Structure of Distillation Regions for Multicomponent Azeotropic Mixtures

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Geometric methods for the conceptual design of nonideal and azeotropic distillation systems have focused primarily on three- and four-component mixtures. A generalization of geometric methods that does not rely on visualization and gives a completely equation-based approach to determine the structure of distillation regions for homogeneous mixtures is described. This method is useful for mixtures with a large number of components, provided a vapor–liquid equilibrium model is available. The approach is applied to assess feasibility and alternative separations in several examples, including a five-component mixture with nine azeotropes and a six-component mixture with seven azeotropes. These methods can be used to rapidly generate process alternatives, and the examples demonstrate that there can be a surprising number of these alternatives for the distillation of azeotropic mixtures.

Introduction and Background

Geometric methods have led to new tools and conceptual designs for distillation systems to separate nonideal mixtures. These include residue curve maps, feasibility methods, minimum reflux algorithms, design methods, and azeotrope calculations (e.g., Widagdo and Seider, 1996; Malone and Doherty, 1995). The principal focus has been on three- and four-component mixtures because it is possible to visualize the results.

For example, in ternary mixtures, distillation boundaries or their limits can be calculated for both infinite and finite reflux (Krolikowski et al., 1996; Davydian et al., 1997). The feasible products for distillation of ternary homogeneous mixtures have been studied in detail (Wahnschafft et al., 1992; Fidkowski et al., 1993a). Methods are also available for assessing the structure of distillation regions in systems with four or five components based on a detailed topological analysis of the separating manifolds (Baburina and Platonov, 1987, 1990a,b; Baburina et al., 1988). Progress continues to be made on treating mixtures containing any number of components (Safrit and Westerberg, 1996; Ahmad and Barton, 1996), but it remains an important area of research.

This article describes a new method for evaluating distillation feasibility. The method identifies the most important splits and applies to all homogeneous mixtures, regardless of the number of azeotropes or components. First we describe the data structures and a method for calculating their properties from a vapor–liquid equilibrium model. Next, we relate these results to feasibility of various splits. This is followed by several examples. We have not attempted to develop a systematic procedure for generating alternative sequences of distillation columns. However, we are optimistic that such a procedure could be readily developed by combining the feasibility methods from this article with the state–task network formalism in (Sargent, 1998).

Representation of the Residue Curve Structure

Pure components and azeotropes are the singular points for the residue curve map equation:

$$dx/d\xi = x - y(x). \qquad (1)$$

Model equations for continuous-column sections have fixed points at total reflux that are the same as the singular points of Eq. 1. This allows the representation of certain limiting cases based on the structure of the residue curves. In mixtures with more than four components, where graphical methods fail, the directed adjacency matrix, A, and a related

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reachability matrix, $\boldsymbol{R}$ (Knight and Doherty, 1990), can be used to represent this structure.

We list these singular points in order of their boiling temperatures since the residue curves connect these points in the direction of increasing temperature (Doherty and Perkins, 1978). The adjacency matrix is defined by $a_{i,j}=1$ if a residue curve joins i to j; otherwise, $a_{i,j}=0$. The reachability matrix $\boldsymbol{R}$ is defined by $r_{i,j}=1$ if there is *any* path from i to j, that is, j is "reachable" from i; otherwise $r_{i,j}=0$. Note that a path may include intermediate singular points and there may be more than one path when j is reachable from i.

Fidkowski et al. (1993b) describe a homotopy continuation method for computing *all* the azeotropes (and their stability) from a vapor–liquid equilibrium model. In addition to the temperatures and compositions of the azeotropes, their stability as well as that of each pure component is required here. This is based on a linearization of Eq. 1 at each singular point and the properties of the Jacobian matrix

$$J_{i,j}=\delta_{i,j}-\partial y_i/\partial x_j. \tag{2}$$

The eigenvectors of the Jacobian show the characteristic directions of the residue curves near a singular point. The eigenvalues are always real and fixed points are either saddles or nodes (Doherty and Perkins, 1978). Node-to-node connections do not form distillation boundaries (Foucher et al., 1991). This leaves saddle–saddle and saddle–node connections to form distillation boundaries.

Connections between singular points on the binary edges can be determined from a knowledge of the boiling temperatures for binary pairs in the mixture. If there is no azeotrope, then the lower-boiling pure component is adjacent to the higher-boiling component. For binary pairs with a single azeotrope, a minimum boiling azeotrope is adjacent to the two pure species; a maximum-boiling azeotrope has both pure components connected to it. (We do not consider the possibility of double azeotropes in binary mixtures because it is rare.)

Once the binary connections have been made, residue curves are computed starting at all binary and higher dimensional saddles to complete the construction of the adjacency matrix. These curves initially follow the eigenvectors, either forward in time for a positive eigenvalue or backward in time for a negative eigenvalue. The end points of these residue curves are "adjacent" to the saddle or the saddle is adjacent to them. The elements of the adjacency matrix are determined simply by repeating this procedure until there are no saddles remaining.

