an *entrainer* that introduces an extra, useful azeotrope, and (2) *extractive distillation*, using a *solvent* that interacts specifically with one or more components to lower their relative volatility. Often, extractive distillation is viewed as a special case of azeotropic distillation and it is usually preferred for several reasons. First, there is a much wider choice of possible solvents than of possible entrainers. Second, energy costs for azeotropic distillation are usually higher, since all of the entrainer must eventually appear in the distillate. Third, extractive distillation is generally regarded as being more flexible. Doherty and Caldarola (1985) distinguish two types of extractive distillation: (1) using a high-boiling solvent to split an azeotrope; and (2) using a high-boiling solvent to split two close-boiling species. These definitions put different requirements on the solvents.

The first azeotropic (batch) distillation was realized by Young (1902), for the production of anhydrous ethanol, using benzene as the added component. In fact, this specific process uses extractive distillation to break the azeotrope. Kubierschky (1915) patented a continuous version of this process, a few years later. The knowledge of azeotropic distillation has come a long way since then and reached a stage of accelerated progress over the last 15 years, largely due to the (re)discovery of the use of residue curve maps.

3. Residue Curve Maps

Theoretically, RCMs can be constructed for any number of components, but they can only be pictured graphically for up to four. A simple McCabe–Thiele diagram (Figure 4), in which the vapor-phase information is already included, suffices for binary mixtures. For ternary mixtures, we plot the liquid-phase compositions on a triangular diagram, similar to that used for liquid–liquid extraction, in which every corner represents a pure component (Figure 1). The three-dimensional tetrahedron, necessary to plot a four-component mixture, is hard to visualize on a flat surface. For five or more components, we need analytical geometry techniques.

Apart from experimentally using the simple batch still, we can also generate RCs mathematically, by integrating the mass and energy balances and thermodynamic equilibrium relationships that describe this simple still (see Appendix B). *Vertices* are the so-called "singular solutions" of these mathematical expressions and the collective topological name for azeotropes and pure components.

3.1. Definitions and Assumptions. If we view azeotropic distillation (justifiably) as a difficult separation step, the method of rank-ordered heuristics for separation sequencing (Nadgir and Liu, 1983) advises us that, in most cases, we should perform this step near the end of our sequence. This implies that we should have removed all nonazeotropic components from the mixture, before attempting to break any azeotrope. We thus hope to be dealing with three components (either with or without an entrainer or a solvent), which would allow us to represent the mixture in a ternary diagram. We apply the "diagram convention", used by Van Dongen and Doherty (1985) and by Foucher et al. (1991), *to have the high-boiling pure component as the lower right corner and the low-boiling pure component as the upper left corner* (Figure 1).

For ternary azeotropic systems, the analogy with binary azeotropic systems basically holds. The presence

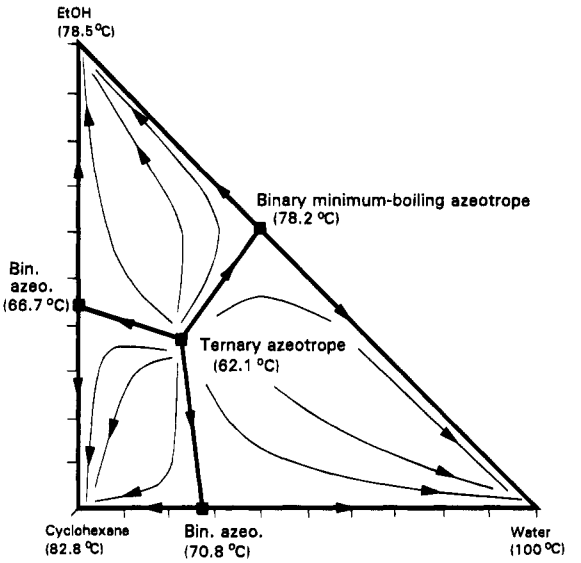

Figure 5. An example of binary and ternary azeotropes involving ethanol (EtOH), cyclohexane, and water.

of azeotropes divides the triangular diagram into separate *distillation regions* by introducing "distillation boundaries". These boundaries can, in a way, be seen as two-dimensional azeotropes. As shown in Figure 5, binary azeotropes are located on the edges of the triangular diagram, while ternary azeotropes are located inside the triangle. *Minimum-boiling azeotropes* have a lower boiling point than that of any of the components involved, while *maximum-boiling azeotropes* have a higher boiling point.

In order to predict where distillation boundaries will occur and to be able to sketch RCMs from minimal experimental data, we need to know more about the characteristics of residue curves (RCs).

3.2. Nodes and Saddles. Much theoretical research has been conducted to investigate azeotropy in multicomponent mixtures, notably in a series of papers by Doherty and Perkins (1978a,b, 1979a, 1982) and by Van Dongen and Doherty (1984). Others (Gani and Cameron, 1992; Matsuyama and Nishimura, 1977; Petlyuk et al., 1975a,b, 1977; Reshetov et al., 1983) have applied the field of mathematical topology and index theory to find relationships in RCMs, leading to the theory of "nodes and saddles". This theory suggests some heuristic guidelines for the construction of fairly accurate RCMs from *minimal* data. These data include the boiling temperatures of all components in the mixture, as well as the boiling temperatures and compositions of all occurring azeotropes (see Appendix A). Applying the heuristic guidelines, in most cases, enables us to construct RCMs, *without* requiring the explicit numerical integration of component mass/energy balances and thermodynamic equilibrium equations (see Appendix B). Numerical computations of exact RCMs are then only necessary for verifying difficult cases, such as those involving "*indeterminacy*", to be discussed in section 3.6.

We have already established that RCs point toward increasing temperature. This implies that they "diverge" from low-boiling vertices (pure components or azeotropes) and converge toward high-boiling vertices. At the same time, intermediate-boiling vertices exist, at which no RC ever starts or ends. From now on, we shall call the starting and end points of RCs "*nodes*", and all other vertices "*saddles*". This jargon comes from the stability theory of ordinary differential equations.

Nodes are either "stable" or "unstable" (Figure 6). A stable node is like a valley, in which a rolling ball will

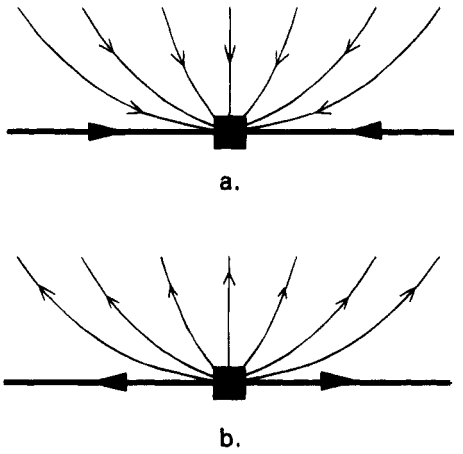

Figure 6. (a) A stable node and (b) an unstable node.

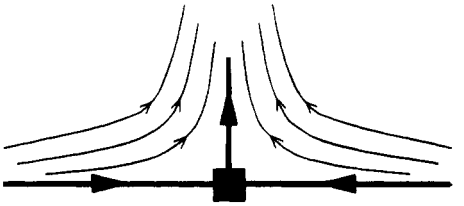

Figure 7. A saddle point.

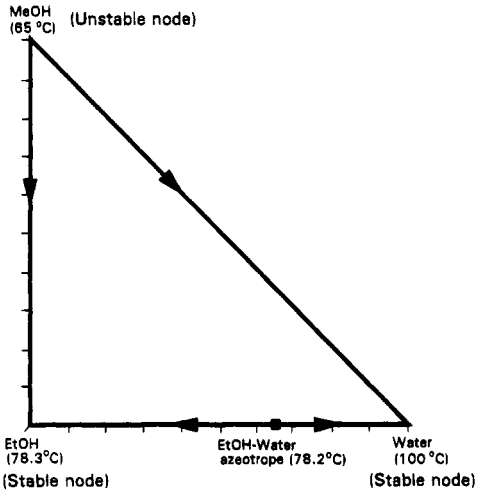

Figure 8. Classifying vertices as stable and unstable nodes: the methanol (MeOH)–ethanol (EtOH)–water system.

settle down in a stable position; all RCs in a distillation region point toward (arrive at) a stable node. In any distillation region, the highest-boiling vertex is a stable node. An unstable node is analogous to a mountain top, from which a ball will roll down toward a more stable position. In any distillation region, the lowest-boiling vertex is an unstable node, from which all RCs in that region will start.

A saddle point, as shown in Figure 7, has no RCs coming in or going out. Moving in one direction along the triangle edge is like going downhill (toward a stable node), while going in another direction resembles going uphill (toward an unstable node).

In order to determine the nature of pure-component vertices, we simply draw arrows on every segment of the ternary diagram's outer border between pure components and binary azeotropes and let these point toward the segment end with the highest boiling temperature (Figure 8). Stable nodes will only have arrows pointing inward, unstable nodes will have all arrows pointing outward, and saddles will have some arrows pointing inward and some pointing outward.

If a ternary azeotrope exists (we assume a maximum of one per ternary system, which is true for practically all industrial cases), we now need to start thinking about its nature as a node or a saddle. Foucher et al. (1991) state that a *ternary saddle azeotrope* must always have four connections to other vertices: two higher-boiling and two lower-boiling vertices, to be exact. If these connections are not available, the ternary azeotrope must be a node. Thus, a ternary azeotrope is a node (1) if it is one of the two highest-boiling or the two lowest-boiling species (excluding pure-component saddles) in the system or (2) when the sum of the number of pure-component nodes and the number of binary azeotropes is smaller than 4. Otherwise, the ternary azeotrope is a saddle.

A ternary node can only be connected to binary saddles and must be connected to at least one.

Knowing these facts, we can classify the rest of our vertices, using important results from topology (Doherty and Perkins, 1979a):

$$N2 = (2 + B - N1 - 2N3 + 2S3)/2 \qquad (1)$$

and

$$S2 = B - N2 \qquad (2)$$

where

B = no. of binary azeotropes

$N1$ = no. of pure-component nodes

$N2$ = no. of binary azeotrope nodes

$N3$ = no. of ternary azeotrope nodes

$S1$ = no. of pure-component saddles

$S2$ = no. of binary azeotrope saddles

$S3$ = no. of ternary azeotrope saddles

We illustrate the use of these equations in the next section.

3.3. Construction of RCMs. Once we have identified the topology of the RCM, we can sketch the distillation boundaries as straight lines with a direction (Figure 5). In reality, the boundaries are usually more or less curved, but at the preliminary design stage, there may be no need to establish a more accurate RCM.

We illustrate the use of eqs 1 and 2 as follows. Suppose that we have a ternary diagram as in Figure 9. Compositions and boiling temperatures have already been entered. By drawing the appropriate arrows on the edges, we find that the system has three binary azeotropes ($B = 3$), three stable pure-component nodes ($N1 = 3$), and no pure-component saddles ($S1 = 0$). We recognize that the ternary azeotrope must be an unstable node, since it has the lowest boiling point in the whole system. This means that the system has one ternary azeotrope node ($N3 = 1$) and no ternary saddle ($S3 = 0$). Our equations now give us $N2 = 0$ and $S2 = 3$, that is, the system has no binary azeotropic node and three binary azeotropic saddles. When no ternary saddle is present ($S3 = 0$), the number of distillation boundaries equals the number of binary saddles ($S2$) and all boundaries connect binary saddles to nodes (Appendix A). We thus obtain the RCM as shown in Figure 5.

