Shortcut Design Method for Columns Separating Azeotropic Mixtures

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A shortcut method is proposed for the design of columns separating homogeneous azeotropic mixtures. Azeotropes are treated as pseudocomponents, and a *C*-component system with *A* azeotropes is treated as an enlarged (*C* + *A*)-component system. This enlarged system is divided into compartments, where each compartment behaves like a nonazeotropic distillation region formed by the singular points that appear in it. The compartment boundary is linearly approximated. A procedure is proposed for transforming vapor−liquid equilibrium behavior in terms of pure components into that in terms of singular points, allowing relative volatilities to be characterized in terms of singular points. The classical Fenske−Underwood−Gilliland method can then be used to design columns separating azeotropic mixtures. This method is extremely computationally efficient and can be applied to homogeneous azeotropic mixtures with any number of components. The results of the shortcut design method are useful for initializing rigorous simulations using commercial software.

Introduction

The composition space of an azeotropic mixture is always divided into distillation regions[1] and compartments,[2,3] thereby restricting feasibility and presenting a challenge for the prediction of feasible separations and for column design. For ternary azeotropic mixtures, graphical tools, such as residue curve maps and distillation line maps, can be used to identify distillation regions and compartments. However, such representations are not applicable for multicomponent mixtures because the visualization of residue curve maps is impossible.

For nonazeotropic mixtures, effective methods exist for the shortcut design of distillation columns. The classical approach is the Fenske−Underwood−Gilliland (FUG) method.[4−10] This method assumes constant molar overflow and constant relative volatility and can be used for columns separating mixtures with any number of components. However, in columns separating azeotropic mixtures, the relative volatilities of all components can vary significantly along the column, and sometimes the volatility order can even change. Therefore, these shortcut methods cannot be used directly.

Several design methods[11−15] for columns separating azeotropic mixtures have been proposed, with many of them concentrating on the calculation of minimum reflux ratios. The methods available for column design are rigorous or semi-rigorous, and are therefore computationally intensive. As a result, these methods cannot conveniently be used to solve larger problems, such as the synthesis and evaluation of distillation flowsheet alternatives. Furthermore, there is still no reliable method for calculating the minimum number of stages for a column separating a multicomponent azeotropic mixture.

This paper proposes a shortcut method for the design of columns separating azeotropic mixtures. In this method, all azeotropes are treated as pseudocomponents, and a *C*-component mixture with *A* azeotropes is treated as an enlarged nonazeotropic system with (*C* + *A*) components. Subsystems within the enlarged composition space in which the volatility order is fixed are defined. The classical Fenske−Underwood−Gilliland shortcut design method is then employed to design columns and evaluate flowsheets separating azeotropic mixtures.

Background

Distillation Regions and Compartments. At an azeotrope, the vapor in equilibrium with the liquid phase has the same composition as the liquid. Therefore, an azeotrope cannot be separated by conventional distillation. For analysis of azeotropic distillation, especially for ternary mixtures, residue curve maps[1] and distillation line maps[16] are widely used. This work uses the convention that the singular points (all pure-component vertices and azeotropes)[1] are numbered in order of increasing boiling temperature.

Azeotropes can result in the formation of compartments and distillation regions. Within a distillation region, all residue curves have the same pair of initial and terminal singular points.[1] Residue curves in two different distillation regions will have different stable or unstable nodes.[1] Two adjacent distillation regions are separated by a distillation boundary, which is generally nonlinear and imposes limitations on the product compositions (and composition profiles) of distillation columns. At total reflux, a feasible split must have two products that lie in the same distillation region.[17] A split with products that lie in one region and a feed in another might also be feasible if the feed lies on the concave side of the distillation boundary (or the two products might even lie in different regions).

Within a distillation region, although all residue curves begin at the same unstable node and end at the

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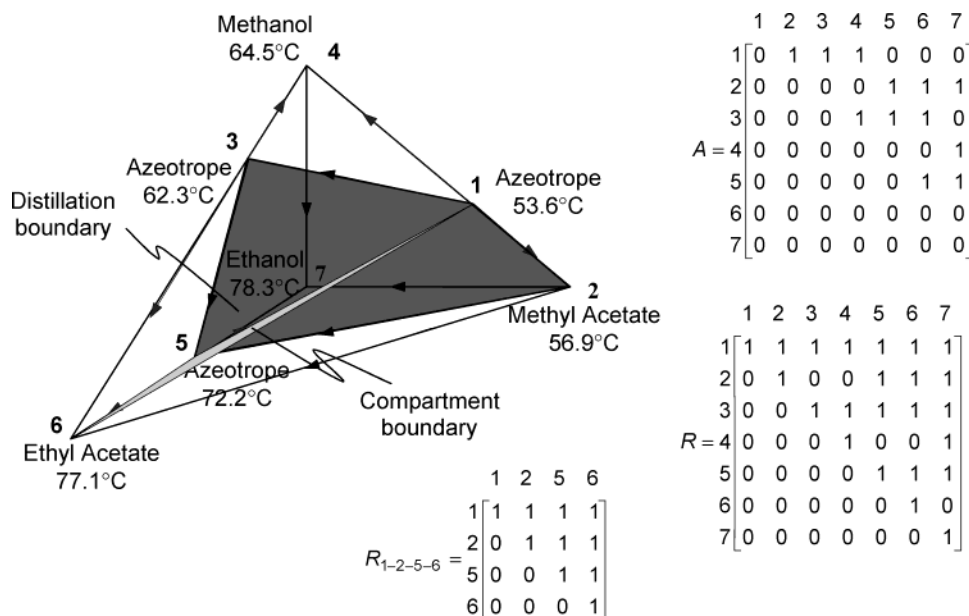† UMIST.
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$$A = \begin{array}{c|ccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ \hline 1 & 0 & 1 & 1 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ 3 & 0 & 0 & 0 & 1 & 1 & 1 & 0 \\ 4 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 5 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}$$

$$R = \begin{array}{c|ccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ \hline 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 2 & 0 & 1 & 0 & 0 & 1 & 1 & 1 \\ 3 & 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 4 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 5 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ 6 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 7 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}$$

$$R_{1-2-5-6} = \begin{array}{c|cccc} & 1 & 2 & 5 & 6 \\ \hline 1 & 1 & 1 & 1 & 1 \\ 2 & 0 & 1 & 1 & 1 \\ 5 & 0 & 0 & 1 & 1 \\ 6 & 0 & 0 & 0 & 1 \end{array}$$

Figure 1. Adjacency and reachability matrices of a quaternary mixture with three azeotropes. One distillation boundary and one compartment boundary are shown by shaded surfaces.

same stable node, sometimes, they can approach different saddle points. In this case, the distillation region is divided into several "continuous distillation regions"[2] or "compartments".[3] In each compartment, all residue curves start from the unstable node, approach saddle points one by one in order of increasing boiling temperature, and end at the stable node. Within a compartment, residue curves can approach all the saddle points that appear in it.[3] This behavior is analogous to that in the composition space of nonazeotropic mixtures. The difference between two neighboring compartments lying in the same distillation region is that they have different saddle points. Two adjacent compartments are separated by a compartment boundary.[3] Single-feed columns can sometimes cross a compartment boundary (i.e., the two products lie in adjacent compartments), and two-feed columns can further facilitate such a split.[3]

For multicomponent azeotropic mixtures, the topology of the composition space (existence and location of distillation regions and compartments and their boundaries) cannot be visualized. However, the approach of Knight and Doherty[18] allows for a mathematical representation of the topology. For a multicomponent azeotropic mixture with singular points numbered in the order of increasing boiling temperature, an adjacency matrix, **A**, and a reachability matrix, **R**, are defined.[18] The elements of the adjacency matrix are defined by $a_{i,j} = 1$ if a residue curve connects singular point i to singular point j and $a_{i,j} = 0$ otherwise. The elements of the reachability matrix are defined by $r_{i,j} = 1$ if there is any path from i to j and $r_{i,j} = 0$ otherwise.

Rooks et al.[19] developed a general procedure for computing the adjacency and reachability matrices for n-component homogeneous mixtures and proposed an algorithmic procedure for identifying the distillation regions. In each distillation region, there is only one pair of stable and unstable nodes, and all saddle points can reach the stable node and can be reached by the unstable node. Thong and Jobson[3] found that the reachability submatrix formed by all singular points comprising a compartment is an upper-triangular matrix. An algorithm for systematically identifying all such

Table 1. Distillation Regions, Distillation Boundaries, Compartments, and Compartment Boundaries in the Quaternary System Shown in Figure 1

distillation regions	1−2−3−5−6	1−2−3−4−5−7
compartments	1−2−5−6	1−2−5−7
	1−3−5−6	1−3−5−7
		1−3−4−7
compartment boundaries	1−5−6	1−5−7
		1−3−7
		1−7
distillation boundary	1−2−3−5	

submatrices and hence all compartments is presented by Thong and Jobson.[3]

Figure 1 illustrates the adjacency and reachability matrices of a quaternary mixture with three azeotropes. Using the procedures of Rooks et al.,[19] it can be determined that the whole composition space is separated into two distillation regions by distillation boundary 1−2−3−5. Two compartments in distillation region 1−2−3−5−6 and three in region 1−2−3−4−5−7 can be identified using the procedure of Thong and Jobson.[3] The distillation regions, compartments, and corresponding boundaries are listed in Table 1.[3] Figure 1 also presents the upper-triangular reachability submatrix, **R**$_{1-2-5-6}$, that corresponds to compartment 1−2−5−6.

Simplified Representation of Azeotropic Systems. Vogelpohl[20] showed that, in distillation, an azeotrope behaves like a pure component and a binary azeotropic system can be simplified into two ideal systems by treating the azeotrope as a pseudocomponent. For example, with the minimum azeotrope between ethanol (A) and benzene (B) treated as a pseudo-pure component, the binary (A−B) system, shown in Figure 2, can be transformed into two ideal systems, system I and system II.[20] When the mole fraction of A is less than $x_{az,A}$, the mixture can be treated as the ideal system of the azeotrope and B in system I. On the other side of the azeotrope, the mixture can be taken as the ideal system of the azeotrope and A in system II.

