

Research Article

A shortcut minimum reflux calculation method for distillation columns separating multicomponent homogeneous azeotropic mixtures

Zheyu Jiang¹¹ Crop Protection Product & Process Technology, Corteva Agriscience™, Indianapolis, USAEmail to zheyu.jiang@corteva.com

Abstract

Chemical, pharmaceutical, and agrochemical industries frequently face the challenge of separating multicomponent mixtures exhibiting one or more azeotropes using distillation. The minimum reflux ratio of a distillation column is directly related to its energy consumption and capital cost. Thus, it is a key parameter for distillation systems design, operation, and comparison. Despite its great scientific significance and practical importance, this problem remains an open challenge to researchers and industrial practitioners due to the highly nonideal nature of azeotropic systems. In this work, I present a simple and easy-to-use shortcut method to analytically calculate the minimum reflux ratio for a broad class of multicomponent homogeneous azeotropic mixture separations. Through an illustrative example, I demonstrate the accuracy and effectiveness of our new approach. I also show that the classic Underwood's method used for ideal multicomponent distillation turns out to be a special case of this generalized method. Compared with existing techniques, this method does not involve any rigorous tray-by-tray calculation and is iteration free. Therefore, it can be easily incorporated into a global optimization framework that enables industrial practitioners to, for the first time, quickly synthesize energy-efficient and cost-effective multicomponent azeotropic distillation systems and determine their optimal operating conditions.

distillation plays a critical role in the workup of active ingredient manufacturing process. For instance, solvent exchange, the distillation operation of switching from one solvent to another while retaining the solutes (e.g., active ingredients or intermediates) in solution, is common in industrial practice [6,22]. In addition, to reduce overall waste and environmental footprint as well as to improve process efficiency and economics, staged distillation is widely used as an effective way to recover and recycle valuable solvents [27]. One common issue these separation tasks frequently face is that the multicomponent systems involved are typically highly nonideal and form one or more azeotropes. As an azeotrope, the vapor that is in equilibrium with the liquid phase has the same composition as the liquid. Therefore, the liquid or vapor at azeotropic composition cannot be further separated by conventional distillation. As illustrated in the residue curve maps [5] of Figure 1, unlike non-azeotropic systems (e.g., Figure 1a), the presence of azeotropes poses a challenge to process engineers as the composition space is divided into two or more distinct distillation regions that restrict the feasible product composition a distillation column can achieve (e.g., Figure 1b), as the composition profile within the column cannot cross from one distillation region to another stay within one distillation region [31]. Moreover, due to the nonideality of the azeotropic system, a distillation region can sometimes be further divided into several distillation compartments (e.g., Figure 1c) in which residue curves within the distillation region start the same unstable node and terminate at the same stable node but approach different saddle points [29]. These characteristics significantly complicate the synthesis and design of energy-efficient and cost-effective azeotropic distillation systems. Process engineers must have a clear understanding of how a distillation column performs (e.g., purity of products) with respect to its internal liquid

Introduction

Distillation is an important separation process that accounts for 90-95% of all liquid separations and consumes more than 40% of energy in the chemical industry [13]. In pharmaceutical and agrochemical industries,

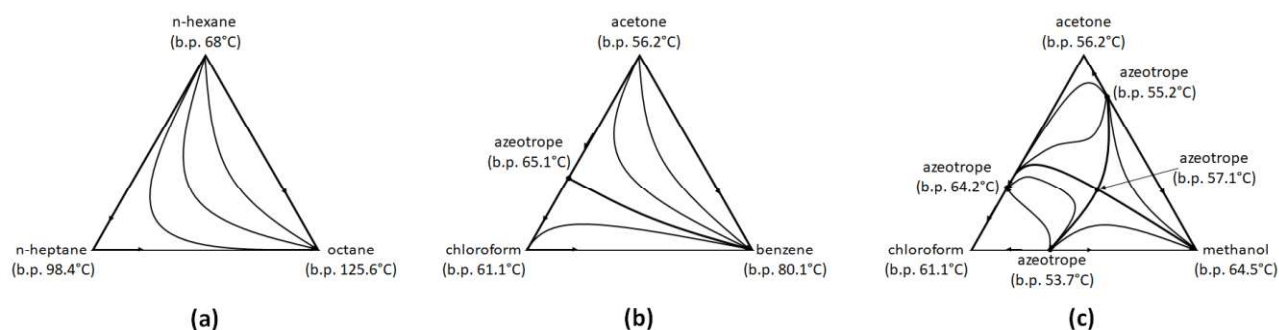


Figure 1. (a) Residue curve map of a typical 3-component zeotropic system, pointing in the direction of increasing time. (b) Residue curve map of a typical 3-component azeotropic system with a binary maximum boiling azeotrope. The composition space is divided by a distillation boundary into two distillation regions. (c) A residue curve map containing two distillation compartments inside a distillation region enclosed by acetone, the binary azeotrope between acetone and chloroform, the ternary azeotrope, and the binary azeotrope between acetone and methanol.

and vapor traffic subject to these complications before drawing any conceptual design.

The minimum reflux ratio of a distillation column, often characterized by the reboiler vapor duty requirement at *minimum reflux condition*, is an important parameter that provides critical information on the column's optimal design and operation [19]. With the knowledge of minimum reboiler vapor duty, process engineers can estimate the actual heat duty corresponding to the column's optimal performance [11]. The minimum reboiler vapor duty of a column also serves as a direct indicator for its capital cost, as it is closely related to the number of stages, height and diameter of the column, as well as the size of reboiler and condenser [14]. Because of these reasons, the minimum total reboiler vapor duty requirement has been extensively chosen as the objective function for comparing and rank listing different distillation configurations [8,9,25]. Hence, a fast and accurate determination of the true minimum reflux ratio is crucial for synthesizing attractive multicomponent distillation systems, whereas failing to do so often leads to inefficient and unnecessarily large columns being built and operated.