The general procedure for computing the adjacency matrix can be summarized as follows:

Algorithm 1: adjacency

1. Given: a mixture, a column pressure, and a *VLE* model.
2. Compute all azeotropes and determine the stability of all the singular points (pure components and azeotropes) using the method of Fidkowski et al. (1993b). Number the singular points in order of increasing boiling temperature.
3. For pairs of components without binary azeotropes, indicate a connection from the lower-boiling component, set $a_{i,j}=1$ where i is lower-boiling.
4. For pairs of components that do exhibit binary azeotropes, set $a_{az,i}=1$ and $a_{az,j}=1$, where az refers to the index of the minimum-boiling azeotrope. For a maximum-boiling azeotrope, set $a_{i,az}=1$ and $a_{j,az}=1$.
5. For each saddle:
   (a) Compute the eigenvectors.
   (b) For each eigenvector corresponding to a positive eigenvalue, integrate Eq. 1 forward in time from the saddle: (i) in a direction along the eigenvector and (ii) in a direction opposite to the eigenvector. Omit directions in the integration that point outside the composition space.
   (c) For each eigenvector corresponding to a negative eigenvalue, repeat the previous step, but integrate backwards in time.
   (d) Integration is stopped when the residue curve approaches any singular point (other than the one it started from) within a Euclidean distance of 0.001. Indicate a connection from the lower-boiling singular point, i, to the higher-boiling singular point, j, by setting $a_{i,j}=1$.

The reachability matrix can be computed from the adjacency matrix by

$$\boldsymbol{R}=\text{Boolean}[\boldsymbol{A}+\boldsymbol{I}]^{\nu-1} \tag{3}$$

where ν is the number of singular points and $\boldsymbol{I}$ is the identity matrix. (The Boolean operation replaces nonzero elements by unity and zero elements remain zero.) This provides a simple and effective method to represent the structure (Knight and Doherty, 1990).

The adjacency matrix has a property that makes it easy to determine which points are stable nodes and unstable nodes. Because the points are connected in the direction of increasing temperature, *an unstable node is indicated by a column of zeros*, since no other point can connect to it. Likewise, *a stable node is identified by a row of zeros*, since a stable node cannot connect to any other point.

Distillation Regions

A distillation region is a family of curves connecting one unstable node to one stable node. A region must also have the same dimension in composition space as the original mixture. Therefore, a distillation region can be identified from a collection of points with one unstable node, one stable node, and a number of intermediate-boiling saddles that satisfy the following properties.

Property 1. The stable node is reachable from the unstable node, that is, $r_{UN,SN}=1$.

Property 2. The nodes and saddles define a $(c-1)$-dimensional composition space.

The number of distillation regions is no greater than the number of pairs of unstable and stable nodes for which $r_{UN,SN}=1$. For example, consider a mixture of methyl acetate, ethyl acetate, methanol, and ethanol that has the residue curve map shown in Figure 1. There are three binary azeotropes for a total of seven singular points numbered as in Figure 1. The adjacency and the reachability matrices are

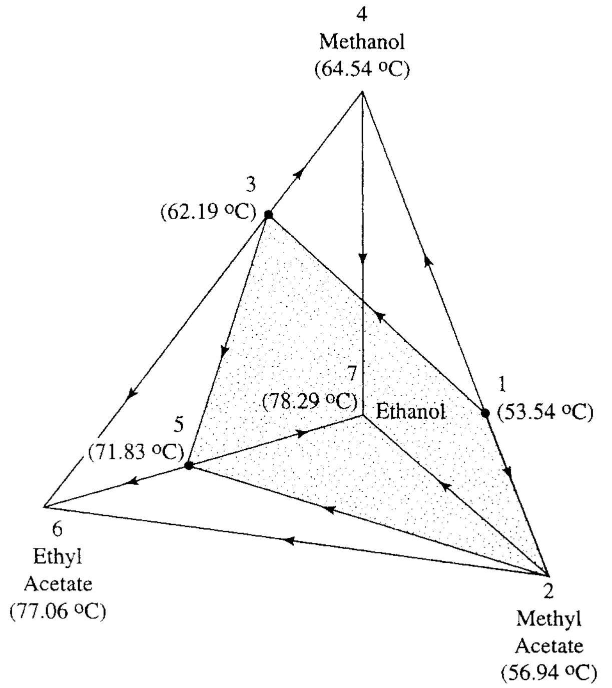

Figure 1. Distillation boundary and residue curve map structure for the mixture of methanol, methyl acetate, ethyl acetate and ethanol.

The distillation boundary is the surface (shaded) that splits the mixture into two distillation regions.

$$A = \begin{bmatrix} 0 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$R = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

Matrix A shows two stable nodes (rows 6 and 7, corresponding to pure ethyl acetate and pure ethanol, respectively) and one unstable node (column 1, corresponding to the methanol–methyl acetate azeotrope). There are two combinations of stable and unstable nodes, (1–6) and (1–7), and no more than two distillation regions since $r_{1,6} = 1$ and $r_{1,7} = 1$.

It is also necessary to determine all of the saddle points that bound a distillation region. This is the set of saddle points for which $r_{i,SN} = 1$ and $r_{UN,i} = 1$. Each region is enclosed either by composition or distillation boundaries connecting these points. A composition boundary is simply the limit of composition space defined by $0 \le x_i \le 1$ and $\Sigma x_i = 1$. Distillation boundaries are created by binary or higher-dimensional saddles, which cause residue curves to break into different families. The vertices that define a distillation boundary can be found by grouping those singular points from a given region that are shared by another region. For example, the mixture of methyl acetate, methanol, and ethyl acetate (Figure 2) has two saddles (points 2 and 3). A distillation boundary joins the methyl acetate–methanol unstable node to the methanol–ethyl acetate saddle and divides the mixture into two distillation regions. The lower region has three composition boundaries defined by the lines joining points (1)–(2), (2)–(5), and (3)–(5). The (1)–(3) connection forms a distillation boundary, since those two points are shared by both the lower and upper regions. Distillation boundaries are of dimension $(c-2)$ and the distillation boundaries of lower-dimensional mixtures form edges of the higher-dimensional boundaries. The structure of the regions can be determined with the following algorithm.