In the last example, the use of eqs 1 and 2 was not absolutely necessary to be able to sketch the RCM. The

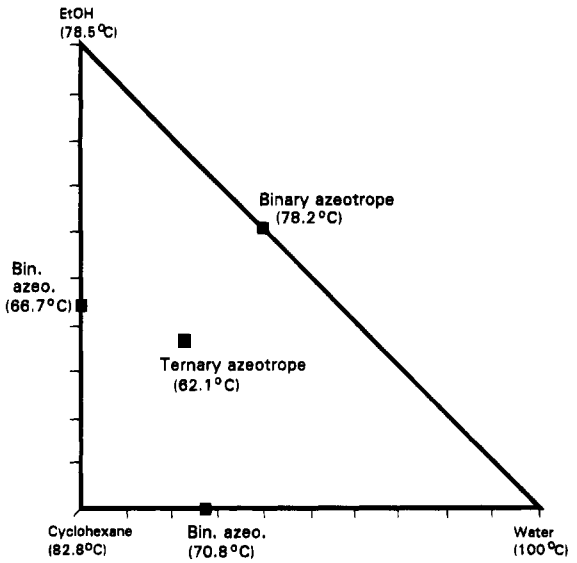

Figure 9. Initial data required to construct the RCM for the ethanol–cyclohexane–water system shown in Figure 5.

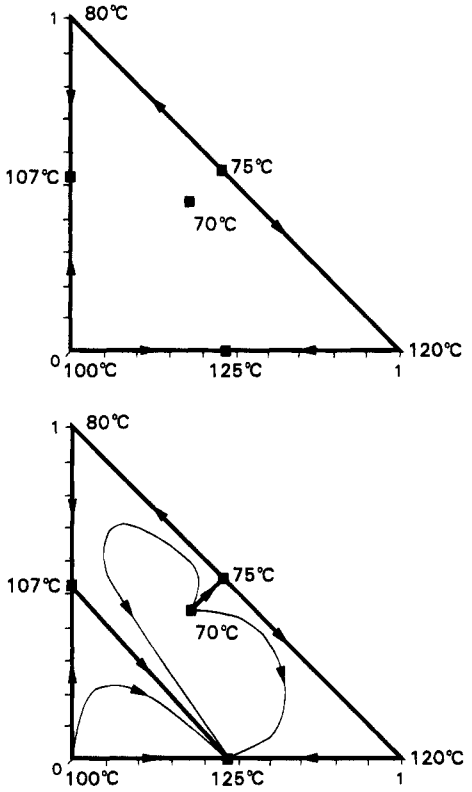

Figure 10. Constructing an RCM, using eqs 1 and 2. (a, top) Minimal data entered in the composition triangle. (b, bottom) The final result.

equations become important when dealing with more complicated systems, as in the next example (Figure 10). In Figure 10a, we have three binary azeotropes (B = 3), one unstable pure-component node ($N1$ = 1), and one ternary azeotrope with the lowest boiling point in the system, which means that it must be an unstable node, giving us $N3$ = 1 and $S3$ = 0. Using eqs 1 and 2, we find that there must be one binary azeotrope node ($N2$ = 1) and two binary azeotrope saddles ($S2$ = 2). Since one of the binary azeotropes has the highest boiling point in the system, this must be the one binary azeotrope node. The binary azeotrope boiling at 75 °C must then be a saddle and therefore have a connection to a lower-boiling species, for which only the ternary azeotrope is available. The binary azeotrope boiling at

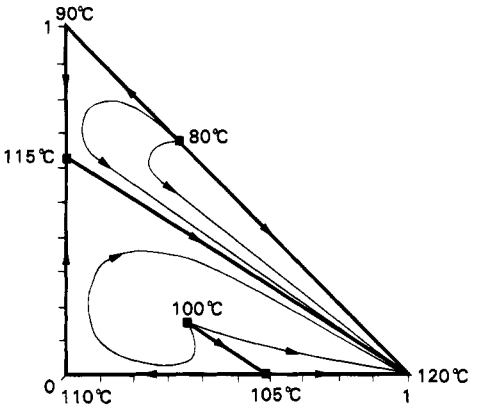

Figure 11. An RCM for which Yamakit's data-consistency checking rules give spurious results (Foucher et al., 1991).

107 °C must also be a saddle and needs a connection to a higher boiling species, for which the only option is the binary azeotrope node, boiling at 125 °C, since pure-component saddles cannot be candidates. We have now found the correct RCM (Figure 10b). Note that in neither example were RCs needed to obtain the final result.

Rev (1992, p 899) distinguishes between *separatrices*, which constitute all RCs that connect two vertices, and *boundaries*, which are only those separatrices that arrive at saddle points. The terms separatrix and boundary are not used consistently throughout the literature.

3.4. Data Inconsistency. If $N2$ or $S2$ comes out negative or noninteger, or if $S2$ is larger than the total number of intermediate-boiling binary azeotropes, then the pure-component and azeotropic data are thermodynamically inconsistent. Yamakita et al. (1983) present a method to check the consistency of ternary azeotropic data, using simple distillation experiments in the neighborhoods of binary azeotropes. They require that the RC has to extend to the point at higher temperature and

$$\sigma_1 + 2\sigma_2 + 4\sigma_3 = 1 \qquad (3)$$

where σ_1 denotes the sum of indices of pure components, and σ_2 and σ_3 represent the sums of indices of binary and ternary azeotropes, respectively. An index is defined to be +1 when it represents a node or −1 when it represents a saddle. A ternary azeotrope gets index +1 if it is the highest- or lowest-boiling species in the system and a −1 otherwise.

Foucher et al. (1991) find this method to be incomplete and recommend not to use it indiscriminately. They give an example to illustrate this incompleteness. As they point out, the method by Yamakita et al. (1983) would falsely diagnose the system in Figure 11 to be inconsistent, because it is unable to assign a correct index to the ternary azeotrope. Since this ternary azeotrope is neither the highest- nor the lowest-boiling species in the system, it should get an index −1. However, there are two pure-component saddles and one pure-component node, $\sigma_1 = -2 + 1 = -1$; two binary azeotrope saddles and one binary azeotrope node (found from the experiments that this method requires), $\sigma_2 = -2 + 1 = -1$; so eq 3 gives us $\sigma_3 = 1$. Obviously, the ternary azeotrope has been assigned two different indices, which, according to Yamakita et al. (1983), should indicate data inconsistency, even though the system is, in fact, fully consistent.

Foucher et al. (1991) present another set of rules for checking data consistency. Their first test consists of

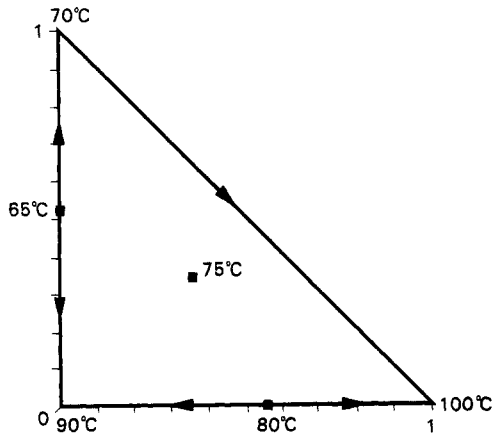

Figure 12. An example of inconsistent thermodynamic data according to the first test rule from Foucher et al. (1991).

counting the number of binary azeotropes that are either the highest- or the lowest-boiling species in the system. If this number is greater than the number of binary nodes, N2, the data are inconsistent. As an example, they provide a hypothetical case, shown in Figure 12. The number of extremum-boiling binary azeotropes is 1 (at 65 °C). The ternary azeotrope has to be a node, since we have to exclude the pure-component saddle at 70 °C as a possible (and necessary) connection for a ternary saddle. We now have two binary azeotropes ($B = 2$), two pure-component nodes ($N1 = 2$), one ternary azeotrope node ($N3 = 1$), and no ternary azeotrope saddle ($S3 = 0$). Using eq 1 we can calculate that $N2 = 0$. This means that, since $N2 < 1$, the thermodynamic data must be inconsistent.

3.5. Classifying RCMs. Not all combinations of azeotropes can freely exist, due to thermodynamic and topological constraints. Matsuyama and Nishimura (1977) reduce the total number of possible configurations to 113, by making the assumption that we can have at most one ternary azeotrope per system and one binary azeotrope per triangle edge. Evidence of systems contradicting this assumption has been reported in literature (e.g., Gaw and Swinton, 1966), but these exceptional systems are very rare in industrial practice.

Matsuyama and Nishimura (1977) find that ternary systems can be classified according to their number and type of azeotropes. The key to their classification system uses the same "diagram convention" we mentioned earlier (Figure 1). Of the three digits, the first one corresponds to the A−B binary pair, the second one to the B−C pair, and the third one to the A−C pair, where A, B, and C represent the lowest-, intermediate-, and highest-boiling components, respectively. The meaning of the digits is:

0: no azeotrope

1: binary *minimum*-boiling azeotrope *node*

2: binary minimum-boiling azeotrope *saddle*

3: binary *maximum*-boiling azeotrope *node*

4: binary maximum-boiling azeotrope *saddle*

If a ternary azeotrope is present, the three-digit code is followed by one of three letters:

m: minimum-boiling azeotrope

M: maximum-boiling azeotrope

S: intermediate-boiling azeotrope

For example, Figure 13 shows systems from classes 324-M and 414-M, while Figure 34 shows an example of a class 222-m system.

The 87 RCM configurations that contain at least one minimum-boiling binary azeotrope are given in Doherty and Caldarola (1985). The cases most commonly encountered in industry are among those 87.

3.6. Indeterminacy. Knight (1986) reports that, in some (rare) cases, multiple RCMs are possible for a given set of boiling points. An example is shown in Figure 13: the 324-M and the 414-M classes can both be constructed from the same minimal data set. Foucher et al. (1991) also discuss this kind of indeterminacy and mention that (1) if a ternary saddle exists ($S3 = 1$) and the sum of the number of pure-component nodes and binary azeotropes is six (i.e., $N1 + B = 6$) or (2) when the number of binary saddles does not equal the number of intermediate-boiling binary azeotropes, indeterminacy occurs. In these cases, it should be a simple matter to calculate a single RC and to determine its direction and thus the correct RCM structure. Fortunately, cases like these are still hypothetical and have not yet been reported from engineering practice.

3.7. RCMs and Reality. At infinite reflux and with an infinite number of stages, the liquid-composition trajectories in continuous distillation (as opposed to the simple batch still we have been discussing so far) practically follow the RCs. For a more practical column, with a finite reflux and a finite number of stages, the composition profiles still exhibit the same general behavior as RCs. Distillation boundaries can shift slightly as a function of reflux ratio and the number of stages. Wahnschafft et al. (1992) show where and by how much this shifting can have notable consequences in systems with simple distillation boundaries of marked curvature. Nevertheless, the error in approximating true boundaries with "simple distillation boundaries" often is so small as to be inconsequential, especially at the flowsheet-synthesis stage.

