Shortcut Methods for Nonideal Multicomponent Distillation: 1. Simple Columns

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Shortcut methods are a prerequisite for the fast evaluation of alternatives in process design. The rectification body method (RBM) for calculating the minimum energy demand of homogeneous, azeotropic multicomponent distillation processes is presented. The new method incorporates both the classical Underwood technique and certain previously proposed techniques as special cases. It employs all pinch point branches of both column sections and thus requires no a priori selection of active pinch points. It is entirely general and can be applied to any type of split of nonideal and azeotropic mixtures irrespective of the number of components. Hence, it significantly extends previous results and practical applicability. Its features are highlighted through examples of nonideal separations with three, four, and five components.

Introduction

There is probably no domain of chemical engineering research which has attracted more attention than distillation. However, in engineering practice the unwieldy procedure applied for the design of distillation arrangements usually involves the detailed specification of the column design (that is, the number of trays, location of the feed tray, and reflux ratio), the analysis of the postulated distillation configuration by means of state-of-the-art flowsheeting software and the trial and error alternation of the chosen column design. The stated methodology leaves the process engineer with the uneasy task of deciding whether nonconvergence of the simulation problem posed is due to bad initial guesses, unlucky choices of some of the design variables, or an inherent infeasibility of the specified separation.

The design of distillation arrangements can effectively be segregated into two subsequent steps. Within the first step, the manner of interest is to decide whether given a certain feed the desired products can be obtained at competitive costs. However, flowsheeting packages are not the best choice for this task. Rather, calculating the minimum energy demand of the separation by means of some suitable shortcut will provide all the information needed *without* requiring a detailed column design. *If* the minimum energy demand can be calculated, there is a strong indication that the specified separation is feasible, and *if* the minimum energy demand is sufficiently low, the capital costs and the energy demand of the realized distillation arrangement will be admissible as well. This piece of information readily allows a decision concerning the most favorable distillation arrangement without tedious trial-and-error simulations.

In the second step, the detailed column design can be undertaken using simulation tools with the reassuring knowledge that this second step has to be performed only a few times for feasible designs and that good initial guesses are at hand. Alternatively, in current research mixed integer nonlinear programming (MINLP) techniques are employed for this design step (Bauer and Stichlmair, 1996).

While suitable shortcut techniques for the minimum energy demand calculation for ideal mixtures have been available for a long time (Underwood, 1948), unfortunately no such general shortcut techniques are available for multicomponent azeotropic and highly nonideal mixtures. As will be outlined in this article, all previously proposed techniques are either restricted to certain splits or require some *a priori* knowledge on the separation, which is usually not available prior to rigorous simulation.

Starting from the established geometrical analysis of the separation profiles in multicomponent azeotropic distillation (Julka and Doherty, 1990), an extension of a shortcut method recently published by the authors (Bausa et al., 1996) is presented which is entirely general and applicable to arbitrary splits. A detailed presentation of the newly developed technique will be given.

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State of the Art: A Critical Review

During the last decade, various shortcut methods for the prediction of minimum reflux for the distillation of azeotropic and nonideal mixtures have been developed. However, these techniques are either restricted to certain types of splits or require some amount of *a priori* knowledge on the particular separation problem. The method introduced in this article intends to set aside these restrictions. Embedding different approaches as special cases, it can be considered as a generalization of the previous work.

In order to relate the new method to previously proposed techniques, a brief overview of these techniques is given. To illustrate the methods, a simple separation example of the ternary azeotropic mixture acetone/methanol/ethanol which exhibits a binary minimum azeotrope will be introduced. The residue curve map and the boiling surface of this mixture can be found in Figure A1 for further reference. The mixture and the type of split were chosen in such a way that all methods can be applied.

Illustrative separation example

In Figure 1 on the left side the plate-to-plate profiles (see Appendix A) of both the stripping and rectifying section under minimum reflux are shown. The limiting case of a column with an infinite number of stages is approximated by a column with a very large number of stages (250). Since the feed stage must be reached by a plate-to-plate calculation from the bottom and from the distillate, both column section profiles have to intersect at that point in composition state space, which corresponds to the liquid composition on the feed stage. Thus, the dashed part of the stripping profile lying behind the point of intersection is not part of the actual column profile. It can only be reached by a plate-to-plate calculation originating at the bottom without introducing the feed.

For a given product and a variable reboiler/condenser duty, pinch point curves can be calculated for each column section (see Appendix B). Figure 1 (righthand side) shows that, in the rectifying section two and the stripping section three, different solution branches occur. If the parameter reboiler/condenser duty is fixed, one solution can be determined on each branch (if $Q_{B/D}$ is inside the parameter range of the branch). Due to the number of unstable and stable eigenvectors, these pinch points can be classified as stable or unstable nodes or as saddles (see Appendix B for stability and classification of pinch points). The pinch points according to the minimum reboiler duty and the corresponding condenser duty are marked in both diagrams. These points are fixed points of the plate-to-plate recurrence under minimum reflux. It can be seen that the course of the plate-to-plate profiles in composition state space is strongly related to the pinch points.

Boundary value method

Levy et al. (1985) introduced the boundary value method (BVM), which is based on the plate-to-plate calculation of column profiles. For fully specified products and an arbitrary condenser duty, the profiles of both column sections can be determined. Since the reboiler duty was chosen arbitrarily, the calculated profiles do not need to correspond to a feasible separation. The criterion for the separation to be feasible requires the column section profiles to intersect in composition state space. The point of intersection corresponds to the feed tray and must be a solution to both the stripping and the rectifying recurrence.

To determine minimum reflux with the BVM means to find the smallest reflux ratio which makes intersection of both profiles possible. In Figure 1 the profile of the rectifying section terminates while touching the profile of the stripping section.

The plate-to-plate profiles exhibit a very high sensitivity for the amount of components that nearly vanish in the product. A manifold of profiles can be determined and has to be checked for intersection, when these components are varied

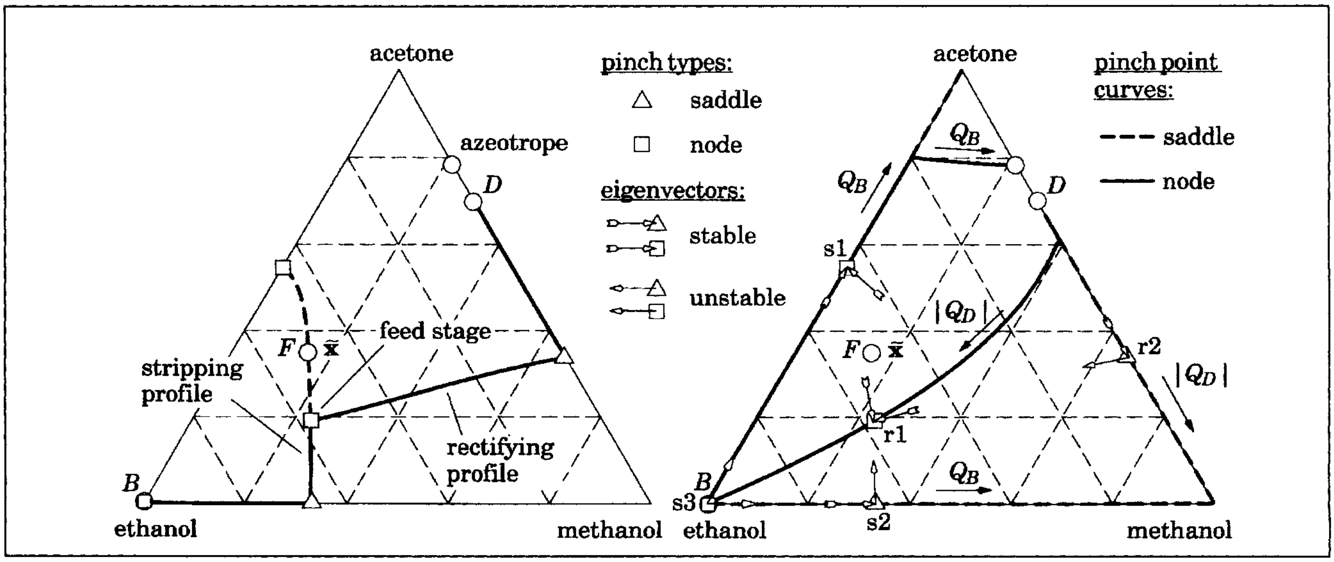

Figure 1. Plate-to-plate profiles (left) and pinch point curves (right) at minimum reflux for a ternary separation example.

For specifications of all examples, see Table 1.

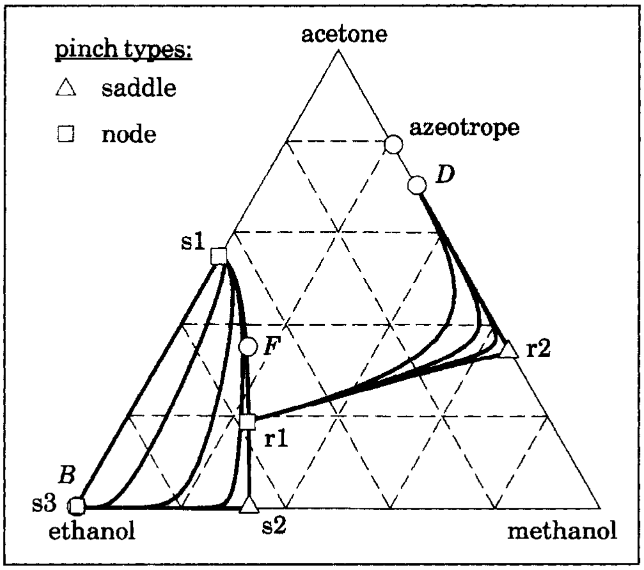

Figure 2. Manifold of plate-to-plate profiles for the example in Figure 1.

(see Figure 2, $x_{B,\text{acetone}} = 10^{-40}, 10^{-30}, 10^{-27}, 10^{-24}$). Hence, not only the minimum reboiler duty, but also the exact amount of the trace components, has to be determined in an iterative procedure with many manual iterations even though these values are of no practical interest.

The BVM cannot be applied to mixtures with more than four components, since the profiles must be checked for intersection and there is no simple graphical representation of the trajectories. However, for up to four components the method gives reliable and accurate results and can be used to "get a feeling" for the behavior of nonideal distillations.

Zero-volume criterion

On the basis of the BVM, Levy et al. (1985) developed an algebraic criterion to determine minimum reflux that was extended by Julka and Doherty (1990) to the zero-volume criterion (ZVC). The ZVC uses pinch points to approximate the course of plate-to-plate profiles instead of calculating profiles repeatedly. The recommended formulation of the criterion applied to the example in Figure 1 requires the point $\tilde{x}$ (which depends on the feed composition and the VLE on the feed plate, but is identical to x_F in this case, see Appendix D), the pinch s2, and the pinch r1 to lie on a straight line. Other formulations would require the pinches s1, s2, and r1 to lie on a straight line or, if eigenvectors are used, the pinch r1 to lie on the line originating at s2 in the direction of the unstable eigenvector. When extended to multicomponent separations, the recommended formulation of the criterion requires $\tilde{x}$ and $C-1$ pinch points to lie in one hyperplane.

Since the criterion can be checked using a simple determinant formulation, it can be applied to any number of components. However, the method can be applied only to direct and indirect cuts, since the topology of the split (the pinch points determining minimum reflux) must be known *a priori:* For the direct cut of a ternary mixture $\tilde{x}$, s1 and r2 must be used, whereas for the indirect cut $\tilde{x}$, s2 and r1 are valid (see Figure 1). For ternary mixtures, Fidkowski et al. (1993) presented a criterion to determine if a given separation corresponds to a direct or an indirect geometry. However, for mixtures with more than three components, corresponding criteria are missing. In addition, in the case of multicomponent mixtures topologies can arise that do not correspond to either a direct or indirect geometry. Thus, most of the conceivable splits (such as the split AB/CD of a quaternary mixture) cannot be taken into consideration.