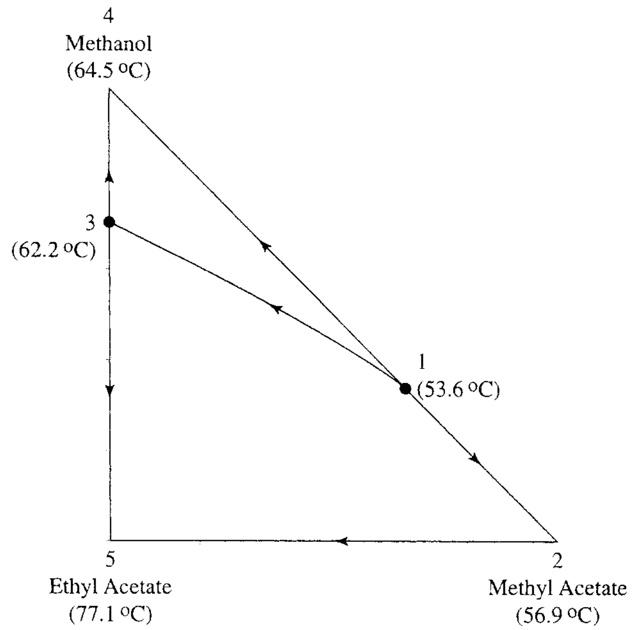

Figure 2. Distillation boundary and residue curve map structure for the mixture of methyl acetate, methanol and ethyl acetate.

Algorithm 2: distillation regions

1. *Candidate Regions and Points.*

(a) Find all pairs of an unstable node (UN) and a stable node (SN) for which $r_{UN,SN} = 1$. The number of pairs is the number of candidate regions.

(b) For each candidate region identified in (a) generate a list of saddle points i for which $r_{i,SN} = 1$ and $r_{UN,i} = 1$, that is, saddles that can reach the stable node and that can be reached from the unstable node.

2. *We Conjecture the Following Test for Property 2.*

(a) Form a separate adjacency matrix for each candidate region using only the vertices identified in step 1. For each candidate region find the number of *distinct paths* joining the UN to the SN. Paths are distinct if they differ by at least one vertex. The number of distinct paths can be found by recursive application of either breadth-first search or depth-first

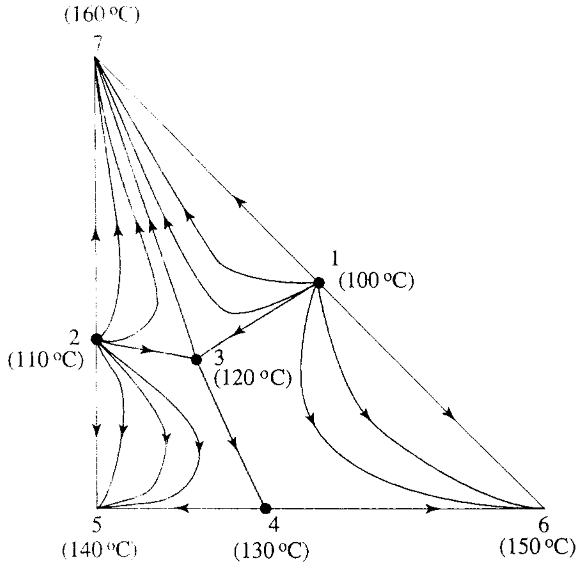

Figure 3. Hypothetical residue curve map with six candidate regions.

Two of the candidate regions are rejected, 1-3-4-5 and 2-3-4-6, leaving four, 1-3-4-6, 1-3-7, 2-3-7, and 2-3-4-5.

search algorithms on the adjacency matrix for the candidate region (Corman et al., 1990; McHugh, 1990).

(b) If the number of distinct paths is at least $(c-1)$ accept the candidate region. Otherwise, reject it.

3. *Identify the Boundaries of Each Region.*

(a) *Composition boundaries.* Group the vertices that are missing one of the pure components. Each group defines one composition boundary. For example, the lower region of the mixture in Figure 2 has three composition boundaries. The first, (1)–(2), is found by grouping those vertices in the lower region that do not contain ethyl acetate (5). The other two composition boundaries (3)–(5) and (2)–(5) are found by grouping vertices in the region that are missing methyl acetate (2) and methanol (4), respectively.

(b) *Distillation boundaries.* Group those vertices that are shared by another region. Each group defines one distillation boundary.

Frequently, Property 2 is satisfied by all candidate regions and step 2 in Algorithm 2 may seem unnecessary. However, Figure 3 gives an example (hypothetical) where Property 2 is *not* satisfied by some of the candidate regions. This example has two unstable nodes (vertices 1 and 2) and three stable nodes (vertices 5, 6 and 7), giving six combinations. All six satisfy Property 1, that is, $r_{1,6}=r_{1,7}=r_{2,5}=r_{2,7}=r_{1,5}=r_{2,6}=1$, but only the first four satisfy Property 2 (i.e., by inspection there are only four distillation regions). Step 2 of Algorithm 2 detects the faulty candidates and correctly rejects them.