Over the past decades, several attempts have been made to determine the minimum reflux condition for highly non-ideal or even azeotropic mixture distillations. Levy et al. [21] introduced the boundary value method (BVM) based on tray-by-tray calculation of column composition profiles. For a separation to be feasible, the rectifying section composition profile must intersect the stripping section profile. The minimum reflux ratio corresponds to the smallest reflux ratio that makes the intersection of both composition profiles possible. Nevertheless, there are two major drawbacks of BVM: first, the tray-by-tray calculation in BVM is highly sensitive to the composition of the vanishing components in the product stream; and second, BVM cannot be applied to mixtures with more than four components. To address these drawbacks, Julka and Doherty [16] extended the BVM and developed the zero-volume criterion (ZVC), an algebraic criterion for minimum reflux based on collinearity of feed composition and different pinch points. Since the ZVC can be checked using a simple determinant formula, it can be applied to any number of components in theory. However, the method is limited to only direct and indirect splits, since the pinch points that determine the minimum reflux ratio must be known *a priori*. Later, Koehler et al. [18] proposed an empirical minimum angle criterion (MAC) and claimed that it improved the ZVC. Yet, the MAC does not really have any physical basis for quaternary separations and above. Also, it was shown that the MAC fails when no pinch point is located at the feed stage and the feed is not introduced as saturated liquid. Poellmann et al. [26] presented an eigenvalue criterion that can be considered as a hybrid of the BVM and ZVC, in the sense that only part of the composition profile is obtained by tray-by-tray calculations and the minimum reflux ratio corresponds to the smallest reflux ratio at which the composition profile within one column section intersects a pinch point of the other column section. However, this approach requires tremendous computational efforts. Finally, Bausa et al. [2] developed the rectification body method (RBM) that has attracted great research attention [3,20,23,34]. The rectification body of a column section is constructed by joining points on the branches of pinch point curves with straight lines. The minimum reflux condition is determined in an iterative manner when the rectification body of the rectifying section just touches that of the stripping section. Unfortunately, the calculation of pinch point curves is known to be computationally intensive [23]. Also, the iterative nature of the RBM algorithm creates additional computational challenges that hinder it from solving large-scale problems or being incorporated into a global optimization framework. In summary, there is a need to develop an

accurate and easy-to-use shortcut method that does not involve rigorous tray-by-tray calculations or tedious iterations.

Preliminaries and Background Information

The singular points in a residue curve map are compositions at which the driving force for the change in liquid composition is zero. Thus, any pure component or azeotropic point in the composition space corresponds to a singular point. In fact, it has been shown that azeotropes behave exactly like pure components for binary [1] and multicomponent systems [33]. Therefore, an azeotrope can be treated as a pseudo-component. In this regard, a distillation region or compartment forms a new composition space. For example, for the binary system of ethanol and benzene, the minimum boiling azeotrope (44.8 mol% ethanol at 1 atm) can be viewed as a pseudo-component (Figure 2), which decomposes the original composition space into two new spaces [32]. Any mixture composition can be linearly transformed to a new coordinate system based on which decomposed composition space the mixture composition lies in. Next, each decomposed space can now be approximated as an ideal binary system, thereby enabling process engineers to use various shortcut methods such as the well-known McCabe-Thiele method to estimate the minimum reflux ratio [1]. While Liu et al. [23] and Yang et al. [34] have successfully extended this concept to multicomponent azeotropic systems, I would like to point out that whether such an extension is possible depends on the specific topology of the azeotropic system. Specifically, for a c -component azeotropic system to be applicable to such extension, every decomposed composition space must contain exactly c singular points with 1 stable node, 1 unstable node, and $c - 2$ saddle points. Most azeotropic systems that were studied and reported in literature satisfy this rule [17], with only a few exceptions such as the acetone/benzene/n-heptane ternary system (Figure 3a). Among the 1783 published 3-component azeotropic systems summarized by Kiva et al. [17], more than 80% of them belong to five major topological classes as illustrated in Figures 3b thru 3f, all of which fulfill this rule.

Minimum reflux calculation using shortcut methods requires relative volatility information of all pure components and azeotropes to be available. Conventionally, relative volatility of a pure component is defined as the ratio of equilibrium constant (K -value) of the component with respect to that of the least volatile pure component. However, in a distillation column, the temperature varies substantially from top to bottom. Consequently, K -values, and in turn relative volatilities, vary substantially across the column. Furthermore, in the presence of an azeotrope, even the

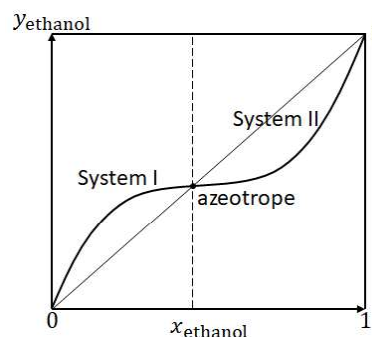


Figure 2. The binary azeotropic system of ethanol/benzene can be decomposed into two distillation zones, each approximated as an ideal binary system. The azeotrope is now treated as a pseudo-component.