Minimum angle criterion

Köhler et al. (1991) proposed the empirical minimum angle criterion (MAC) that requires the angle that is spanned by x_F and one pinch in each column section to be minimal at minimum reflux. In our ternary example this criterion is equivalent to the recommended formulation of the ZVC: The points x_F, s2 and r1 lie on a straight line, thus the angle is zero (see Figure 1). However, suitable pinch solutions have to be chosen carefully, since there are multiple solution branches.

According to Köhler et al., the MAC can also be applied to multicomponent mixtures. Thus, it might be considered as an application of the ternary setup of the ZVC to an unrestricted number of components. However, while the ZVC requires $C-1$ pinch solutions and has a physical explanation, the MAC must always be applied to only two pinch solutions and lacks a physical explanation for more than three components. Since the number of solution branches of the pinch equation increases with the number of components, the selection of the *two relevant* solutions can be very complicated for multicomponent mixtures.

Using the secant condition at minimum reflux (Appendix D), it can be shown that the MAC cannot be applied to separations without a pinch at the feed stage when the feed is not introduced as boiling liquid. This restriction can be important when columns with side columns are taken into considerations: Using the decomposition of the complex column into a sequence of simple columns proposed by Carlberg and Westerberg (1989), the feed state of the second column of the analogous sequence will always be subcooled or superheated. In addition, for more than three components, most of the conceivable splits will have *no* pinch at the feed stage.

Eigenvalue criterion

Pöllmann et al. (1994) presented the eigenvalue criterion (EC), which can be considered as a mixture of the BVM and the ZVC. In their procedure, only the part of the column profile after the pinch point actually occurring is calculated using a plate-to-plate algorithm. In Figure 1 this is the pinch s2 in the stripping section. However, in an infinite column two pinch points will occur in the rectifying section: r2 and r1. Thus, it is not obvious which one to choose, although in this case both pinch points will lead to a correct solution.

When the pinch r1 is chosen, the rectifying profile does not need to be calculated, since r1 is a stable node and the rectifying profile terminates in this point. The stripping profile calculation starts from a point close to the pinch s2, that is located to a small extent in the direction of the corresponding unstable eigenvector. In the next step the pinch r1 and the stripping profile are checked for intersection. The minimum reflux condition is achieved at the smallest reflux ratio, which makes the intersection possible. In Figure 1 the criterion requires the pinch r1 to lie on the column profile between s2 and s1.

Since Pöllmann (1995) presented an optimization procedure to perform the checkup for the intersection, the EC can be applied to any number of components. However, the selection of the pinch points actually occurring in the column profile is not a simple task. Frequently, the active pinches cannot be determined solely from the product specifications, as will be shown later. In this case the column profile, which is, of course, not available at this stage, needs to be analyzed in order to determine the loci of the trajectories and the relevant subset of active pinch points.

When more than one unstable eigenvector exists in one pinch point, a manifold of profiles can be calculated. For multicomponent mixtures, multidimensional manifolds of column profiles have to be calculated and checked for intersection. Thus, the computational effort will increase drastically for higher numbers of components.

To tackle this problem Pöllmann et al. (1994) proposed approximate column profiles using the unstable eigenvectors. This formulation of the EC is equivalent to a special formulation of the ZVC. Applied to Figure 1, the criterion requires the pinch r1 to lie on a straight line through the pinch s2 in the direction of the unstable eigenvector. However, this formulation is even more sensitive for the correct selection of pinch points. Although the pinches r2 and s2 will occur in an infinite column under minimum reflux, they cannot be used to apply the criterion, since each pinch has an unstable eigenvector and, thus, the EC would only require two straight lines to intersect, which is always fulfilled for nonparallel eigenvectors. (The rectifying profile is approximated by a straight line through r2 and the stripping profile by a straight line through s2 in the direction of the corresponding unstable eigenvector.) Besides, using an incorrect pair of pinches (such as s1 and r2), the criterion can be satisfied but still can lead to an incorrect result.

New Criterion to Determine Minimum Reflux

The new procedure introduced in this article is based on a geometrical analysis of plate-to-plate profiles. After fixing all product compositions, the amount of the trace components has to be set to a nonzero value, since all feed components have to appear in both products in a finite column. When the concentration of the trace components is varied below the allowed impurity, a manifold of plate-to-plate profiles can be calculated for each reflux ratio (see Figure 2). Using the BVM would require checking all profiles for intersection. Rather than calculating the manifold of plate-to-plate profiles, the new method *approximates* the manifold using all available information.

The first piece of information is, of course, that all profiles originate at the given product composition. The next piece of information that can be obtained is the pinch points for a specified reflux ratio. Figure 2 shows that the plate-to-plate trajectories are strongly related to the pinch points. Thus, the information about the number, the position, the type, and the thermodynamic properties of the pinch points will be used for an approximation of the profiles.

Ordering of pinch points

An analysis of plate-to-plate profiles leads to the fact that, under minimum reflux, all profiles will touch one or more pinch points. However, how must the pinch solutions be ordered to obtain paths that correspond to plate-to-plate profiles? For this task, the information of the eigenvalues that describe the behavior of the profiles in the vicinity of the pinch can be used:

Unstable Nodes: If all eigenvalues are greater than unity, the column profile will always leave the pinch point. Thus, the pinch can only be a point of the trajectory, if the trajectory originates in this point. However, in this case the pinch is identical to the product composition and supplies no further information (pinch s3 in Figure 2). Thus, unstable nodes do not need to be considered.

Stable Nodes: If all eigenvalues are smaller than unity, the profile will always approach the pinch. Thus, a stable node can only be the final point of the trajectory (pinches s1 and r1 in Figure 2).

Saddles: If there are eigenvalues smaller and greater than unity, the profile will approach the pinch in one direction (which is a linear combination of the stable eigenvectors), but will leave the pinch in another direction (a linear combination of the unstable eigenvectors). Thus, a saddle point can only occur in the middle part of a profile (pinches s2 and r2 in Figure 2).

This can be generalized to the following rule: *The number of stable eigenvectors in the pinch points touched by each plate-to-plate profile must increase strictly monotonously.* Applied to the stripping section in Figure 2, we obtain two relevant *paths:* B-s2-s1 and B-s1. The starting point of the trajectory is fixed through the given product composition $x_B = x_{s3}$. The pinch s1 is the only stable node; thus, it must be the final point of all trajectories. Since s2 is a saddle, it can only occur between B and s1. Figure 2 shows that for both paths corresponding plate-to-plate profiles exist.

Checking for thermodynamic consistency

Since only local information of the mixture (VLE and enthalpy data) in the vicinity of the pinch points was used to generate the paths, the existence of corresponding trajectories cannot be guaranteed. Thus, it would be desirable to check the paths at least for consistency, although this will not guarantee that corresponding trajectories exist.

It has been stated in literature that the temperature profile of a column must always be monotonously increasing from the top to the bottom for all reflux ratios (Stichlmair, 1988) or at least for total reflux (Pöllmann et al., 1996; Van Dongen and Doherty, 1984). Thus, one might think that checking the temperature profile of a path might be used as a check for consistency. However, to the authors' knowledge there is no physical foundation for the strict monotony of the temperature profile at finite reflux. In addition, it turned out that examples can be found where the temperature profile has local extrema (cf. the subsection on highly nonideal topology).

However, first principles give rise to a very simple check for thermodynamic consistency: Using an entropy balance, the entropy production in the column section between product withdrawal and pinch can be calculated, since all streams leaving and entering are given

$$S_{\mathrm{irr}} = -\sum_{j} N_j s_j - \sum_{k} \frac{Q_k}{T_k}. \qquad (1)$$

Due to the second law of thermodynamics, S_{irr} must always be positive. Thus, paths that lead to a negative value of S_{irr} do not correspond to plate-to-plate profiles.

For a vanishing driving force in the reboiler and condenser, the entropy production in the stripping section between bottom and pinch si can be calculated by

$$S_{\mathrm{irr}}^{si} = V_{si} s_{si}^{V} - L_{si} s_{si}^{L} + B s_B - \frac{Q_B}{T_B}, \qquad (2)$$

and in the rectifying section between head and pinch ri by

$$S_{\mathrm{irr}}^{ri} = L_{ri} s_{ri}^{L} - V_{ri} s_{ri}^{V} + D s_D - \frac{Q_D}{T_D}, \qquad (3)$$

where T_B and T_D are the boiling temperatures (K) of the products.

The entropy production must be positive in each part of the column. Thus, S_{irr} for the first pinch must be positive and the series of S_{irr} of all pinch points must increase strictly monotonously. Applied to the stripping section in Figure 2 the two possible paths require

$$0 < S_{\mathrm{irr}}^{s2} < S_{\mathrm{irr}}^{s1} \quad \text{and} \quad 0 < S_{\mathrm{irr}}^{s1}. \qquad (4)$$

However, the first claim includes the second and both are fulfilled in this case. Thus, both paths are thermodynamically consistent.

Rectification bodies

The generated paths can now be used to approximate the manifold of column profiles. Figure 2 shows that the manifold of trajectories in the stripping section is enclosed by the two possible paths. Since the points of the second path B-s1 are a subset of the points of the first path B-s2-s1, the triangle that is built by all points of the first path can be used as an approximation of the manifold of trajectories. This triangle shall be named *rectification body* (see Figure 3).

In the rectifying section only two pinch points exist. This also leads to two possible paths: D-r2-r1 and D-r1. Checking the entropy production proves that both paths are thermodynamically consistent. Thus, the triangle $\langle D, \text{r2}, \text{r1}\rangle$ can be used as an approximation for the manifold of the rectifying profiles. Although, in opposition to the stripping section, only a part of the rectifying body is covered by the trajectories, the triangle is a good approximation for the column profiles in the area where the intersection of rectifying and stripping profiles takes place.

Now, instead of checking the manifolds of trajectories for intersection, the rectification bodies are considered. If they intersect, there should also be intersecting profiles; thus, the separation is feasible.

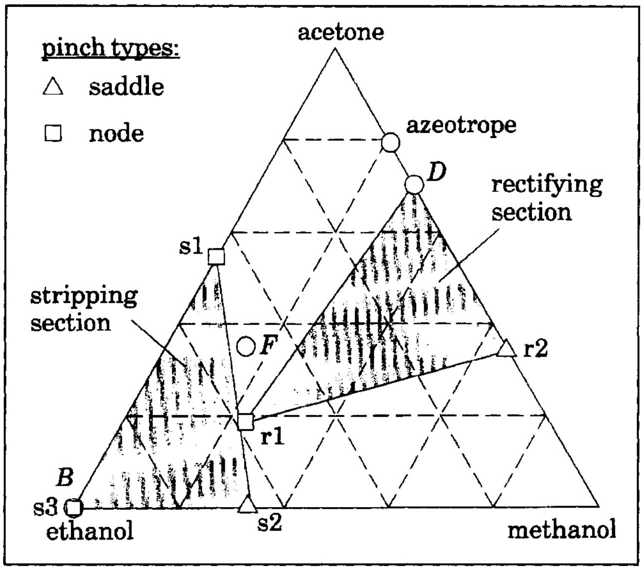

Figure 3. Geometric approximation of the manifold of plate-to-plate profiles at minimum reflux through rectification bodies.

To determine minimum reflux with the new criterion means to find the smallest reflux ratio that makes intersection of both simplexes possible. If they do not touch at all, the separation is below minimum reflux (Figure 4, left). If they penetrate each other, the separation is feasible with the specified reflux ratio, but above minimum reflux (Figure 4, right). Using a bisection algorithm, the minimum energy demand that allows the rectification bodies just to touch can be determined (Figure 3).

The criterion can be applied to an unrestricted number of components: Although the check for intersection of the rectification bodies can be done graphically only for mixtures with up to four components, a mathematical check for intersection can be applied to any dimension and thus to any number of components.

In the case of a direct or an indirect split a special formulation of the ZVC that requires C pinch points to lie in a hyperplane is equivalent to the new criterion. (In Figure 1 the pinches s1, s2, and r1 would be required to lie on a straight line). Besides, the new criterion can be considered in analogy with the graphical representation of Underwood's method (see Köhler et al., 1995), with the difference that pinch points with negative concentrations are replaced by the product composition.