As shown in Figure 2, each system can be treated as an independent system, and the composition of any mixture can be transformed to the new coordinate system. In the transformed system, the relative volatili-
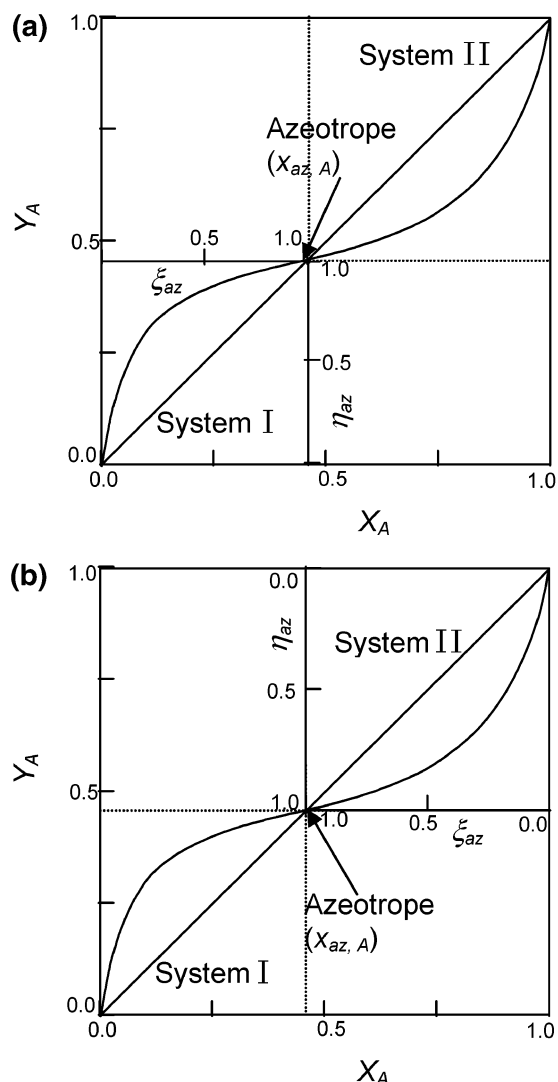
(a)

(b)

Figure 2. Binary system, ethanol (A)−benzene (B), with one azeotrope, can be transformed into two transformed systems with the azeotrope treated as a pseudocomponent.[20]

ties of the pure component and the pseudocomponent, the azeotrope, can be calculated according to the transformed composition. For example, in transformed system II, the relative volatilities of compositions between the azeotrope and A can be calculated using eq 1.[20]

$$\alpha_{az,A} = \frac{\eta_{az}(1 - \xi_{az})}{\xi_{az}(1 - \eta_{az})} \tag{1}$$

For the mixture of ethanol (A) and benzene (B) at 1 bar, it was shown that the relative volatility in system II, $\alpha_{az,A}$ has an almost constant value (4.32 ± 0.32), so this transformed system can be treated as an ideal system.[20] System I can also be treated as an ideal system, as the relative volatility between B and the azeotrope is also approximately constant.[20]

Vogelpohl[21] recently extended this work for ternary systems. However, claims that the method is generally applicable for multicomponent systems[21] have not been substantiated. In this method, with azeotropes treated as pseudocomponents, a ternary azeotropic system with *A* azeotropes can be treated as an enlarged system with (3 + *A*) components. The enlarged system can be separated into several approximately ideal subsystems.
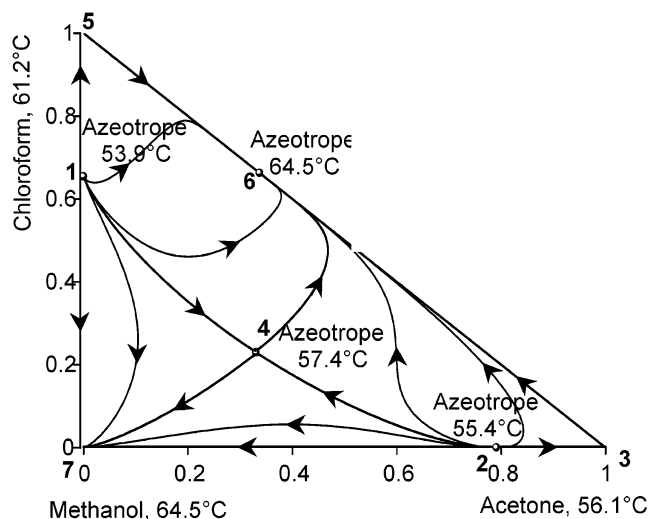

Figure 3. Residue curve map of the ternary system of acetone, chloroform, and methanol.

For example, there are four azeotropes in the ternary system of acetone, chloroform, and methanol, as shown in Figure 3. Vogelpohl[21] proposed that the composition space could be treated as a seven-component system with three "quaternary" ideal subsystems, namely, 1−4−5−6, 1−2−4−7, and 2−3−4−6. In each subsystem, the relative volatilities of pure components and azeotropes are assumed to be constant and can be calculated using eq 2[21]

$$\alpha_{ik} = \frac{\gamma_i p_i^0}{\gamma_k p_k^0} \tag{2}$$

where γ_i and γ_k are the activity coefficients and p_i^0 and p_k^0 are the vapor pressures of any pure component or azeotrope *i* and *k*, respectively.[21] In this equation, an azeotrope *i* is treated as a pseudocomponent, and its γ_i p_i^0 value is given by that of any of its constituent pure components.

Applying the distillation theory of ideal systems and eq 2 to calculate the relative volatilities of the pure components and azeotropes, the distillation lines or other information related to vapor−liquid equilibrium in the subsystem can be calculated, and an approximate prediction of the actual system behavior can be made.[21] For a simple system, such as a ternary system with only one azeotrope, distillation lines calculated using this method are in good agreement with those calculated rigorously. For a complex system, such as the ternary system shown in Figure 3, the deviation between the distillation lines calculated using this method and those calculated rigorously is large.[21]

Another problem with this method is that there is no clear definition of what constitutes a subsystem. For the example shown in Figure 3, subsystem 1−2−4−7 contains two distillation regions, 1−4−7 and 2−4−7, whereas subsystem 1−4−5−6 corresponds to a single distillation region. Therefore, this method cannot be systematically applied.

Shortcut Design Method for Columns Separating Nonazeotropic Mixtures. For the design of columns separating nonazeotropic mixtures, the Fenske−Underwood−Gilliland (FUG) method[4−10] is the most widely used shortcut method. The Fenske equa-

tion,[4] the Underwood equations,[5−8] and the Gilliland correlation[9,10] are employed in this method. This method needs the separation between two key components, the light key (LK) component and the heavy key (HK) component, to be specified. The light key component has a specified maximum recovery in the bottom product, whereas the recovery or mole fraction of the heavy key component in the top product is specified. The Fenske and Underwood equations assume constant relative volatilities in the column.

When operated at total reflux, a column can achieve the desired separation with the minimum number of stages. The Fenske equation,[4] given in eq 3, can be used to calculate the minimum number of stages, which includes the reboiler and partial condenser

$$N_{min} = \frac{\log\left[\left(\frac{x_A}{x_B}\right)_d / \left(\frac{x_A}{x_B}\right)_b\right]}{\log(\alpha_{AB})} \quad (3)$$

where A and B denote key components; d and b denote the distillate and bottom product, respectively; and N_{min} is the minimum number of stages.

Using an infinite number of stages, the desired separation can be achieved by a column operated at the minimum reflux ratio, which can be determined using the Underwood equations,[5−8] eqs 4 and 5

$$1 - q = \sum_{i=1}^{N} \frac{\alpha_i x_{i,F}}{\alpha_i - \theta} \quad (4)$$

$$R_{min} + 1 = \sum_{i=1}^{N} \frac{\alpha_i x_{i,D}}{\alpha_i - \theta} \quad (5)$$

where α_i, $x_{i,F}$, and $x_{i,D}$ are the average relative volatility of component i ($i = 1, 2, ..., N$) and the mole fractions of i in the feed and in the distillate, respectively, and q, R_{min}, and θ are the feed thermal condition, the minimum reflux ratio, and the dimensionless root of eq 4, respectively.

Assuming constant molar overflow, the Underwood equations can also be used to calculate the minimum vapor flow rate, corresponding to the minimum reflux ratio. The Underwood equations are insensitive to the distribution of impurities (nonkey components) in the products.[22]

When the two key components are adjacent to each other in volatility, only one solution for θ lies between α_{LK} and α_{HK}. Otherwise, there are several solutions for θ lying between α_{LK} and α_{HK}. In this case, it is difficult to determine which θ value allows eq 5 to give a good prediction of the minimum reflux ratio. The iterative procedure employed to solve for θ should be highly accurate.[22] However, if the denominator $(\alpha_i - \theta)$ (for any i) is very small, the Underwood equations cannot give good results, even if x_i is also small.

Once the minimum reflux ratio and the minimum number of stages are known, the Gilliland correlation relates the number of equilibrium stages and the operating reflux ratio.[9,10] This correlation, which is based on stage-by-stage calculations for over 50 binary and multicomponent distillations, was first developed as a plot.[9] Many attempts have been made to represent
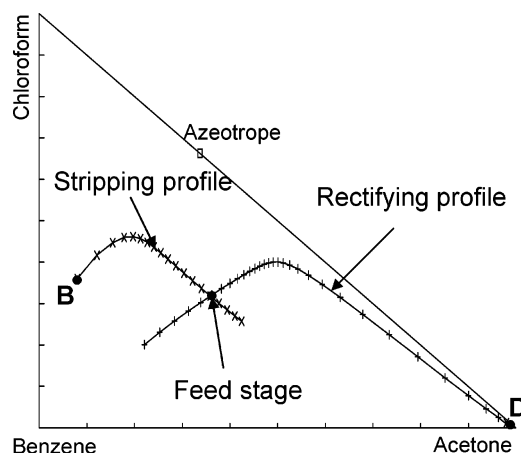

Figure 4. Feasible ternary split with two intersecting composition profiles.