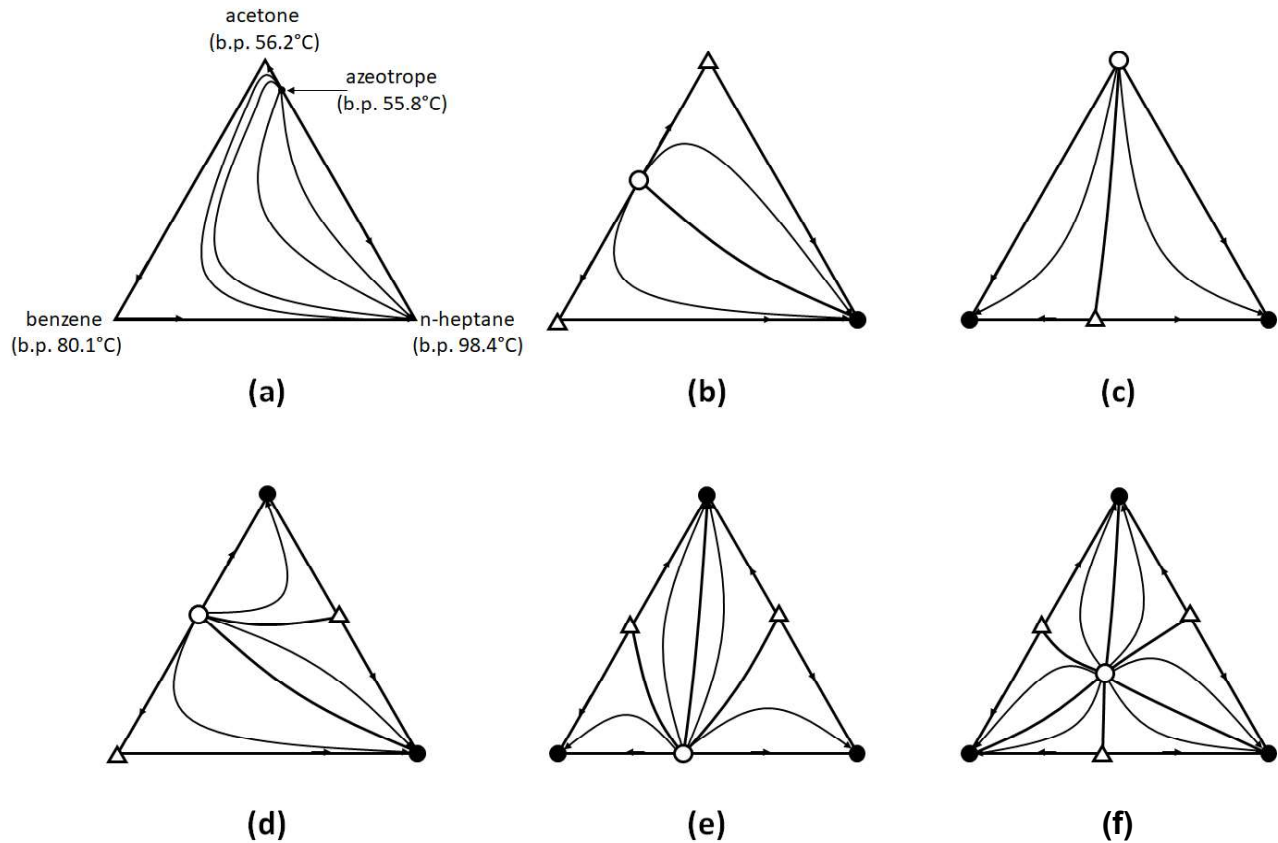


Figure 3. (a) An exception case to the general rule of composition space decomposition and transformation, since not every decomposed composition space contains exactly 1 stable node, 1 unstable node, and 1 saddle point. (b)-(f) Topological structures of the five most common ternary azeotropic systems. In these figures, unfilled circles, triangles, and filled circles represent unstable nodes, saddle points, and stable nodes, respectively.

order of relative volatility of each pure component and azeotrope changes from one distillation region/compartment to another. Thus, to treat each decomposed composition space as an ideal system and to utilize the constant relative volatility assumption in our shortcut method, I develop an alternative approach to estimate relative volatilities of pure components and azeotropes. For c -component azeotropic mixture separation, given a distillation region/compartment in which the feed composition lies, I first generate a series of residue curves by rigorous simulations and transform them into the new coordinate system corresponding to the respective decomposed composition space. Then, I solve an unconstrained minimization problem that determines the relative volatilities $\{\alpha_i\}_{i=1}^c$ for the c components and pseudo-components such that the transformed residue curve VLE can be closely approximated by the ideal VLE surrogate of Equation 1 in least-square error sense:

$$\bar{y}_i = \frac{\alpha_i \bar{x}_i}{\sum_{j=1}^c \alpha_j \bar{x}_j} \quad \forall i \in \{1, \dots, c\}, \quad (1)$$

where \bar{x}_i and \bar{y}_i respectively denote the liquid and vapor phase molar fraction of component or pseudo-component i in the transformed composition space, and α_i is the relative volatility of component i with respect to the least volatile component (component 1). By convention, we have $\alpha_c > \alpha_{c-1} > \dots > \alpha_2 > \alpha_1 = 1$.

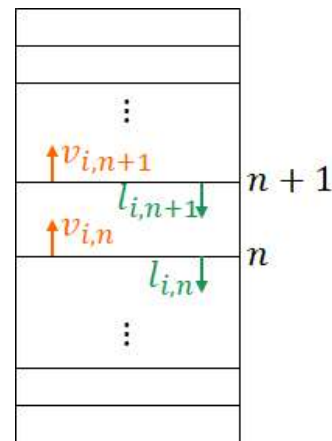


Figure 4. Schematic diagram of the rectifying section, in which the vapor and liquid flow rate for component i leaving stage n based on the transformed composition are respectively given by $v_{i,n}$ and $l_{i,n}$.

Mathematical Formulation

Let us consider the rectifying section of an azeotropic distillation column (Figure 4) that involves a total of c pure components and pseudo-components. The same analysis approach follows for the stripping section. Under the simplifying assumption of constant molar overflow

For internal use only

(CMO) that has been extensively used and validated [15,24], the total vapor and liquid flow rate, respectively denoted as V and L , do not change from stage to stage within the column section. As a result, the overall distillate flow, defined as $D := V - L$, is constant as well. In terms of each individual component/pseudo-component i , its distillate flow rate d_i , which is given by $d_i = v_{i,n} - l_{i,n+1}$ for every $i = 1, \dots, c$ and $n = 1, 2, \dots$, also remains unchanged within the rectifying section. Here, $v_{i,n}$ and $l_{i,n}$ stand for the rectifying section vapor and liquid flow rate for component/pseudo-component i in the transformed composition space. In other words, $v_{i,n} = V\bar{y}_{i,n}$ and $l_{i,n} = L\bar{x}_{i,n}$. Note that for the rectifying section (resp. stripping section), $d_i \geq 0$ (resp. $d_i \leq 0$) for every component/pseudo-component i involved. Following the notations and conventions defined so far, the ideal VLE surrogate of Equation 1 is combined with the component mass balance equation above stage 1:

$$\begin{pmatrix} l_{1,2} \\ \vdots \\ l_{c,2} \end{pmatrix} = \frac{V}{\sum_j \alpha_j l_{j,1}} \begin{pmatrix} \alpha_1 l_{1,1} \\ \vdots \\ \alpha_c l_{c,1} \end{pmatrix} - \begin{pmatrix} d_1 \\ \vdots \\ d_c \end{pmatrix} = \frac{1}{\sum_j \alpha_j l_{j,1}} \mathbf{A} \begin{pmatrix} l_{1,1} \\ \vdots \\ l_{c,1} \end{pmatrix}, \quad (2)$$

in which the $c \times c$ matrix \mathbf{A} is defined as:

$$\mathbf{A} := \begin{pmatrix} \alpha_1(V - d_1) & \cdots & -\alpha_c d_1 \\ \vdots & \ddots & \vdots \\ -\alpha_1 d_c & \cdots & \alpha_c(V - d_c) \end{pmatrix}. \quad (3)$$

Note that all elements in matrix \mathbf{A} are independent of stage number. Clearly, the system of Equation 2 is highly nonlinear. To linearize it, I define new variables \mathcal{L}_1 and \mathcal{L}_2 , and rewrite the original nonlinear relation as:

$$\mathcal{L}_2 := \begin{pmatrix} l_{1,2} \\ \vdots \\ l_{c,2} \end{pmatrix} \sum_{j=1}^c \alpha_j l_{j,1} = \mathbf{A} \mathcal{L}_1 := \mathbf{A} \begin{pmatrix} l_{1,1} \\ \vdots \\ l_{c,1} \end{pmatrix}.$$

In general, \mathcal{L}_{n+1} is defined as:

$$\mathcal{L}_{n+1} := \begin{pmatrix} l_{1,n+1} \\ \vdots \\ l_{c,n+1} \end{pmatrix} \prod_{j=1}^n \sum_{i=1}^c \alpha_i l_{i,j}$$