If we plot the bubble-point of every possible liquid composition, using an axis perpendicular to the triangular plane, we have a three-dimensional "*T-x-y* diagram", resembling a hilly surface with valleys and ridges. Rev (1992) gives an excellent discussion on the traditional misconception that distillation boundaries must coincide with these temperature ridges and valleys. The same misconception, which also seems to appear in the early articles by Doherty and Perkins (1978a,b), had already been noted by Van Dongen and Doherty (1984). Rev shows that the boundaries usually do not coincide, even though the boundaries and the ridges/valleys both start from the vertices. Good examples are the ternary systems of methanol and acetone with chloroform or methyl acetate. At present, distillation boundaries are thought to be unrelated to simple thermodynamic functions like (1) $\alpha_{ij} = 1$(relative volatility of i with respect to j); (2) $K_i = 1$(equilibrium ratio of i: vapor mole fraction/liquid mole fraction); (3) valleys/ridges in the temperature surface. Swietoslawski (1963) was apparently the first to note the discrepancies between ridges and boundaries.

3.8. Distillation Lines. RCs are not to be confused with *distillation lines*, which are smooth representations

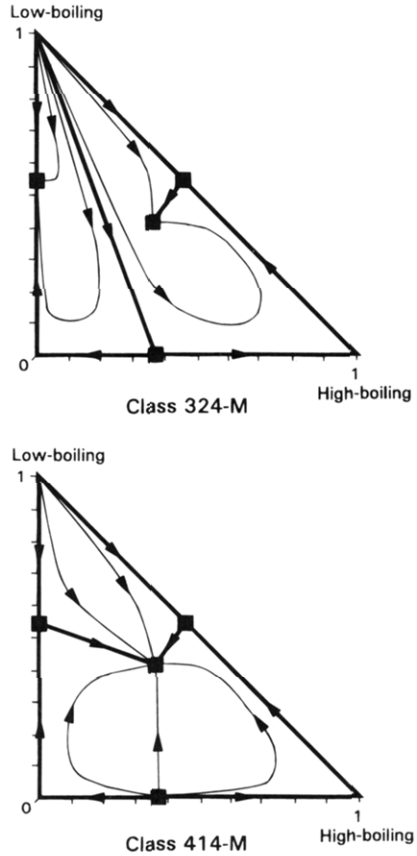

Figure 13. Examples of indeterminacy: different RCM classes, based on the same initial data set.

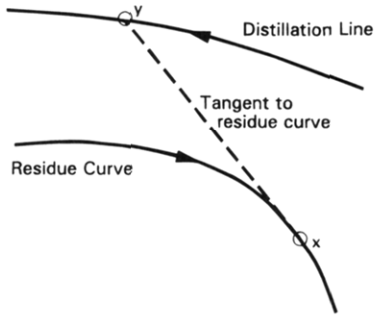

Figure 14. Residue curves and distillation lines: vapor composition y, in equilibrium with liquid composition x, must be on the distillation line and must lie on the tangent to the residue curve in x.

of liquid composition profiles in staged columns, operating at total reflux. Any given point on an RC is connected by its tangent to the corresponding point on a distillation line (Figure 14 and Appendix B). Furthermore, as the generally accepted convention, the direction of the RC is toward increasing temperature, whereas distillation lines point toward decreasing temperature. RCs are generally better understood, better defined in a thermodynamic sense, and easier to verify experimentally than distillation lines, but "the difference between RCs and distillation lines is normally not very significant" (Wahnschafft et al., 1992). Stichlmair et al. (1989, 1992) use distillation lines extensively.

4. Separation Processes and RCMs

4.1. Introduction. RCMs and related ternary diagrams are capable of representing many important features of the mixture to be separated and of the process involved. An incomplete list of such (superimposed) features includes distillation boundaries and

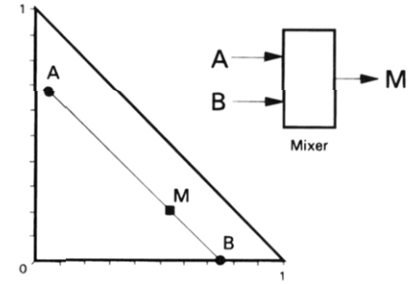

Figure 15. A stream-mixing balance line.

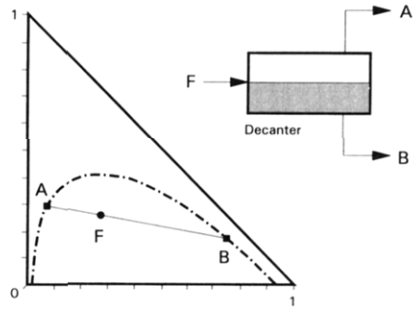

Figure 16. A phase-separation balance line.

azeotropes, saddle products, material-balance lines, regions of low volatility ("pinch" regions), liquid−liquid immiscibility, and liquid−solid immiscibility. In the following sections, we shall discuss how some of these features are represented and how we can apply them toward the design of feasible separation sequences.

4.2. Material-Balance Lines. Analytical material balances are graphically represented in RCMs by straight lines connecting stream compositions. Relative stream flow rates can be found by the well-known "lever rule".

For distillation systems, we commonly encounter three types of material balances: (1) stream-mixing balances, (2) distillation-column balances, and (3) phase-separation balances.

When two streams are combined, the resulting mixture must have an intermediate composition on the material-balance line connecting the two feed points: the stream-mixing balance line (Figure 15).

A distillation-column balance line represents the result of a simple (binary) distillation, in which one feedstream is split into a distillate and a bottoms product stream. The product compositions give the endpoints of the balance line, which is governed by two important constraints (Laroche et al., 1992a): the feed, distillate, and bottoms compositions must lie on the same straight line, which is segmented according to the lever rule; and (2) the bottoms and distillate compositions must lie on the same residue curve and therefore in the same distillation region.

Phase-separation balance lines usually play a role in heterogeneous distillation when, at one point or another, a distillation-column balance line enters a liquid−liquid immiscibility region and phase separation occurs. The resulting liquid phases should have compositions on the border of the immiscibility region, connected by a mass-balance tie line, with segments that represent the relative flow rates of the liquid phases, according to the lever rule (Figure 16).

Two important distillation-column balance lines are those representing the direct and indirect splits. The *direct-split* balance line connects the feed composition and the lowest-boiling vertex in a distillation region, indicating a sharp split with the lowest-boiling species as pure *top* product. The *indirect-split* balance line

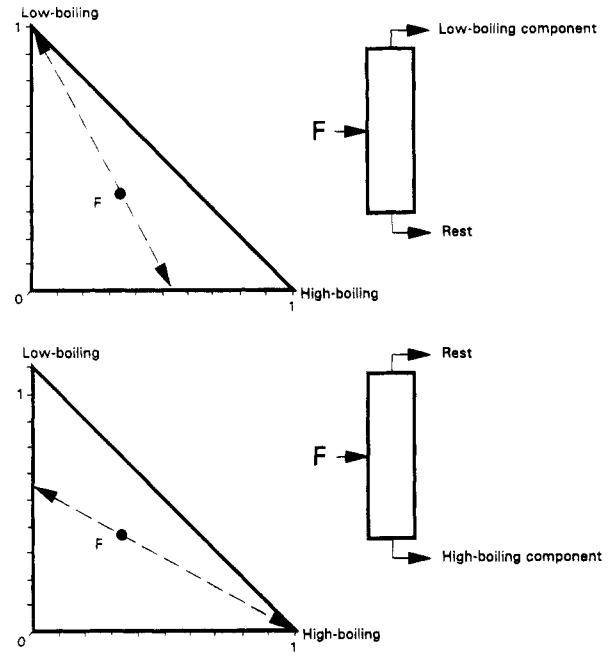

Figure 17. (top) Direct- and (bottom) indirect-split balance lines.

connects the feed composition to the highest-boiling vertex in a distillation region, indicating a sharp split with the highest-boiling component as pure *bottoms* product (Figure 17). Because the temperature in a simple distillation column must decrease monotonically toward the top stage, it is normally impossible to obtain an intermediate-boiling component (saddle point) as pure product from either the top or the bottoms of a single column. Exceptions can occur in systems with intermediate-boiling azeotropes, as discussed by Laroche et al. (1991) and Wahnschafft and Westerberg (1993).

None of these types of balance lines is necessarily confined to one specific distillation region.

4.3. Crossing Boundaries. Doherty and Caldarola (1985) assume, as a practical working approximation, that "[distillation-column] material-balance lines must remain local to the distillation region that contains the column feed". They are, of course, aware that mixing of streams from different regions causes the balance line for a process to cross the boundary between those regions. However, even distillation-column balance lines are (theoretically) able to cross distillation boundaries. Bossen et al. (1993), who discuss boundary crossing extensively, therefore propose to label them more accurately as "possible distillation boundaries". In order to effectively prohibit all distillation across a boundary, that boundary would have to be a straight line, which they propose to label as a "true distillation boundary".

Boundary crossing by distillation can be demonstrated as follows. Suppose that we have an RCM with a single (extremely) curved distillation boundary, as in Figure 18. If our feed composition (F) is located close enough to the concave side of the boundary, a distillation-column balance line may give us top and bottoms products that are located on the same RC (as required) but with the feed and the products on opposite sides of the distillation boundary (Laroche et al., 1992b). This "trick" is very sensitive to the exact curvature of the boundary and therefore to the accuracy of the vapor–liquid-equilibrium model used. It can also be expected that, even if a design for such a split worked, it would tend to be rather expensive and difficult to control (Foucher et al., 1991; Stichlmair and Herguijuela, 1992; Westbrook and Knight, 1992).

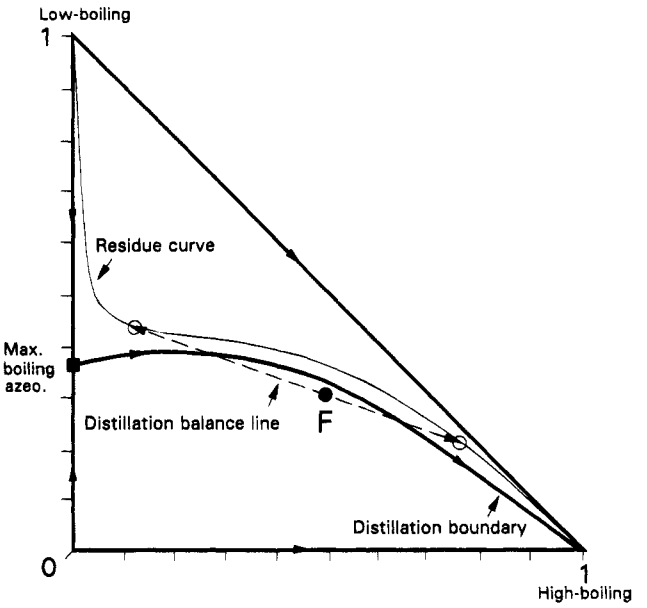

Figure 18. Crossing a distillation boundary.

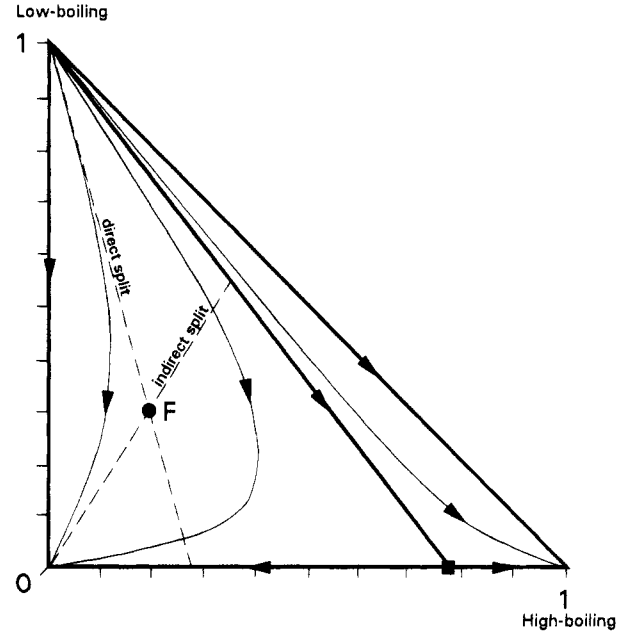

Figure 19. Construction of the bow-tie region: drawing direct- and indirect-split balance lines in the residue curve map, containing a minimum-boiling binary azeotrope.