Moreover, when Algorithm 2 is applied to the examples in Figures 1 and 2 it correctly predicts two distillation regions in each case.

Feasible Splits

The feasibility of products for mixtures with three components has been worked out in detail (Wahnschafft et al., 1992; Fidkowski et al., 1993a; Krolikowski et al., 1996). The most important splits occur very close to the edges of the composition triangle where one of the components has been nearly eliminated from a product stream. These often correspond to "sharp" splits between components with adjacent boiling points. Components with nonadjacent boiling points can also be split; these are sometimes called "nonsharp" splits. We also use these terms to refer to splits with compositions on distillation boundaries in azeotropic mixtures. To determine these, we need a feasibility test that can be used in higher dimensions, and this test should also be practical to compute.

We consider a somewhat simpler test than the full analysis described in the references just cited, which is much easier to implement. A ternary mixture of methyl acetate, methanol, and ethyl acetate has the residue curve map structure shown in Figure 2 at atmospheric pressure. For feed compositions in the lower distillation region, the bottoms composition can lie either below the azeotrope on the methanol–ethyl acetate binary edge or along the methyl acetate–ethyl acetate binary edge essentially free of methanol. Stripping profiles for the first case are shown in Figure 4a. As the reboil ratio is increased, the stripping profile approaches the distillation boundary. For the second case, Figure 4b, the stripping profile approaches the binary edge between pure methyl acetate and the methyl acetate–methanol azeotrope as the reboil ratio is increased.

For a feed composition as shown in Figure 5, suppose we seek a distillate composition very close to the distillation boundary. The rectifying profile will first approach the saddle (3), and then the stable node (5). The feasible bottoms composition (mass balance indicated by the solid line) lies on the (3–5) edge. A bottoms composition (mass balance indicated by the dashed line) on the (2–5) binary edge is infeasible because the stripping profile approaches the saddle at methyl acetate (2) and then the unstable node (1). *For feasible sharp splits, it is necessary for the rectifying and stripping profiles to approach the same saddle at large reflux.* We call this the *common saddle test*.

These ideas extend to four-component mixtures using the concept of a rectifying manifold (Julka and Doherty, 1993). For the general case of n components, the feasible products can be determined in the following manner (starting from the unstable node, other splits can be found starting from the stable node).

Algorithm 3: feasibility

1. Specify a feed composition, a pressure, and a *VLE* model.

2. Compute the adjacency matrix using Algorithm 1 and the reachability matrix using Eq. 3.

3. Determine the singular points that bound each of the regions using Algorithm 2.

4. Determine which region contains the feed by integrating a residue curve through the feed and matching the stable and unstable nodes of the residue curve to the nodes of each region determined in step 3.

5. Select a distillate composition between the unstable node and an adjacent saddle.

6. Find a mass balance through the distillate and feed compositions and extend this until a composition boundary is

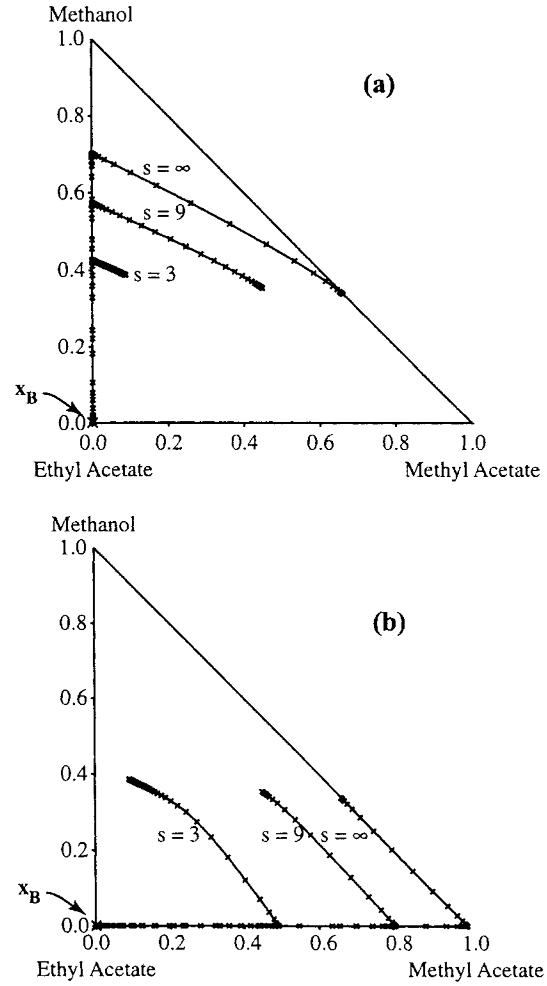

Figure 4. Series of composition profiles for the stripping section of a column for a mixture of methyl acetate, methanol, and ethyl acetate.

See Fig. 2 for the residue curve map and the boiling temperatures. The upper figure (a) represents those profiles that have a bottoms product on the methanol–ethyl acetate binary edge. The lower figure (b) represents those profiles that have a bottoms product on the methyl acetate–ethyl acetate binary edge.

reached at point x. If x is in the same distillation region as the distillate (integrate a residue curve from the bottoms composition to check this), then x is a feasible bottoms composition and lies on a composition boundary of the distillation region. Otherwise, search over the material balance line from x to the feed composition until a point is found (very close to a distillation boundary) that first produces a residue curve in the same region as the distillate. This point is a feasible bottoms composition.

