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SHORTCUT METHODS FOR THE DESIGN OF HETEROAZEOTROPIC DISTILLATION OF MULTICOMPONENT MIXTURES

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Abstract
Shortcut methods are valuable tools in the early stages of chemical process design, where numerous flowsheet alternatives need to be evaluated to determine the most energy-efficient, feasible flowsheet. Various shortcut methods based on tray-to-tray calculation and pinch point analysis for the inspection of feasibility and the determination of the minimum energy demand (MED) for homogeneous nonideal distillation have been published in the literature. Recently, Kraemer et al.[1] presented the feed pinch method (FPM) for heterogeneous azeotropic mixtures of any number of components. While the FPM returns an accurate representation of the MED, it still requires tray-to-tray calculations for one column section and it can only be applied to separations with a feed pinch, i.e. usually direct or indirect splits. In this work, we propose the feed angle method (FAM) which resolves both of these issues as it does not rely on numerous tray-to-tray calculations and can be applied to any kind of sharp split. The FAM is illustrated by ternary and quaternary heteroazeotropic separations with direct, indirect and intermediate splits.

Keywords: Heteroazeotropic distillation, shortcut method, feed angle method

1. Introduction

When designing a sustainable distillation process for an azeotropic multicomponent mixture, numerous alternative flowsheets and entrainer candidates have to be evaluated in order to determine the most energy-efficient flowsheet. In industrial practice, usually a small number of possible flowsheets are selected by heuristics and evaluated manually by repetitive simulation studies, which require detailed design specifications in the early design phase. Despite this tedious, iterative procedure, no guarantee concerning the quality of the solution can be given. Shortcut methods for distillation column design, however, allow for an inspection of feasibility and an efficient and robust calculation of the minimum energy demand (MED) without the need for detailed column specification. Some powerful and recent shortcut methods based on rigorous thermodynamics for nonideal and azeotropic mixtures are reviewed in brief in the following[2]. Subsequently, the application to the heterogeneous case is shown. The restrictions of the existing methods, especially for heterogeneous mixtures, are pointed out in order to motivate the development of a novel method for heteroazeotropic distillation which can be viewed as an extension of the existing methods to overcome their limitations.

2. Existing shortcut methods for nonideal distillation

Levy et al.[3] proposed the boundary value method (BVM) for the determination of the MED of nonideal distillation. Here, column tray-to-tray profiles are calculated for each column section from the respective column ends by balancing components and energy and considering chemical equilibrium on each tray. The lowest energy duty that allows an intersection of column profiles defines the MED. For sharp splits, traces have to be specified for every component, since the profiles would not leave the subspace of the product components otherwise. The manifold of stripping section profiles for different trace components in the bottom product of an example separation is shown in Figure 1. The search for the MED therefore requires a tedious simultaneous optimization of the energy and the trace components. Considering that the intersection of profiles needs to be checked manually, the application of the BVM is effectively limited to ternary mixtures.

In order to overcome the dependency of the shortcut results on trace components in the products, pinch based shortcut methods have been proposed by various authors. Pinch curves for a given product and a variable reboiler/condenser duty can be calculated for each column section as solution branches of the tray-to-tray equations. For a specific energy duty, pinch points are identified as fixed

points of the plate-to-plate recurrence on the pinch point curves (cf. Figure 1). These pinch points, which are insensitive towards the choice of trace components, can be classified as stable or unstable nodes or as saddles depending on the number of stable eigenvectors. The zero-volume criterion (ZVC)[4] and the minimum angle criterion (MAC)[5] require a subset of pinch points to be on a straight line or to form a minimum angle, respectively, for MED. While the ZVC relies on a constant molar overflow assumption, the MAC can be inaccurate for mixtures with more than three components. Both criterions share the drawback that they can only be applied to separations with a feed pinch.