Gilliland's correlation analytically. Equation 6 is the correlation of Eduljee.[10]

$$\frac{N - N_{min}}{N + 1} = 0.75\left[1 - \left(\frac{R - R_{min}}{R + 1}\right)^{0.566}\right] \quad (6)$$

To use eq 6, either the ratio between the operating reflux and the minimum reflux or the ratio between the number of equilibrium stages and the minimum number of stages is specified, so that the number of equilibrium stages or the operating reflux ratio can be determined.

In the FUG method, both the Underwood and Fenske equations assume constant relative volatilities. Even for ideal and near-ideal systems, the relative volatility between any two components does vary through the column. Standard practice is to use a characteristic value for the relative volatility, e.g., that of the feed or the arithmetic or geometric mean of the values for the overhead and bottom products. The performance of the shortcut design equations is sensitive to the method used to calculate characteristic relative volatilities, even for well-behaved systems.[23] For a column separating an azeotropic mixture, the relative volatilities will generally change significantly along the column, and sometimes the volatility order will even change. The FUG method cannot be used directly to design columns separating such mixtures.

Design Methods for Columns Separating Azeotropic Mixtures. (i) Boundary Value Method. The boundary value method, proposed by Levy et al.,[11] can be used to determine the minimum reflux ratio and feasible design parameters for a column separating a ternary homogeneous azeotropic mixture. This method requires fully specified product compositions, the feed composition, and the feed thermal condition. Once these specifications have been made, only one degree of freedom remains between the reflux and boil-up ratios. With a specified reflux (or boil-up) ratio, rectifying and stripping composition profiles can be calculated from the fully specified products, and the intersection of these two profiles indicates the feasibility and design parameters of this split. Figure 4 shows a ternary split with two intersecting profiles. The minimum reflux ratio can be found through repeated calculation for different reflux ratios.
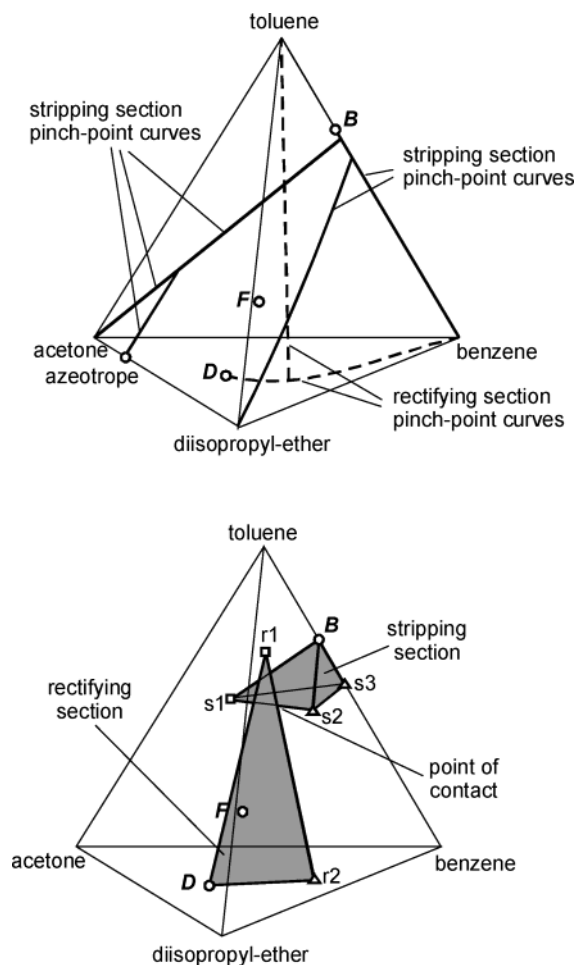
Figure 5. Branches of the pinch-point curves for two product compositions and rectification bodies at a particular value of the reflux ratio.[14] (Reproduced with permission from Wiley & Sons.)

Julka and Doherty[13] extended the boundary value method to apply to multicomponent mixtures. In this procedure, a feasible split is indicated when two stages that lie on the composition profiles of two different sections have the same liquid compositions. However, in columns separating multicomponent azeotropic mixtures, section composition profiles are very sensitive to impurity concentrations in the product, and it is difficult to find exact intersections between the rectifying and stripping profiles. The feasibility criterion of Julka and Doherty[13] can be relaxed by defining a maximum allowable difference between two stages.[24,25] The accuracy of the results then depends on the specified maximum allowable difference. Suitable maximum allowable distances are different for different azeotropic mixtures and cannot easily be specified a priori.

The boundary value method can also be used to test the feasibility of splits. For an infeasible split, the two section profiles will not intersect for any reflux ratio. This feasibility test is iterative in nature and therefore computationally time-consuming.

(ii) Rectification Body Method (RBM). Bausa et al.[14] proposed the rectification body method (RBM) for the determination of minimum energy requirements of a specified split. For a specified product, branches of the pinch-point curves can be found. Rectification bodies can be constructed by joining points on the branches of pinch-point curves with straight lines, as shown in Figure 5. For either section of a column, a rectification body can be constructed; its size and position depend

on the corresponding reflux or boil-up ratio. The intersection of the rectification bodies of two sections of a column indicates its feasibility. The minimum reflux ratio can be obtained through an iterative search of the intersections of rectification bodies corresponding to different reflux ratios. Because this method utilizes only the pinch-point curves to construct rectification bodies, it can, in principle, easily be applied to mixtures with any number of components. Although the method requires the complete specification of both product compositions, it is not as sensitive to impurity concentrations as the boundary value method.[3] Furthermore, the intersection (in higher dimension) between linear "edges" or "surfaces" can be easily assessed using algebraic equations or geometric relations.

The rectification body method can be used to calculate the minimum reflux ratio and minimum energy cost and to test the feasibility of a split. Because faces on rectification bodies are linearly approximated by joining branches of pinch-point curves using straight lines, this method cannot guarantee accurate results. The minimum reflux ratio might be inaccurately predicted, or feasible splits might be incorrectly identified as infeasible. No information about column design (number of stages and operating reflux ratio) is obtained from the RBM. The calculation of pinch-point curves is, furthermore, computationally intensive.

(iii) Column Design Method Using Manifolds. Thong and Jobson[26] proposed a column design method using manifolds. Instead of fully specifying product compositions, only the mole fractions of principal components and the sum of the mole fractions of the impurities are specified in this method. A product specified in this way is known as a "product region". Several characteristic compositions are chosen to represent the specified product region, and composition manifolds, analogous to points on a composition profile, can be formed from the section profiles calculated from these representative compositions.[26] The intersection of a pair of rectifying and stripping manifolds indicates feasible column design parameters, including the reflux (and boil-up) ratio, total number of stages, and feed stage.

This method overcomes the limitations of the boundary value method by eliminating the requirement of fully specified product compositions. However, this method is more computationally intensive than the boundary value method, especially for multicomponent mixtures: to build two sets of section manifolds at a certain reflux (or reboil) ratio, many profiles must be calculated for each pair of product regions.

Representation of the Vapor−Liquid Equilibrium (VLE) Behavior in Terms of Singular Points

Relative volatility is a key driving force in distillation. Only when the relative volatility between two components differs from unity can these components be separated by distillation. The more the relative volatility differs from unity, the easier the separation. Azeotropes, which cannot be separated in an equilibrium flash stage, behave like pure components in distillation.[20,21] This means that an azeotrope will affect the design of a column as an individual component would, rather than as its constituents would. This work presents a new application of the classical FUG approach to column design by treating azeotropes in a system as pseudocom-
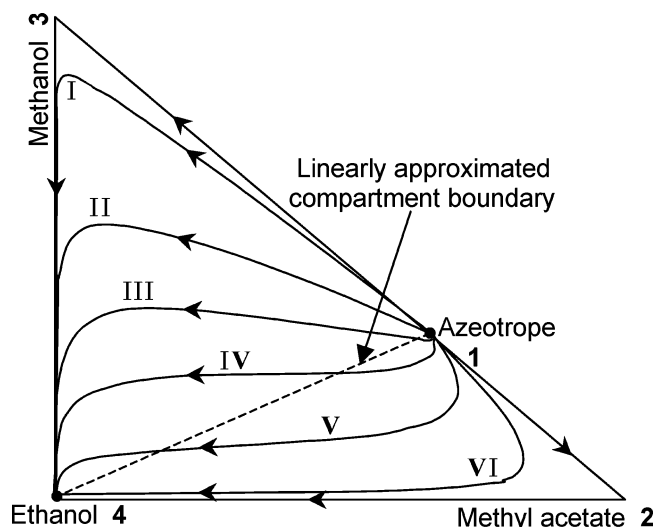
Figure 6. Ternary azeotropic system of methyl acetate, methanol, and ethanol. The composition space is separated into two compartments, $1-2-4$ and $1-3-4$.

Figure 7. Ternary system of methyl acetate, methanol, and ethanol, with singular point compositions expressed in terms of pure components.

ponents. The formulation requires that the relative volatilities of the azeotropes can be characterized.

Azeotropes are treated as pseudocomponents, and a C-component system with A azeotropes is treated as an enlarged $(C + A)$-component system, where all singular points constitute its components. Vapor−liquid equilibrium compositions in terms of pure components can be transformed into vapor−liquid equilibrium compositions in terms of singular points. Relative volatilities of all singular points (i.e., pure components and azeotropes) can then be calculated.

Compartments as Subsystems in the Composition Space. A compartment is the largest subsystem of composition space required to consistently treat azeotropic mixtures as nonazeotropic mixtures of pseudocomponents. First, it is necessary to identify compartment boundaries. In a distillation region, by testing the saddle points approached (i.e., moved toward and away from) by residue curves passing through different compositions, the compartments to which these compositions belong can be identified in principle, as can the compartment boundaries. However, it is not a straightforward matter to identify which saddle points are approached by a given residue curve. In particular, inflections in residue curves might indicate that saddle points lying in two different compartments are "approached".