7. The last step does not tell us *which* composition or distillation boundary contains the bottoms composition. We determine this as follows:

(a) If the bottoms composition is free of one of the pure components, then the singular points that compose the composition boundary are the set of singular points enclosing the region that do not contain that pure component *and* that form a distillation region in the lower-dimensional mixture that also does not contain that pure component.

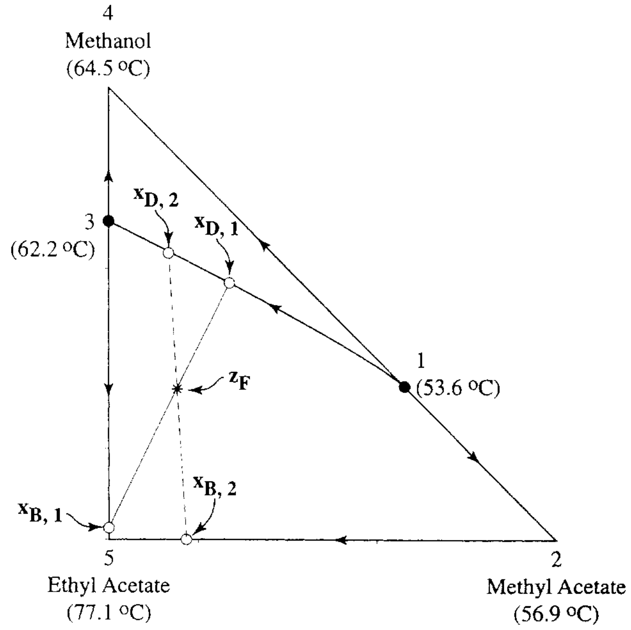

Figure 5. Two candidate splits for the same feed.

The dashed line is infeasible and the solid line is feasible. Point 3 is the common saddle.

(b) Otherwise, compute two residue curves, starting at points along the mass-balance line on either side of the bottoms composition (which is on a distillation boundary). Each of these residue curves will lie in a different distillation region. The distillation boundary is enclosed by the set of vertices shared by both regions.

8. If the lowest-boiling saddle on the bottoms boundary is reachable from the distillate composition, then this saddle is common to both the distillate and bottoms, and the split is feasible.

9. Repeat step 5 for each saddle adjacent to the unstable node.

This method provides a sufficient condition for product feasibility. It is not a necessary condition, and there are other alternative splits that are feasible and that do not fulfill these criteria. Fortunately, many common splits are covered by this method.

Implementing Algorithm 3 for Feed A in Figure 6, we find the range of sharp splits shown in the figure. Adding methyl acetate to the feed alters the range of feasible splits. For instance, with Feed B it is possible to obtain complete recovery of methanol in the distillate, and ethyl acetate in the bottoms simultaneously. This is not possible with the original feed.

Example 1

A mixture of methyl acetate, ethyl acetate, methanol, and ethanol has three binary azeotropes at atmospheric pressure as shown in Figure 1. These are the methanol–methyl acetate unstable node, the methanol–ethyl acetate saddle, and the ethyl acetate–ethanol saddle. This results in two distillation regions, one with a stable node at ethyl acetate and another with a stable node at ethanol. The distillation boundary (shaded) has vertices at each of the binary azeotropes, plus pure methyl acetate.

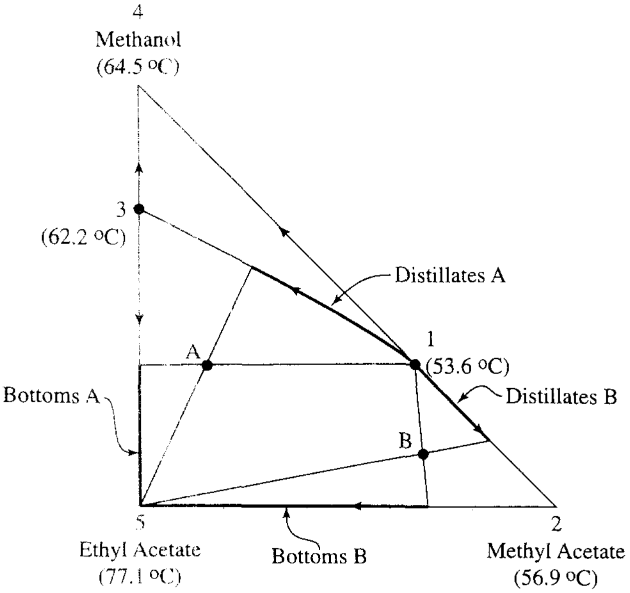

Figure 6. Feasible splits for two different feeds, *A* and *B*, in a mixture of methyl acetate, methanol, and ethyl acetate.

Consider a feed at the approximate center of the region behind the distillation boundary. One feasible split removes the methanol–methyl acetate azeotrope as a distillate and leaves methanol, ethyl acetate, and ethanol in the bottoms (split #1). This is the analog of a "direct" split in simpler mixtures. For a high recovery of methyl acetate, the bottoms composition can be chosen near the composition boundary, defined by points (7–4–3–5). The lowest-boiling saddle in this set is (3), which we must reach at step 8 of Algorithm 3. There are three saddles adjacent to the unstable node, (2), (3), and (4). When saddle (2) or (4) is selected in step 5, the reachability matrix shows that saddle (3) is not reachable from (2) or (4) since $r_{2,3}=0$ and $r_{4,3}=0$. The remaining saddle (3) is a common saddle since $r_{3,3}=1$. Therefore, this is a feasible split, and possible stream compositions are given in Table 1.