Wahnschafft et al. (1992) report that distillation boundaries for columns at total reflux can be crossed at finite reflux ratios, when the relative volatilities between the azeotrope-forming species depend on the presence of other components in the mixture. We are not aware of many industrial applications of this type of separation, but some do exist (e.g., Stichlmair et al., 1989). Also, Wahnschafft and Westerberg (1993) define the conditions for using entrainers whose function is based on boundary crossing. Wahnschafft et al. (1992) mention that "the extent of crossing of simple distillation boundaries will hardly ever be large enough to make a species, which introduces such a boundary between the components to be separated, a good choice as an entrainer. However, processes that exploit the ability to cross boundaries may be attractive if a species already present in the original mixture can function as the separating agent".

4.4. Bow-Tie Regions. A very useful "shortcut design tool" is the so-called *bow-tie region*, which gives

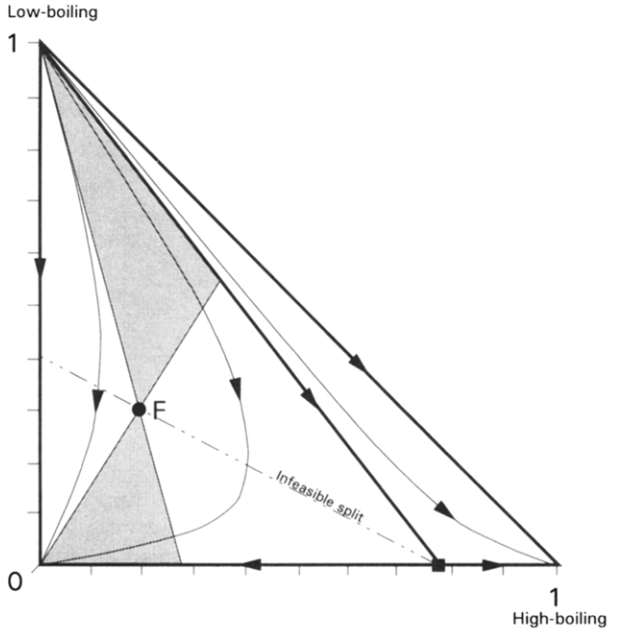

Figure 20. Construction of the bow-tie region: drawing the (impossible) intermediate-split balance line and shading the two regions not crossed by this balance line.

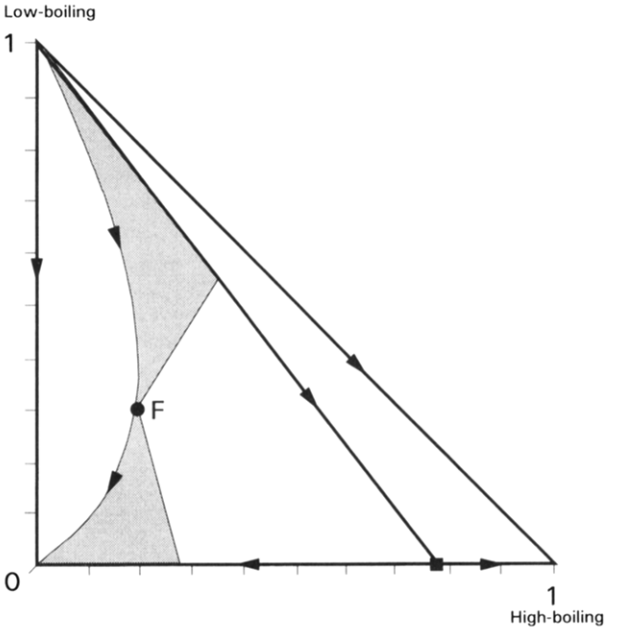

Figure 21. Construction of the bow-tie region: drawing the final bow-tie region.

the feasible combinations of distillate and bottoms compositions for a specified feed composition (Van Dongen, 1983; Van Dongen and Doherty, 1985). In other words, a bow-tie region gives the feasible distillation-column mass-balance lines for a specific feed. We construct a bow-tie region (for a total-reflux column) as follows: (1) Draw the material-balance lines for direct and indirect splits in the RCM, thereby dividing the distillation region, in which the feed composition is located, into four sections. Note that these balance lines are constrained by the distillation boundaries (Figure 19). (2) Next, imagine the balance line for the (impossible) intermediate split and shade the two regions that are *not* crossed by this last, impossible, mass-balance line (Figure 20). (3) We observe that each feasible RC must go through both shaded regions, in order to get feasible top *and* bottoms products, that lie on a material-balance line passing through the feed. This means that we should take as the final bow-tie region the shaded section on the convex side of the RC that goes through the feed composition (Figure 21). Although step 2 (Figure 20) seems instinctively correct, rare exceptions to it are known. Step 3 is more rigorous and makes step 2 superfluous.

We can also generate bow-tie regions mathematically (Van Dongen, 1983; Wahnschafft et al., 1992). The resulting regions usually turn out somewhat smaller than the "true" regions but with the same general features and sufficient accuracy for use in preliminary design.

If the feed composition is located on an RC near an inflection point, the bow-tie region becomes complicated (Figure 22) and cannot be defined simply in terms of direct and indirect split lines (Wahnschafft et al., 1992).

It is important to realize that the bow-tie region is a shortcut design tool, giving a set of feasible mass-balance lines, which may rule out certain feasible top and bottoms products for columns with finite reflux or in case of distillation-boundary crossing (Wahnschafft, 1992).

Recognizing that many industrially important separation methods are unable to achieve sharp splits in single-unit processes, Liu et al. (1990) and Wahnschafft et al. (1993) describe strategies for developing the multicomponent separation sequences required to achieve the overall separation goal by combining nonsharp splits. In the following, we shall focus on the use of RCMs in developing sequences for the separation of ternary azeotropic mixtures.

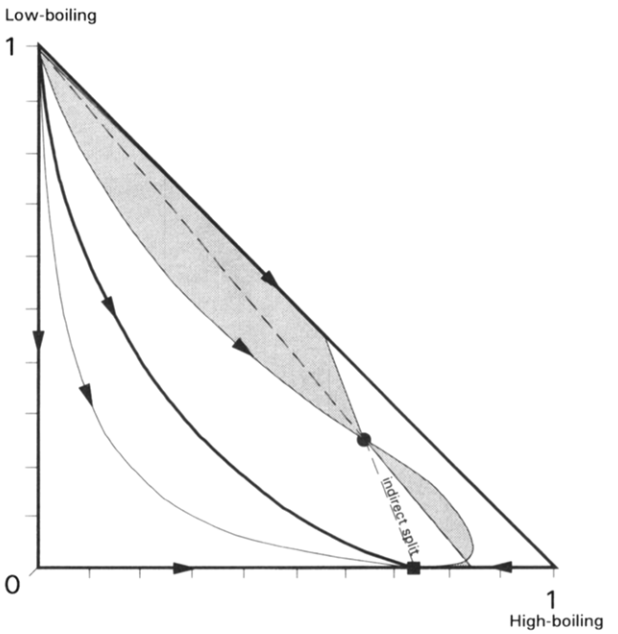

Figure 22. An example illustrating the difficulty of drawing the bow-tie region: feed composition near an inflection point.

5. Sequencing of Azeotropic Distillation Processes

5.1. Homogeneous Azeotropic Distillation Processes. Homogeneous azeotropic distillation of ternary mixtures refers to the distillative separation of a three-component azeotropic mixture, in which all components are fully miscible over their whole concentration range. We shall demonstrate the use of RCMs for the synthesis of feasible separation sequences, beginning with a simple example from ordinary (nonazeotropic) distillation.

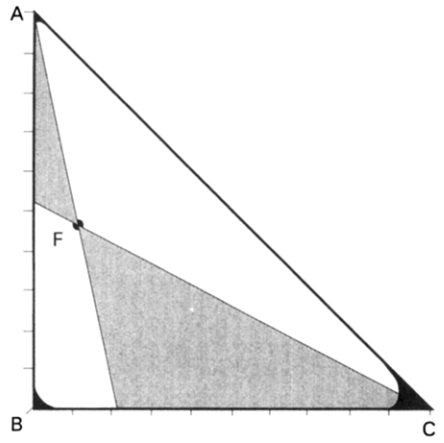

Figure 23. Product specifications and bow-tie region for a nonazeotropic ternary mixture. The darkened areas near the three pure-component vertices represent the minimum purity requirements of components A, B, and C (90−98%).

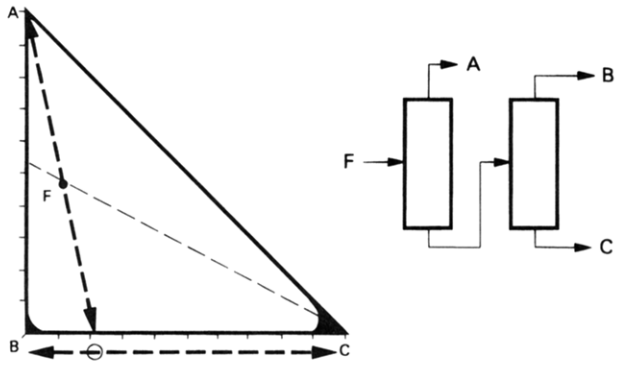

Figure 24. A direct split followed by a binary split.

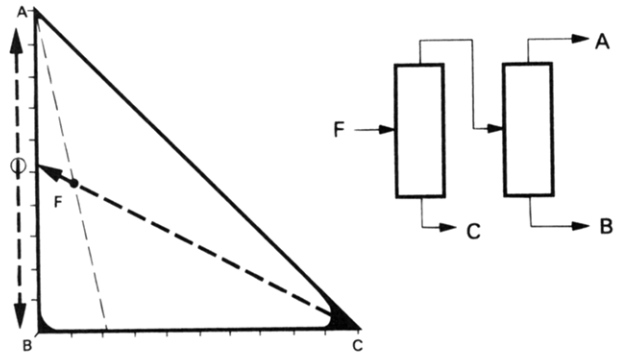

Figure 25. An indirect split followed by a binary split.