Residue curves in a compartment behave analogously to those in the whole composition space of a nonazeotropic mixture.[3] That is, the residue curves generally start from the unstable node, approach the saddle points that appear in the compartment one by one in order of increasing temperature, and end at the stable node, as illustrated in Figure 6. In this ternary system of methyl acetate, methanol, and ethanol, there is one minimum-boiling azeotrope (1) between methyl acetate (2) and methanol (3), and the whole composition space is separated into the two compartments $1-2-4$ and $1-3-4$. The saddle point 2 can only appear in compartment $1-2-4$, whereas saddle point 3 can only appear in compartment $1-3-4$. The linearly approximated compartment boundary is the straight line connecting stable node 4 and unstable node 1. In compartment $1-2-4$, residue curves, such as residue curves I, II, and III, start from unstable node 1, approach saddle point 2, and end
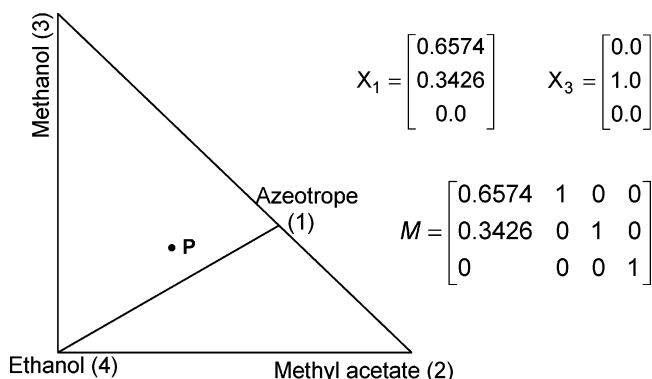
at stable node 4. The behavior of this compartment is analogous to that of the nonazeotropic system with singular points 1, 2, and 4. Similarly, the behavior of compartment $1-3-4$ is analogous to that of the nonazeotropic system with singular points 1, 3, and 4. Although there are residue curves in Figure 6, such as residue curves IV and V, that approach both saddle points 2 and 3, residue curves generally approach only one saddle point.

In this work, the compartment boundary is linearly approximated by connecting all singular points that appear in both of two neighboring compartments by straight lines. Because the feasibility of splits crossing a compartment boundary does not depend on the boundary's curvature,[3] the linear approximation of the compartment boundary is not a limiting assumption.

This work treats an azeotropic system as an enlarged system with all singular points as the constituents. In this respect, this work is like that of Volgelpohl.[20,21] In this approach, however, compartments, which can be rigorously defined and linearly approximated, are defined as the subsystems that are treated as nonazeotropic composition regions. In each compartment, an azeotrope acts as a pure component, and any mixture can be treated as a mixture of the singular points that appear in this compartment. A systematic approach for expressing compositions in terms of singular points, rather than in terms of pure components, is presented below.

Transformation of Compositions. In a C-component azeotropic system, each singular point can be taken as the mixture of the pure components; thus, the system composition in terms of pure components is known and can be expressed by a C-dimensional vector. For example, in the methyl acetate, methanol, and ethanol system shown in Figure 7, two C-dimensional vectors, $\mathbf{X}_1$ and $\mathbf{X}_3$, can be used to represent to the compositions of singular points 1 and 3, respectively.

In a C-component azeotropic system with A azeotropes, $(C + A)$ C-dimensional vectors can be built to represent the compositions of singular points and can form a $C \times (C + A)$ matrix. Each column of this matrix represents the composition of a singular point, and each row represents a pure component. The pure components are ordered with respect to boiling temperature at the system pressure, as are the singular points. This matrix relates the compositions of all singular points to pure components and is defined in this work as the transformation matrix. For example, in Figure 7, all of the singular point compositions are expressed in the 3×4-dimensional transformation matrix $\mathbf{M}$.

In the enlarged system with all singular points as its constituents, the composition of a point can be expressed in terms of these singular points. As mentioned previously, a compartment behaves as the nonazeotropic mixture of the singular points it contains. Singular points that are not included in the compartment are inactive, or irrelevant to the VLE behavior of the compartment. Therefore, when the composition of a point lying in a compartment is expressed in terms of all singular points, the mole fractions of singular points that do not appear in the compartment of interest can be set to zero. The transformation matrix and the C-dimensional and $(C + A)$-dimensional composition vectors form a set of linear equations. The procedure for setting up and solving these equations is illustrated by example in Figure 7.

For a stream with composition vector **P**, shown in Figure 7, the following is true:

(1) The molar composition, in terms of pure components, is

$$\mathbf{X} = [0.33 \quad 0.33 \quad 0.34]^T$$

(2) The composition in terms of all singular points is

$$\mathbf{S} = [s_1 \quad s_2 \quad s_3 \quad s_4]^T$$

where s_i (i = 1, 2, 3, or 4) represents the mole fraction of singular point i.

(3) Because point P lies in compartment $1-3-4$ and singular point 2 does not appear in this compartment, $s_2 = 0$.

(4) The linear equations to be solved are

$$\mathbf{X} = \mathbf{M} \cdot \mathbf{S} \tag{7}$$

where **M** is included in Figure 7. Hence, the composition of vector **P**, in terms of all singular points, is

$$\mathbf{S} = [0.5020 \quad 0 \quad 0.1580 \quad 0.34]^T$$

Note that a composition can only be expressed as a mixture of the singular points lying in the same compartment. For example, point P in Figure 7 lies in compartment $1-3-4$ and can be taken as the mixture of singular points 1, 3, and 4, but not as a mixture of singular points 1, 2, and 4.

A restriction of this method is that, in a C-component azeotropic system, the number of singular points that lie in the compartment of interest must be equal to C. When the number of singular points lying in the compartment of interest is not equal to C, there is no solution for the set of linear equations $\mathbf{X} = \mathbf{M} \cdot \mathbf{S}$. For example, in the ternary system shown in Figure 8, there is a minimum azeotrope (1) between the lightest component, acetone (2), and the heaviest component, n-heptane (4). The whole composition space is a compartment, as can be seen in the residue curve map. In this three-component compartment, the number of singular points is 4, and the compositions in terms of pure components cannot be transformed into compositions in terms of singular points by the above procedure.

In a multicomponent azeotropic system, the compartment in which a given composition lies can be identified if the saddle point approached by the residue curve containing this composition is known. Because the compositions of points lying on the residue curve are expressed in terms of pure components, it is difficult to
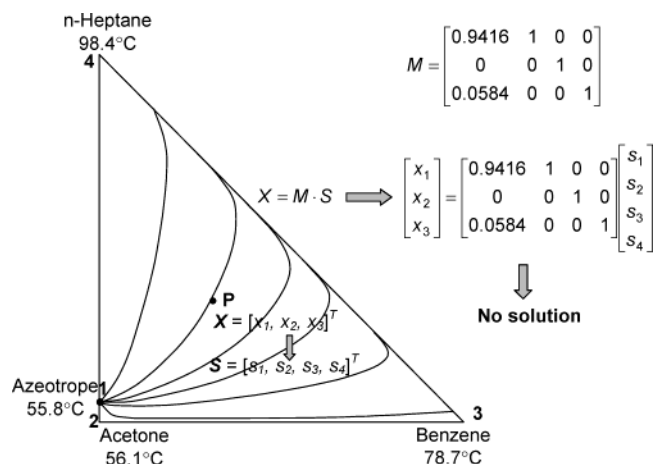

Figure 8. Ternary system with one minimum-boiling azeotrope. The whole composition space is one compartment. It is impossible to transform a composition in terms of pure components into a composition in terms of singular points.

identify which saddle point is approached by the residue curve. With the composition transformation procedure, this problem can be easily solved by searching through different compartments; calculation of the residue curve is not necessary. We can assume that a given composition lies in one of the compartments identified using the procedures of Rooks et al.[19] and Thong et al.[3] The assumptions can be checked by trying to transform a given mixture's composition in terms of pure components into a composition in terms of singular points using the transformation procedure. Only if there is a solution can it be concluded that this assumption is correct. The candidate compartments (within a given distillation region) must be tested in turn until a solution to eq 7 is obtained.

For example, the composition space of the quaternary system of methyl acetate, methanol, ethanol, and ethyl acetate is separated into five compartments, as shown in Figure 1 and Table 1. For a mixture P with composition

$$\mathbf{X} = [0.1315 \quad 0.5229 \quad 0.1466 \quad 0.2]^T$$

the composition transformation procedure is used to identify the compartment in which this mixture lies. According to the compositions of singular points in terms of pure components, the transformation matrix, **M**, is

$$\mathbf{M} = \begin{bmatrix} 0.6574 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0.3426 & 0 & 0.7088 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0.2912 & 0 & 0.5345 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0.4655 & 0 & 1 \end{bmatrix}$$

If we assume that mixture P lies in compartment $1-2-5-7$, using the transformation procedure, there is no solution to eq 7. Therefore, the mixture does not lie in the proposed compartment. Similarly, the mixture does not lie in compartment $1-3-5-7$. When compartment $1-3-4-7$ is assumed to be the compartment in which mixture P lies, a solution to eq 7, namely

$$\mathbf{S} = [0.2 \quad 0 \quad 0.5 \quad 0.1 \quad 0 \quad 0 \quad 0.2]^T$$

is obtained. Therefore, mixture P lies in compartment $1-3-4-7$. DISTIL 5.0 was used to compute the residue curve passing through the composition of mixture P,
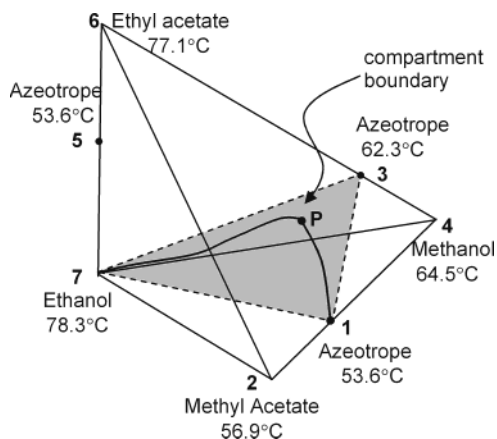
Figure 9. In the quaternary system of methyl acetate, methanol, ethyl acetate, and ethanol, the composition transformation procedure can be used to identify the compartment in which a composition lies.
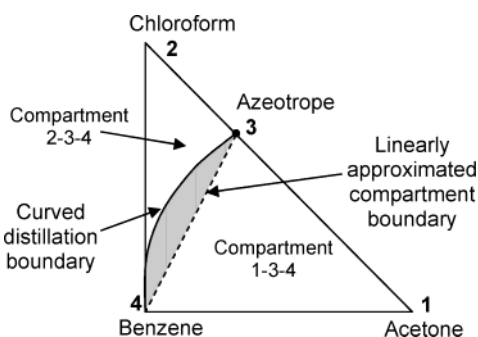

Figure 10. Ternary azeotropic system with a curved distillation boundary that is also the compartment boundary.

which is illustrated in Figure 9. Figure 9 shows that mixture P and the residue curve passing through it lie in compartment 1−3−4−7.