Table 1. Feed, Distillate, and Bottoms Compositions for the Mixture of Methyl Acetate, Methanol, Ethyl Acetate, and Ethanol*

	Split #1	Split #2
Feed		
$z_{F,1}$	0.25	0.25
$z_{F,2}$	0.25	0.25
$z_{F,3}$	0.25	0.25
$z_{F,4}$	0.25	0.25
Distillate		
$x_{D,1}$	0.6622	0.2767
$x_{D,2}$	0.3378	0.2767
$x_{D,3}$	6.519×10^{-6}	0.2767
$x_{D,4}$	4.412×10^{-8}	0.17
Bottoms		
$x_{B,1}$	1.0×10^{-6}	4.659×10^{-10}
$x_{B,2}$	0.1967	5.551×10^{-5}
$x_{B,3}$	0.4016	1.255×10^{-7}
$x_{B,4}$	0.4016	0.9999

*The number of the components in the table is methyl acetate (1), methanol (2), ethyl acetate (3), and ethanol (4).

Note that other feasible splits can be found for distillate compositions along the (1–3) edge of the distillation boundary, but not along the (1–2) or (1–4) edges.

A second feasible split is the analog of the "indirect" split, where a composition near pure ethanol (the stable node) is taken out as a bottoms stream (split #2). The mass balance and the geometry of the mixture confine the distillate composition to lie near the distillation boundary, because we do not attempt to cross these (also see the additional comments in the "Discussion and Conclusions" section). Therefore, the distillate contains all four components, and high recovery of methanol in the bottom product is not possible. Saddle (5) is a common saddle, indicating that the split is feasible.

More feasible splits can be found. For instance, a distillate can be taken along the (1–3) boundary. For certain feed compositions, the bottoms can be close to the (5–7) binary edge and nearly free of methyl acetate. Saddle (3) is adjacent to the distillate. Saddle (5) is adjacent to the bottoms composition and is also reachable from (3) so (5) is the common saddle. Note that these splits, though feasible, may not be very practical because disturbances in the feed composition may be difficult to accommodate.

Example 2

Next, consider a mixture of ethanol, methanol, chloroform, benzene, and acetone, which cannot be so easily visualized. Nine azeotropes are predicted by the Wilson model at 1-atm pressure (Fidkowski et al., 1993b) for a total of 14 singular points. One of the azeotropes is a quaternary saddle, two are ternary saddles, and six are binary saddles or nodes. The adjacency matrix reveals two unstable nodes and two stable nodes and the reachability matrix shows that there are at most four distillation regions. (These matrices are reported in Rooks, 1997.) Algorithm 2 indicates that there are exactly four distillation regions. The vertices of these regions, along with their stability classification and boiling temperatures, are given in Table 2.

For an equimolar feed of all five components, there are few splits with high recoveries. The distillate can be near the chloroform–methanol azeotrope (unstable node), but this leads to a bottoms composition on or near a distillation boundary containing all five components (split #1, Table 3). Another split is possible with a bottoms that is primarily ethanol (stable node); however, the distillate lies on a distillation boundary that also contains all the components (split #2, Table 3). Therefore, with this feed composition, it is not possible to achieve complete recovery of any component in either of the product streams.

We can also explore alternative feed compositions and the possibility of recycling certain components in order to alter the feasible splits within a given distillation region using the approach described in the Appendix. This approach is also considered in the next example.

Example 3

We consider a six-component mixture of methanol, methyl acetate, ethanol, ethyl acetate, water, and acetic acid at 1-atm pressure modeled with the NRTL equation. Table 4 shows the stability characteristics and boiling temperatures for each singular point. For details of the vapor–liquid equilibrium

Table 2. Four Distillation Regions in a Five-Component Mixture of Acetone, Methanol, Ethanol, Chloroform, and Benzene*

UN	53.9	Chloroform–methanol
SA	57.5	Acetone–chloroform–methanol–benzene
SA	57.6	Acetone–chloroform–methanol
SA	58.1	Methanol–benzene
SA	59.9	Chloroform–ethanol
SA	63.9	Acetone–chloroform–ethanol
SA	64.5	Methanol
SA	67.8	Ethanol–benzene
SN	78.3	Ethanol
UN	53.9	Chloroform–methanol
SA	57.5	Acetone–chloroform–methanol–benzene
SA	57.8	Acetone–chloroform–methanol
SA	58.1	Methanol–benzene
SA	59.9	Chloroform–ethanol
SA	61.8	Chloroform
SA	63.9	Acetone–chloroform–ethanol
SA	65.5	Acetone–chloroform
SA	67.8	Ethanol–benzene
SN	80.0	Benzene
UN	65.5	Acetone–methanol
SA	56.1	Acetone
SA	57.5	Acetone–chloroform–methanol–benzene
SA	57.6	Acetone–chloroform–methanol
SA	58.1	Methanol–benzene
SA	63.9	Acetone–chloroform–ethanol
SA	64.5	Methanol
SA	67.8	Ethanol–benzene
SN	78.3	Ethanol
UN	64.6	Acetone–methanol
SA	56.1	Acetone
SA	57.5	Acetone–chloroform–methanol–benzene
SA	57.6	Acetone–chloroform–methanol
SA	58.1	Methanol–benzene
SA	63.9	Acetone–chloroform–ethanol
SA	65.5	Acetone–chloroform
SA	67.8	Ethanol–benzene
SN	80.0	Benzene