Under this definition, one can show by induction that I have successfully transformed the nonlinear system of Equation 2 into the following linear recursive system:

$$\mathcal{L}_{n+1} = \mathbf{A} \mathcal{L}_n \quad n = 1, 2, \dots \quad (4)$$

The linear recursive relation of Equation 4 also leads us to further investigate the mathematical properties of \mathbf{A} as they may contain key information about the fixed-point solutions of the system. It can be verified that the characteristic polynomial of \mathbf{A} is given by:

$$\det(\lambda \mathbf{I} - \mathbf{A}) = \frac{1}{V} \left(V - \sum_{i=1}^c \frac{\alpha_i d_i}{\alpha_i - \lambda/V} \right) \prod_{i=1}^c (V \alpha_i - \lambda).$$

We can easily see that the eigenvalues of \mathbf{A} are simply:

$$\begin{aligned} \lambda_i &= V \alpha_i & \forall i \text{ such that } d_i &= 0, \\ \lambda_i &= V \gamma_i & \forall i \text{ such that } d_i &\neq 0, \end{aligned}$$

where γ_i represents the i th root of the following equation:

$$\sum_{j=1}^c \frac{\alpha_j d_j}{\alpha_j - \gamma_i} = V \quad \forall i = 1, \dots, c. \quad (5)$$

I follow the convention that $\alpha_c > \gamma_c > \alpha_{c-1} > \gamma_{c-1} > \alpha_{c-2} > \dots > \alpha_1 > \gamma_1$. Surprisingly, Equation 5 has the same mathematical form as the famous Underwood's distillate equation [30], except that $\{d_i\}_{i=1}^c$ are now in the transformed composition space. For each eigenvalue λ_i as determined in Equation 5, the corresponding eigenvector \mathbf{z}_i can be derived as:

$$\mathbf{z}_i = \left(\frac{\gamma_i d_1}{\alpha_1 - \gamma_i}, \dots, \frac{\gamma_i d_c}{\alpha_c - \gamma_i} \right)^T \quad \forall i = 1, \dots, c.$$

It turns out that these eigenvectors are closely related to the pinch zone composition. Recall that a pinch zone is a region within a column section where the liquid or vapor composition remains unchanged from stage to stage. When the section is pinched, the operating line of the distillation column intersects the VLE curve, resulting in zero dividing force for mass transfer from one stage to another. As discussed by *Franklin and Forsyth* [10] in the context of ideal multicomponent mixture distillations, each γ root to Equation 5 is associated with a unique pinch composition. Similarly, one can show that the liquid pinch composition associated with γ_i in the transformed space, denoted as Z_i , is simply given by:

$$Z_i = \frac{\mathbf{z}_i}{L} = \frac{1}{L} \left(\frac{\gamma_i d_1}{\alpha_1 - \gamma_i}, \dots, \frac{\gamma_i d_c}{\alpha_c - \gamma_i} \right)^T \quad \forall i = 1, \dots, c. \quad (6)$$

From Equations 5 and 6, all the c liquid pinch compositions are fully determined once $\{d_i\}_{i=1}^c$ as well as the total vapor or liquid flow are fixed. As a result, these pinches are intrinsic characteristics of the rectifying section, and they correspond to the fixed-point solutions to Equation 2. Furthermore, one can show that these c liquid pinch compositions are affinely independent. Geometrically, the convex hull of $\{Z_i\}_{i=1}^c$ forms a $(c-1)$ -dimensional simplex called the Z -simplex whose c vertices correspond to pinch compositions $\{Z_i\}_{i=1}^c$ and c facets, namely $\{z_i = 0\}_{i=1}^c$, are determined as:

$$z_i = \sum_{j=1}^c \frac{\alpha_j \bar{x}_j}{\alpha_j - \gamma_i} = 0 \quad \forall i = 1, \dots, c, \quad (7)$$

in which $\bar{X}:(\bar{x}_1, \dots, \bar{x}_c)$ establishes the coordinate system for the transformed composition space. And it is obtained through a linear mapping $T: X \rightarrow \bar{X}$ from the original composition space $X:(x_1, \dots, x_c)$. Any pinch composition Z_i simultaneously satisfies $z_j = 0$ of Equation 7 for all index $j \neq i$. It turns out that the exact composition profile within the rectifying section as well as the minimum reflux condition can be determined based on the information above. To understand this, let us consider any two adjacent stages, namely stages $n+1$ and n , in the rectifying section. Without substantiating the entire mathematical derivation, it can be shown that:

$$\frac{\sum_{k=1}^c \frac{\alpha_k \bar{x}_{k,n+1}}{\alpha_k - \gamma_i}}{\sum_{k=1}^c \frac{\alpha_k \bar{x}_{k,n+1}}{\alpha_k - \gamma_j}} = \left(\frac{\gamma_i}{\gamma_j} \right) \frac{\sum_{k=1}^c \frac{\alpha_k \bar{x}_{k,n}}{\alpha_k - \gamma_i}}{\sum_{k=1}^c \frac{\alpha_k \bar{x}_{k,n}}{\alpha_k - \gamma_j}} \quad \forall i \neq j \quad (8)$$

$\in \{1, \dots, c\}; n = 1, 2, \dots$

Equation 8 is analogous to the well-known Fenske equation [7] which relates the liquid composition on any two stages in a distillation column

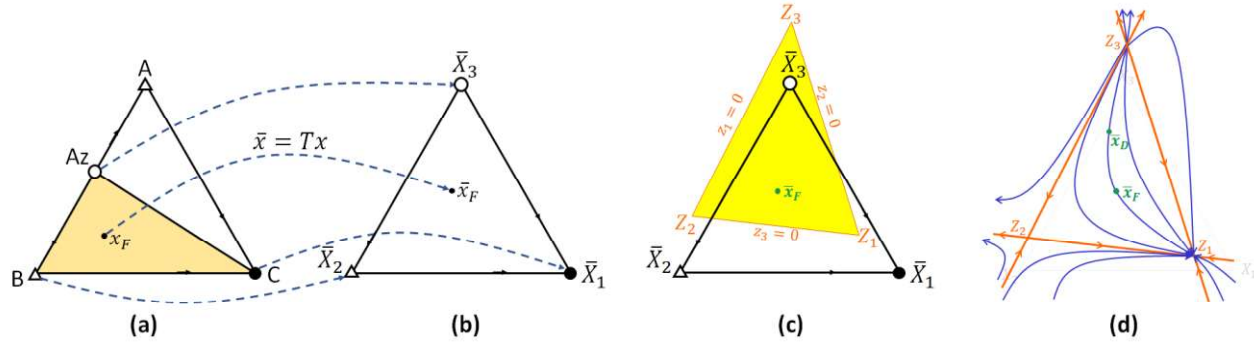


Figure 5. (a) The distillation region of interest drawn in the original composition space. (b) Through a linear mapping $T: X \rightarrow \bar{X}$, the original distillation region is transformed into a new composition space. (c) A Z-simplex can be constructed under the transformed composition space. (d) The Z-simplex can be used to generate all liquid composition profile patterns subject to a given distillate composition and total vapor or liquid flow rate in the column section. The arrows in these liquid composition profiles indicate the direction where liquid composition evolves as we move downward in the column section.

operated at total reflux condition. Solving Equation 8 recursively allows us to relate the liquid composition on any two stages in the transformed composition space. As this process is repeated infinitely many times in either forward or backward direction (i.e., the stage of interest lies infinitely above or below the starting point of stage n), the liquid composition will reach one of the pinch compositions $\{Z_i\}_{i=1}^c$.