The assumption that compartment boundaries are linear restricts the applicability of this transformation procedure. For example, in a composition space with several distillation regions, a distillation boundary is sometimes also a compartment boundary. To transform a composition in terms of pure components into a composition in terms of singular points, such a distillation boundary needs to be approximated linearly. In this case, compositions lying on the concave side of a curved distillation boundary will be assigned to the wrong compartment.

Figure 10 illustrates this limitation for a ternary system in which the composition space is separated into two distillation regions, 1−3−4 and 1−2−4. Each distillation region is also a compartment, so the distillation boundary is also a compartment boundary. As shown in Figure 10, compositions lying in the shaded region belong to distillation region 1−3−4. To transform compositions in terms of pure components into compositions in terms of singular points, the boundary is linearly approximated, and compositions lying in the shaded region will be incorrectly classified as lying in distillation region 1−2−4.

Relative Volatility Calculation Based on Transformed Composition. For an azeotropic mixture, vapor−liquid equilibrium behavior in terms of pure components can be calculated using suitable liquid-phase and vapor-phase models. Compositions of the equilibrium vapor and liquid, in terms of pure components, can then be transformed into compositions in
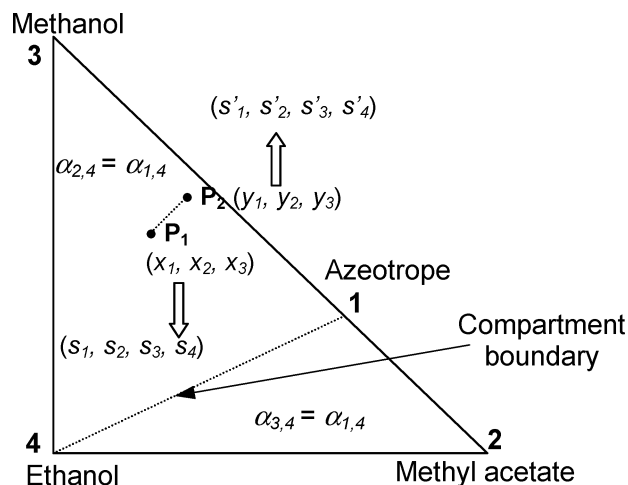

Figure 11. Vapor−liquid equilibrium relationships in terms of pure components can be transformed into vapor−liquid equilibrium relationships in terms of singular points.

terms of singular points. The transformed vapor and liquid compositions still represent an equilibrium pair, because the transformation procedure is based on the principle that each compartment behaves like a non-azeotropic mixture of the singular points appearing in it and will not distort the vapor−liquid equilibrium relations within the compartment. In Figure 11, points P_1 and P_2 correspond to the equilibrium liquid and vapor compositions, respectively. Their compositions in terms of pure components, which are represented by (x_1, x_2, x_3) and (y_1, y_2, y_3), respectively, are known and can be transformed into corresponding compositions in terms of singular points. After transformation, points P_1 and P_2, with transformed compositions (s_1, s_2, s_3, s_4) and (s_1', s_2', s_3', s_4'), respectively, are still in equilibrium with each other.

Because a compartment behaves like a nonazeotropic mixture of the singular points that appear in it, the equilibrium vapor and liquid compositions generally lie in the same compartment. In this case, both the vapor and liquid can be taken as mixtures of the singular points lying in the compartment of interest. After the composition transformation, the relative volatilities of these singular points can be calculated according to the definition of relative volatility, which is shown in eq 8

$$\alpha_{i,H} = \frac{s_i'/s_i}{s_H'/s_H} \qquad (8)$$

where i is a singular point and H is the heaviest singular point.

The relative volatility of singular point j lying outside the compartment of interest can be represented by that of the singular point k, which lies in the compartment of interest and has the composition most similar to the composition of j. For example, in the ternary system shown in Figure 11, singular point 2 does not appear in compartment 1−3−4; therefore, its relative volatility in this compartment can be set to be equal to that of singular point 1, the azeotrope containing this singular point. Similarly, in compartment 1−2−4, the relative volatility of singular point 3, lying outside this compartment, is set to be equal to that of singular point 1.

In relative volatility calculations for ideal mixtures, the relative volatilities of components in a mixture are dependent on the mixture composition only to the extent

that the boiling temperature of the mixture is affected by its composition. For example, the distribution of trace impurities is unlikely to affect relative volatilities significantly. On the other hand, eq 8 implies that the mixture composition directly affects relative volatility values. In practice, however, the dependence does not appear to be very strong. The effect of the purity of the mixture and the distribution of trace impurities was tested for a number of mixtures and found not be significant.

The composition of a given liquid might lie in a different compartment from that of the equilibrium vapor. In this case, the vapor and liquid behave like the mixtures of two different sets of singular points that appear in two neighboring compartments. The singular points lying on the boundary between the two compartments are active in both phases and are generally a stable–unstable node pair. For these singular points, their transformed mole fractions are not zero, and their relative volatilities can be calculated according to eq 8, where the stable node can be taken to be the heavy component. For singular points that are active in only one of these two compartments, their mole fractions are zero in either the vapor or the liquid phase. The relative volatilities of these singular points cannot be calculated using eq 8, nor can suitable values be assigned.

Vogelpohl's method[21] treats each subsystem as an ideal system (i.e., with relative volatilities that are constant and independent of composition) of the singular points that appear in the system. On the other hand, this method treats each compartment as a nonazeotropic mixture of the singular points that appear in it, for which VLE behavior is rigorously calculated in terms of pure components. As a result, the relative volatilities calculated using this method are more reliable than those used in the method of Vogelpohl.[21] Furthermore, in this work, a systematic approach to the identification of subsystems is used. Because no visual tools are needed, this method can be applied to azeotropic mixtures with any number of components, as long as the number of singular points in a given compartment is equal to the number of components present.

Shortcut Method for Column Design

With azeotropes treated as pseudocomponents and a C-component system with A azeotropes treated as a ($C + A$)-component system, a column separating a C-component azeotropic mixture can be treated as a column separating a ($C + A$)-component nonazeotropic mixture. Using the assumption of constant molar overflow, the classical FUG method can be used to design the column on the condition that the relative volatilities of singular points do not change significantly along the column. As for nonazeotropic mixtures, mean relative volatilities are used in the Fenske and Underwood equations. Relative volatilities in terms of singular points can be calculated using the new method. The characteristic relative volatilities are derived from rigorous vapor–liquid equilibrium calculations, rather than by assuming them to be constant and independent of composition, as in the method of Vogelpohl.[21]

Calculation of Minimum Reflux Ratio Using the Underwood Method. When the relative volatilities, expressed in terms of singular points, do not change significantly along a column separating an azeotropic mixture, it will be shown that the Underwood equations can be used to calculate the minimum reflux ratio. As
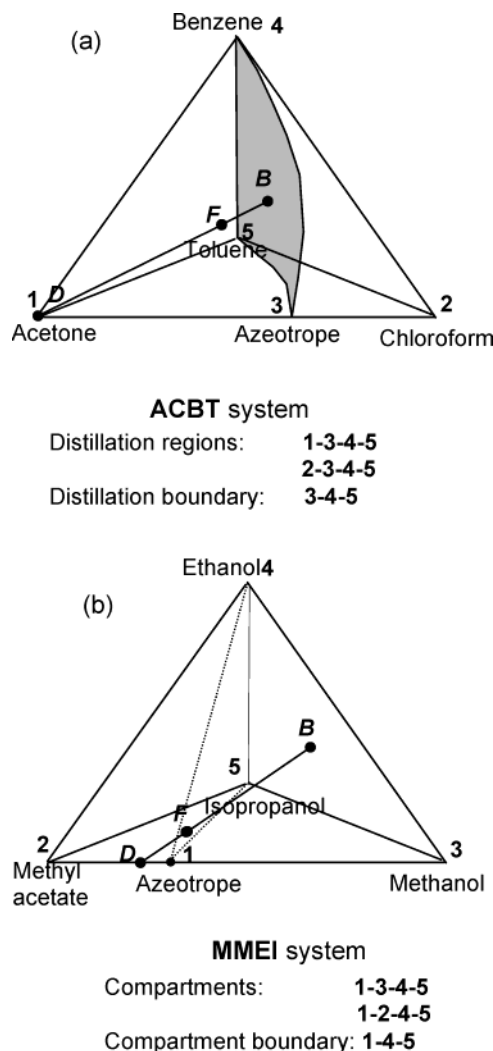
Figure 12. Separations of quaternary azeotropic mixtures (details given in Table 2).

for nonazeotropic mixtures, mean relative volatilities of singular points need to be calculated, as the relative volatilities of singular points are not constant in the column. A characteristic set of mean relative volatilities in terms of singular points is used in the Underwood equations. Different ways of calculating these mean relative volatilities will give more or less satisfactory results.