Highly nonideal topology

Although the mixture in the last example exhibits an azeotrope, its behavior and the topology of pinch points and plate-to-plate profiles is very similar to an ideal mixture. However, even in the ternary case, topologies of higher complexity can occur.

Figure 5 shows an example for the mixture acetone/chloroform/benzene (see Figure A1) where additional pinch point curves occur due to nonideal behavior of the mixture. At minimum reflux, four pinch points can be determined for the rectifying section: r3 = D, r2, r1a, and r1b. Ordering by the number of stable eigenvectors leads to four possible paths: D-r2-r1a, D-r1a, D-r2-r1b, and D-r1b. These paths corre-

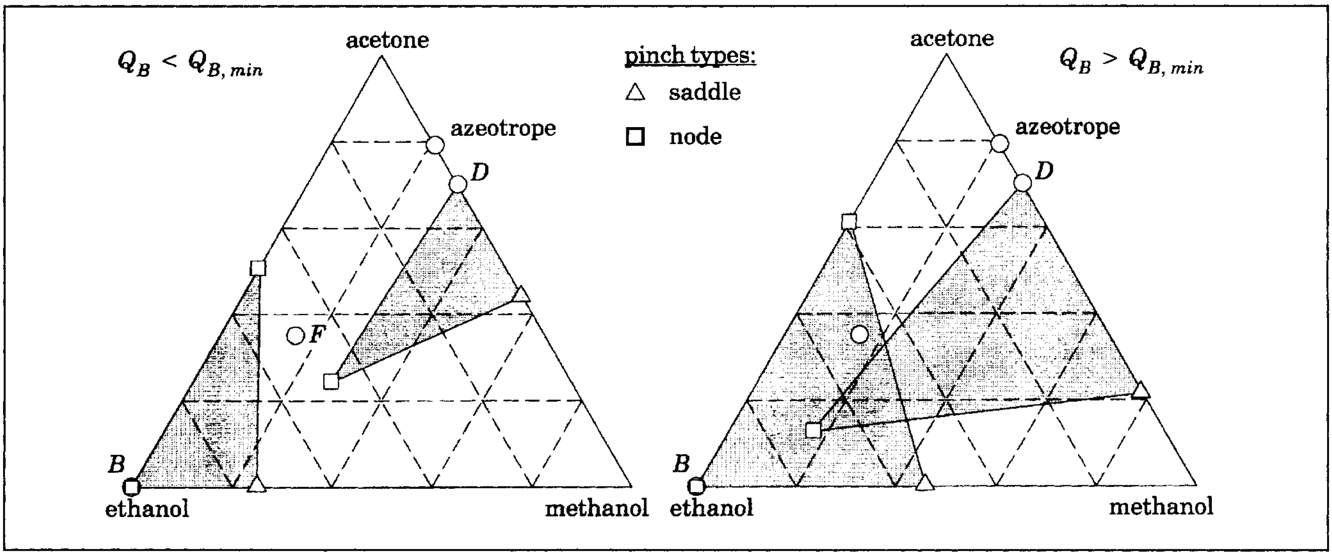

Figure 4. Rectification bodies below and above minimum reflux.

spond to two rectification bodies and manifolds of column profiles as can be seen in Figure 6. Thus, in this case not only one, but a set of rectification bodies (the triangles ⟨D, r2, r1a⟩ and ⟨D, r2, r1b⟩) approximate all possible profiles.

In the next step, the two paths are checked for thermodynamic consistency. This check can be visualized through the entropy production surface: For the given product and condenser duty each point in the composition triangle is regarded as the liquid composition on an imaginary plate of the column. Then, using energy and component balances and the information that all streams in the column are at bubble or dew point, the vapor and liquid streams passing each other inside the column at this virtual plate are calculated

$$V - L - D = 0, \quad (5)$$

$$Vy - Lx - Dx_D = 0, \quad (6)$$

$$Vh^V(y, T^D(y)) - Lh^L(x, T^B(x)) - Dh_D + Q_D = 0. \quad (7)$$

Now, assuming a reversible condenser ($\Delta T = 0$), the entropy production inside the control volume can be determined using

$$S_{\text{irr}} = -Vs^V + Ls^L + Ds_D - \frac{Q_D}{T_D}. \quad (8)$$

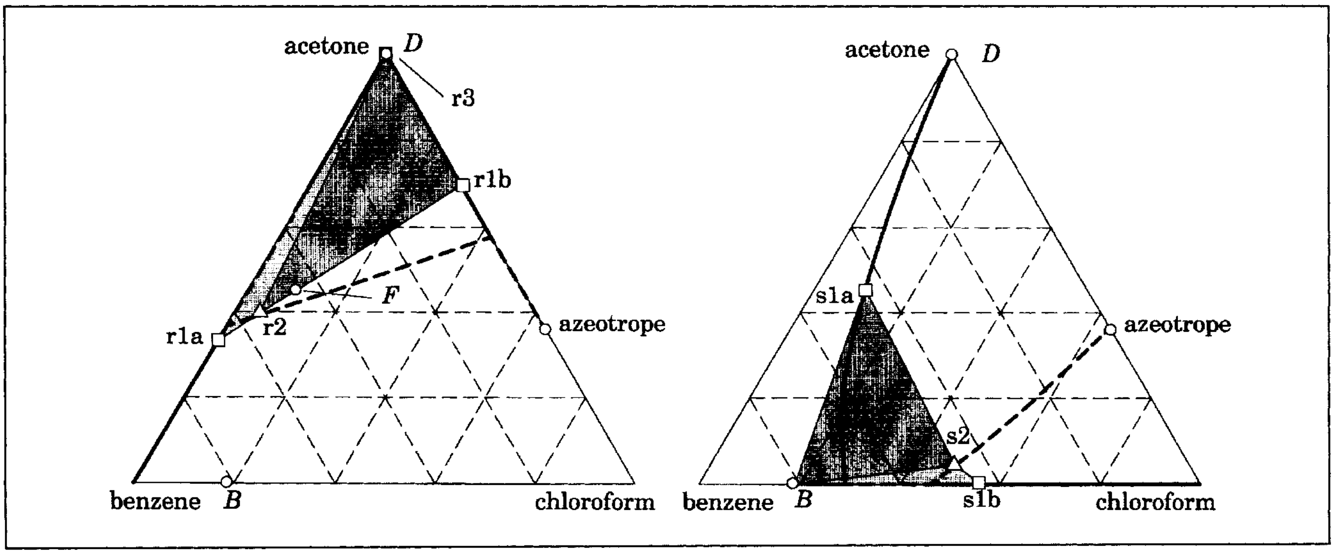

Figure 5. Pinch point curves, pinch points, and rectification bodies at minimum reflux for the rectifying section (left) and the stripping section (right).

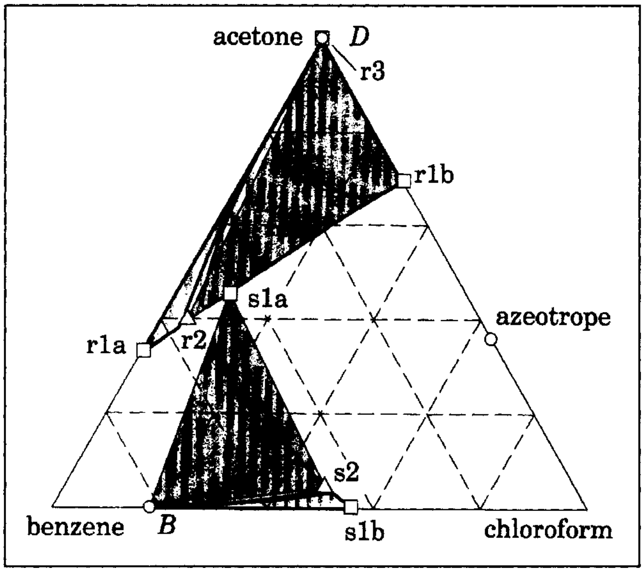

Figure 6. Rectification bodies and manifold of column profiles at minimum reflux.

Figure 7 shows the entropy production surface and the manifold of plate-to-plate profiles for the rectifying section at minimum reflux. Since entropy production must be positive on each tray, the plate-to-plate profiles must always go uphill, which is fulfilled by all profiles. Due to this restriction, it is intuitively comprehensible that the profiles will never cross the ridge between r1a and r1b, which is nearly identical with the lower boundary of the two rectification bodies of the rectifying section. Besides, it is obvious that both paths are thermodynamically consistent, since the entropy production at the pinch r2 is positive and smaller than the entropy production at r1a and r1b.

It can be shown that the condition $\partial S_{\text{irr}} = 0$ is equivalent to the pinch equations (the symbol ∂ denotes a variation of first order, see Appendix E). Thus, the local extrema and saddle points of the entropy production surface correspond to pinch points. (Note that in Appendix E S_{irr} was regarded as a function of l_i, v_i, T^L, and T^V, whereas in Figures 7 and 8, S_{irr} is a function of x_1 and x_2 only. Thus, the gradient is not always zero at pinch points (such as r1b)). In addition, the type of extremum corresponds to the type of pinch: A minimum corresponds to an unstable node, a saddle to a saddle-type pinch, and a maximum to a stable node.

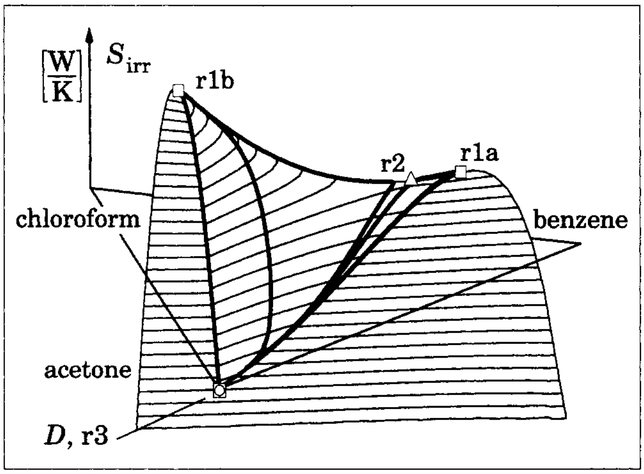

Figure 7. Entropy production surface and plate-to-plate profiles for the rectifying section under minimum reflux.

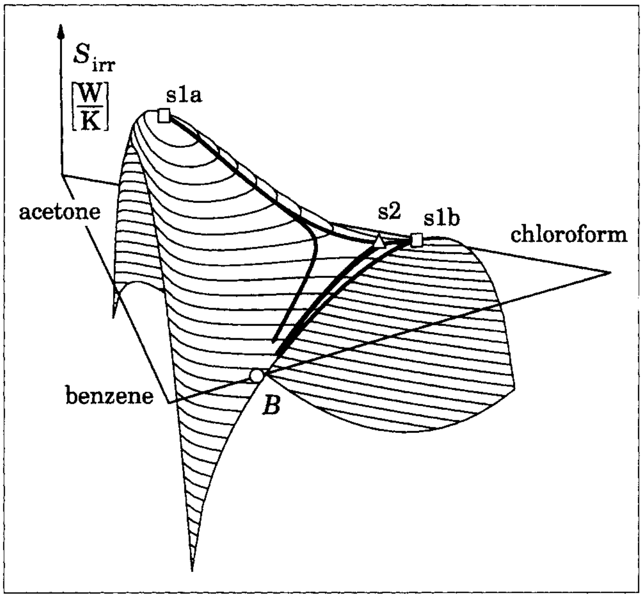

Figure 8. Entropy production surface and plate-to-plate profiles for the stripping section under minimum reflux.