Bausa et al.[2] introduced the rectification body method (RBM) as an algorithmically accessible procedure to estimate the MED of multicomponent distillation. Here, possible paths along pinch points with an increasing number of stable eigenvectors are generated and checked for thermodynamic consistency by excluding paths, where the entropy production does not increase strictly monotonously. Linear rectification bodies that approximately describe the manifold of all profiles are then constructed for each section by linearly connecting the pinch points contained in the paths (cf. Figure 1). The MED is calculated by iteratively identifying the lowest reboiler duty that results in an intersection of a set of bodies. The check for intersection of the convex rectification bodies can be performed very efficiently and, therefore, the method is applicable and automatable for any number of components in the mixture and for any kind of split. Nevertheless, the RBM only returns an accurate indication of the MED as long as the profiles between the pinch points are close to a linear approximation. Most homogeneous mixtures, however, exhibit only very mild nonlinear behavior. Lucia et al.[6] proposed the shortest stripping line approach (SSL) to find the MED in distillation. They calculate stripping profiles until a pinch occurs and then switch to the rectifying profile. The shortest stripping line which produces a feasible result, i.e. where the distillate product is reached by the rectifying profile, marks the MED. While the SSL is based on a constant molar overflow assumption and can only be applied to separations with a feed pinch, it was automated and applied to homogeneous zeotropic and azeotropic mixtures of up to six components and multi-unit processes.

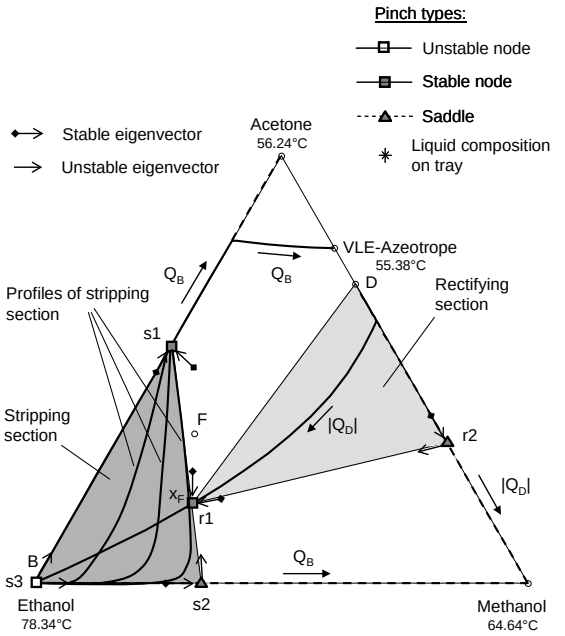

Figure 1. Stripping section profiles, pinch points and rectification bodies at MED for a separation of the homogeneous mixture of acetone, methanol and ethanol

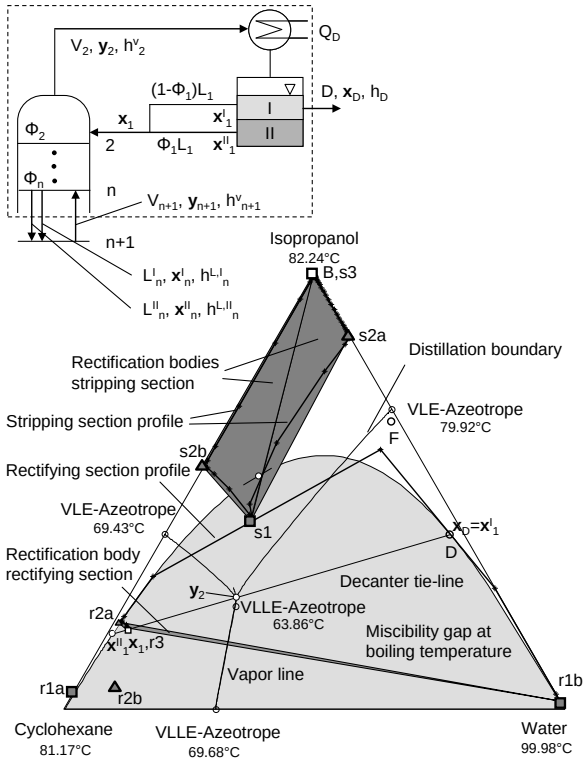

Figure 2. Section profiles and relevant rectification bodies for the heteroazeotropic separation of isopropanol, water and cyclohexane

Table 1. Compositions and MEDs for heteroazeotropic separation of i-propanol, water, cyclohexane

Molar comp.	x_F 0.66/0.32/0.02	x_D 0.4/0.57/0.03	x_B 1/0/0	$Q_{b,min}/F$ [MJ/kmol]	rigorous 30.3	RBM 65.9	FPM 30.3	FAM 30.7