The two quaternary systems shown in Figure 12 provide examples. The first split (Figure 12a) lies within a single compartment that is bounded by a simple distillation boundary. In the second split (Figure 12b), the two products lie in different compartments. The minimum reflux ratios of these two splits were calculated rigorously using HYSYS[27] (for a column with 90 stages); details of the feeds and design results (including product compositions and minimum reflux ratio) are presented in Table 2. With the same feed composition and the product compositions specified as listed in Table 2, the minimum reflux ratio was calculated using the Underwood method, with the relative volatilities averaged in three different ways. It can be seen in Table 2 that minimum reflux ratios based on the geometric-mean relative volatility are in good agreement with those calculated by rigorous simulation. The Underwood prediction of R_{min} is within 8 and 26% of the rigorously calculated values. Results based on the relative volatility of the feed exhibit the greatest deviation from the

Table 2. Minimum Reflux Ratios Calculated Rigorously and Using the Underwood Equations[a]

| | composition specification | | | | minimum reflux ratio, R_{min} | | | |
| | | | | | Underwood | | | exact |
	feed	distillate	bottom	D/F	α_{geom}[b]	α_{alg}[b]	α_f[b]	HYSYS
			ACBT 1/3−4−5					
acetone	0.2261	0.99	0.06					
chloroform	0.2743	0.009	0.332	0.179	5.79	3.53	2.37	6.26
benzene	0.1784	0.001	0.217					
toluene	0.3212	1.0×10^{-7}	0.391					
			MMEI 1−2/3−4−5					
methyl acetate	0.1282	0.7889	1.0×10^{-7}					
methanol	0.0968	0.2111	0.0746	0.162	3.33	2.50	6.24	2.65
ethanol	0.0625	1.0×10^{-7}	0.0746					
2-propanol	0.7125	1.0×10^{-7}	0.8507					

[a] Feed and products are saturated liquids at 1 atm. [b] $\alpha_{geom} = \sqrt{\alpha_D \alpha_B}$, $\alpha_{alg} = (\alpha_D + \alpha_B)/2$, $\alpha_f = \alpha_{feed}$.
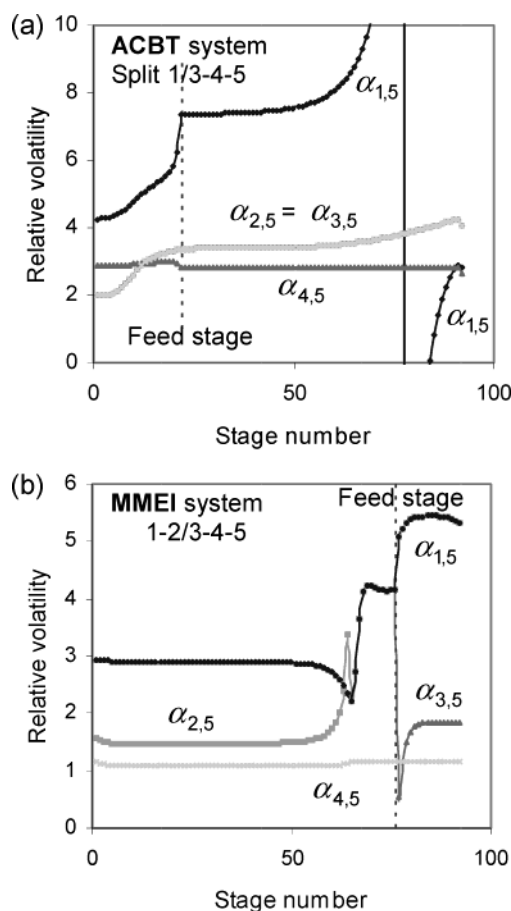

Figure 13. Relative volatility profiles (in terms of singular points) for the separations simulated using HYSYS[27] at the minimum reflux ratio and with the feed and product compositions shown in Table 2.

rigorous simulation results. Numerous other examples studied gave the same general result. In the remainder of this paper, the geometric-mean relative volatility is used in the Underwood and Fenske equations.

Figure 13 presents details of the relative volatility behavior in the columns simulated using HYSYS[27] at the minimum reflux ratio. From Figure 13, it can be seen that the relative volatilities in terms of singular points can change significantly in the column, especially at the feed stage. The change in volatility order seen in the ACBT system is related to the linear approximation of the compartment boundary. Figure 13 provides insights into why the R_{min} values predicted in Table 2 are so sensitive to the method used for averaging the relative volatilities.

Table 3 compares the minimum energy demands, for different splits in different systems, calculated using the Underwood equations with those determined by other rigorous or semi-rigorous methods, including the rectification body method (RBM),[14] boundary value method,[11] and rigorous simulation using ASPEN PLUS.[28] It can be seen that the Underwood method gives a good approximation of the minimum energy demand, with deviations of up to 12%. Although the accuracy of the Underwood method is poorer than those of the rectification body and boundary value methods, the Underwood method is much more computationally efficient. It can be concluded that Underwood method can be used to estimate the minimum reflux ratio of a column separating an azeotropic mixture.

The Underwood method assumes constant relative volatilities in the columns and is most reliable in cases in which relative volatilities (in terms of singular points) are relatively constant. In particular, when one or both product compositions of a column lie near a nonlinear distillation boundary or compartment boundary, this approach will lead to a poor approximation of the VLE behavior of the nonideal mixture. In these cases, the minimum reflux ratio calculated using the Underwood equations would be less accurate. The results of the Underwood equations are also affected by the accuracy with which relative volatilities are calculated.

Calculating Minimum Number of Stages by the Fenske Equation. When a column separating a C-component azeotropic mixture is treated as a column separating a $(C + A)$-component nonazeotropic mixture, the Fenske equation can be used to calculate the minimum number of stages, assuming that the relative volatilities of singular points are constant throughout the column. The minimum number of stages depends only on the separation of the two key components or, in this case, pseudocomponents (singular points).

For the four-column sequence shown in Figure 14, the Fenske equation is used to calculate the minimum number of stages. In Table 4, the results are compared with those calculated by rigorous simulation using HYSYS.[27] The product compositions calculated using HYSYS[27] are almost the same as the values specified in the shortcut method. From Table 4, it can be seen that column II has the largest error in the prediction of the minimum number of stages. This column crosses a curved distillation boundary that is linearly approximated for the composition transformation procedure. Such an approximation of this distillation boundary is an oversimplification; as a result, the relative volatilities of the singular points are not well estimated in this case.

Table 3. Comparison of Minimum Energy Demand Determined with ASPEN PLUS, Boundary Value Method, Rectification Body Method, and Underwood Method[a]

system	feed and product molar compositions and flow ratios				$Q_{B,min}/F$ (10^6 J/kmol)			
	feed	distillate	bottom	D/F	ASPEN	BVM	RBM	Underwood
acetone	0.35	0.7	1.0×10^{-7}					
methanol	0.15	0.3	1.0×10^{-7}	0.5	47.0	46.0	46.8	50.4
ethanol	0.5	1.0×10^{-7}	1.0					
acetone	0.46	1.0	1.0×10^{-7}					
chloroform	0.1026	1.0×10^{-7}	0.19	0.46	44.5	44.4	44.4	49.6
benzene	0.4374	1.0×10^{-7}	0.81					
acetone	0.3	0.4958	1.5×10^{-6}					
chloroform	0.3	0.4876	0.0127	0.605	71.5	67.8	67.6	62.9
benzene	0.2	0.0165	0.4810					
toluene	0.2	1.0×10^{-7}	0.5063					

[a] Separation specifications and ASPEN PLUS, BVM, and RBM results taken from Bausa et al.[14] Feed and products are saturated liquids at 1 atm.

Table 4. Comparison of the Results of Shortcut Design and Rigorous Simulation of a Distillation Sequence (ACBT System)

	splits			
	column I (1/3−4−5)	column II (2−3/4−5)	column III (2/3)	column IV (4/5)
x_F	0.26/0.32/0.21/0.21	0.09/0.39/0.26/0.26	0.16/0.83/0.01/0	0/0.02/0.48/0.50
x_D	0.93/0.04/0.03/0	0.16/0.83/0.01/0	0/1/0/0	0/0.02/0.98/0
x_B	0.09/0.39/0.26/0.26	0/0.02/0.48/0.50	0.31/0.67/0.02/0	0/0/0/1.0
v_F[a]	1	1	1	1
v_D[a]	0	0	0	0
v_B[a]	0	0	0	0
D/F	0.21	0.47	0.41	0.5
		Shortcut Method		
R_{min}	5.12	1.95	5.35	2.29
N_{min}	25	26	23	11
R	6.14	2.34	6.42	2.75
N	53	58	48	25
		HYSYS		
R_{min}	6.06	2.5	4.5	2.12
N_{min}	28	20	20	9
R	6.3	3.1	7.26	2.96
N	53	58	48	25
		error		
R_{min}	−16%	−22%	+19%	+8%
N_{min}	−11% (−3)	+30% (+6)	+15% (+3)	+22% (+2)
R	+2%	−24%	−12%	−7%

[a] v_F, v_D, and v_B are the vapor fractions of feed, distillate, and bottom, respectively. Mole fractions less than 10^{-6} are shown as 0.
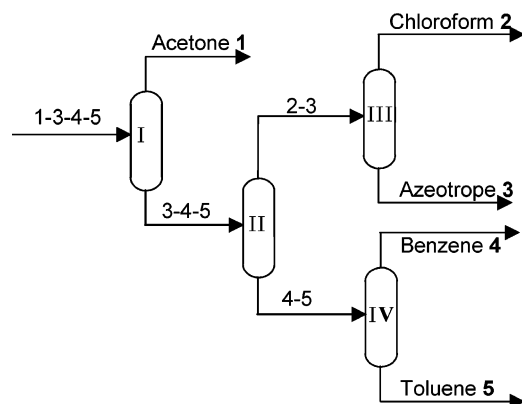
Figure 14. Four-column distillation sequence separating the quaternary mixture of acetone, chloroform, benzene, and toluene shown in Figure 12a.

In the remaining columns, the predictions for N_{min} are up to three stages different to the rigorously simulated values, illustrating the applicability of the Fenske equation for this sequence. The calculation of N_{min} is extremely quick and simple, especially compared to

other available methods, such as the boundary value method[11] or the use of manifolds.[26]

Calculating the Operating Reflux Ratio and Number of Equilibrium Stages Using the Gilliland Correlation. Once the minimum reflux ratio and minimum number of stages of a column separating a multicomponent azeotropic mixture have been determined, the Gilliland correlation can be used to calculate the operating reflux ratio and number of equilibrium stages. Either the ratio between the actual and minimum reflux ratios is specified and the number of equilibrium stages is calculated using the Gilliland correlation, or the ratio between the number of equilibrium stages and the minimum number of stages is specified and the operating reflux ratio is calculated.