Let Figure 23 be the ternary diagram representing a nonazeotropic ternary mixture of components A, B, and C. According to our labeling convention, component B must be the intermediate-boiling component. The feed composition (F) and the bow-tie region are already drawn in. Suppose that our product specifications are as follows: minimum purity of A stream, 98%; minimum purity of B stream, 95%; minimum purity of C stream, 90%. We represent these specifications in the ternary diagram by small darkened areas near the pure-component vertices in Figure 23. We have three basic sequence options to reach the product specifications. We can start with the (sharp) *direct* split, which leads to a two-column design (Figure 24). We can start with the (sharp) *indirect* split, which also leads to a two-column design (Figure 25), or we can first perform a nonsharp split, which eventually leads to a three-column design (Figure 26). To minimize the number of columns, we generally distill to a "composition of interest" (e.g., pure components or azeotropes) rather than to an arbitrary

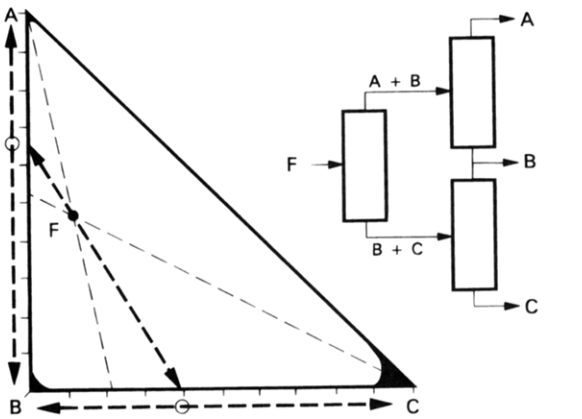

Figure 26. A nonsharp split followed by two binary splits.

composition. We should, therefore, prefer sharp splits, unless azeotropes and distillation boundaries get in the way. Reasons for preferring a nonsharp split can come from heat integration, balancing molar flow rates to other columns, or isolating a difficult separation. Nonsharp splits are usually found in preconcentrators, which are used to prepare a stream for further processing by roughly removing unwanted quantities of one or more components. Anderson and Doherty (1982) give a design method for this type of column.

This example, which did not really require an RCM analysis, gives a basic idea of the usefulness of a ternary diagram. At the same time, it demonstrates the freedom we have when designing a nonazeotropic separation sequence. Many more splits are feasible than in azeotropic distillation, and the combinatorially large number of possible sequences can be narrowed down by applying rank-ordered heuristics to find good initial designs (Nadgir and Liu, 1983). In azeotropic distillation, however, many splits are prevented by azeotropes and distillation boundaries, allowing many fewer feasible sequences. To find these sequences, we use heuristic and thermodynamic guidelines, in the form of RCMs. To determine the optimal column sequence from several alternative separation trains, Knight (1986) presents a systematic procedure, involving rank-order and proximity parameters, developed by Fisher et al. (1985).

We continue with two examples taken from Stichlmair and Herguijuela (1992, p 1529). In both examples, the distillation borders are curved, which makes these (hypothetical) cases more realistic and interesting. Figure 27 shows the RCM (type "020") for the mixture a,b,e, according to our labeling convention. Component e is the entrainer. Figure 28 represents a process for an "a−b" minimum-boiling azeotrope, with an entrainer that boils lower than the minimum-boiling azeotrope. The process consists of three separation steps and two recycles.

Feed stream F lies in the region where component a can be obtained as a pure bottoms product. Stichlmair and Herguijuela suggest to mix F with the (still imaginary) bottoms stream B3, to obtain feed mixture M1. M1 is fed to column C-1 and separated into distillate D1 and bottoms B1 (indirect split). Mixing D1 with (still imaginary) stream D3 gives M2, the feed for column C-2. C-2 performs another indirect split, giving bottoms product B2 (pure b) and distillate D2. D2 is fed to column C-3, to be split into products D3 and B3, which are now no longer imaginary. Since we want to keep D2 small, in order to keep recycle streams D3 and B3 small, the lever rule tells us that the length D2−M2 should be large with respect to B2−M2. This requires

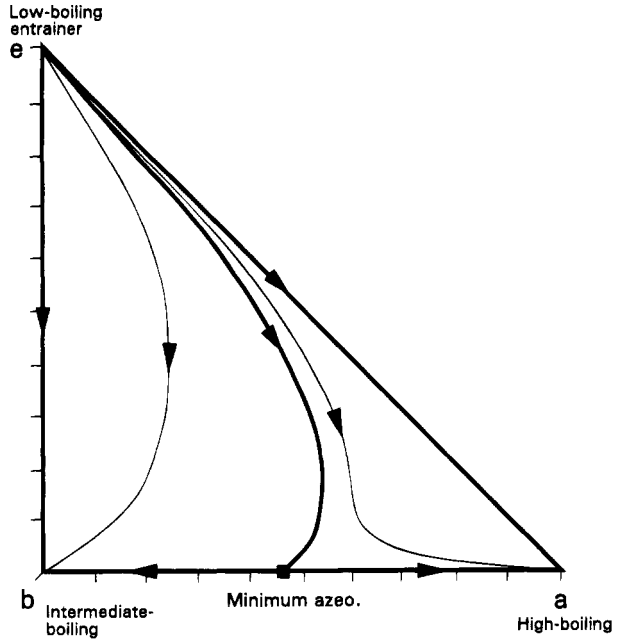

Figure 27. The RCM of a system with a minimum-boiling azeotrope and a low-boiling entrainer.

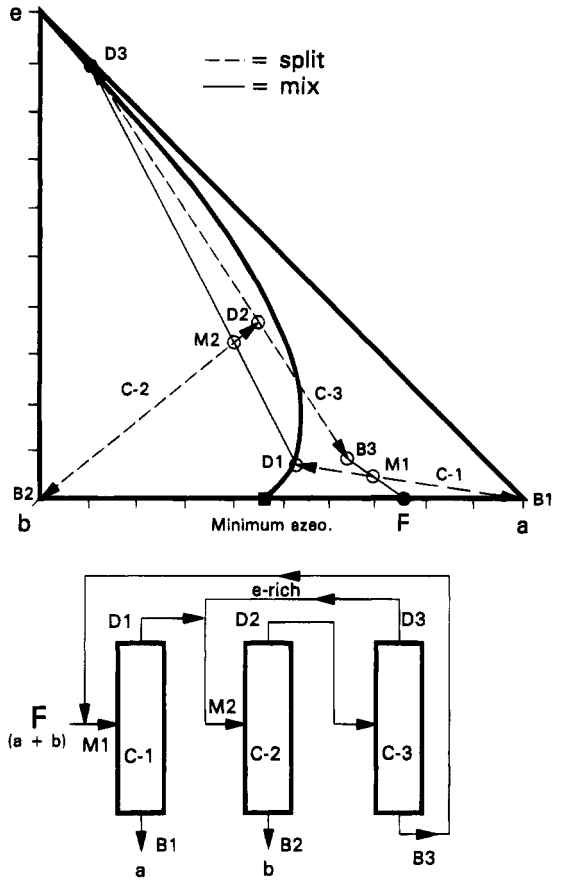

Figure 28. Splitting a minimum-boiling azeotrope with a low-boiling entrainer (Stichlmair and Herguijuela, 1992). (a, top) The "RCM design" of a separation sequence. (b, bottom) A flowsheet corresponding to the "RCM design" in a.

a highly curved distillation border and an optimal position of M2.

Figure 29 represents another flowsheet when the feed F lies in the region where high-boiling component b can be separated first. In this case, since stream D1 must be the sum of streams M2 and B3, the RCM shows D1, M2, and B3 to lie on one material-balance line. As

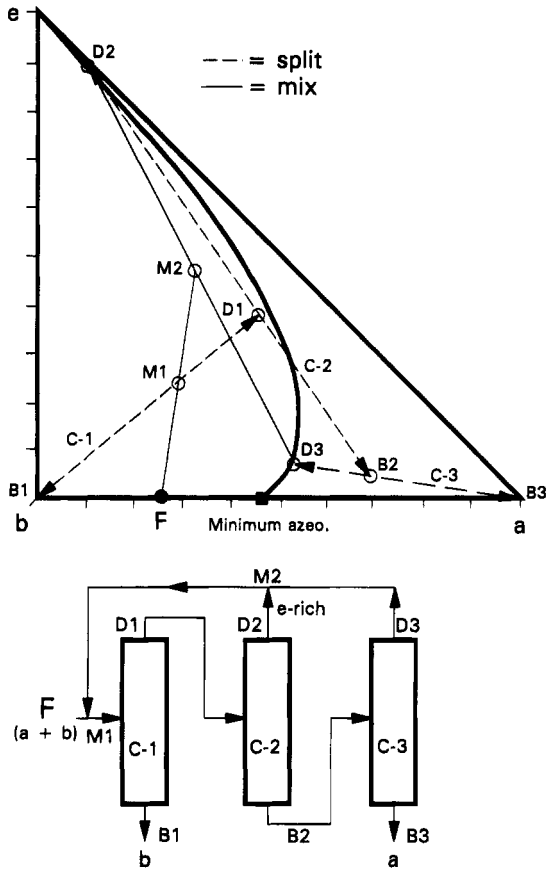

Figure 29. Another flowsheet for splitting a minimum-boiling azeotrope with a low-boiling entrainer. (a, top) The "RCM design" of a separation sequence. (b, bottom) A flowsheet corresponding to the "RCM design" in a.

mentioned earlier, this process becomes more economical as the curvature of the distillation border increases.

If, instead, a high-boiling azeotrope occurs, products a and b are obtained as distillate fractions of column C-1 and C-2, and the flowsheet would resemble an upside-down version of Figure 28b (Stichlmair, 1991). In this case, a high-boiling entrainer is required to obtain a and b as pure components.

The general flowsheets in Figure 28 and Figure 29 can be quite expensive in terms of investment and operating costs. Therefore, Stichlmair and Herguijuela (1992) present examples of cost-effective process simplification. We shall here illustrate their example, in which an azeotropic mixture of benzene and cyclohexane is separated, using 2-propanol as a high-boiling entrainer. This system contains a ternary azeotrope (Figure 30a). The curvature of the distillation border, running from the benzene–cyclohexane azeotrope to the ternary azeotrope, is sufficient to allow for pure benzene as the bottoms product of column C-2. Both the RCM design and the corresponding flowsheet in Figure 30 parts a and b should, by now, be self-explanatory. We see that in order for the two-column model to work, the recycle-stream composition must be that of the ternary azeotrope, such that the top and bottoms products of the second column appear on one RC. A large number of stages would be required to obtain the azeotrope at sufficient purity, raising operating costs considerably. Most likely, a make-up stream of 2-propanol is needed as well.

Doherty and Caldarola (1985) give a good discussion of a possible pitfall in separation sequencing. In an imaginary case, an unspecified entrainer is used to separate water and ethanol. The entrainer *forms* a

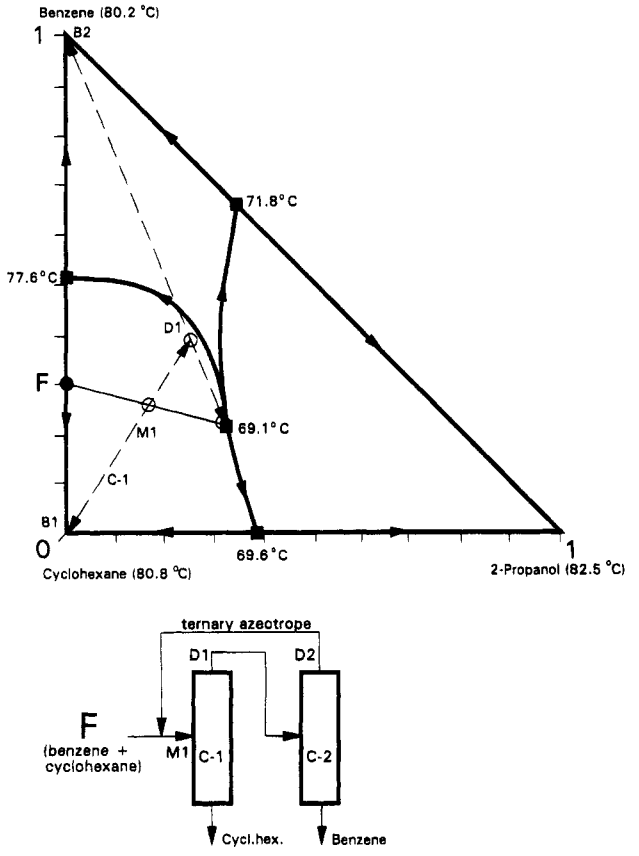

Figure 30. A sequence for separating benzene and cyclohexane, using 2-propanol as a high-boiling entrainer (Stichlmair and Herguijuela, 1992). (a, top) The RCM design by Stichlmair and Herguijuela (1992). (b, bottom) A flowsheet corresponding to the RCM design in a.