For better illustration of Equation 8 and the entire process, let us study the most common 3-component azeotropic system whose topological structure is drawn in Figure 3b [17]. With a binary minimum boiling azeotrope Az between the intermediate component B and the heaviest component C , the original composition space is decomposed into two distinct distillation regions. Suppose the feed composition lies in the lower distillation region enclosed by Az , B , and C (Figure 5a). Through $T: X \rightarrow \bar{X}$, all feasible compositions within the distillation region are mapped to the transformed composition space (Figure 5b) whose vertices are given by $\bar{X}_3 = (0,0,1)$ (mapped from azeotrope Az), $\bar{X}_2 = (0,1,0)$ (mapped from component B), and $\bar{X}_1 = (1,0,0)$ (mapped from component C). Under the transformed composition space, a 2-dimensional Z-simplex, $Z_3Z_2Z_1$, is drawn (Figure 5c) by solving Equations 5 thru 7 for a given distillate product flows $\{d_i\}_{i=1}^c$ and rectifying section vapor flow V . Next, the liquid composition profile bundle that captures all possible liquid composition profile patterns is obtained from Equation 8 at different starting compositions in the transformed space (Figure 5d). As we can see, if the starting composition (e.g., distillate liquid composition x_D) lies in the interior of $Z_3Z_2Z_1$, then applying Equation 8 infinitely many times in the forward and backward direction ultimately leads to Z_3 as the unstable node pinch and Z_1 as the stable node pinch. Z_3 , on the other hand, corresponds to a saddle pinch that can only be reached when the starting liquid composition lies on the simplex facets $z_3 = 0$ or $z_1 = 0$. In general, for a c -component system, Z_c and Z_1 represent the stable node pinch and unstable node pinch, respectively. All other vertices of the Z-simplex, namely Z_{c-1} to Z_2 , are saddle pinches that can only be reached when the starting liquid composition resides on a facet or intersection of facets.

Like the rectifying section, a $(c-1)$ -dimensional Z-simplex can also be constructed for the stripping section given the stripping section vapor flow and bottoms product component flows $\{b_i\}_{i=1}^c$ in the transformed space. To do this, one can solve the stripping section version of Equation 5 for $\{\phi_i\}_{i=1}^c$:

$$\sum_{j=1}^c \frac{\alpha_j b_j}{\alpha_j - \phi_i} = -V' \quad \forall i = 1, \dots, c, \quad (9)$$

where V' stands for the stripping section vapor flow and is related to the rectifying section vapor flow V via the vapor balance: $V' + V_{\text{feed}} = V$. Here, V_{feed} stands for the feed stream vapor flow. $\{\phi_i\}_{i=1}^c$ follow the convention that $\phi_c > \alpha_c > \phi_{c-1} > \alpha_{c-1} > \dots > \phi_1 > \alpha_1 = 1$. Recognize that Equation 9 has the same mathematical form as Underwood's bottoms equation [30], except that $\{b_i\}_{i=1}^c$ are now in the transformed composition space.

After all, $\{\phi_i\}_{i=1}^c$ roots are determined, construct the Z-simplex for the stripping section by locating all of the c liquid pinches $\{Z'_i\}_{i=1}^c$:

$$Z'_i = \frac{1}{L'} \left(-\frac{\phi_i b_1}{\alpha_1 - \phi_i}, \dots, -\frac{\phi_i b_c}{\alpha_c - \phi_i} \right)^T \quad \forall i = 1, \dots, c, \quad (10)$$

as well as the c facets, namely $\{z'_i = 0\}_{i=1}^c$, are determined as:

$$z'_i = \sum_{j=1}^c \frac{\alpha_j \bar{x}_j}{\alpha_j - \phi_i} = 0 \quad \forall i = 1, \dots, c. \quad (11)$$

Minimum Reflux Condition for Azeotropic Distillation

To determine the minimum reflux ratio of an azeotropic distillation column, the Z-simplices for both rectifying and stripping sections are constructed simultaneously. When the distillation column is operated above the minimum reflux, the desired separation can be achieved with finite number of stages; whereas when the column is at minimum reflux, the desired separation can be achieved using infinite number of stages. In other words, both column sections are pinched at minimum reflux condition. When a given separation can be achieved, this means that the composition profile within the column is continuous and the desired product specifications (flow rate and composition) are met for both product streams. If the reflux ratio is further reduced below the minimum reflux ratio, even by an infinitesimal amount, the desired separation can no longer be achieved, even with infinite stages, because the composition profile in the column does not form a continuous path anymore.

How is this related to the Z-simplex? As shown for a 3-component separation example of Figure 6, a continuous path that connects the distillate composition (red dot) and the bottoms composition (black dot) is required

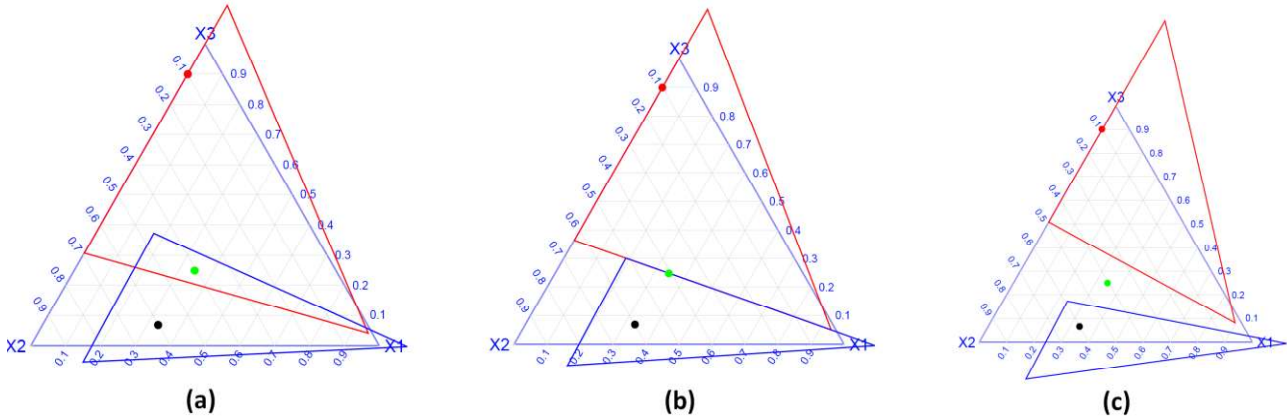


Figure 6. The Z-simplex diagram of a distillation column operated (a) above minimum reflux; (b) at minimum reflux; (c) below minimum reflux. The red and blue Z-simplices describe the rectifying section and stripping section, respectively. The red, green, and black dots represent the liquid composition of distillate, feed, and bottoms product in the transformed composition space, respectively. Note that the feed is not in saturated liquid state, otherwise the feed composition is colinear with distillate and bottoms product compositions.