This demonstrates clearly that the full information about the VLE is included in the entropy model. Thus, care must be taken to use consistent models for the calculation of VLE and entropy data. Otherwise, the check of the entropy production may lead to the result that a special path is infeasible, although a corresponding plate-to-plate profile exists. Note that inconsistencies may arise from the use of independent models for vapor pressure, heat of vaporization, and molar volume, since the models will in general not fulfill the Clausius-Clapeyron equation

$$\frac{dp_0}{dT} = \frac{\Delta h^{\text{VAP}}}{T(v^V - v^L)}. \tag{9}$$

It is an interesting property of the separation example considered that the column temperature profile is not monotonously increasing from top to bottom. Not only plate-to-plate trajectories following the path D-r2-r1b, but also the column profile (rectifying and stripping section) exhibit a local maximum in the vicinity of the pinch r2. [The temperatures at the fixed points and product withdrawals are: $t^B(x_D) = 56.24°\text{C}$, $t^B(x_{\text{r2}}) = 64.88°\text{C}$, $t^B(x_{\text{r1b}}) = 61.82°\text{C}$, $t^B(x_{\text{s1a}}) = 64.03°\text{C}$, $t^B(x_{\text{s2}}) = 70.47°\text{C}$, $t^B(x_B) = 76.90°\text{C}$.] However, it is not clear if this behavior corresponds to a physical phenomenon or if it was caused by uncertainties in the thermodynamic model parameters. Ewell and Welch (1945) reported a similar phenomenon while experimentally investigating the same mixture by employing a batch distillation system with a packed tower. They found local extrema in the temperature profile of the overhead vapors (see Doherty and Perkins (1978) for an interpretation of that work).

In the stripping section three pinch points can be determined that form four possible paths: *B*-s2-s1a, *B*-s1a, *B*-s2-s1b, and *B*-s1b (see Figure 5, right). Checking the entropy production leads to the fact that all paths are consistent (see Figure 8). Thus, the rectification bodies $\langle B$, s2, s1a$\rangle$ and $\langle B$, s2, s1b$\rangle$ are used to approximate the manifold of stripping profiles (see Figure 6).

Now, the sets of rectification bodies are checked for intersection. In this example, four combinations must be considered. If intersection is found, there should also be intersecting profiles and the separation is feasible. Hence, to find minimum reflux means to find the smallest reflux ratio where intersection occurs. It can be seen in Figure 6 that the triangles $\langle D$, r2, r1b$\rangle$ and $\langle B$, s2, s1a$\rangle$ just touch at minimum reflux. Thus, trajectories corresponding to *D*-r2-r1b and *B*-s2-s1a (or subpaths of these) will exist at minimum reflux, which is true, as can be seen in Figure 6.

Applying the ZVC, MAC or EC to this example, the increased number of pinch points must be taken into account and suitable pinch points must be selected (such as s1a and not s2 must be used in the stripping section for the ZVC and MAC). Since these methods include no automated ordering of pinch points, the correct set of active pinch branches must be determined *a priori* typically by some rigorous simulations.

Rectification body method (RBM)

The novel procedure to determine minimum reflux can be summarized as follows:

(1) Specify, consistently, composition, flow rate, and thermal state of the feed and all products and the column pressure.

(2) Calculate all branches of the pinch equation for both column sections.

(3) Estimate the reboiler duty.

(4) Calculate the condenser duty using an energy balance for the whole column.

(5) Determine all pinch points on the pinch point curves of the rectifying section corresponding to the condenser duty.

(6) Generate all possible paths: Each path consists of the product composition as the first point and pinch points with an increasing number of stable eigenvectors. Exclude paths that contain an unstable node or do not contain a stable node.

(7) Check for thermodynamic consistency: Calculate the entropy production for each pinch, then exclude paths where the entropy production of the first pinch is negative or which do not increase strictly monotonously.

(8) Determine the set of rectification bodies corresponding to all paths, that are not subpaths to other paths.

(9) Work out the set of rectification bodies of the stripping section analogously to Steps 5–8.

(10) Check all members of both sets for intersection against each other.

(11) If there are intersecting rectification bodies decrease the reboiler duty, if not, increase the reboiler duty. If the accuracy requirement is met, stop, otherwise go to Step 4.

Since all pinch points are used, no *a priori* selection of relevant pinch solutions is required. This is essential for multicomponent separations, when the topology and the occurrence of pinch points is not known *a priori*. The topology of the separation is taken into account by using the information of the pinch points and the geometry of the rectification bodies.

Due to the ordering of pinch points, it is guaranteed that each rectification body consists of at most C points. Since the composition state space has $C-1$ degrees of freedom, the rectification bodies will always be convex. Thus, a very simple and fast procedure that is valid for any dimension can be used to check the rectification bodies for intersection, allowing the application to separations with an unrestricted number of components.

Only in the case of tangent pinches pinch solutions are discharged. In the case of a tangent pinch three pinch points can be determined on one pinch point curve, if the condenser/reboiler duty lies in the interval between the two local extrema. However, according to our experience and the literature only the pinch nearest to the product will affect the separation. Hence, only the first pinch on each pinch point curve is used, as proposed by Fidkowski et al. (1991). If the absolute value of the heat exchanger duty exceeds the minimum/maximum, there is again only one solution that is located after the extrema. Thus, the pinch will make a jump and the rectification body will expand greatly. If the intersection is determined directly after this jump, minimum reflux is controlled *only* by the tangent pinch and the rectification bodies will not only touch but cut into another. Note, that the heuristic to use only the pinch nearest to the product composition could be avoided if the region of attraction of each pinch is determined. In nonlinear dynamics, procedures have been proposed for this task (such as Kreuzer, 1987). However, their computational demand makes them unsuited for a shortcut procedure.

In the examples presented in this article none of the generated paths were excluded due to a negative entropy production. However, topologies which lead to thermodynamically inconsistent combinations of pinch points are conceivable. Consider an entropy production surface similar to Figure 7, but with a third local maximum r1c on the ridge between r1a and r1b. In this case the entropy production will have two saddles r2a and r2b between the maxima. Now, in opposition to Figure 7, the entropy production corresponding to, for example, saddle r2a can be higher than the entropy production corresponding to, for example, r1a. Using only local information at the pinch points (such as the type of pinch), the path *D*-r2a-r1a seems to be feasible, whereas the entropy production criterion proves the path to be infeasible in a very simple way.

Limitations

The RBM requires the specification of feasible products. To determine feasible products, various procedures have been proposed in literature (such as Fidkowski et al., 1993; Pöllmann et al., 1996; Safrit and Westerberg, 1997). If the specified products are not attainable by distillation (such as due to the presence of a separatrix), the RBM will lead to the result that no intersecting rectification bodies can be found.

Since the rectification bodies are only a linear approximation of the curved plate-to-plate trajectories (see Figures 2 and 6), the results of the shortcut are not identical with the results obtained by the BVM. However, accuracy could be increased by using the direction of the eigenvectors in the pinch points to define rectification bodies with a curved surface. Since the computational effort will increase clearly and the accuracy of linear approximations is sufficient in most cases, up to now the information of the eigendirections is not used.

In the case where the desired products contain all species, only one pinch can be found for each column section and the rectification bodies are finite straight lines that intersect at the feed pinch, one of the pinch points. Thus, the actual column profile will never reach the other pinch and there is no pinch in the corresponding column section. Since the finite straight line is a rather poor approximation for the curved profile of this section, the minimum reflux estimation will also be relatively inaccurate. However, the described split can only be performed in a column with a finite and fixed number of plates in the column section, where no pinch occurs. If the number of plates is increased, the products will become better than the specifications. Thus, it is questionable if the described split corresponds to a minimum reflux situation.

Applications

In this section the RBM will be applied to different separation examples with three, four, and five components. A comparison of the minimum energy demand determined with ASPEN PLUS, the BVM and the RBM for all examples can be found in Table 1.

Ternary systems

Example 1. For the ternary examples, the mixture acetone/chloroform/diisopropyl-ether, which exhibits three binary azeotropes (see Figure A1) was chosen. This split is of the type AC/BC that can only be achieved due to the occurrence of azeotropes.

Table 1. Comparison of ASPEN PLUS, the BVM and the RBM ($p = 1.013$ bar)*

	Specification			$Q_{B,\min}/F$ (10^6J/kmol)		
Figures	x_F x_D x_B	v_F v_D v_B	D/F	ASPEN	BVM	RBM
1, 2, 3, 4	0.35/0.15/0.5	0	0.5	47.0	46.0	46.8
	0.7/0.3/0	0				
	0/0/1	0				
5, 6, 7, 8	0.46/0.1026/0.4374	0	0.46	44.5	44.4	44.4
	1/0/0	0				
	0/0.19/0.81	0				
9	0.2/0.2/0.6	1	0.5	33.2	32.7	32.7
	0.4/0/0.6	0				
	0/0.4/0.6	0				
10	0.483/0.151/0.367	1	0.7	—$^+$	13.7	21.2
	0.69/0/0.31	0				
	0/0.5/0.5	0				
11 and 13	0.28/0.28/0.23/0.21	1	0.7	13.3	13.2	13.5
	0.4/0.4/0.2/0	0				
	0/0/0.3/0.7	0				
11 and 12	0.28/0.28/0.23/0.21	1	0.7	30.5	30.3	30.3
	0.4/0.4/0.2/0	0				
	0/0/0.3/0.7	0				
14 and 15	0.3/0.3/0.2/0.2	0	0.605	71.5	67.8	67.6
	0.4958/0.4876/0.0165/0					
	1.5E-6/0.0127/0.4810/0.5063					
Example 5a	0.2/0.2/0.2/0.2/0.2	0	0.4	48.6	—**	48.8
	0.5/0.5/0/0/0	0				
	0/0/0.33/0.33/0.33	0				
Example 5b	0.2/0.2/0.2/0.2/0.2	0	0.6	67.4	—**	67.7
	0.33/0.33/0.33/0/0	0				
	0/0/0/0.5/0.5	0				
Example 5c	0.2/0.2/0.2/0.2/0.2	1	0.6	12.7	—**	12.5
	0.33/0.33/0.33/0/0	0				
	0/0/0/0.5/0.5	0				

*The results of the BVM can be considered as a reference since the number of stages during simulation was high ($N = 200\ldots300$) and the same physical property routines as for the RBM were used. There are two reasons for the ASPEN PLUS results to differ from the BVM results: (1) The results of ASPEN PLUS are in most cases slightly higher than the results of the BVM and the RBM since the number of stages in ASPEN PLUS is limited ($N \leq 150$) in order to achieve convergence; (2) There are some differences in the formulation and the parameters used for physical property calculations by ASPEN PLUS and the BVM.

**The BVM cannot be applied to systems with five components since the profiles cannot be checked for intersection visually.

$^+$Convergence was not achieved.

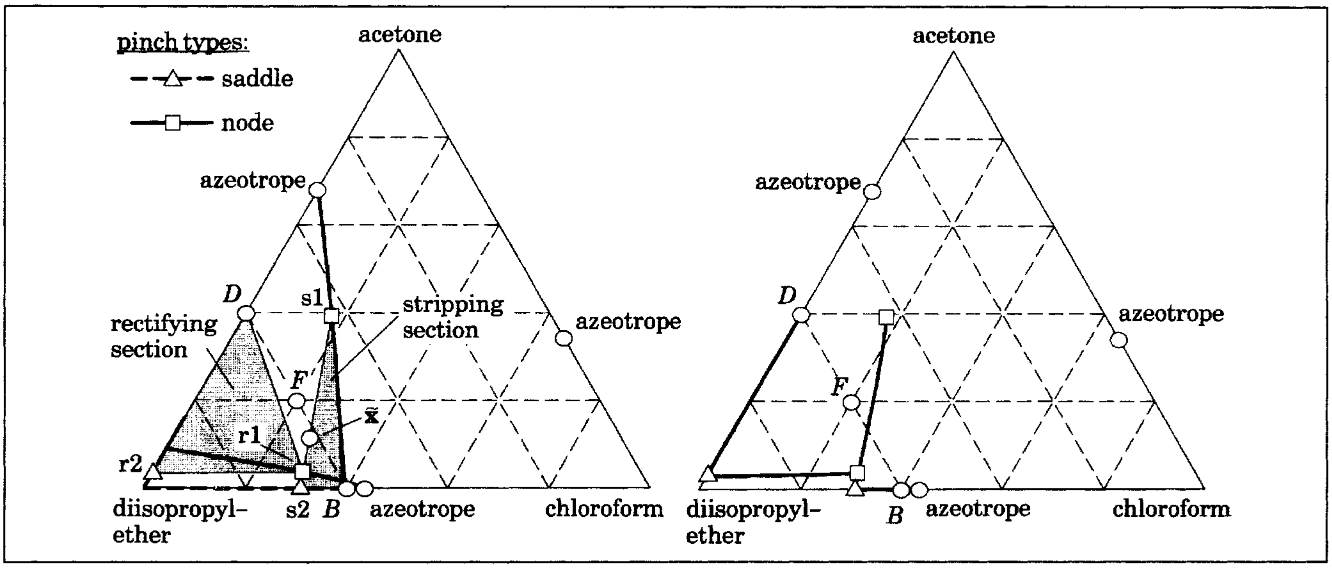

Figure 9. Ternary separation example: Pinch curves and rectification bodies (left) and plate-to-plate profiles for the reboiler duty determined with the RBM (right).