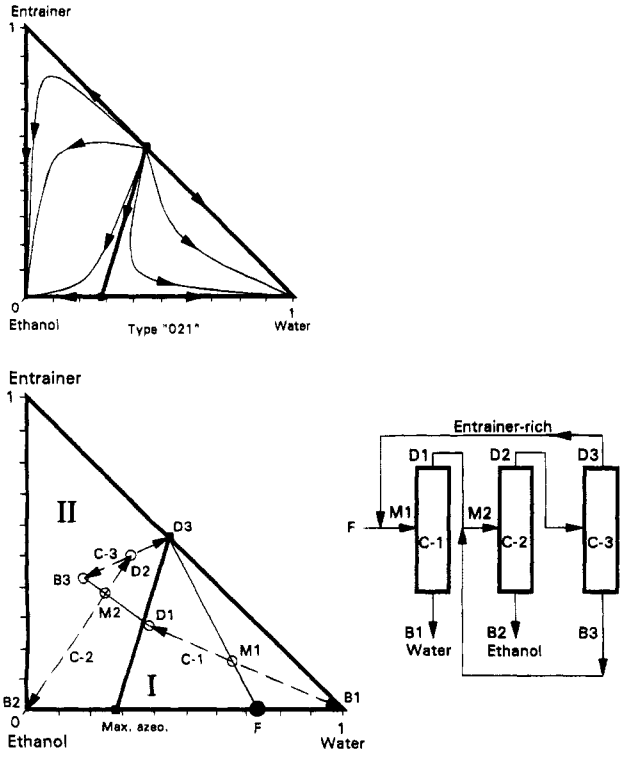

Figure 31. An imaginary case of a homogeneous azeotropic distillation sequence from Doherty and Caldarola (1985). (a, top) A sketch of the RCM for the mixture used in b. (b, bottom) A distillation sequence with an internal recycle.

binary azeotrope with water only. Figure 31a shows a sketch of the RCM. We can synthesize a column sequence as follows (Figure 31b).

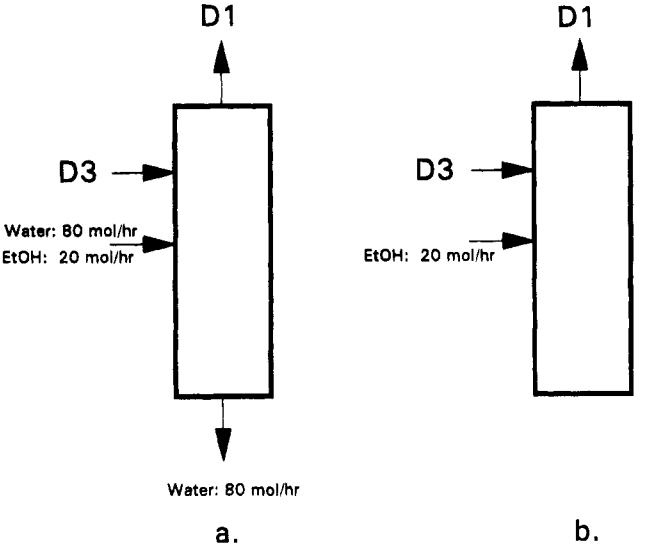

Figure 32. A demonstration of sequence infeasibility for the example in Figure 31.

Feed F is plotted in the RCM and mixed with top product D3 from (future) column C-3, giving the feed mixture (M1) for column C-1. Pure water (B1) leaves the bottom of this first column. Distillate D1 is mixed with bottoms B3, from (future) column C-3, thereby crossing the distillation boundary to give feed stream M2 for column C-2. M2 is split into pure ethanol (B2) and distillate D2, which is fed to column C-3, giving the already mentioned products D3 and B3, which are used to "cross the boundary".

After synthesizing a separation sequence like this, we should attempt a more detailed simulation, to make the material balance for the entire separation train converge. Here, a fundamental error emerges. In order to have no mass accumulation in the system, all the water present in F, must be in the pure water stream B1, while all ethanol must be in B2. This means that we can represent column C-1 as in Figure 32a, which, from a mass-balance perspective, is equivalent to Figure 32b. In a ternary diagram, D3, D1, and B2 must therefore be on one material-balance line, requiring D1 to be in distillation region II. This cannot be achieved by the simple distillation column C-1. From this and other case studies, Doherty and Caldarola (1985) conclude that "distillation boundaries within the composition triangle can never be crossed by simple recycle methods [only] and that other sequencing techniques need to be employed." Several researchers (e.g., Laroche et al., 1991) have challenged this heuristic and find it to be correct only when distillation boundaries are linear and the system is homogeneous. If we view the exploitation of liquid/liquid equilibria through decantation (Figure 16) as one of the "other sequencing techniques" and not as a simple recycle method, Doherty and Caldarola's statement does hold true for heterogeneous systems. Curved boundaries, however, still represent an exception to the preceding heuristic by Doherty and Caldarola (1985).

The last two examples stress the importance of always keeping the material balances in mind.

5.2. Heterogeneous Azeotropic Distillation Processes. The term "heterogeneous" indicates that somewhere in the separation process, liquid–liquid immiscibility occurs and is being exploited. Phase separation can be used as a cheap and efficient way to cross distillation boundaries, simply because it is not restricted by the rules of relative volatility that apply to

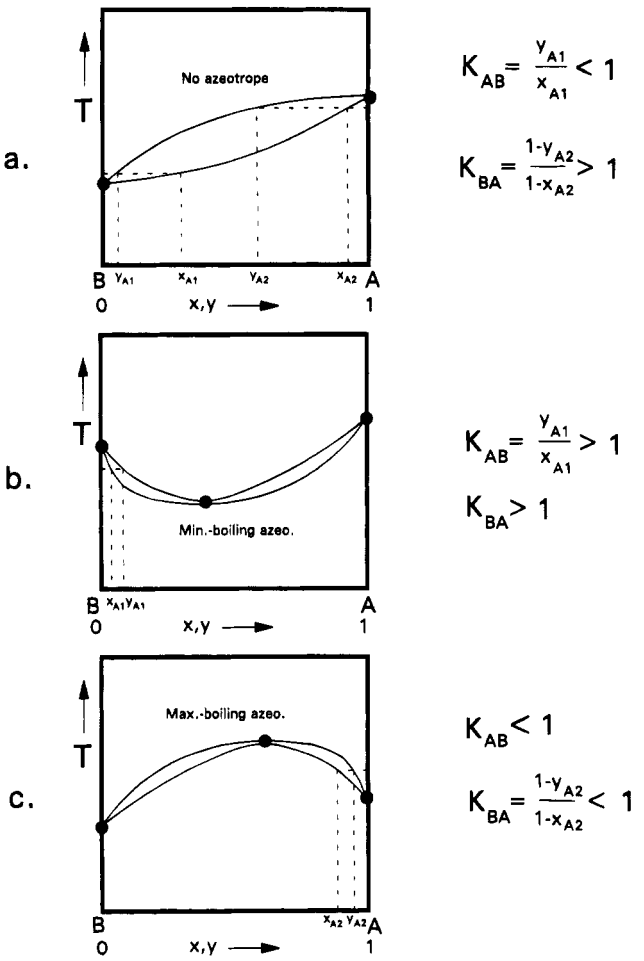

Figure 33. An illustration of the azeotrope heuristic from Wahnschafft and Westerberg (1993).

Table 1. Heuristics for Predicting Binary Azeotrope Types (Wahnschafft and Westerberg, 1993)

	K_{AB}	K_{BA}
minimum-boiling azeotrope	>1	>1
maximum-boiling azeotrope	<1	<1
heterogeneous minimum-boiling azeotrope	>10	>10

distillation. The RCM can therefore be constructed in the same manner as discussed so far. Pham (1987, pp 58–59) provides an algorithm for computing heterogeneous RCMs. Bossen et al. (1993) give a shortcut method for detecting heterogeneity.

The "immiscibility region" only comes into play when we start drawing in the material-balance lines for our separation sequence. As soon as a top or bottoms product lies inside the immiscibility region, two new phases will form, with compositions (ideally) located on the region's border. The compositions of the "total product stream" and the two newly formed streams must lie on the same material-balance line, namely, the aforementioned "phase-separation mass balance".

Separation takes place in a *decanter,* from which the two resulting phases are withdrawn and either recycled or fed to a next separation step. Typically, the lighter (entrainer/solvent-rich) phase is recycled to the column as reflux.

Binary or ternary azeotropes that are located inside the phase-separation region are called "heterogeneous azeotropes". Wahnschafft and Westerberg (1993) give a heuristic for identifying a binary heterogeneous minimum-boiling azeotrope, based on the two relevant K-values at infinite dilution (K_{AB} and K_{BA}). These K's can be found from the ratio of the mole fraction in the

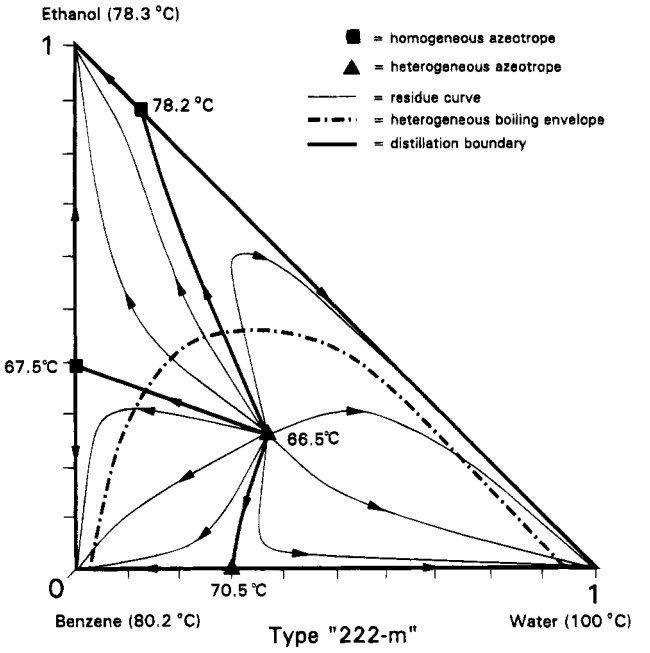

Figure 34. The RCM for a mixture of ethanol–benzene–water at 1 atm.