*The normal boiling points (°C) are shown along with the stability of the vertices: UN—unstable node; SN—stable node; SA—saddle. Entries showing more than one component correspond to azeotropes.

model and parameters, see Rooks (1997). The adjacency and reachability matrices, numbered according to the singular points listed in Table 4, are

$$A = \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

and

Table 3. Two Feasible Splits for an Equimolar Feed of Acetone, Methanol, Chloroform, Ethanol, and Benzene*

	Distillate	Bottoms
Split #1	Chloroform Methanol	Acetone Chloroform Methanol Ethanol Benzene
Split #2	Acetone Chloroform Methanol Ethanol Benzene	Ethanol

*The feed is in the first region listed in Table 2.

$$R = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 1 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

There is one six-component distillation region for this mixture. For an equimolar feed, there are four splits shown in Table 5. It is possible to remove methyl acetate with high recoveries as a distillate (split #1), but not in high purity because of the methanol–methyl acetate azeotrope. It is also possible to completely recover pure acetic acid in an indirect split (split #3).

Starting with these splits, and applying the algorithms recursively, many alternative sequences to separate the original mixture into its pure components can be generated.

For example, if all of the methyl acetate is removed in the distillate as an azeotrope with methanol, the resulting bottoms will contain the remaining components, which form a single distillation region. Instead, if the acetic acid is re-

Table 4. Singular Points for Example 3

No.	Component or Azeotrope	Boiling Point, °C	Stability
1	Methyl acetate–methanol	53.5	UN
2	Methyl acetate–water	56.4	SA
3	Methyl acetate	56.9	SA
4	Methanol–ethyl acetate	62.2	SA
5	Methanol	64.5	SA
6	Ethyl acetate–ethanol–water	70.7	SA
7	Ethyl acetate–ethanol	71.8	SA
8	Ethyl acetate–water	71.9	SA
9	Ethyl acetate	77.1	SA
10	Ethanol–water	78.27	SA
11	Ethanol	78.29	SA
12	Water	100.0	SA
13	Acetic acid	117.9	SN

Table 5. Four Splits for an Equimolar Feed of Methanol, Ethanol, Methyl Acetate, Ethyl Acetate, Acetic Acid, and Water

Split	Distillate	Bottoms
#1	Methyl acetate Methanol	Methanol Ethyl acetate Ethanol Water Acetic acid
#2	Methyl acetate Methanol Ethyl acetate	Ethyl acetate Ethanol Water Acetic acid
#3	Methyl acetate Methanol Ethyl acetate Ethanol Water	Acetic acid
#4	Methyl acetate Methanol Ethyl acetate Ethanol Water	Acetic acid Water

moved as a bottom product, the remaining components will appear in the distillate. These components form three distillation regions that can be determined as follows. Delete row 13 and column 13 in the preceding adjacency matrix. Three singular points (9, 11, and 12) become stable nodes since those rows in the reduced adjacency matrix contain only zeros. Point 1 remains the only unstable node and all three stable nodes can be reached from this unstable node, giving three candidate regions. (Generally, this requires recalculation of the reachability matrix.) All three of these satisfy Property 2, and therefore there are three distillation regions. This split may seem undesirable because of the complicated structure of the distillate mixture and because at least 83% of the feed mixture must be vaporized. However, this split avoids the difficult separation of water from acetic acid, which is expensive. A design and cost estimate for some or all of the columns in the sequences is needed to rank them, for example, using a branch-and-bound approach.

The particular alternative shown in Figure 7 can be constructed starting with recovery of the methyl acetate as an azeotrope with methanol in the distillate. This mixture can be separated using known technology such as extractive, azeotropic, or perhaps pressure-swing distillation (we do not follow these binary separations any further). Methanol is added in sufficient quantity to the resulting bottoms product so that all of the ethyl acetate can be recovered in the distillate as an azeotrope with ethyl acetate (see the Appendix). This methanol addition avoids a split involving the ethyl acetate-ethanol-water azeotrope, which is not easily separated.

The bottoms stream from the second split is sent to another column, where pure methanol can be recovered in the distillate. A fourth split removes acetic acid as the bottoms product; this is liable to be expensive if high purities are desired. The ethanol/water mixture can be split in a conventional extractive distillation subsystem, for example, using ethylene glycol as entrainer.