For each of the splits shown in Figure 14 and Table 4, the ratio between the operating reflux and the minimum reflux, as calculated by the Underwood equations, is set to be 1.2, and the number of equilibrium stages is calculated using the equation of Eduljee[10] to represent the Gilliland correlation. In the rigorous simulation of each column using HYSYS, the number of stages is chosen to be the same as that calculated by
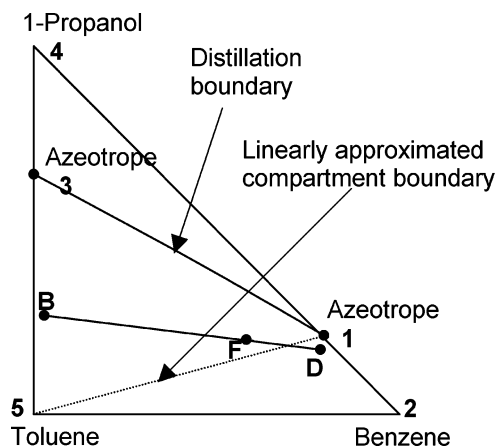
Feed and product compositions of split 1-2/3-5

	F	D	B
Benzene	0.5894	0.7803	0.0372
1-propanol	0.2085	0.1854	0.2754
Toluene	0.2021	0.0343	0.6874

D/F	R_{min}	N_{min}	R	N
0.7432	0.13	980	0.16	2842

Figure 15. Infeasible split crossing a compartment boundary in the system benzene, 1-propanol, and toluene.

the Gilliland correlation, and the operating reflux ratio is determined.

From Table 4, it can be seen that the reflux ratios determined by the FUG shortcut method and rigorous simulation are in good agreement. Except for column II, the error in the reflux ratio obtained by the FUG method is less than 12%. Because column II crosses a curved distillation boundary, both its products lie near the boundary. As discussed previously, the shortcut method proposed in this work is least accurate for such splits.

Other analytical forms of the Gilliland correlation[29−31] have been applied to estimate the number of stages, but give inferior results in this case. The methods of Molokonov[29] and Rusche[30] predict numbers of stages that are almost the same as the minimum predicted by the Fenske equation. The method of Liddle[31] predicts between 6 and 15 stages less than that of Eduljee,[10] which would further widen the difference between the shortcut predictions of the reflux ratio and the rigorous simulation results.

The shortcut method developed in this work employs the Fenske equation, Underwood equations, and Gilliland correlation to design columns separating azeotropic mixtures. Before the classical FUG method can be applied to azeotropic mixtures, vapor−liquid equilibrium compositions in terms of pure components need to be transformed into vapor−liquid equilibrium compositions in terms of singular points. Because only linear equations need to be solved to perform this transformation, applying the FUG shortcut method to azeotropic distillation is as computationally efficient as applying it to nonazeotropic mixtures. As for nonazeotropic mixtures, the FUG method can be used to initialize rigorous simulations using commercial software, such as HYSYS.

Identifying Infeasible and Very Difficult Splits Using the Shortcut Method. One can infer from the Fenske equation (eq 3) when a proposed split will be very difficult or even infeasible. When the relative volatility between two components or singular points is near unity, the value of $\log(\alpha_{LK,HK})$ will be nearly zero. The minimum number of stages, N_{min}, which is inversely proportional to $\log(\alpha_{LK,HK})$ in the Fenske equation, will become very large. The number of equilibrium stages, N, determined by the Gilliland correlation, will be even larger. Therefore, the Fenske−Underwood−Gilliland shortcut design method can easily identify such splits. Compared with other feasibility tests, such as the

boundary value and rectification body methods, this method is much more computationally efficient.

For example, the ternary split with feed and product compositions shown in Figure 15 crosses a compartment boundary. For a saturated liquid feed and the ratio R/R_{min} taken to be 1.2, the shortcut design method gives the reflux ratio and number of stages as 0.16 and 2842, respectively. It can be concluded that this separation is either infeasible or very difficult. The boundary value method (with the same product specifications) and rigorous simulation using HYSYS[27] (specifying D/F and the mole fraction of benzene in the bottom product) also indicate that this separation is infeasible.

Application to Sequence Evaluation

To recover all pure or nearly pure constituents of a multicomponent azeotropic mixture using simple columns, a sequence with several columns and several recycles is needed. To evaluate a distillation sequence, column design parameters, such as the number of stages and reflux ratio, need to be calculated, together with recycle flow rates. The existence of recycles makes such an evaluation an iterative procedure. Because rigorous or semi-rigorous column design methods, such as the boundary value method, are iterative and need stage-by-stage calculations at different reflux ratios, applying them to evaluate a distillation sequence is time-consuming. The shortcut method developed in this work is computationally efficient and can be applied to mixtures with any number of components. Therefore, sequences can be evaluated quickly and easily. A more complete description of sequence evaluation using the shortcut method is presented by Liu.[32]

In the five-component system of acetone, benzene, 1-propanol, toluene, and styrene, two azeotropes form; all singular points, calculated using DISTIL[33] (Wilson activity model with default model parameters), and the transformation matrix of this five-component system are presented in Table 5. Using the procedures of Rooks et al.[19] and Thong et al.,[3] it can be determined that the whole composition space of this system is a single distillation region that is separated into three compartments, namely, 1−2−3−6−7, 1−2−4−5−7, and 1−2−4−6−7. In this system, a mixture with composition

$$\mathbf{X}_F = [0.2 \quad 0.16 \quad 0.17 \quad 0.27 \quad 0.2]^T$$

is to be separated into pure components. Using the

Table 5. All Singular Points in the Five-Component Azeotropic Mixture of Acetone, Benzene, 1-Propanol, Toluene, and Styrene

singular point	component or azeotrope	boiling point (°C)	transformation matrix
1	acetone	55.68	
2	benzene−1-propanol	75.28	
3	benzene	78.32	
4	1-propanol−toluene	92.66	
5	1-propanol	96.83	
6	toluene	110.18	
7	styrene	144.95	

$$\mathbf{M} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.7863 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0.2137 & 0 & 0.6489 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0.3511 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

composition transformation procedure, it can be established that the mixture lies in compartment 1−2−4−6−7.

The many distillation sequences that can be used to separate this mixture can be identified using the method of Thong and Jobson;[34] one of these is the six-column sequence illustrated in Figure 16. Four recycles are specified for this sequence; different recycle streams with different flow rates will affect the feasible design parameters of individual columns and therefore the operating and capital costs of this sequence. The aim of the evaluation procedure is to search for the best set of recycle flow rates, corresponding to the minimum total annualized cost of the flowsheet. In the evaluation of this sequence, recycle flow rates can be varied over a wide range [e.g., from 0 to 3F, where F is the molar flow rate of the mixture to be separated (100 kmol/h)] in search steps of 0.2F.

The optimization procedure used is shown in Figure 17 and is outlined below. The compositions of the final products (products that cannot be further separated in the sequence, such as the products of column C6) can initially be estimated assuming complete recovery of pseudocomponents "lighter" than the light key compo-

nent of the distillate and complete recovery of components "heavier" than the heavy key component of the bottom product. Once the recycle flow rates are set, the mass balance of the sequence can be closed backward. For example, after the final product compositions and recycle flow rates are specified, the mass balance of columns C5 and C6 can be closed. Thus, the compositions and flow rates of the feeds of these two columns,
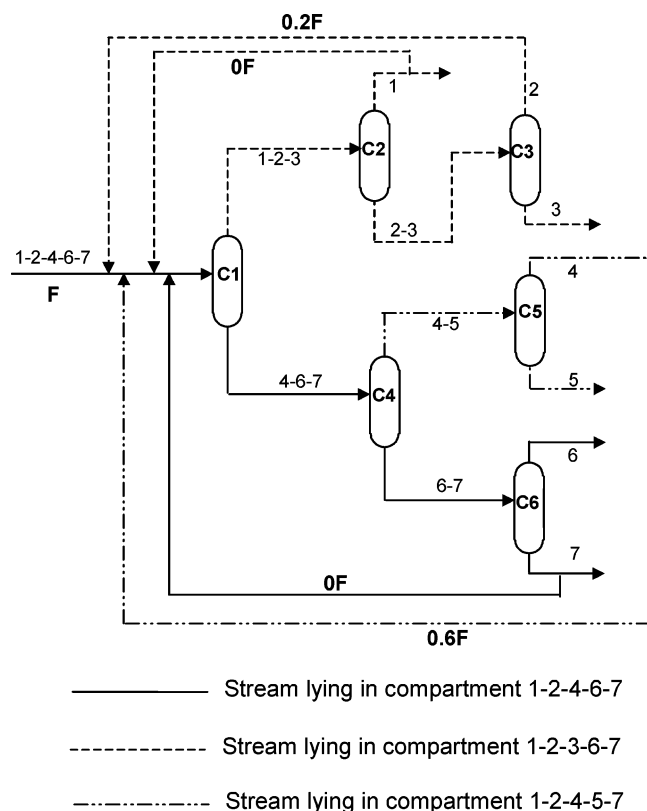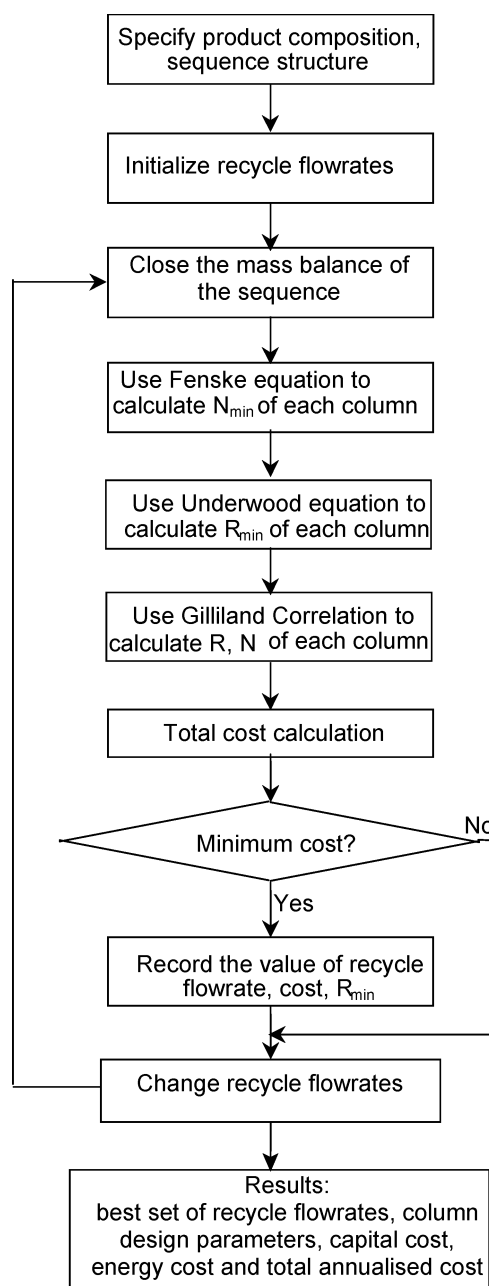

Figure 16. Six-column distillation sequence with recycles. Flow rates indicate optimization results, where F is the molar flow rate of the feed.