Figure 9 shows that for each column section two solution branches of the pinch equation exist. At minimum reflux, there are two consistent paths in each column section (*D*-r2-r1 and *D*-r1 or *B*-s2-s1 and *B*-s1, respectively), leading to the rectification bodies 〈*D*, r2, r1〉 and 〈*B*, s2, s1〉. The minimum reflux condition is achieved when the two triangles just touch. The right diagram in Figure 9 and the results in Table 1 show that the BVM leads to the same result.

Other methods can only be applied to this example if the relevant solution branches are known and if it is clear that the pinch r1 rather than s1 will occur at the feed stage [such as using the criterion proposed by Fidkowski et al. (1993) for ternary mixtures]. Since the feed was not introduced as boiling liquid, the ZVC and the MAC must be applied to the point $\tilde{x}$ instead of x_F. The EC requires r1 to lie on the stripping profile between s2 and s1, or, when the linear approximation is used, to lie on a straight line through s2 in direction of the unstable eigenvector (not shown in Figure 9). All three methods will lead to nearly the same result, if the relevant solution branches are known *a priori*.

Example 2. This split is also of the type AC/BC, but takes place in another concentration region. A comparison of Figure 10 and Figure A1 shows that the column profile crosses the distillation boundary formed by the residue curve between the azeotropes acetone/chloroform and chloroform/diisopropyl-ether.

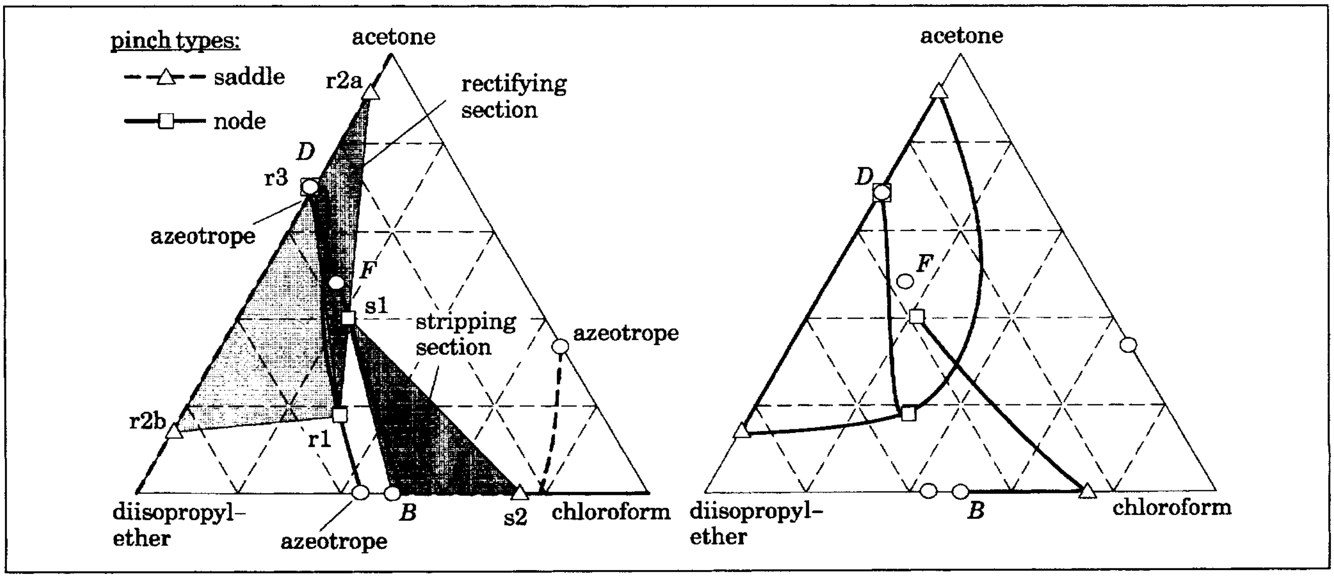

Figure 10. Rectification bodies and column profiles for the second ternary example.

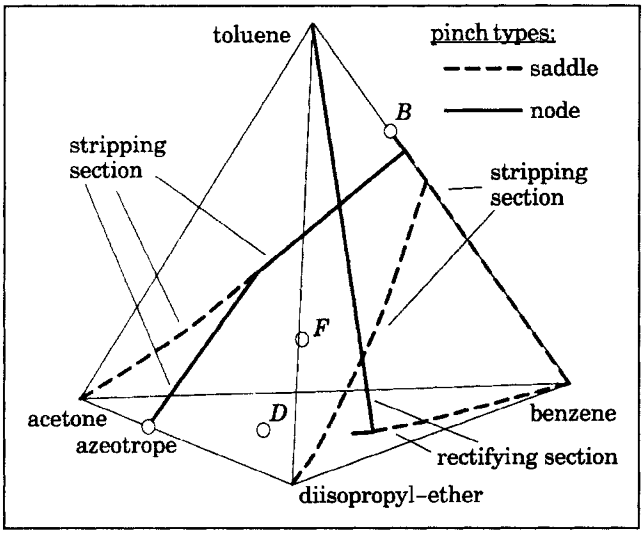

Figure 11. Pinch point curves for the quaternary example 1.

In this case the column profile of the rectifying section that will prevail under minimum reflux is strongly curved. Thus, the linear approximation via pinch points is poor and the minimum energy demand is overestimated. However, other methods that use linear approximations will have the same problems. A higher accuracy can only be obtained when either column profiles are calculated (BVM and EC using plate-to-plate profiles) or if the information of the eigenvectors is used to define curved rectification bodies.

Quaternary systems

When extended to quaternary systems, rectification bodies cannot only be triangles, but also tetrahedrons, depending on the number of pinch points.

Example 1. In this example the split AB/CD of the mixture acetone/diisopropyl-ether/benzene/toluene is analyzed. Pinch point curves for both column sections are shown in Figure 11.

Figure 12 shows the rectification bodies and column profiles at minimum reflux for a liquid feed. In the rectifying section the two pinch points r1 and r2 and the distillate composition form a triangle. In the stripping section four pinch points can be determined, forming a set of rectification bodies consisting of the tetrahedrons ⟨*B*, s3, s2a, s1⟩ and ⟨*B*, s3, s2b, s1⟩. At minimum reflux, the lower surface of the tetrahedron ⟨*B*, s3, s2a, s1⟩ is just touched by the vertex of the rectifying sections triangle.

Since the rectification bodies are used as an approximation of the profiles, their point of contact corresponds to the intersection of the plate-to-plate profiles and thus to the feed tray. Figure 12 shows that the point of contact is achieved at the pinch r1 that will occur in the column profile at the feed tray.

Figure 13 shows the rectification bodies for the separation specified in Figure 11 but with a vapor feed. Since the enthalpy of the feed is different, the energy balance for the whole column gives a different condenser duty for a specified reboiler duty. Although the products, the feed composition and the pinch curves are identical in both cases, the different feed state results in a qualitatively different separation: In Figure 13 the triangle touches one edge of the tetrahedron with one of its sides at minimum reflux. Thus, there is no pinch at the point of contact and no pinch will occur in the column profile at the feed stage. Since in both cases the specification of flow rate and composition of all streams were identical, the occurrence of pinch points cannot be determined based on this information. While in the ternary case the topology of a separation can be determined using a simple criterion (Fidkowski et al., 1993), this is not possible in the quaternary case.

The BVM can be used to determine minimum reflux in both cases, but with a high effort. If the occurrence of pinch

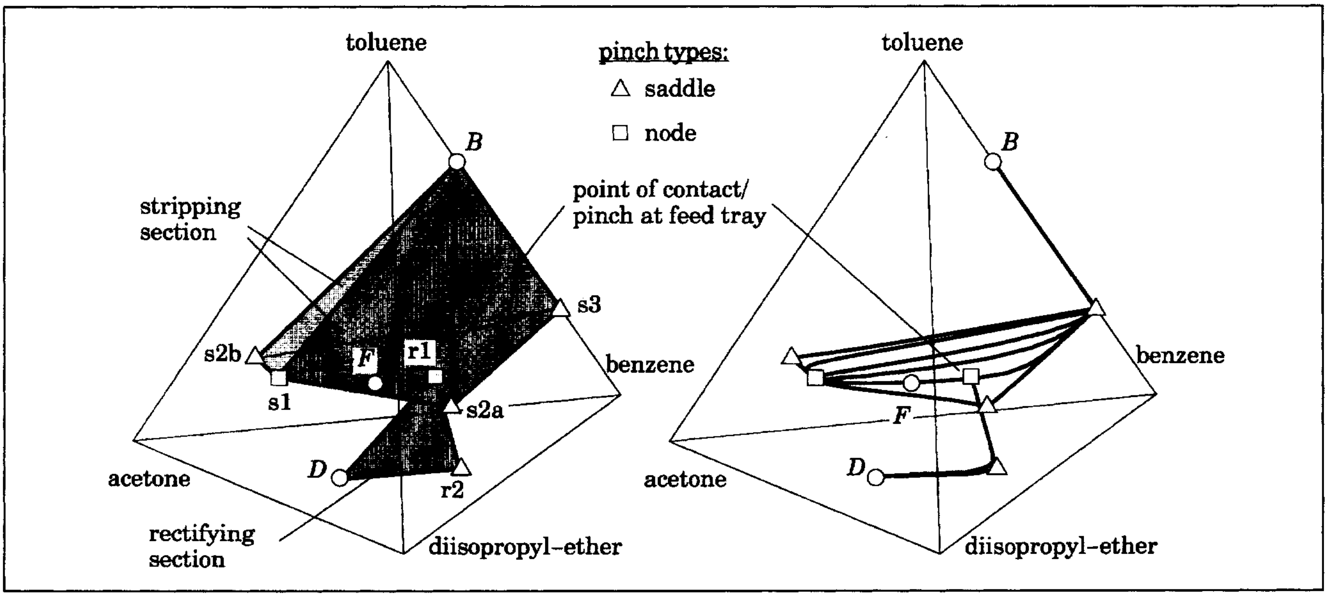

Figure 12. Quaternary example 1: rectification bodies and column profiles for a *liquid* feed at minimum reflux.