3. Application to heterogeneous mixtures

Many industrially relevant mixtures exhibit immiscibilities in the liquid phase. Moreover, the use of a heterogeneous entrainer allows for a crossing of distillation boundaries to separate azeotropic multicomponent mixtures. In typical designs, a heterogeneous stream is produced at the top of the column which is then split in a decanter into an entrainer-lean distillate and an entrainer-rich reflux. Heterogeneous systems always exhibit strong nonlinearities. Shortcut methods for homogeneous systems cannot be applied without an adaptation to handle the decomposition of the liquid phase in the decanter but also on the heterogeneous trays within the column. Hence, there are very few publications on shortcuts for heterogeneous systems; most of these consider immiscibilities only in the decanter. A thorough analysis of the properties of heteroazeotropic distillation has been presented by Urdaneta et al.[7]. The application of the shortcut methods for homogenous distillation reviewed above is illustrated in this section with the ternary heteroazeotropic mixture of isopropanol, water and cyclohexane. A ternary feed is to be separated into a bottom product of pure isopropanol and a cyclohexane-lean product on the decanter tie-line through the minimum boiling ternary azeotrope (cf. Figure 2). The limitations of the existing shortcut methods are demonstrated and the novel shortcut method is presented subsequently.

RBM. Urdaneta et al.[7] have extended the procedure for the calculation of the pinch points of a separation to handle heterogeneous systems. Based on these pinch point solutions, the RBM can also be in principle applied to heterogeneous systems. However, the accuracy of the RBM can be low for these systems, as heterogeneous mixtures usually exhibit strongly curved profiles in and around the region of immiscibility. The profile of the rectifying section for the example mixture is strongly curved towards the isopropanol vertex (cf. Figure 2). While the linear combinations of pinch points at MED approximate the stripping profiles very well, they miss the curved profiles of the rectifying section by a large margin as shown in Figure 2. The rectification bodies can be brought to intersection at a significantly higher reflux than the minimum reflux leading to a significant overestimation of the MED (cf. Table 1).

BVM. Pham et al.[8] have extended the BVM to heteroazeotropic distillation but only considered designs with homogeneous column trays. For columns with heterogeneous behavior in the rectifying section, however, the courses of the profiles are not only dependent on the specification of trace components in the products, but also on the specification of the number of heterogeneous trays k and the liquid phase ratio Φ_k on the last heterogeneous tray as shown by Urdaneta et al.[7]. Factoring in the graphical check for intersection required by the BVM, it becomes clear that this method is not suited for heterogeneous mixtures.

FPM. Kraemer et al.[1] developed the feed pinch method (FPM) in order to overcome the limitations towards the number of components or the inaccuracies of the above mentioned methods. The FPM is initialized by the RBM to gain an initial value for the MED and identify the relevant separation pinch points, particularly the feed pinch point. The FPM then requires the calculation of one tray-to-tray profile starting from the feed pinch point. This single profile is only calculated for the section that does not contain the feed pinch, i.e. when the feed pinch is the stable node pinch of the stripping section, the rectifying section profile is calculated upwards from the feed pinch and vice versa. The profile of the section to which the feed pinch belongs does not need to be calculated as the stable pinch can always be reached by a profile of the respective section. Feasibility of the separation is detected, when the calculated profile reaches the product composition or the decanter tie line. The lowest reflux, for which this is possible, denotes the MED. Note that the FPM does not require the specification of trace components as well as k and Φ_k for the determination of feasibility and MED[1]. Hence, the profile is a function of the energy duty only. In addition, the FPM offers a simple check for feasibility; it is algorithmically accessible and applicable to heterogeneous mixtures of any number of components. The only restriction of the FPM is the requirement of a feed pinch point. While direct or indirect splits always have a feed pinch point, non-sharp or sloppy splits do not necessarily exhibit a feed pinch point.

The FPM is similar to the SSL approach, which cannot easily be applied to separations without a feed pinch either. Contrary to the SSL, however, the FPM does not rely on a constant molar overflow assumption since energy balances and rigorous thermodynamics are considered. In addition, balances and equilibrium for heterogeneous trays and a computationally cheap but reliable phase stability test[9] are included. Furthermore, the FPM identifies the feed pinch a priori by the initialization with the RBM such that the tray-to-tray calculations only need to be carried out in one direction starting

from the feed pinch. The application of the FPM to the ternary example mixture is shown in Figure 3. The profile of the rectifying section at MED starts at the feed pinch, i.e. the stable pinch of the stripping section and reaches the unstable pinch of the rectifying section on the decanter tie line, which marks the composition of the reflux from the decanter. The FPM detects the correct MED as listed in Table 1.