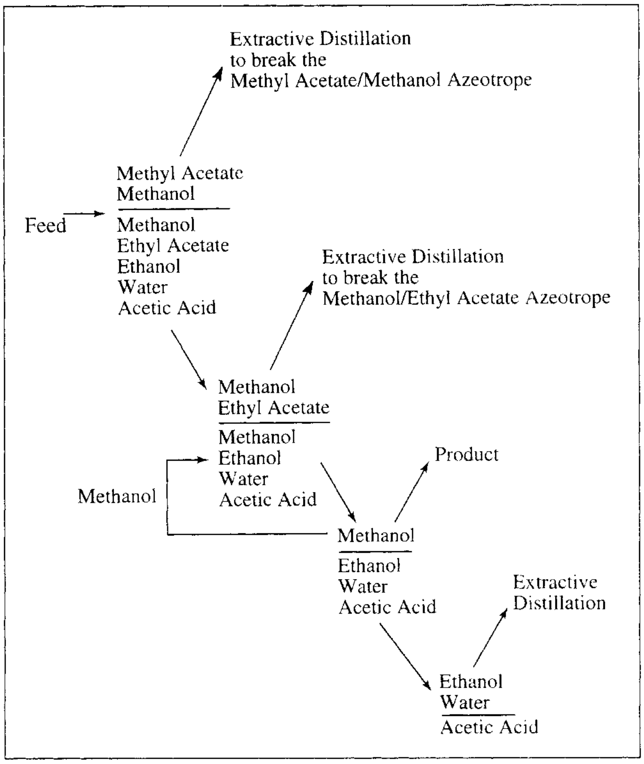

Figure 7. One sequence to separate equimolar feed of methyl acetate, methanol, ethyl acetate, ethanol, water and acetic acid.

Rooks (1997) determines that at least 26 alternative sequences can be generated to separate this mixture, not taking into account sidestream columns, entrainer selection, and nonsharp splits!

Discussion and Conclusions

The methods described here provide feasibility tests and sequencing of distillation columns to separate nonideal mixtures containing many components. With these tools, the residue curve map structure of complex multicomponent mixtures can be calculated rapidly, for example, in less than one or two minutes on a typical workstation. The development avoids crossing distillation boundaries and exploiting liquid-liquid phase behavior. Either of these two effects can give rise to additional alternatives, with the latter effect typically being of greatest practical importance. The methods described here apply strictly to homogeneous mixtures, but also provide a basis for studying heterogeneous mixtures, chemically reacting mixtures (and even to solid-liquid equilibrium systems for multicomponent crystallization). The main obstacle is the lack of a robust method for calculating all the azeotropes (eutectics, peritectics, and compounds) in such mixtures. Once this is achieved the methods developed here should apply.

Because of the difficulty of constructing feasible sequences of distillation columns for azeotropic mixtures, it is easy to conclude that there may not be many alternatives, and that as soon as one feasible alternative is found it is less important to develop others. The examples given earlier demonstrate that there can be a surprisingly large number of alternatives for the distillation of azeotropic mixtures, and Rooks (1997) has shown that some of them are much more attractive than others.

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Notation

$a_{i,j}$ = element of the adjacency matrix
c = total number of components in a mixture
$\delta_{i,j}$ = Kronecker delta
$\mathbf{J}$ = Jacobian matrix
$r_{i,j}$ = element of the reachability matrix
$\mathbf{x}$ = vector of liquid compositions
x_i = mole fraction of component i in the liquid phase
$x_{B,i}$ = mole fraction of component i in the bottoms stream
$x_{D,i}$ = mole fraction of component i in the distillate stream
$\mathbf{y}$ = vector of vapor compositions
y_i = mole fraction of component i in the vapor phase
$z_{F,i}$ = mole fraction of component i in the feed

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Appendix: Feed Compositions Allowing Complete Recovery

In some mixtures containing distillation boundaries, such as Example 2, it is not possible to completely recover any component in either product stream. However, for other feed compositions within the same distillation region, it may be possible to recover one or more components in a single product stream. In this Appendix we describe a systematic method to determine a feed composition that allows complete recovery of one of the components in a product stream.

The stable node of a distillation region can always be removed as a bottoms product. First, we find the composition boundaries of the given region that do not contain one of the components present in the stable node. If a distillate composition is located on such a composition boundary then one component can be completely recovered in the bottoms product. If we completely recover a component in the bottoms stream, then the distillate composition will lie on the lower-dimensional face that does not contain the recovered component. This face may have one or more distillation regions and a distillate composition could lie in any one of these lower-dimensional distillation regions, depending on the feed composition. Thus, different locations of the distillate composition will lead to different separation sequences.

The following algorithm provides a method for determining typical feed compositions that lead to complete recovery of a component in one of the product streams. It is described for starting at the stable node, though a similar procedure can be followed starting with the unstable node as a distillate.

Algorithm 4: typical feed compositions

1. Compute the adjacency and reachability matrices for the full mixture.
2. Determine the number of distillation regions.
3. For each of the distillation regions:
    (a) Find a set of vertices that do not contain one of the pure components present in the stable node.
    (b) Compute the lower-dimensional adjacency matrix.

(The adjacency matrix of a lower-dimensional system can be computed from a higher-dimensional system by replacing all of the elements in the row(s) and column(s) of singular points containing the missing component by zeros.)

(c) Use Algorithm 2 on the lower-dimensional problem generated in steps (a) and (b).

(d) For each lower-dimensional distillation region, compute an average composition for each component from the mean value of the mole fractions at each singular point.

(e) Compute a midpoint between the stable node and the average composition in the lower-dimensional distillation region. At this point, a feed composition can be located that allows complete recovery of one of the components in the bottoms stream. (A collateral benefit may be that another component is completely recovered in the distillate, for example, feed B in Figure 6.)

(f) There is a neighborhood of feed points enclosing the line connecting the stable node to the average composition in the lower-dimensional distillation region that give the desired separation. The best one can only be found by optimization.

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