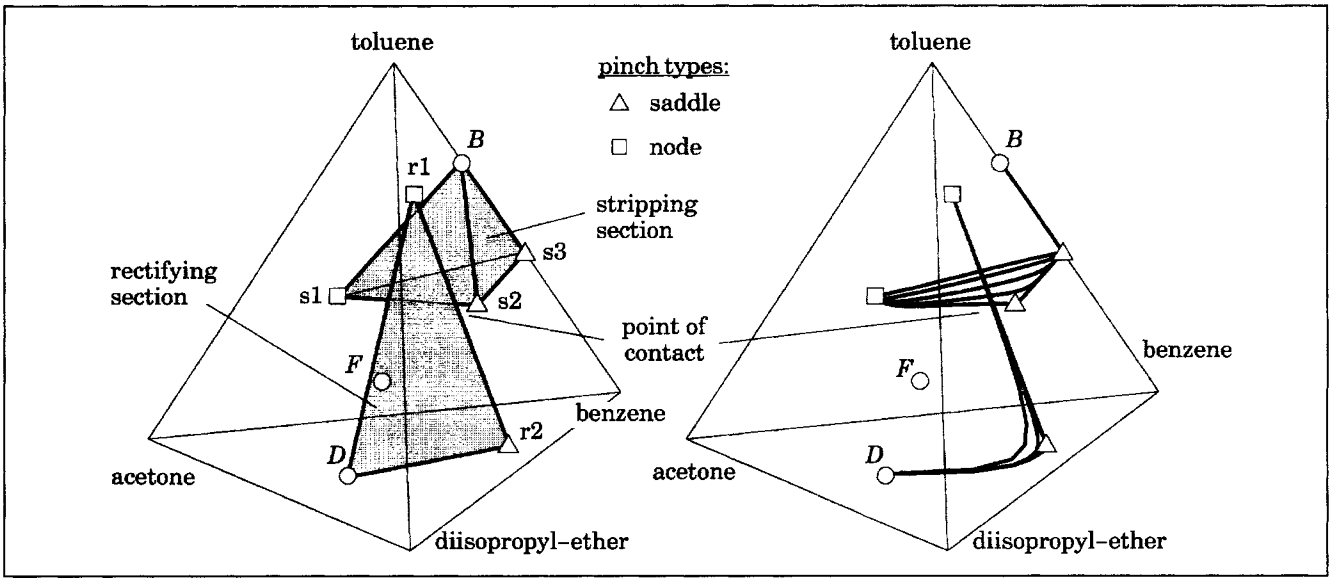

Figure 13. Quaternary example 1: rectification bodies and column profiles for a *vapor* feed at minimum reflux.

points is known *a priori*, the ZVC can only be applied in the case of a feed pinch. Since the MAC relies on the secant condition, it cannot be applied to Figure 13 where no feed pinch occurs and the feed is not introduced as boiling liquid (see Appendix D). However, since there is no physical explanation for its applicability for more than three components, it also seems questionable if the MAC can be applied to Figure 12. The EC can be applied in both cases, but only if the relevant pinch points are known. In Figure 13 the plate-to-plate calculations must be initiated in r2 and s2, whereas in Figure 12 r1 and s3 must be used.

Example 2. This example has been taken from Köhler et al. (1994, Table 3, No. 9) and has also been treated by Pöllmann (1995). It shows clearly the problems connected with the selection of pinch solutions especially for nonideal mixtures. Since the column section profiles in Figure 14 intersect, the separation is obviously feasible, which was also verified using ASPEN PLUS.

However, using the EC, Pöllmann found the separation to be infeasible. In opposition to Köhler et al. (1994) he sets $x_{B,\text{acetone}} = 0$. Thus, chloroform is the light key and Pöllmann concludes that the ternary stripping pinch (s1b) must be used for the EC, which would have been true for an ideal mixture. Since there is no unstable eigenvector in this pinch, the EC yields the separation to be infeasible. (If the plate-to-plate profile reaches s1b it will terminate there since s1b is a stable

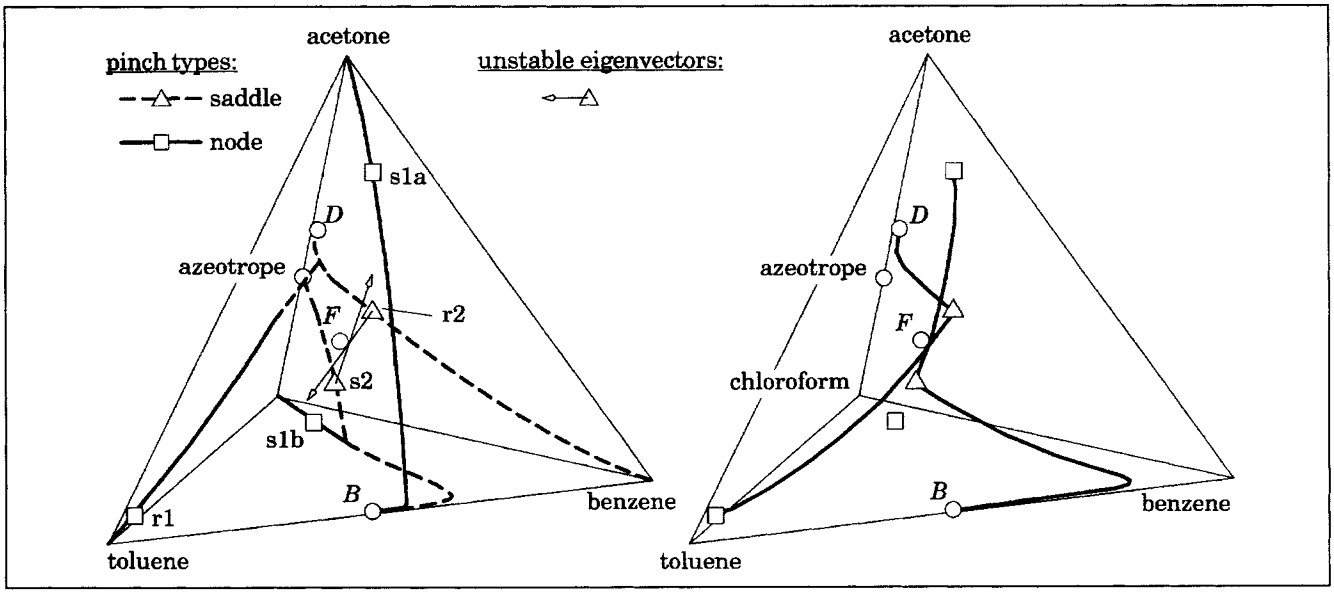

Figure 14. Quaternary example 2: pinch curves, pinch points (left) and column profiles (right) under minimum reflux.

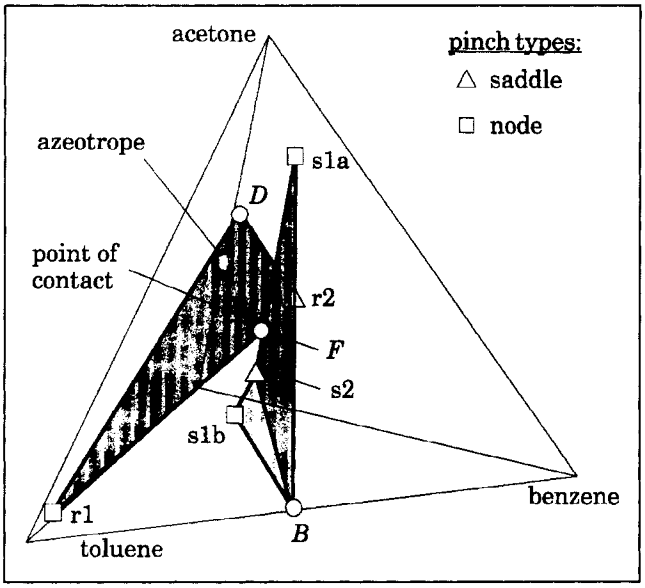

Figure 15. Rectification bodies according to the quaternary example 2.

node.) Using $x_{B,\mathrm{acetone}} = 1.5 \times 10^{-6}$ and stating acetone as the light key he would have found that the pinch s1a has to be used, which also has no unstable eigenvector and leads to the same result. Due to the nonideal behavior of the mixture the quaternary pinch s2, which has one unstable eigenvector, has to be used for the EC and would probably lead to the correct result. However, this information cannot be found based only on the product composition.

Figure 15 shows the application of the RBM to this separation example. In the stripping section three pinch points can be determined that form a set of two rectification bodies (the triangles ⟨B, s2, s1a⟩ and ⟨B, s2, s1b⟩). In the rectifying section two pinch points and the distillate composition also form a triangle. At minimum reflux, one of the stripping and the rectifying triangle touch each other at their sides.

The minimum energy demand was calculated using ASPEN PLUS, the BVM and the RBM (see Table 1). The results obtained by Köhler are $Q_B/F = 67.1 \times 10^6$ J/kmol for ASPEN PLUS and $Q_B/F = 64.7 \times 10^6$ J/kmol for MAC. However, it is not clear which pinch points were used and how they were selected. The ZVC cannot be applied to this split since it is neither a direct nor an indirect split.

Systems with five components

The RBM can be applied to mixtures with five components in the same way as to ternary and quaternary mixtures. Unfortunately, there is no simple graphical representation of the pinch curves, pinch points and column profiles; thus, it is not possible to discuss the separations in detail or to apply the BVM. However, minimum reflux can be determined with the RBM and compared with the results obtained by ASPEN PLUS.

For Examples 5a and 5b, the system ethanol/i-propanol/propanol/i-butanol/butanol was chosen and, for 5c, acetone/chloroform/benzene/toluene/p-xylene was chosen. The type of split is AB/CDE (5a) and ABC/DE (5b, 5c). Since there are no direct or indirect cuts, the ZVC cannot be applied. Due to the considerations in Appendix D, it is questionable if the MAC can be applied to these separations, even if the relevant pinch solutions are known. If they are known, it should be possible to use the EC to determine minimum reflux for all three examples.

Conclusions

The rectification body method (RBM), a novel shortcut technique for the calculation of the minimum energy demand of nonideal and azeotropic distillations, has been developed. The method is entirely general and can be applied to any arbitrary separation without limitations regarding the number of components or the type of split. In contrast to previous techniques, the RBM is well suited for separations with one or several distributing components when the type of the controlling pinch points can no longer be concluded from the knowledge of the specified products alone. In particular, the RBM can be applied in a straightforward manner to separations which are neither a direct nor an indirect split.

It is a particular characteristic of the RBM that it does not require any *a priori* knowledge on the type and number of pinch points prevailing in the separation under consideration. Neither the information concerning which pinch solutions will occur in the column profile nor whether there is a pinch at the feed stage is necessary to apply the RBM. Instead, all solutions of the pinch equations are exploited for the determination of the minimum energy demand. Using the information of the eigenvalues and thermodynamic data, pinch points are ordered to generate paths that approximate the column profile. If the number of pinch solutions increases due to bifurcations, these pinch points can also be used in a straightforward manner. The topology and thus the type of split is taken into account through the geometric criterion. However, all other methods to determine minimum reflux based on pinch points need to be applied only to special pinch solutions. Thus, they require an *a priori* selection of pinch solutions, which in many cases is not possible due to the unknown topology (quaternary example 1) or nonideal behavior of the mixture (quaternary example 2). For more than four components, this problem is even harder to solve, since qualitatively new types of splits may occur and pinch curves, pinch points, and column profiles can no longer be visualized.

The RBM can be considered as a generalization of certain previously proposed techniques. The Zero Volume Criterion by Julka and Doherty (1990) for direct and indirect splits can be considered as a special case. Further, the RBM reduces to the classical Underwood technique in case of ideal separations.

As the numerical implementation of the RBM is extremely fast and robust, computation time is negligible. The method is capable to account for superheated or subcooled feeds in a natural way without any additional computational burden. The comparison of the RBM to results obtained by rigorous simulation shows excellent agreement even for a suite of notorious examples where previous techniques are known to fail.

It has to be stated that a necessary prerequisite of all minimum energy shortcut calculation methods is the specification of feasible products. Finding feasible products for azeotropic, multicomponent mixtures can be rather involved, in particular when a graphical visualization of the residue curve map is no longer possible. It is another—maybe the most valuable—benefit of the new shortcut technique to indicate the feasibility of a certain product specification once the pinch lines have been calculated. Trying to resolve this problem using rigorous simulation tools leaves the user with the cumbersome problem to assess whether nonconvergence is due to bad initial guesses or to an inherent infeasibility of the simulation problem posed. Note that azeotropic distillation simulations are rather demanding in terms of initial guesses.

Due to its sound theoretical basis, its excellent performance, and its relatively simple use, we believe that the method proposed constitutes a mature foundation for a comprehensive toolkit of minimum energy shortcut methods for azeotropic and highly nonideal mixtures. Thus, in our future publications the method will be extended to certain complex distillation arrangements.