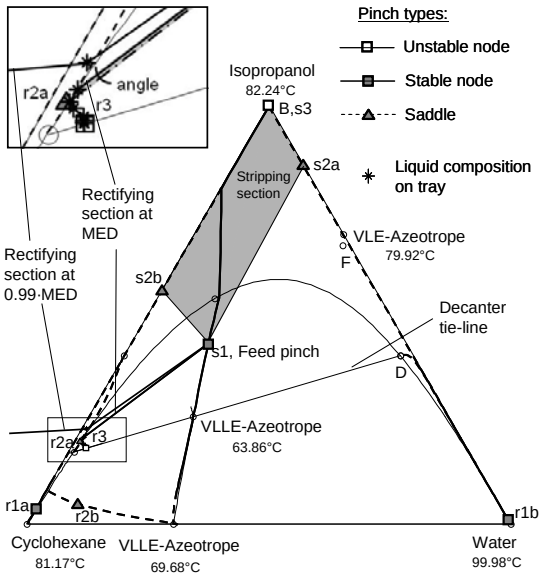

Figure 3. Rectifying section profiles for MED and 0.99·MED calculated with the FPM and angle calculated with the FAM for the heteroazeotropic separation of isopropanol, water and cyclohexane

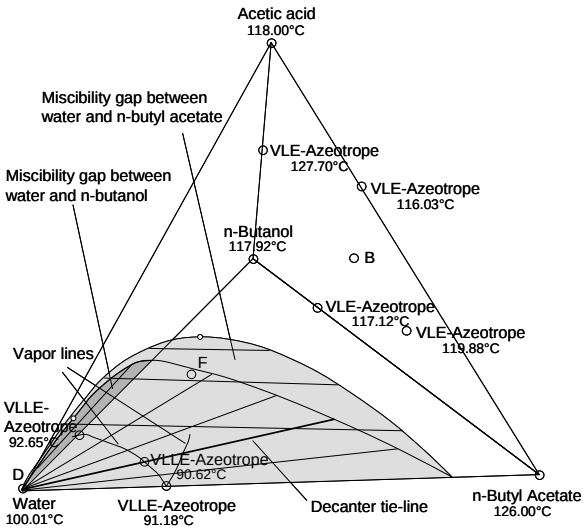

Figure 4. Quaternary heterogeneous system of water, n-butyl acetate, n-butanol, acetic acid

4. Novel shortcut method: Feed angle method (FAM)

While the FPM returns an accurate representation of the MED, it still requires tray-to-tray calculations for one column section and it can only be applied to separations with a feed pinch, i.e. usually direct or indirect splits. The feed angle method (FAM), which we propose in this paper, resolves both of these issues as it does not rely on numerous tray-to-tray calculations and can be applied to any kind of sharp split. In order to achieve this goal, the FAM revives conceptual elements of the MAC/ZVC and combines these with the FPM such that only one tray has to be calculated per non-pinched section.

Like the FPM, the FAM is initialized by the RBM, which provides information about the relevant pinch points and determines an initial value for the MED. For the application of the FAM we need to distinguish between separations with or without a feed pinch. When a feed pinch is identified in the initialization by the RBM, the pinched section can be approximated by a rectification body as in the FPM. The FAM then checks feasibility and approximates the MED by the calculation of only one tray above or below the feed pinch in the non-pinched column section. In the case of the example separation (Figure 3), we compute the rectifying tray above the pinched feed tray. In an algorithmic optimization procedure, we then minimize the angle between the line connecting the feed pinch and the tray above (below) the feed pinch and the line connecting the feed pinch s1 and the relevant saddle pinch r2a of the rectifying (stripping) section (Figure 3). Feasibility is determined and the MED is found when the angle is minimized to zero. The MED determined in this manner is a very good approximation: for the example separation, it is only 1.3% larger than the MED calculated with the more rigorous FPM (cf. Table 1).

In mixtures with more than three components, more than two pinch solutions are taken into account. We illustrate the application to higher dimensional systems with the quaternary mixture of water, n-butyl acetate, n-butanol, acetic acid with three heterogeneous and four homogeneous azeotropes as well as two binary miscibility gaps between water and n-butyl acetate and between water and n-butanol (cf. Figure 4). The specified separation, which is given in Table 2, is accomplished by a heteroazeotropic column setup with a decanter at the top of the column, where pure water is drawn off. Bausa[10] inspected this separation with the RBM (cf. Figure 5): the tray-to-tray profiles of the

rectifying section display a distinct curvature and pass by the stripping section with a considerable distance to the edges of the stripping section rectification body. The RBM therefore overestimates the MED by a considerable amount (cf. Table 2). The application of the FAM is shown in Figure 6. Like in the ternary case, the selection of the relevant pinch points can be achieved by application of the RBM: we select the feed pinch s1 and the saddle pinches r2 and r3 which constitute the edges of the intersecting rectification planes. Then, the angle between the line connecting the feed pinch s1 with the tray above the feed pinch and the hyperplane defined by the relevant saddle pinches is minimized to a value of zero by adjusting the reboiler duty. The MED approximated in this way constitutes a very good approximation when compared to the more rigorously determined value by the FPM (cf. Table 2)