for a feasible separation. This implies that, with the distillation and bottoms product composition respectively lying on the $z_1 = 0$ boundary of rectifying section Z-simplex and inside the stripping section Z-simplex, these two Z-simplices must share a common region (Figure 6a). As the reflux ratio decreases, both Z-simplices start to move and eventually just touch each other by sharing a common edge (Figure 6b). This corresponds to the minimum reflux condition. If the reflux ratio is further reduced, the two Z-simplices are completely separated (Figure 6c). From Equations 7 and 11, it can be immediately observed that the minimum reflux condition illustrated in Figure 6b is equivalent to the relation $\gamma_3 = \phi_2$, which I denote as $\theta_2 \in (\alpha_2, \alpha_3)$. Substituting this root equality into Equations 5 and 9 and combining with overall mass balance produces the following equation:

$$\sum_{j=1}^3 \frac{\alpha_j f_j}{\alpha_j - \theta_2} = V_{\text{feed}},$$

where $f_i = d_i + b_i$ represents the feed flow rate of component/pseudo-component i in the transformed composition space. Once θ_2 is determined from the equation above, it is substituted back to Equation 5 for minimum rectifying section vapor flow calculation, from which the minimum reflux ratio is immediately implied: $R_{\min} = \frac{L}{D} = \frac{V}{D} - 1$. In the general case of a c -component system, one can directly solve for a total of $c - 1$ θ roots to the equation:

$$\sum_{j=1}^c \frac{\alpha_j f_j}{\alpha_j - \theta_i} = V_{\text{feed}} \quad \forall i = 1, \dots, c - 1. \quad (12)$$

Recognize that Equation 12 matches with Underwood's feed equation [30]. In other words, the classic Underwood's method for determining the minimum reflux condition for ideal multicomponent distillation turns out to be just a special case of Equation 12 when decomposition/no composition space transformation is applied. I believe that the derivations presented above contribute the first rigorous shortcut method that calculates

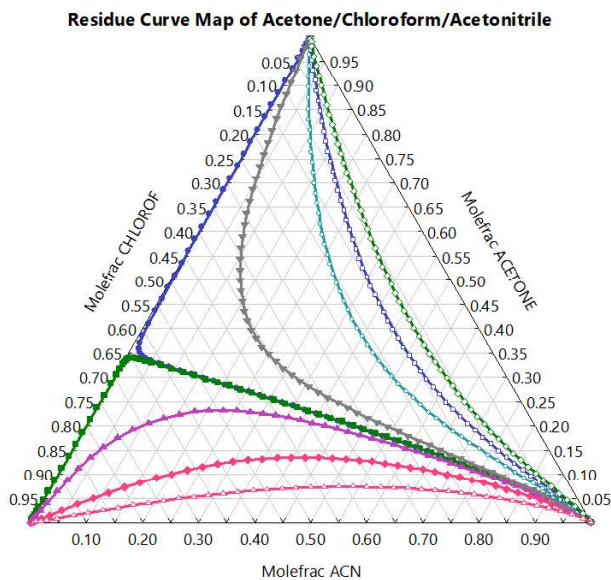


Figure 7. The residue curve map of acetone/chloroform/acetonitrile ternary system, with a binary maximum boiling azeotrope at 34.1 mol% acetone/65.9 mol% chloroform.

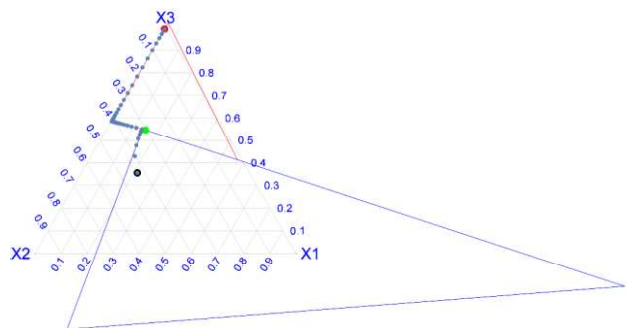


Figure 8. The Z-simplex diagram at minimum reflux. The rectifying and stripping section Z-simplices share a common edge in which the feed composition lies. The blue dots correspond to the actual liquid composition profile within the distillation column at minimum reflux, which is obtained from rigorous Aspen Plus simulations.

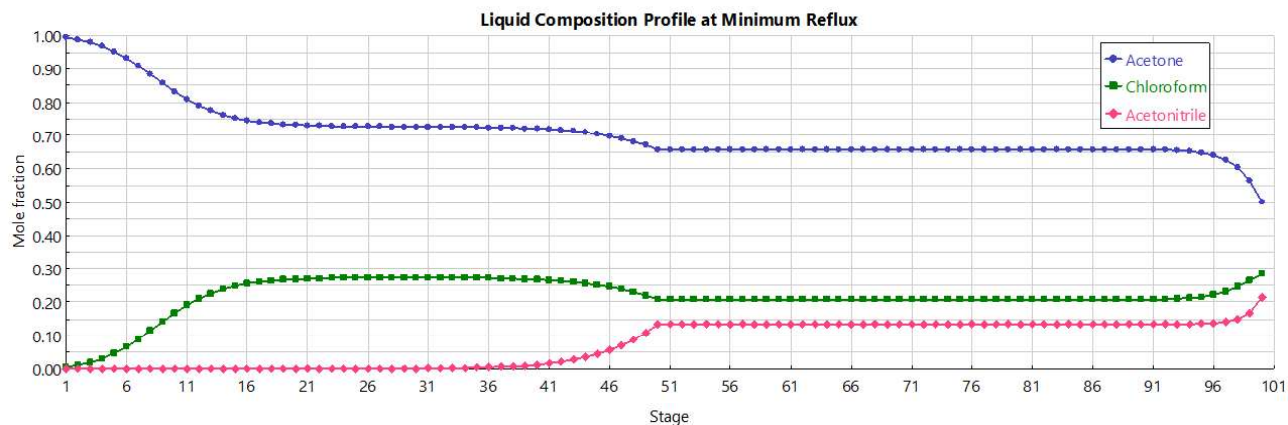


Figure 9. The actual liquid composition profile within the column at minimum reflux. Both column sections are given sufficient number of stages to ensure that the true minimum reflux is achieved.

the minimum reflux ratio for multicomponent azeotropic distillation columns. Also, depending on what the light and heavy key components are, there may be more than one active θ root that needs to be identified from Equation 12 and evaluated in Equation 5 for minimum reflux ratio calculation. In fact, the true minimum reflux ratio corresponds to the largest reflux ratio calculated from Equation 5 using all active θ roots, the ones that lie within the relative volatilities of the heavy and light key components. In the example of Figure 6b, since the distillate product is free of the heaviest component 1 and the bottoms product contains all three components in significant amount, the light and heavy key components for this separation are components 3 and 2, respectively [12]. As a result, the active θ root to Equation 12 corresponds to $\theta_2 \in (\alpha_2, \alpha_3)$.