Acknowledgment

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Notation

B = bottom product flow rate, kmol/s
C = number of components
D = distillate flow rate, kmol/s
F = feed flow rate, kmol/s
h = molar enthalpy, J/kmol
H = enthalpy stream, W
l_i = liquid flow rate of component i, kmol/s
L = liquid flow rate, kmol/s
p = pressure, bar
p_0 = vapor pressure of a pure component, bar
q = thermal state (1 = liquid, 0 = vapor)
Q = energy, W
s = molar entropy, J/(K kmol)
S = entropy stream, W/K
t = temperature, °C
$\hat{t}$ = parameter of the residue curve
T = temperature, K
v = molar volume, m^3/kmol
v = vapor fraction, kmol/kmol
v_i = vapor flow rate of component i, kmol/s
V = vapor flow rate, kmol/s
x_i = liquid-phase composition, kmol/kmol
y_i = vapor phase composition, kmol/kmol

Subscripts

B = bottom
D = distillate
f = feed tray
F = feed
i = component
irr = irreversible
n = tray
P = pinch point

Superscripts

B = bubble point
D = dew point
L = liquid phase
V = vapor phase
VAP = vaporization
$*$ = equilibrium state
r = rectifying section
ri = pinch i in the rectifying section
s = stripping section
si = pinch i in the stripping section

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Appendix A: Plate-to-Plate Calculations

Balancing components and energy, the following equations can be formulated (Levy et al., 1985; Pöllmann et al., 1994)

$$y^*(x_{n+1}) = \frac{L_n}{L_n + D} x_n + \frac{D}{L_n + D} x_D; \quad n = 1 \ldots n_f, \tag{A1}$$

$$h_{n+1}^V = \frac{L_n}{L_n + D} h_n^L + \frac{D}{L_n + D} h_D - \frac{Q_D}{L_n + D}; \quad n = 1 \ldots n_f. \tag{A2}$$

If the product composition, the product flow rate, the condenser duty, and the composition on plate n are given, all values on plate $n+1$ can be calculated. Thus, the profile of the column section can be calculated successively from *plate-to-plate* starting at the product withdrawal.

Appendix B: Pinch Points

From a mathematical point of view, the plate-to-plate Eqs. A1 and A2 can be considered as an implicit recurrence: x_{n+1} is a function of x_n. Thus, they have fixed points where $x_{n+1} = x_n$ (Levy et al., 1985; Pöllmann et al., 1994)

$$y^*(x_P) - \frac{L_P}{L_P + D} x_P = \frac{D}{L_P + D} x_D; \tag{B1}$$

$$h_P^V - \frac{L_P}{L_P + D} h_P^L = \frac{D}{L_P + D} h_D - \frac{Q_D}{L_P + D}. \tag{B2}$$

When product composition and flow rate are given, this set of equations still has one degree of freedom. Solving with different values of the condenser duty yields a curve in composition state space, which can have multiple solution branches and bifurcation points. When the parameter condenser duty is fixed, fixed points can be determined on each solution branch.

At total reflux, each pure component and azeotrope is a fixed point. Thus, at total reflux, the number of fixed points equals the number of components plus the number of azeotropes. When reflux is decreased, some of the fixed points move on their solution branch outside the composition space, while others move inside. Thus, the number of fixed points changes with the reflux ratio.

From a distillation point of view, the fixed points of the plate-to-plate recurrence correspond to pinch zones in the column profile. In a pinch zone the meeting vapor and liquid streams approach equilibrium. Thus, the driving force for mass transfer between the streams is vanishing and there is no change in composition over several stages.

In literature many methods have been proposed to solve Eqs. B1 and B2 (such as Köhler et al., 1991; Aguirre and Espinosa, 1996; Pöllmann and Blass, 1994; Julka and Doherty, 1990). However, none of these methods can guarantee the determination of all solution branches, especially when branching between two solution branches occurs. To find all solution branches, continuation methods *and* bifurcation analysis (Seydel and Hlaváček, 1987) must be applied. However, until now, a very simple continuation algorithm with a secant predictor and a Newton corrector was used for the calculations presented in this article.

The Jacobian of the plate-to-plate equations ($J = \partial x_{n+1}/\partial x_n$) has $C-1$ positive eigenvalues λ_i and corresponding eigenvectors. These eigenvalues describe the local behavior of plate-to-plate profiles in the vicinity of a pinch point. Eigenvalues greater than unity correspond to plate-to-plate profiles leaving the pinch in the direction of the corresponding unstable eigenvector. Eigenvalues smaller than unity correspond to stable eigenvectors and to approaching profiles (Pöllmann et al., 1994; Julka and Doherty, 1990).

In this article pinch points were classified as proposed by Julka and Doherty (1990). The name of a pinch point consists of a letter denoting the column section (s or r) and the number of the unstable eigenvectors plus one. If two or more fixed points with the same classification occur, they are differentiated using a second letter (such as s2a and s2b in Figure 12).

Appendix C: Residue Curves

Residue curves describe the change in composition of an open still in simple distillation (Doherty and Perkins, 1978)

$$\frac{dx}{d\hat{t}} = x - y^*(x). \tag{C1}$$

They can be used to visualize the nonideal behavior of ternary mixtures. In Figure A1 residue curve maps and boiling surfaces can be found for three ternary mixtures.

Appendix D: Secant Condition at Minimum Reflux

Although not mentioned by Köhler et al. (1991), the secant condition at minimum reflux, stated by Julka and Doherty (1990), Appendix D, can give a physical explanation for the minimum angle criterion (MAC). Using balance equations for both the stripping and the rectifying section as well as for the feed tray, the secant condition

$$L^r \Delta x_M^r + L^s \Delta x_{N+1}^s = F(\tilde{x} - x_f) \tag{D1}$$

with

$$\tilde{x} \equiv x_F + (1 - q_F)(x_f - y_f) \tag{D2}$$

is obtained. (The index of plates in the rectifying section is m in the stripping section n. They are counted from the product withdrawal in direction of the feed plate. The feed plate is plate M of the rectifying and plate N of the stripping section: $x_f = x_M = x_N$. L^r is the liquid stream in the rectifying section, and L^s in the stripping section. Both streams are assumed to be constant. The backward difference operator Δ is defined as follows: $\Delta x_k = x_k - x_{k-1}$.) Δx_M^r gives the difference between the composition on the feed plate M and plate $M-1$ and can be interpreted as a secant to the rectifying profile. Δx^s_{N+1} is a secant to the stripping profile. (In this case the secant lies between the feed stage N and stage $N+1$. However, this plate will never be reached by the column profile, since it is part of the stripping section but lies *above* the feed stage. It can only be determined calculating plate-to-plate from the bottom upwards without introducing the feed.)

Interpreting Eq. D1 geometrically yields that $\tilde{x}$ lies in the plane spanned by Δx^r_M and Δx^s_{N+1} through the point x_f. If one of the profiles pinches at the feed tray, the corresponding secant vector is zero and the composition on the feed tray equals to the pinch composition. A pinch x^s_P in the stripping section leads to

$$\Delta x^s_{N+1} = 0, \quad x_f = x^s_P, \quad \tilde{x} = x_F + (1-q_F)(x^s_P - y^s_P). \tag{D3}$$

Equation D1 holds

$$\Delta x^r_M = \frac{F}{L^r}(\tilde{x} - x^s_P), \tag{D4}$$

$$\tilde{x} = x^s_P + \frac{L^r}{F}(x^s_P - x^r_{M-1}). \tag{D5}$$

The pinch composition, the composition on the plate above the feed plate and the point $\tilde{x}$ are lying on a straight line, as can be seen in Figure A2 on the left. In this case $\tilde{x}$ is not equal to x_F, since the feed was introduced as vapor ($q_F = 0$).

A feed pinch in the rectifying section leads to

$$\Delta x^r_M = 0, \quad x_F = x^r_P, \quad \tilde{x} = x_F + (1-q_F)(1-q_F)(x^s_P - y^s_P). \tag{D6}$$

From Eq. D1 can be derived

$$\Delta x^s_{N+1} = \frac{F}{L^s}(\tilde{x} - x^r_P), \tag{D7}$$

$$\tilde{x} = x^r_P + \frac{L^s}{F}(x^s_{N+1} - x^r_P). \tag{D8}$$

Thus, the composition on plate $N+1$, the pinch and $\tilde{x}$ must lie on a straight line, as can be seen in Figure A2 on the right. Since the feed was introduced as boiling liquid ($q_F = 1$), $\tilde{x}$ is equal to the x_F. In the figure the real plates $N-1$ and N as well as the virtual plate $N+1$ are depicted.

Using the secant condition, a physical explanation of the MAC for special splits can be obtained: If a feed pinch occurs in one column section, $\tilde{x}$ must lie on the extension of the profile of the other column section beyond the feed plate. If the profile of this column section can be approximated by the line through saddle pinch and feed plate $\tilde{x}$, the saddle and the feed plate (that is, the feed pinch) are lying on a straight line. Only if the feed is introduced as boiling liquid, Eq. D2 holds $\tilde{x} = x_F$ and the MAC is fulfilled. For any other

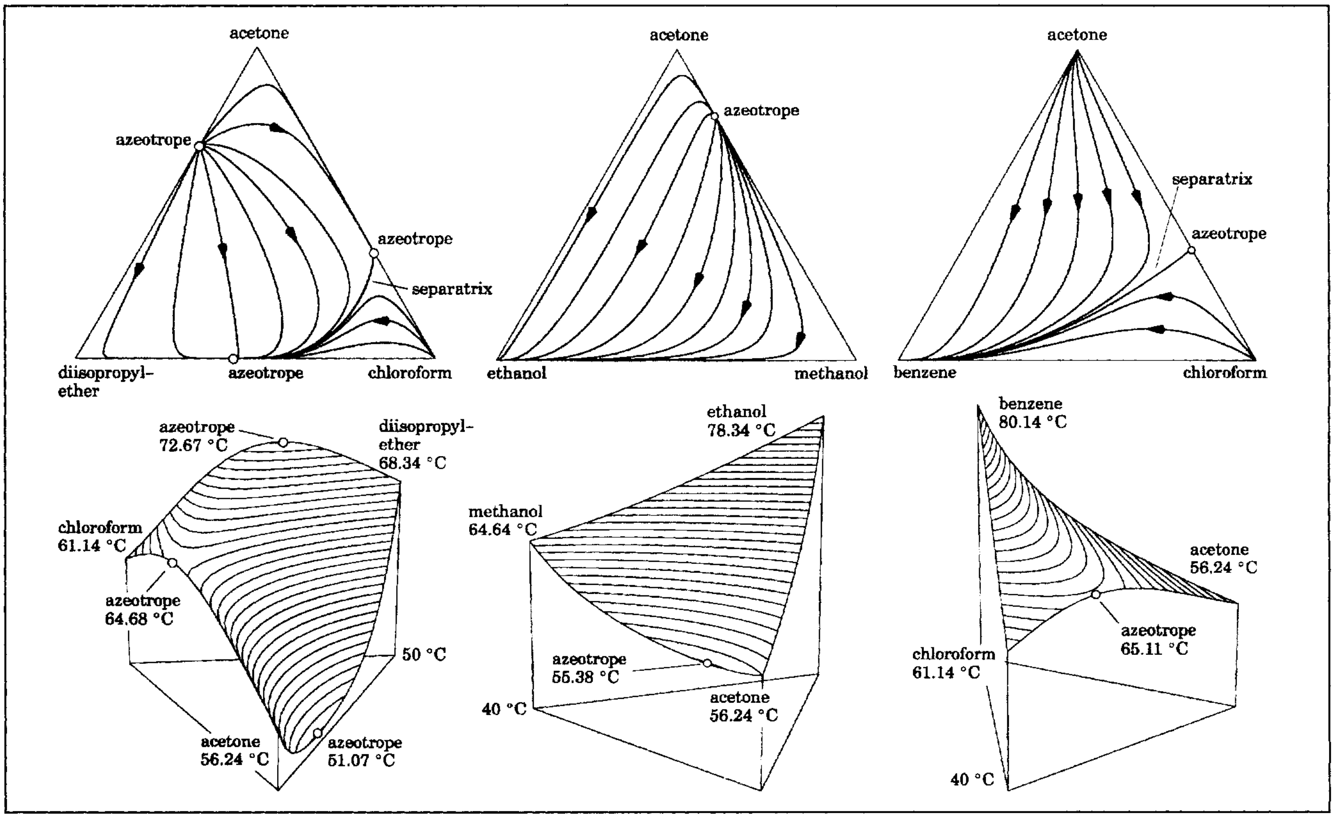

Figure A1. Residue curve maps and boiling surfaces at 1.013 bar.