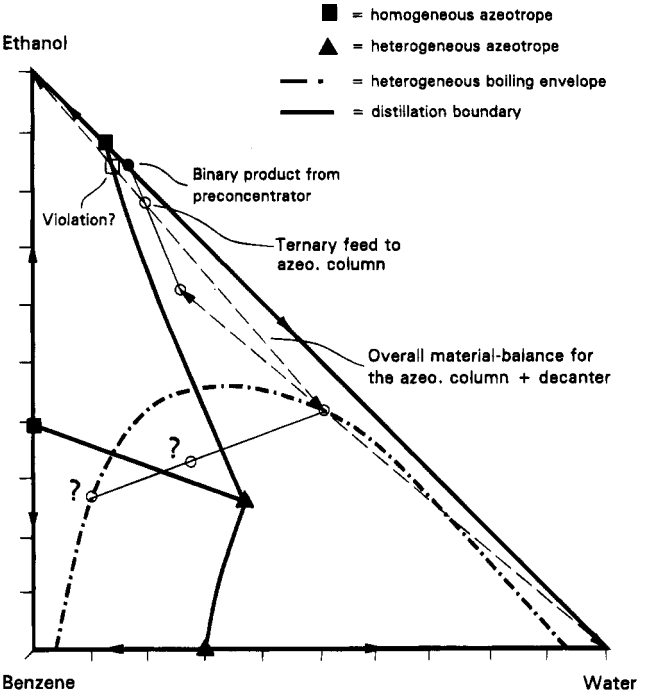

Figure 35. A representation of a separation sequence for the ethanol–benzene–water system (Ryan and Doherty, 1989).

vapor phase (dew-point curve) to that in the liquid phase (bubble-point curve) in a T-x-y diagram (Figure 33). No azeotrope occurs if one of these K's is greater than 1 and the other is smaller than 1. The rest of the heuristic is summarized in Table 1. Pham (1987) shows that liquid-phase heterogeneity forbids the presence of maximum-boiling heterogeneous azeotropes.

The literature contains many examples of heterogeneous azeotropic distillation sequences. These generally consist of three or four columns and apply various methods of entrainer recycling. Kovach and Seider (1987) even present a (rare) case in which the phase tie lines are such to allow the entrainer recovery to be left out. Pham and Doherty (1990) give a detailed review of most techniques.

Ryan and Doherty (1989) present a useful heuristic,

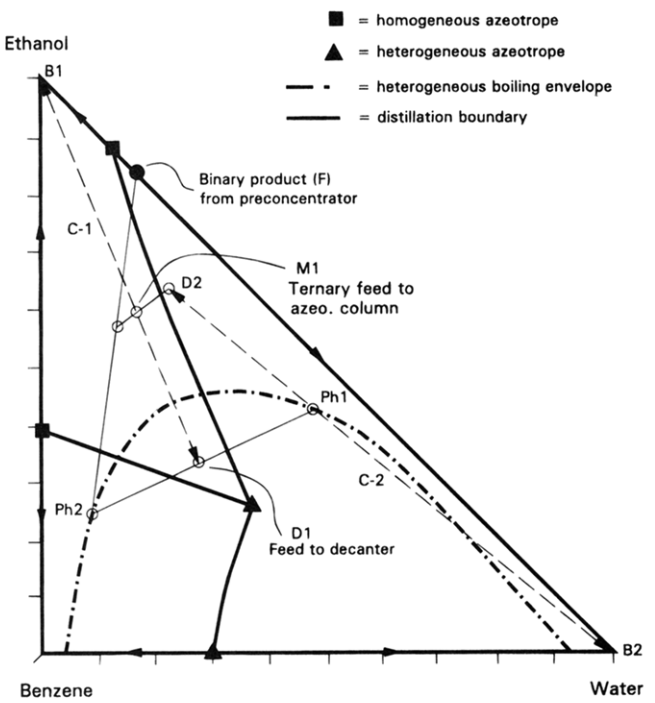

Figure 36. An alternative representation of the separation sequence for the ethanol–benzene–water system of Figure 35.

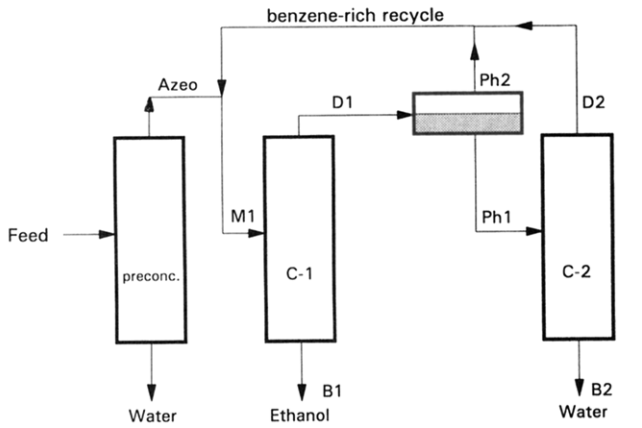

Figure 37. A flowsheet corresponding to Figure 36.

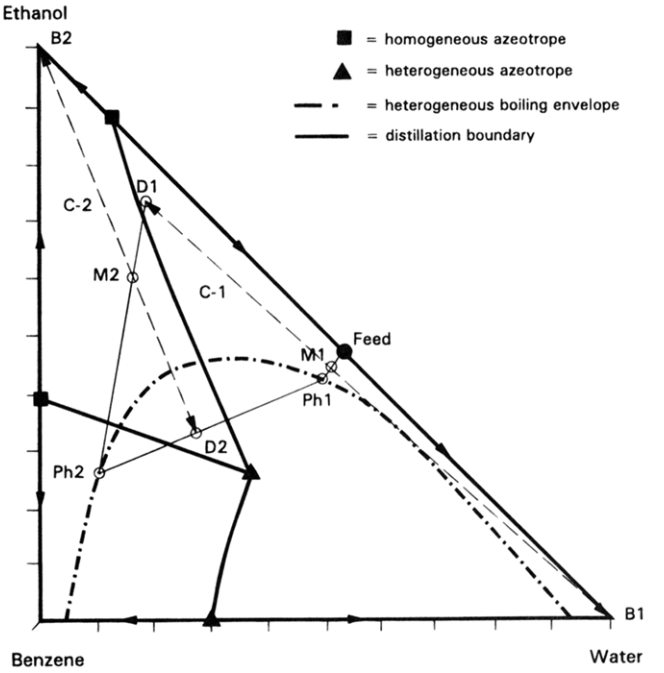

Figure 38. A two-column design for the ethanol–benzene–water system (without preconcentrator).

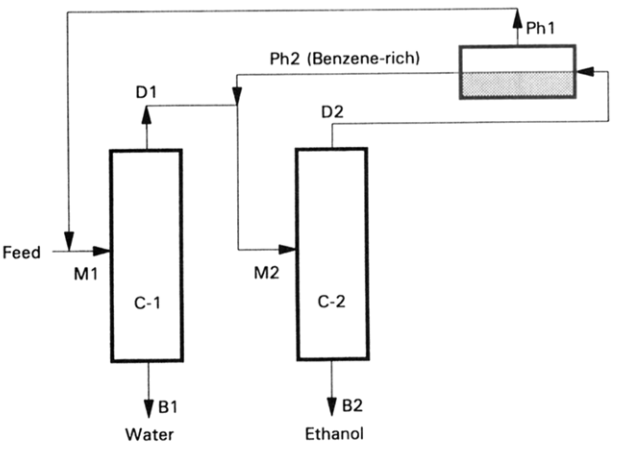

Figure 39. A flowsheet corresponding to Figure 38.

which states that the distillate composition from the entrainer-recovery column should be set close to the distillation boundary, thereby removing it from the list of optimization variables. We continue with one of their examples, in which they develop a three-column separation sequence for a system of water and ethanol with benzene as entrainer, using the RCM shown in Figure 34. The material-balance lines given in Figure 6 of their article (Figure 35) can be somewhat confusing, however, and seem to ignore distillation boundaries. Their overall feed composition to the azeotropic column lies in the wrong distillation region for obtaining ethanol as pure bottoms product. Furthermore, their decanter feed seems to have no origin, even though it should clearly be the top product of the azeotropic column. The reason for this apparent confusion is that they combine azeo-column and decanter inside one material-balance envelope. The mix of binary feed and recovery-column top product enters this envelope, while the azeo-column bottoms product and the entrainer-recovery feed are the exiting streams. This gives the overall material-balance line in Figure 35. An alternative representation clarifying the details of this process is shown in Figures 36 and 37. The binary feed to the azeotropic column comes from a preconcentrator, which gives it a composition close to the ethanol–water azeotrope.

Ryan and Doherty (1989) also give a two-column sequence for the same separation. Again, their material-balance lines could be confusing and an alternative version is shown in Figures 38 and 39. They mention that the main difference between the three- and two-column sequences is the modification of the entrainer-recovery column to accept the dilute ethanol feedstream. The azeotropic column remains unchanged, with respect to its target products, minimum reflux ratio, and number of trays.

We emphasize that our alternative representations in Figures 36–39 are included here with the sole purpose of clarifying the important figures in Ryan and Doherty (1989) to help our readers understand the original reference. These figures are not meant to be in any way critical of the significant work of Ryan and Doherty.

6. Process Synthesis and Operability

When designing a separation sequence, it is usually important to have an understanding of the problems and difficulties that may arise during operation. In

particular, the controllability of azeotropic columns can turn out to be much more complex than would be expected at first.

6.1. Maximum Reflux Ratio. An example of the extra complications in azeotropic column design and operation is the fact that the Underwood method for finding the minimum reflux ratio cannot be relied upon to give accurate results for nonideal mixtures (Levy et al., 1985). Julka and Doherty (1990) offer a simple algebraic method for calculating the minimum reflux ratio for nonideal multicomponent distillation columns. The method is quite general and applies to ideal, nonideal, and azeotropic mixtures. It can even be extended to include multicomponent reactive distillation columns.

Azeotropic separations, which are feasible at total reflux, are also feasible at finite reflux, but the converse is not automatically true. *Separations that are infeasible at infinite reflux may be feasible at finite reflux.* This means that conventional methods for determining the minimum number of stages with total reflux will not work. For instance, separation is never feasible at total reflux for mixtures in Matsuyama's "100-class", which is the most common class encountered in industry, describing extractive distillation (heavy-boiling entrainer and two feeds). Yet, separation of systems in this class is almost always feasible at some finite reflux (Laroche et al., 1992a).

Wahnschafft et al. (1992) give a criterion to determine the finite *maximum* reflux ratio for an adiabatic column with a single feed (which excludes extractive distillation), achieving a specific separation.

6.2. Bifurcation Pressures. Another important phenomenon is the so-called "bifurcation pressures", at which new azeotropes appear and/or existing azeotropes disappear. In between bifurcation pressures, the thermodynamic behavior of a mixture will remain globally unchanged. Knapp (1990) reports a method for finding these bifurcation pressures, which can be used to construct a set of different RCMs for a single mixture, thus allowing the designer to choose the optimal pressure(s) at which to operate the separation sequence, or possibly "pressure-swing distillation", as mentioned in section 2. It is important not to operate a column too close to a bifurcation pressure. First of all, because "tangent pinches" (that is "near azeotropes") will be severe, making separation difficult and operation expensive. Second, because a small change in pressure conditions could result in drastically different column behavior.

6.3. Multiple Steady States. Recently, Bekiaris et al. (1993) reported on their derivation of necessary and sufficient conditions for the existence of multiple steady states in azeotropic distillation columns. Petlyuk and Avetyan (1971) were apparently the first to propose the possibility of such multiple steady states, where different composition and temperature profiles correspond to the same set of operating parameters. The explanation for this unexpected behavior, shown to actually exist by Magnussen et al. (1979), does not require a heterogeneous distillation regime. To visualize and understand the conditions derived by Bekiaris et al. (1993) using RCMs, the reader may refer to the original reference for details.

6.4. Problems in Heterogeneous Distillation. Heterogeneous distillation generally is very sensitive to process disturbances, which can lead to unusual operability and control problems. Probably the most notable sensitivity is the drastic swing in composition and temperature profiles, accompanying very small changes in the level of trace impurities in the product stream.