Figure 17. Optimization of a sequence using shortcut column design.

Table 6. Design Results of Each Column Shown in Figure 16[a]

column:	C1	C2	C3	C4	C5	C6
reflux ratio:	5.28	2.89	2.97	0.99	4.46	1.08
number of stages:	233	63	28	55	31	17
reboiler duty (10^6 kJ/h):	13.42	2.51	2.43	5.53	12.95	2.04
Feed Composition and Flow Rate (kmol/h)						
acetone	0.1056	0.3393	0	0	0	0
benzene	0.1815	0.5835	0.8826	0	0	0
1-propanol	0.3393	0.0772	0.1174	0.4576	0.7334	0.0057
toluene	0.2594	0	0	0.3765	0.2641	0.5607
styrene	0.1143	0	0	0.1659	0.0025	0.4336
flow rate	180	56	36	124	77	47
Distillate Composition and Flow Rate (kmol/h)						
acetone	0.3393	0.9500	0	0	0	0
benzene	0.5834	0.0450	0.7965	0	0	0
1-propanol	0.0772	0.0500	0.2035	0.7334	0.6651	0.0095
toluene	0	0	0	0.2641	0.3344	0.9429
styrene	0	0	0	0.0025	0.0005	0.0476
flow rate	56	20	20	77	60	27
Bottom Composition and Flow Rate (kmol/h)						
acetone	0	0	0	0	0	0
benzene	0	0.8826	0.9903	0	0	0
1-propanol	0.4576	0.1174	0.0097	0.0057	0.9745	0.0005
toluene	0.3765	0	0	0.5607	0.0159	0.0449
styrene	0.1659	0	0	0.4336	0.0095	0.9546
flow rate	124	36	16	47	17	20

[a] Mole fractions of less than 10^{-6} are shown as 0. All feeds and products are saturated liquids.

which are the products of column C4, can be calculated, and the mass balance over column C4 can be closed. In this way, the mass balance of the whole sequence can be closed. The shortcut method is then used to calculate the reflux ratio and number of stages of each column. This allows capital and operating costs of each column and of the whole sequence to be determined. Simple cost correlations, such as those of Peters and Timmerhaus,[35] can be used to estimate capital costs. Trial and error can be used to search for the best set of recycle flow rates, with which the sequence has the minimum annualized total cost (the annualization factor is taken as 0.33).

When an exhaustive search is used to identify the optimum set of recycle flow rates, where the search step size of all recycle flow rates is $0.2F$, the results can be obtained in less than 30 min (AMDXP 2000+, 512 MB of RAM). The best set of recycle flow rates is shown in Figure 16, and the design parameters, together with the feed and product compositions, are reported in Table 6. Using the same computer and the same search procedure but replacing the shortcut method by the boundary value method, the same results were obtained as for the shortcut method. Using this rather crude search strategy and calculating vapor–liquid equilibrium for each stage, the calculations for the boundary value method took around 70 h.

Each column shown in Figure 16 was also rigorously simulated using HYSYS. The feed composition and flow rate, distillate flow rate, and number of stages were specified to be the same as those in Table 6. The reflux ratios, which result in product compositions in good agreement with those presented in Table 6, were determined by trial and error. The results, including the product compositions, reflux ratios and reboiler duties, are shown in Table 7. Comparing the results reported in Tables 6 and 7, it can be seen that the results of the sequence evaluation using the shortcut column design method are in good agreement with those obtained by rigorous simulation. Furthermore, it can be seen that the product compositions predicted by the shortcut

Table 7. Results of Rigorous Simulation (Using HYSYS) of Columns Shown in Figure 16 and Table 6[a]

column:	C1	C2	C3	C4	C5	C6
reflux ratio:	4.93	2.4	2.25	0.91	4.28	1.04
reboiler duty (10^6 kJ/h):	10.976	2.064	2.225	5.925	12.54	1.914
Distillate Composition						
acetone	0.3392	0.9423	0	0	0	0
benzene	0.5296	0.0577	0.7907	0	0	0
1-propanol	0.1205	0	0.2093	0.6803	0.6613	0.0099
toluene	0.0107	0	0	0.3194	0.3387	0.9527
styrene	0	0	0	0.0003	0	0.0374
Bottom Composition						
acetone	0.0001	0.0042	0	0	0	0
benzene	0.0243	0.8757	0.9975	0	0	0
1-propanol	0.4380	0.1201	0.0025	0.0927	0.9888	0
toluene	0.3716	0	0	0.4701	0	0.0316
styrene	0.1659	0	0	0.4372	0.0112	0.9684

[a] Mole fractions of less than 10^{-6} are shown as 0. All feeds and products are saturated liquids.

approach are generally in good agreement with those obtained by rigorous simulation.

It can be concluded that the evaluation of a distillation sequence using the proposed shortcut column design method is efficient and can give good results. A more elegant search method, such as Newton's method or a simplex search, should reduce the optimization time further.

Conclusions

A distillation compartment behaves like a nonazeotropic mixture of the singular points appearing in it. A new shortcut method based on this observation has been developed for the design of columns separating homogeneous multicomponent azeotropic mixtures. In this method, azeotropes are treated as pseudocomponents, and a C-component system with A azeotropes is treated as an enlarged $(C + A)$-component nonazeotropic system. The relative volatilities of these $(C + A)$ singular points can be characterized using a simple transformation of rigorously calculated phase equilibrium behavior.

Thereafter, columns can be designed using the Fenske–Underwood–Gilliland method.

In each compartment, with the compartment boundary approximated linearly, a transformation relates vapor–liquid equilibrium behavior in terms of pure components to that in terms of singular points. The transformation requires a set of linear equations to be solved and allows the relative volatilities of all singular points to be calculated. Because this calculation is based on rigorous models of equilibrium behavior, satisfactory results can be obtained. However, when the mixture composition is near a compartment or distillation boundary, its relative volatilities will be poorly approximated, because of the linear approximation of compartment and distillation boundaries. Nevertheless, such separations, even separations crossing a curved distillation boundary, can be modeled approximately by this method.

Once the relative volatilities of singular points are obtained, the classical Fenske–Underwood–Gilliland method can be used to design columns separating azeotropic mixtures. This shortcut method can be applied to homogeneous azeotropic mixtures with any number of components. Although this method is less accurate than more rigorous approaches, such as the boundary value method, the error is within a tolerable range. As there is no need to calculate pinch-point curves, nor stage-by-stage mass balance and equilibrium relationships, this method is extremely computationally efficient. The absence of efficient methods for estimating the reflux ratio and number of stages of a column separating an azeotropic mixture makes this shortcut method highly attractive.

In multicomponent azeotropic systems, for which the composition space cannot be visualized, the composition transformation procedure can also be used to identify the compartment in which a given composition point lies. The shortcut method is also valuable in that it allows one to identify very difficult and infeasible splits through simple calculations. The results of the shortcut design method are useful for initializing rigorous simulations using commercial software, such as HYSYS.[27] The shortcut method facilitates the efficient evaluation of distillation sequences with recycles.

Notation

A = number of azeotropes
$\mathbf{A}$ = adjacency matrix of the azeotropic system
B = molar flow rate of the bottom product
C = number of pure components
D = molar flow rate of the distillate product
F = molar flow rate of the feed
$\mathbf{M}$ = transformation matrix
N = number of stages in a column
p_i^0 = vapor pressure of pure component or azeotrope i
q = feed thermal condition (ratio of heat required to vaporize 1 mol of feed to molar latent heat of vaporization)
Q = energy demand of the reboiler
R = reflux ratio
$\mathbf{R}$ = reachability matrix of the azeotropic system
s_k = mole fraction of singular point k in the liquid phase
s'_k = mole fraction of singular point k in the vapor phase
$\mathbf{S}$ = vector of mole fractions in terms of singular points (pure components and azeotropes)
v = vapor fraction of a mixture (molar)
x_i = mole fraction of pure component i in the liquid phase
$\mathbf{X}$ = vector of mole fractions in terms of pure components
y_i = mole fraction of pure component i in the vapor phase

Greek Letters

α_{ij} = relative volatility of singular point or pure component i with respect to j
γ_i = activity coefficient of component or pseudocomponent i
η_k = mole fraction of singular point k in the vapor phase
θ = root of the Underwood equation, eq 5
ξ_k = mole fraction of singular point k in the liquid phase

Subscripts

az = azeotrope
F = feed of the column
D, d = distillate product
B, b = bottom product
i = singular point or pure component i
j = singular point or pure component j
k = singular point or pure component k
min = minimum value
H = heaviest singular point in an azeotropic system

Acronyms

FUG = Fenske–Underwood–Gilliland method for column design
RBM = rectification body method
VLE = vapor–liquid equilibrium

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