Arrows indicate the direction of increasing time and parameter $\hat{t}$.

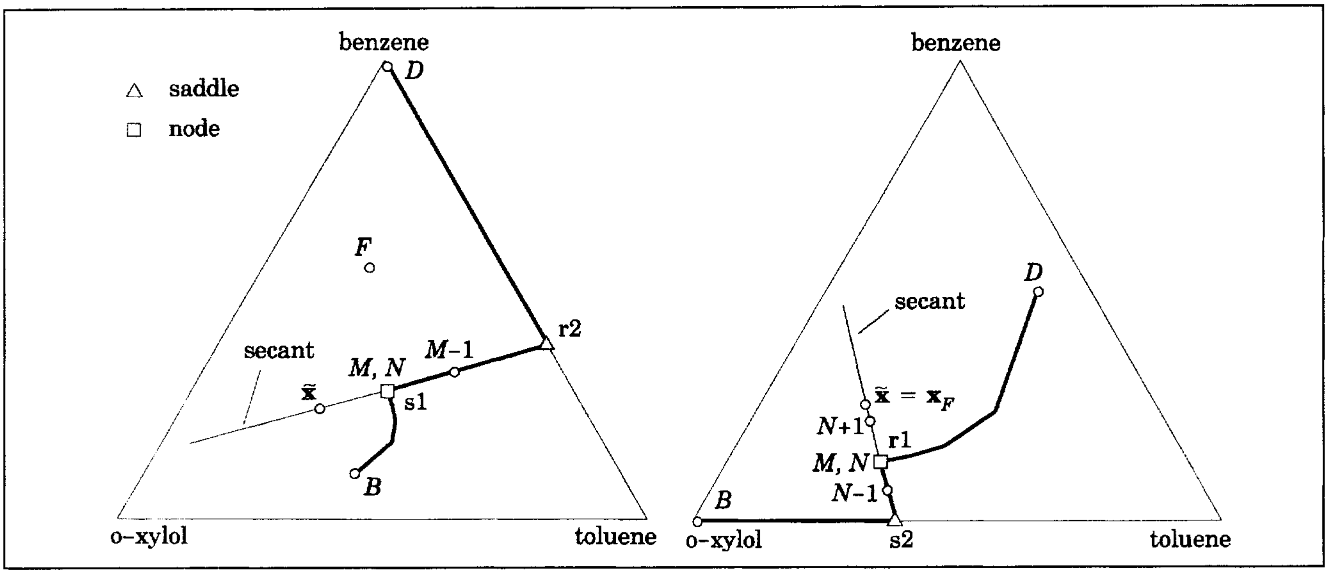

Figure A2. Secants of the column profile for a feed pinch in the stripping (left) and in the rectifying profile (right).

thermal state of the feed, the MAC *must* be formulated using $\tilde{x}$ instead of x_F.

These considerations lead to the limitations of the MAC: In multicomponent distillation often more than one unstable eigenvector exists in the saddle pinch and the profile is curved between saddle and feed plate (such as in Figure 12). Thus, $\tilde{x}$ and the two pinch points will not lie on a straight line. However, the minimum of the angle between these points can often be used to approximate the minimum reflux condition.

When no feed pinch occurs, the secant condition (Eq. D1) only states that $\tilde{x}$ lies in the plane spanned by the secant vectors in the feed plate composition. However, a minimum of the angle spanned by $\tilde{x}$ and the two pinch points cannot be proven. Further, the composition on the feed plate is not known. Thus, $\tilde{x}$, which must be used to formulate the MAC (see Figure A2, left), can only be determined for $q_F = 1$ (see Eq. D2).

Appendix E: Definition and Stability of Equilibrium States

In opposition to many textbooks on thermodynamics we use a general definition of equilibrium as proposed by Gibbs (1906). With equilibrium, we denote a state, where driving forces for all exchange processes vanish, that is, $p' = p''$, $T' = T''$, $\mu_i' = \mu_i''$. In this definition nothing is said about stability. Thus, equilibrium states can be distinguished according to the stability of the system (such as p, T-flash or U, V-flash) considered at this state (note that the stability of different systems does *not* need to be the same for the same state). However, in literature on thermodynamics stability is often included in the definition of equilibrium neglecting unstable equilibrium states.

In a closed system the condition $(\partial S)_{U,V,N} = 0$ is equivalent to an equilibrium state (see, for example, Modell and Reid, 1983). Equilibrium states that correspond to a minimum of S can only be produced artificially and will not prevail, since they are not stable against small perturbations that are always present due to statistical fluctuations. Saddle-type equilibrium states can theoretically be reached, but are also unstable to small perturbations and will thus not prevail for $t \rightarrow \infty$. Only local maxima are stable against small perturbations. However, if finite disturbances are allowed, local maxima may also not prevail, depending on the strength of the disturbances and the properties of the system. Thus, for many systems, only the global maxima of S is of interest (such as liquid-liquid equilibria).

In a steady-state flow process the condition $(\partial S_{\text{irr}})_{p,H,N} = 0$ is equivalent to an equilibrium state (see below). The number of plates of a column section can be considered as a coordinate in analogy to the coordinate time of the closed system. Thus, for a bounded system (that is, a finite number of plates) unstable equilibrium states (minima and saddles of S_{irr}) can prevail. In addition, the steady-state flow process considered can be stabilized from outside (from the other half of the column), since one of the streams that are regarded as degrees of freedom actually enters the balance. For a closed system, this is impossible, since it would require an influence from the future. For an unbounded system (an infinite column section), only a stable equilibrium state, which corresponds to a maximum of S_{irr}, will prevail for the steady-state flow process. However, the stable equilibrium state must not be a global maximum.

Note that the stability of equilibrium states (x, y, p, T) according to the steady-state flow process does *not* correspond to the stability of the same state according to a closed system. In particular all pinch states calculated for this article are stable according to a closed system.

Stationary points of entropy production

It will be shown that the stationary points of the entropy production in a column section at steady state correspond to equilibrium states and thus to pinch points. The stationary points of the entropy production are characterized through the condition $\partial S_{\text{irr}} = 0$, where ∂ denotes a variation of first order.

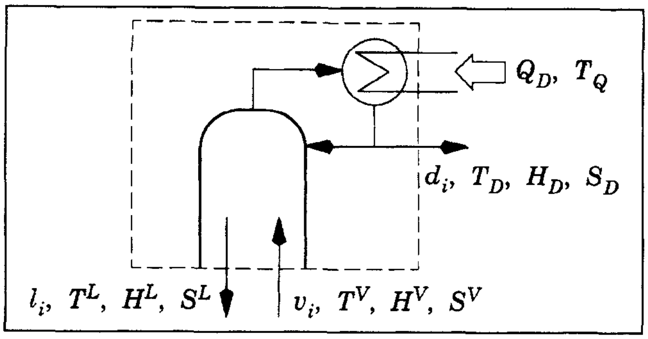

Figure A3. Balancing the rectifying section to calculate the entropy production.

The entropy production in a column section as depicted in Figure A3 can be expressed by

$$S_{\text{irr}} = S^L - S^V + S_D - \int \frac{dQ_D}{T_Q}. \qquad \text{(E1)}$$

However, S_{irr} is constrained by energy and component balances:

$$0 = H^L - H^V + H_D - Q_D, \qquad \text{(E2)}$$

$$0 = \boldsymbol{l} - \boldsymbol{v} + \boldsymbol{d}. \qquad \text{(E3)}$$

The degrees of freedom are the flow rates and temperatures of the passing streams. Product flow rates, product temperature, the condenser duty, the temperature at which the condenser duty is supplied, and the column pressure shall be fixed. To find the stationary points of the entropy production, a Lagrange formulation is used

$$\Phi(\boldsymbol{l}, \boldsymbol{v}, T^L, T^V, \lambda_0, \boldsymbol{\lambda}) = S^L - S^V + S_D - \int \frac{dQ_D}{T_Q} + \lambda_0 (H^L - H^V + H_D - Q_D) + \sum_{i=1}^{C} \lambda_i (l_i - v_i + d_i). \qquad \text{(E4)}$$

Now the derivatives of Φ with respect to l_i, v_i, T^L, and T^V are set to zero

$$\frac{\partial \Phi}{\partial l_i} = \frac{\partial S^L}{\partial l_i} + \lambda_0 \frac{\partial H^L}{\partial l_i} + \lambda_i := 0 \quad ; \quad i = 1 \ldots C \qquad \text{(E5)}$$

$$\frac{\partial \Phi}{\partial v_i} = -\frac{\partial S^V}{\partial v_i} - \lambda_0 \frac{\partial H^V}{\partial v_i} - \lambda_i := 0 \quad ; \quad i = 1 \ldots C \qquad \text{(E6)}$$

$$\frac{\partial \Phi}{\partial T^L} = \frac{\partial S^L}{\partial T^L} + \lambda_0 \frac{\partial H^L}{\partial T^L} := 0 \qquad \text{(E7)}$$

$$\frac{\partial \Phi}{\partial T^V} = -\frac{\partial S^V}{\partial T^V} - \lambda_0 \frac{\partial H^V}{\partial T^V} := 0 \qquad \text{(E8)}$$

Applying Maxwell's relation for the total differential of the fundamental equation for the enthalpy to a steady-state flow process

$$dH = TdS + Vdp + \sum_{k=1}^{C} \mu_k dN_k \qquad \text{(E9)}$$

the derivatives of S can be substituted by

$$\left(\frac{\partial S}{\partial N_i}\right)_{T,p,N_{j \neq i}} = \frac{1}{T}\left[\left(\frac{\partial H}{\partial N_i}\right)_{T,p,N_{j \neq i}} - \mu_i\right]; \; i = 1 \ldots C \qquad \text{(E10)}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_{p,N_j} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,N_j}. \qquad \text{(E11)}$$

This gives

$$\frac{1}{T^L}\left(\frac{\partial H^L}{\partial l_i} - \mu_i^L\right) + \lambda_0 \frac{\partial H^L}{\partial l_i} + \lambda_i = 0 \quad ; \quad i = 1 \ldots C \qquad \text{(E12)}$$

$$-\frac{1}{T^V}\left(\frac{\partial H^V}{\partial v_i} - \mu_i^V\right) - \lambda_0 \frac{\partial H^V}{\partial v_i} - \lambda_i = 0 \quad ; \quad = 1 \ldots \text{C} \qquad \text{(E13)}$$

$$\frac{\partial H^L}{\partial T^L}\left(\frac{1}{T^L} + \lambda_0\right) = 0 \qquad \text{(E14)}$$

$$-\frac{\partial H^V}{\partial T^V}\left(\frac{1}{T^V} + \lambda_0\right) = 0 \qquad \text{(E15)}$$

Now, Eqs. E14 and E15 give

$$T^L = T^V = -\frac{1}{\lambda_0}. \qquad \text{(E16)}$$

Inserting Eq. E16 in Eqs. E12 and E13 results after addition of both equations in

$$\mu_i^L = \mu_i^V; \qquad i = 1 \ldots C. \qquad \text{(E17)}$$

Thus, the condition $\partial S_{\text{irr}} = 0$ corresponds to equilibrium states of the system. This is a generalization of the known fact that for reversible distillation ($S_{\text{irr}} = 0$) pinch solution branch and column profile coincide (Köhler et al., 1991).

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