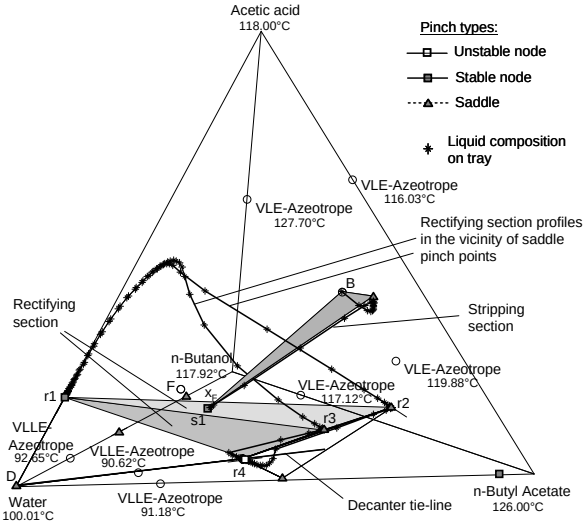

Figure 5. Rectification bodies and profiles at MED as determined by the RBM for the heteroazeotropic separation of water, n-butyl acetate, n-butanol, acetic acid

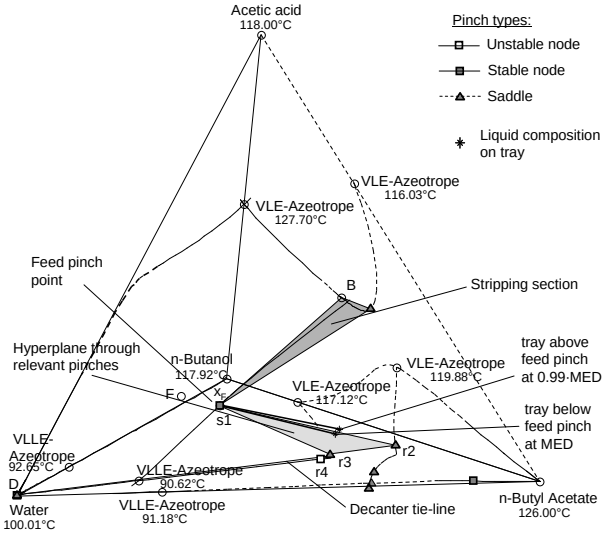

Figure 6. FAM: trays above feed pinch for MED and 0.99·MED and hyperplane through relevant pinch points for the heteroazeotropic separation of water, n-butyl acetate, n-butanol, acetic acid

Table 2. Molar compositions of water, n-butyl acetate, n-butanol, acetic acid and MEDs

x_F	x_D	x_B	$Q_{b,min}/F$	rigorous	RBM	FPM	FAM
0.5/0.17/0.17/0.17	0.99/2e-3/8e-3/0	0/0.33/0.34/0.33	[MJ/kmol]	35.2	44.5	35.2	35.2

The application of the FAM to separations without a feed pinch is illustrated by the quaternary azeotropic heterogeneous system of acetone, chloroform, benzene and toluene. We have specified an intermediate split as given in Table 3. The rectification bodies detected in the initialization by the RBM are shown in Figure 7. It can be clearly seen that the rectification bodies intersect at the edges and, thus, the separation does not exhibit a feed pinch. In fact, this separation will never have a feed pinch, no matter how many trays or how much energy is specified. Figure 7 also shows that the column section tray-to-tray profiles calculated with the MED as identified by the RBM do not intersect. Therefore, one can conclude that the RBM underestimates the MED for this heterogeneous example.
The task of the FAM now is to find a feed tray composition and an energy duty such that the tray above and the tray below the feed tray point towards the respective saddle pinches (cf. Figure 8). The point of intersection of the rectification bodies can be used as initial feed tray composition in the FAM. The angles between the trays and the saddle pinches in the respective sections are determined as described above. These angles are minimized by solving a nonlinear programming problem (NLP) where the feed tray composition and the energy duty remain variable. When the angles in the resulting NLP can be minimized to zero, feasibility of the separation can be assumed and the MED is detected (Table 3). Additionally, we have calculated full tray-to-tray profiles for both column sections at the MED which was determined by the FAM. These profiles intersect at the optimized feed tray composition verifying the results of the FAM. Note that the CPU time on a 3 GHz PC for the FAM optimization was about one second since only two trays and three pinches have to be calculated.