Finally, I believe that, compared to existing approaches published in the literature, this shortcut method is particularly amenable to be incorporated into a global optimization framework. The equations are structurally simple and possess several properties that are useful in constructing tight LP/MIP relaxations that are critical to the convergence of any standard branch-and-bound algorithm. Additionally, compared to existing approaches, the proposed algorithm for calculating the minimum reflux ratio does not involve rigorous tray-by-tray calculations. Furthermore, advanced bound tightening strategies and effective relaxation techniques for nonlinear constraints like Equations 5, 9, and 12 have been deeply studied, developed, and implemented in the operations research community [25,28]. Discussion and implementation of a global optimization framework built upon this shortcut method will be presented in a separate article.

An Illustrative Example

To demonstrate the accuracy and effectiveness of this shortcut method, I examined a ternary system of acetone/chloroform/acetonitrile, which consists of a binary maximum boiling azeotrope (b.p. 64.04 °C) at 34.1 mol% acetone/65.9 mol% chloroform. The topological class of this azeotropic system is shown in Figure 3c [17]. The residue curve map (Figure 7) is synthesized via rigorous Aspen Plus simulations using the NRTL (Non-Random Two-Liquid) activity coefficient model. The residue curve map shows, the distillation boundary between acetonitrile and the binary azeotropic point (Az) separates the composition space into two distillation regions. In this example, let us consider distilling 1000 mol/hr. of saturated liquid feed with 65 mol% acetone, 20 mol% chloroform, and 15 mol% of acetonitrile. The feed composition lies in the distillation region

enclosed by acetone, the azeotrope Az , and acetonitrile. Hence, one can apply the following linear mapping that transforms this distillation region into a new ternary composition space:

$$T = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{0.659} & 0 \\ 0 & 1 - \frac{1}{0.659} & 1 \end{pmatrix}.$$

It can be shown that acetone (original coordinate (0,0,1)), azeotrope (original coordinate (0,0.659,0.341)), and acetonitrile (original coordinate (1,0,0)) have been mapped to $\bar{X}_3 = (0,0,1)$, $\bar{X}_2 = (0,1,0)$, and $\bar{X}_1 = (1,0,0)$, respectively.

Using the parameter estimation procedure described above, I calculate the relative volatilities of acetone (i.e., α_3) and azeotrope Az (i.e., α_2) with respect to acetonitrile to be 2.1 and 1.2, respectively. The distillate product has a flow rate of 300 mol/hr. and contains 99.50 mol% of acetone, 0.50 mol% of chloroform, and negligible quantity of acetonitrile. Hence, the bottoms product flow rate is 700 mol/hr. and contains 50.21 mol% of acetone, 28.36 mol% of chloroform, and 21.43 mol% of acetonitrile. The distillate and bottoms products in the transformed space are calculated to be $(d_1, d_2, d_3) = 300 \times (0.9924, 0.0076, 0)$ and $(b_1, b_2, b_3) = 700 \times (0.2143, 0.4303, 0.3554)$, respectively. Based on this information, one can readily see that the active θ root to Equation 12 is given by θ_2 , which is substituted to Equation 5 to give:

$$R_{\min} = \frac{1}{D} \sum_{j=1}^3 \frac{\alpha_j d_j}{\alpha_j - \theta_2} - 1 = 2.183.$$

I constructed the Z-simplex diagram shown in Figure 8 to visualize the minimum reflux condition. As can be seen, the two Z-simplices share a common edge which corresponds to the root equality of $\theta_2 = \gamma_3 = \phi_2$. If the reflux ratio is ever reduced, these two Z-simplices no longer intersect. It is further verified the minimum reflux condition for separation by rigorous tray-by-tray calculations using Aspen Plus. Each of the two column sections is given 50 theoretical stages to ensure that the true minimum reflux is truly achieved (Figure 9). Aspen Plus gives its minimum reflux ratio prediction of 2.174, which is only 0.46% different compared to our

shortcut calculation result. The actual liquid composition profile determined from rigorous simulation is also mapped to the new composition space and drawn along with the Z -simplex diagram in Figure 8. As can be seen, the actual liquid composition inside the distillation column nicely follows the liquid composition profile bundle corresponding to the Z -simplex as shown in Figure 5d. Keep in mind that this shortcut method only involves simple, noniterative computations and can be completely automated into a straightforward algorithm.

Conclusion

Multicomponent azeotropic distillation is an important separation process extensively used in chemical, pharmaceutical, and agrochemical industries. The minimum reflux ratio of a distillation column is related to its energy consumption and capital cost, and thus is a key parameter in distillation column design and operation. In this work, I present the first rigorous shortcut method to calculate the minimum reflux ratio of a distillation column separating a broad class of multicomponent azeotropic distillation systems. To solve the longstanding problem in chemical engineering, I first decompose the composition space into distinct distillation regions based on the specific topological structure of the azeotropic system. Then, each distillation region is transformed into a new composition space by treating azeotropes as pseudo-components. By carefully choosing the relative volatility parameters, the VLE relations for all components and pseudo-components in the transformed composition space can be accurately approximated by an ideal VLE surrogate, which, when coupling with constant molar overflow assumptions, gives the first shortcut mathematical model for multicomponent azeotropic distillation. I then studied the mathematical properties associated with this model and explored the geometric interpretation of minimum reflux condition based on simplex geometry. These geometric interpretations are equivalent to a set of algebraic constraints which can be incorporated into an optimization algorithm with guaranteed global optimality by using state-of-the-art global solvers such as BARON [28]. Compared with existing approaches, our proposed method is simple, accurate, and easy-to-use. As expected, the mathematical model and constraints developed in this work reduces to the classic Underwood's method in the case of ideal mixture separations.