Ryan and Doherty (1989) find that "for many problems, all the optimization variables, except for the position of the decanter tie line, can be either set by heuristics or calculated at their bounds. The shape of the liquid–liquid envelope, however, varies so much from one system to the other, that no general rule for tie-line positioning can be developed. Therefore, this is expected to be the main optimization variable in most new problems".

Since premature phase separation inside the column is a serious risk, care must be taken in the design to make sure that phase separation is limited to the decanter only. This ensures optimum column efficiencies and a better separation in the decanter (Davies et al., 1987; Ryan and Doherty, 1989). Also, the column models can now be similar to those used for homogeneous distillation sequences. A good entrainer for heterogeneous distillation should cause phase separation over a broad range of compositions in the ternary diagram.

7. Conclusions

It seems safe to state that the design of separation sequences for azeotropic mixtures requires a substantially bigger effort than for "ideal mixtures". We have here discussed only part of that extra effort, directed mainly toward the heuristic synthesis and shortcut design of separation sequences. At the same time, however, there are significant complications in entrainer selection, column design, and process control. Selecting the optimal entrainer is often the solution to many problems. In-depth discussion of entrainer selection lies outside the scope of this article, and readers are referred to Foucher et al. (1991), Laroche et al. (1991, 1992b), and Stichlmair and Herguijuela (1992) for more information. *Residue curve maps are an excellent tool for entrainer feasibility screening.*

Lately, much progress was made in using RCMs in the field of *reactive distillation* (Barbosa and Doherty, 1988; Doherty and Buzad, 1992). Here, as mentioned earlier, the entrainer is chosen to react preferentially (and sometimes reversibly) with one of the azeotropic components, in order to eliminate one or more distillation boundaries and to offer new options for separation.

When a single chemical reaction takes place during distillation, the number of degrees of freedom decreases by one, leaving us with a simplified RCM. Thermochemical data need to be very accurate, in order to correctly describe the distillation of reactive mixtures. Because of the possible formation of distillation boundaries in reactive distillation, even of ideal mixtures, traditional synthesis techniques, like the Fenske–Underwood–Gilliland method, may not be applicable to reactive-distillation columns (Barbosa and Doherty, 1988).

The in-situ removal of product from the reaction zone causes equilibrium-limited reactions to be shifted forward by LeChatelier's principle, thus allowing high conversion. This can make reactive distillation very economical, especially when a liquid-phase reaction must be carried out with a large excess of one reactant. However, most high-temperature and/or high-pressure reactions do not qualify as candidates.

Reactive distillation has already been successfully implemented in important industrial processes, such as the patented Eastman Chemical methyl acetate process (Agreda and Partin, 1984), the nylon-6,6 process, and

the MTBE (methyl *tert*-butyl ether) process (Doherty and Buzad, 1992).

After reviewing the construction, features, and use of residue curve maps, we tend to agree with a statement made by Colberg et al. (1992), that "residue curve maps will be as important for separation synthesis as composite curves are for heat-exchanger network synthesis". This conclusion is based on a number of observations, among which are the facts that: (1) RCMs in ternary diagrams provide important physical insight into the process of multicomponent separation, just like composite curves in temperature–enthalpy diagrams provide insight into heat integration. (2) RCMs and related ternary diagrams are a simple graphical tool. However, the graphical nature of such diagrams should not be relied upon for any form of detailed design. Convergence of mass/energy balances still needs to be achieved numerically, when adequate physical and thermodynamic property data are available or can be predicted. Unfortunately, to our knowledge, good tools for flowsheet analysis *at the conceptual design stage* have not yet been fully developed. (3) The principles of ternary diagrams containing azeotropic data allow a wide range of applicability. Theoretically, all equilibrium-based separation methods can be represented in these diagrams. Current applications can be found in nonazeotropic, azeotropic, extractive, reactive, and batch distillation. Potential applications of analogous ternary diagrams are in extraction and crystallization. (4) Already, many large international companies have started to effectively use analysis of RCMs in ternary diagrams in their engineering practice, recognizing it as a powerful tool for the synthesis and evaluation of separation sequences for multicomponent azeotropic systems. Indeed, Aspen Technology, Inc., Cambridge, MA, is incorporating the latest advances in the fundamentals and practice of ternary diagrams with RCMs, as reviewed in this article, into their commercial process-integration software system, ADVENT, for public release in 1994.

Acknowledgment

We are grateful to Dr. Richard D. Colberg, Eastman Chemical Company, for his inspiring lectures, given at Virginia Tech in November 1992 (Colberg et al., 1992) that motivated us to study residue curve maps, and for his careful review of the manuscript, and to Honeywell, Inc., for a Futuristic Scholarship Award to G.J.F.

Nomenclature

B = bottoms product composition (mole fraction)
B = no. of binary azeotropes
c = no. of components present (dimensionless)
C = indicator for distillation column in figures
D = top product composition (distillate) (mole fraction)
e = entrainer
F = feed composition (mole fraction)
H = liquid molar holdup (mol/h)
K_i = equilibrium ratio of i: vapor fraction/liquid fraction (dimensionless)
K_{ij} = equilibrium ratio of i at infinite dilution in j (dimensionless)
M = overall composition of mixed streams (mole fraction)
P = total column pressure (kPa)
P_i° = saturation pressure of i (kPa)
Ph = liquid phase (from decanter)
Q = added heat (kW)
x = liquid composition (mole fraction)
y = vapor composition (mole fraction)
α_{ij} = relative volatility of i with respect to j (dimensionless)
γ_i = activity coefficient of i (dimensionless)
ξ = dimensionless time coordinate in eqs B.1 and B.2
σ_1 = sum of indices of pure components, eq 3
σ_2 = sum of indices of binary azeotropes, eq 3
σ_3 = sum of indices of ternary azeotropes, eq 3

Appendices

A. Sketching RCMs from Minimal Data. Needed are (only) the boiling temperatures of all components that make up the mixture, plus boiling temperatures and compositions of all occurring azeotropes.

1. Put the pure components and their boiling temperatures on the vertices of the diagram, preferably in a conventional order, e.g. with the low-boiling component at the left-top corner and the high-boiling component at the right-bottom corner of a right triangle.
2. Plot all azeotropes in the diagram, and label them with their boiling temperatures.
3. Draw arrows on the edges of the diagram, pointing in the direction of the higher boiling point.
4. From the arrows, determine if pure component vertices are nodes ($N1$) or saddles ($S1$).
5. If a ternary azeotrope exists, determine its nature as a node ($N3$) or a saddle ($S3$).
6. Applying the topological constraint equations (1 and 2), determine the number of binary nodes ($N2$) and saddles ($S2$).
7. Sketch the RCM, using all the information collected so far, keeping in mind that, in rare cases, more than one RCM may be possible for a given set of data.
8. If more than one RCM seems possible (indeterminacy), calculate one residue curve mathematically (see Appendix B) to help determine the correct RCM.

Hints to aid in drawing distillation boundaries: The heaviest-boiling species (pure component or azeotrope) in the *entire* system must be a stable node. The lightest-boiling species must be an unstable node. Each distillation region will have *exactly* one stable node and one unstable node. There can be more than one saddle per region. Adjacent distillation regions may share *either* the same stable *or* the same unstable node. However, they cannot share both without being the same region. It is impossible for a residue curve *or a distillation boundary* to end at a pure-component saddle. A ternary saddle azeotrope must have four connections; two with higher boiling temperature than the azeotrope and two with lower boiling temperature. If a system does not contain a ternary *saddle* azeotrope (which is usually the case), all distillation boundaries connect binary saddle azeotropes to (pure-component or azeotropic) nodes. A minimum-boiling binary saddle must connect to an unstable (pure-component, binary, or ternary) node or to a ternary saddle.

Heuristic predictions of existence, boiling point, composition, and pressure sensitivity of binary azeotropes are covered by Barnicki (1993). Empirical correlations, especially suitable for water–alcohol and water–ester systems, can be used in the preliminary design phase.

Matsuyama and Nishimura (1977) mention that the experimental effort required to obtain the data for a ternary azeotrope is almost 1 order of magnitude larger than that for a binary azeotrope. Especially, ternary saddle azeotropes are very difficult to measure experimentally.

Knight (1986) gives a good introduction on the use of "composition", "adjacency", and "reachability matrices", which are used for *automated* RCM construction, requiring the same set of minimal data. Developing tools

for automatic RCM construction was coined the "coding problem" (Doherty, 1985).

Foucher et al. (1991) give a flowchart of a computer algorithm for RCM construction.

B. Calculating Distillation Residue Curves. Although calculating RCs is in most cases overly detailed for the presynthesis phase, the situation may arise, where this mathematical exercise becomes necessary (e.g., indeterminacy, section 3.6). Simple distillation residue curves are defined as the trace in time of the liquid composition remaining from a simple batch distillation process. The curves are described by the following set of differential equations (Doherty and Perkins, 1978a,b, 1979a, 1982; Van Dongen and Doherty, 1985):

$$\frac{dx_i}{d\xi} = x_i - y_i \qquad i = 1, 2, \ldots c-1 \qquad \text{(B.1)}$$

where x_i and y_i are the mole fractions of component i in the liquid and the vapor phase, respectively, c is the number of components present in the feed, and ξ is a dimensionless time coordinate, defined by

$$\xi(t) = \ln\left[\frac{H(0)}{H(t)}\right] \qquad \text{(B.2)}$$

$H(0)$ and $H(t)$ are the total liquid molar holdup in the column at "zero time" and at time "t". The movement of liquid composition x is always in a direction that makes the temperature (boiling point of the residue) increase.

Viewing the composition variables x_i and y_i as vectors, we can deduce from eqs B.1 that the tangent to a residue curve connects a liquid composition to the corresponding vapor composition.

Equations B.1 have singular solutions whenever $x_i - y_i = 0$. These show up as pure-component vertices, binary and ternary azeotropes, etc., which are all nodes or saddles. To solve eqs B.1, we need a relationship between y_i and x_i. Under isobaric conditions, we have

$$y_i = y_i(P, T(\boldsymbol{x}), \boldsymbol{x}) \qquad \text{(B.3)}$$

For an ideal vapor mixture in equilibrium with a nonideal liquid, we can use

$$Py_i = P_i^\circ(T)\, x_i \gamma_i(T, P, \boldsymbol{x}) \qquad \text{(B.4)}$$

where

P = total column pressure

P_i° = saturation pressure of component i

γ_i = liquid-activity coefficient of component i

A useful liquid-activity coefficient model for use in RC calculation is that of "regular solutions". This model is sufficiently simple to allow a tractable analysis, while being a plausible thermodynamic model for many nonideal systems. The regular solution model gives particularly simple conditions for the nature of a singular point and can be recommended for the investigation of the qualitative behavior of RCMs. However, it is incapable of describing high-order nonidealities and multiple azeotropy in particular (Doherty and Perkins, 1978b). "A basic and difficult step is to find the temperatures and compositions of *all* the azeotropes, predicted by a [thermodynamic] model", as Fidkowski et al. (1993) state in their latest paper on computing azeotropes in multicomponent mixtures. They focus on isobaric models that use activity and fugacity coefficients to describe nonideal behavior. Arc length and homotopy continuation techniques are used to give an efficient and robust solution model.

It has to be kept in mind that RCMs tend to change abruptly at each bifurcation pressure and remain globally invariant up to the next bifurcation pressure (Knapp, 1990).

Bossen et al. (1993) give a good description of a number of computational tools for simulation, design, and analysis of azeotropic distillation operations.

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