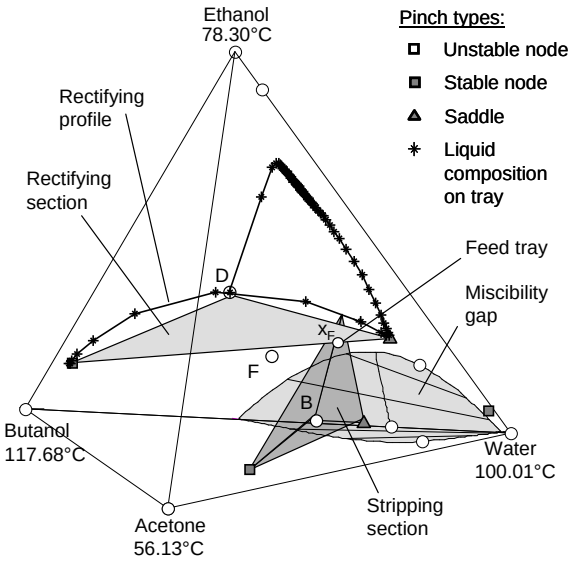

Figure 7. Rectification bodies and rectifying profile at MED as determined by the RBM for the intermediate separation of the heterogeneous mixture of acetone, ethanol, water, butanol

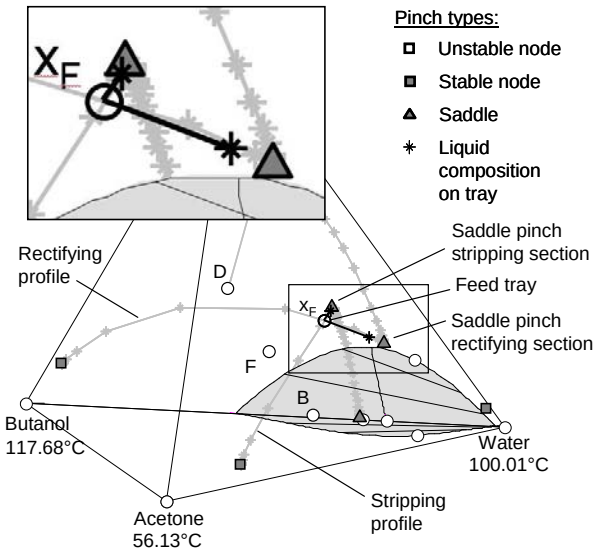

Figure 8. FAM: trays above and below the optimized feed tray at MED for the intermediate separation of the heterogeneous mixture of acetone, ethanol, water, butanol

Table 3. Compositions of acetone, ethanol, water, butanol, and MEDs

Molar composition	x_F 0.23/0.23/0.35/0.2	x_D 0.45/0.45/0.1/0	x_B 0/0/0.6/0.4	$Q_{b,min}/F$ [MJ/kmol]	RBM 39.6	FAM 44.2

5. Conclusions

The shortcut methods for heteroazeotropic distillation in the literature are either restricted by inaccuracies due to highly curved column profiles (RBM) or constant molar overflows (MAC, SSL), limited to ternary mixtures (BVM, MAC), or limited to separations with a feed pinch (MAC, ZVC, FPM, SSL). In this work, we proposed the feed angle method (FAM), which is based on rigorous thermodynamics, applicable to heterogeneous azeotropic mixtures with any number of components, and to any kind of sharp split. Initial values and the identification of the relevant pinch points are determined in an initialization with the RBM. In a way, the FAM can be interpreted as a sequential refinement of the RBM for highly nonideal mixtures, where an additional vertex is added to the linearized rectification bodies at the line or plane of intersection in order to account for the curvature of the profiles. The FAM requires the calculation of the separation pinches and only one tray per non-pinched column section. As consequence, the FAM is a highly efficient method which can easily be automated. It is expected that the computational efficiency of the FAM make it very attractive for the evaluation of multicolumn processes with recycles in future work.

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