References

1. Anderson N.J. and Doherty M.F. An approximate model for binary azeotropic distillation design. *Chemical Engineering Science* **1984**, 39, 11-19.
2. Bausa J., Watzdorf R.V. and Marquardt W. Shortcut methods for nonideal multicomponent distillation: 1. Simple columns. *AIChE Journal* **1998**, 44, 2181-2198.
3. Brüggemann S. and Marquardt W. Shortcut methods for nonideal multicomponent distillation. 3. Extractive distillation columns. *AIChE Journal* **2004**, 50, 1129-1149.
4. Carlberg N.A. and Westerberg A.W. Temperature-heat diagrams for complex columns. 2. Underwood's method for side strippers and enrichers. *Industrial & Engineering Chemistry Research* **1989**, 28, 1379-1386.
5. Doherty M.F. and Perkins J.D. On the dynamics of distillation processes III. The topological structure of ternary residue curve maps. *Chemical Engineering Science* **1979**, 34, 1401-1414.
6. Fazlollahi F. and Wankat P.C. Novel solvent exchange distillation column. *Chemical Engineering Science* **2018**, 184, 216-228.
7. Fenske M.R. Fractionation of straight-run Pennsylvania gasoline. *Industrial & Engineering Chemistry* **1932**, 24, 482-485.
8. Fidkowski Z. and Agrawal R. Multicomponent thermally coupled systems of distillation columns at minimum reflux. *AIChE Journal* **2001**, 47, 2713-2724.
9. Fidkowski Z. and Królikowski L. Minimum energy requirements of thermally coupled distillation systems. *AIChE Journal* **1987**, 33, 643-653.
10. Franklin N.L. and Forsyth J.S. The interpretation of minimum reflux conditions in multi-component distillation. *Transactions of the Institution of Chemical Engineers* **1953**, 31, S56 - S81.
11. Gilliland E.R. Multicomponent rectification. *Industrial and Engineering Chemistry* **1940**, 32, 1101-1106.
12. Halvorsen I.J. and Skogestad S. Minimum energy consumption in multicomponent distillation. 1. Vmin diagram for a two-product column. *Industrial & Engineering Chemistry Research* **2003**, 42, 596-604.
13. Humphrey J.L. and Siebert A.F. Separation technologies: An opportunity for energy savings. *Chemical Engineering Progress* **1992**, 88, 32-41.
14. Jiang Z., Mathew T.J., Zhang H., Huff J., Nallasivam U., Tawarmalani M. and Agrawal R. Global optimization of multicomponent distillation configurations: Global minimization of total cost for multicomponent mixture separations. *Computers & Chemical Engineering* **2019**, 126, 249-262.
15. Jiang Z., Tawarmalani M. and Agrawal R. An accurate minimum reflux calculation method for multi-feed, multi-product distillation columns distilling ideal multicomponent mixtures: 1. Mathematical model. In preparation. **2020**
16. Julka V. and Doherty M.F. Geometric behavior and minimum flows for nonideal multicomponent distillation. *Chemical Engineering Science* **1990**, 45, 1801-1822.
17. Kiva V.N., Hilmen E.K. and Skogestad S. Azeotropic phase equilibrium diagrams: a survey. *Chemical Engineering Science* **2003**, 58, 1903-1953.
18. Koehler J., Aguirre P. and Blass E. Minimum reflux calculations for nonideal mixtures using the reversible distillation model. *Chemical Engineering Science* **1991**, 46, 3007-3021.
19. Koehler J., Poellmann P. and Blass E. A review on minimum energy calculations for ideal and nonideal distillations. *Industrial & Engineering Chemistry Research* **1995**, 34, 1003-1020.
20. Kossack S., Kraemer K. and Marquardt W. Efficient optimization-based design of distillation columns for homogeneous azeotropic mixtures. *Industrial & Engineering Chemistry Research* **2006**, 45, 8492-8502.
21. Levy G.S., Van Dongen D.B. and Doherty M.F. Design and synthesis of homogeneous azeotropic distillations. 2. Minimum reflux calculations for nonideal and azeotropic columns. *Industrial and Engineering Chemistry Fundamentals* **1985**, 24, 463-474.
22. Li Y.E., Yang Y., Kalthod V., and Tyler S.M. Optimization of solvent chasing in API manufacturing process: constant volume distillation. *Organic Process Research & Development* **2009**, 13, 73-77.
23. Liu G., Jobson M., Smith R. and Wahnschafft O.M. Shortcut design method for columns separating azeotropic mixtures. *Industrial & Engineering Chemistry Research* **2004**, 43, 3908-3923.
24. Madenoor Ramapriya G., Selvarajah A., Jimenez Cucaita L.E., Huff J., Tawarmalani M. and Agrawal R. Short-cut methods versus rigorous methods for performance-evaluation of distillation configurations. *Industrial & Engineering Chemistry Research* **2018**, 57, 7726-7731.
25. Nallasivam U., Shah V.H., Shenvi A.A., Huff J., Tawarmalani M. and Agrawal R. Global optimization of multicomponent distillation configurations: 2. Enumeration based global minimization algorithm. *AIChE Journal* **2016**, 62, 2071-2086.

26. Poellmann P., Glanz S. and Blass E. Calculating minimum reflux of non-ideal multicomponent distillation using eigenvalue theory. *Computers & Chemical Engineering* **1994**, 18, S49-S53.
27. Seyler C., Capello C., Hellweg S., Bruder C., Bayne D., Huwiler A. and Hungerbühler K. Waste-solvent management as an element of green chemistry: A comprehensive study on the Swiss chemical industry. *Industrial & Engineering Chemistry Research* **2006**, 45, 7700-7709.
28. Tawarmalani M. and Sahinidis N.V. A polyhedral branch-and-cut approach to global optimization. *Mathematical Programming* **2005**, 103, 225-249.
29. Thong D.Y.C. and Jobson M. Multicomponent homogenous azeotropic distillation. 1. Assessing product feasibility. *Chemical Engineering Science* **2001**, 56, 4369-4391.
30. Underwood A.J.V. Fractional distillation of multicomponent mixtures – Calculation of minimum reflux ratio *Journal of the Institute of Petroleum* **1946**, 32, 614-626.
31. Van Dogen D.B. and Doherty M.F. Design and synthesis of homogeneous azeotropic distillations. 1. Problem formulation for a single column. *Industrial & Engineering Chemistry Research* **1985**, 24, 454-463.
32. Vogelpohl A. Die näherungsweise Berechnung der Rektifikation von Gemischen mit binären Azeotropen. *Chemie Ingenieur Technik* **1974**, 46, 195.
33. Vogelpohl A. On the relation between ideal and real systems in ternary distillation. *Chemical Engineering Research and Design* **1999**, 77, 487-492.
34. Yang X., Dong H.G. and Grossmann I.E. A framework for synthesizing the optimal separation process of azeotropic mixtures. *AIChE Journal* **2012**, 58, 1487-1502.