

A SHORTCUT MODEL FOR MULTICOMPONENT HOMOGENEOUS AZEOTROPIC DISTILLATION

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Abstract

Distillation of multicomponent mixtures forming one or more azeotropes is ubiquitous in chemical process industries. 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. However, this problem remains an open challenge to researchers and industrial practitioners due to the highly nonideal nature of azeotropic systems. In this work, we 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. Compared with existing techniques, this method does not involve any rigorous tray-by-tray calculation and is iteration free. Through an illustrative example, we demonstrate the accuracy and effectiveness of this new approach.

Keywords

Multicomponent distillation, Azeotropic Distillation, Shortcut model, Minimum reflux ratio.

Introduction

Distillation is an important separation process that accounts for 90-95% of all liquid separations and consumes more than 40-70% of energy in chemical process industries (Humphrey, 1992). For multicomponent distillation, one common challenge frequently faced by process engineers is that the multicomponent systems involved are highly non-ideal and form one or more azeotropes. At 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 of Figure 1, unlike zeotropic systems (*e.g.*, Figure 1a), the presence of azeotropes poses complexities to the separation task 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 (Van Dongen and Doherty, 1985). Moreover, due to the non-ideality of the azeotropic system, a distillation region can sometimes be further divided into several distillation compartments (*e.g.*, Figure 1c) in which residue curves belonging to different compartments start from the same unstable node and terminate at the same stable node but approach different saddle points (Thong and Jobson, 2001). To synthesize and design efficient azeotropic distillation systems, process

engineers must have a clear understanding of how operating parameters (*e.g.*, reflux ratio, internal liquid and vapor traffic) affect column performance (*e.g.*, product purity).

The minimum reflux ratio of a distillation column, which directly translates to its reboiler vapor duty requirement at minimum reflux condition, is an important parameter that provides key information on the column's optimal design and operation (Koehler et al., 1995). With the knowledge of minimum reflux ratio, process engineers can estimate the actual heat duty requirement of the distillation column in operation. The minimum reflux ratio also serves as a direct indicator for the capital cost of a distillation column, as it is closely related to the number of stages, column diameter and height, as well as reboiler and condenser sizes (Jiang et al., 2019). Because of these reasons, the minimum reflux ratio has been commonly chosen as the objective function for optimizing, comparing and ranklisting different distillation column designs (Tumbalam Gooty et al., 2019). Hence, a fast and accurate determination of minimum reflux ratio is crucial for synthesizing and designing attractive multicomponent distillation systems, and failing to do so often leads to inefficient and unnecessarily large columns being built and operated.

Over the past decades, a number of research efforts have been made on minimum reflux calculation for highly non-ideal and azeotropic mixture distillations. Levy et al. (1985) introduced the boundary value method (BVM) based on tray-by-tray calculation of column composition profiles. The minimum reflux ratio corresponds to the smallest reflux ratio that ensures rectifying and stripping section composition profiles intersect with each other. However, such tray-by-tray calculation is highly sensitive to the composition of the key com-

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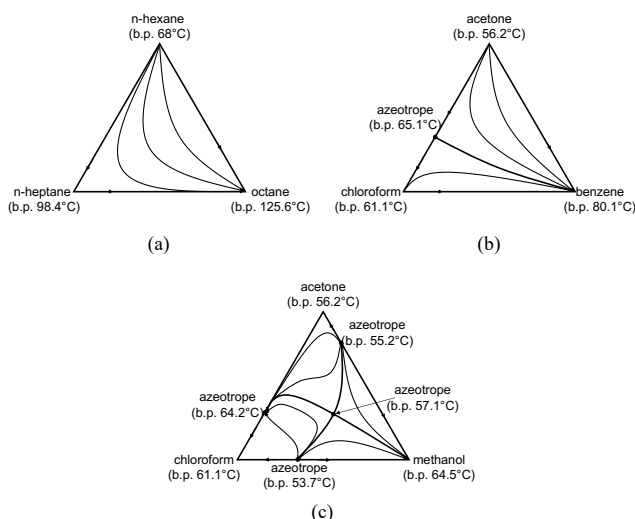


Figure 1: (a) Residue curve map of a typical 3-component zeotropic system, pointing in the direction of increasing time. (b) Residue curve map of a typical 3-component azeotropic system with a binary maximum boiling azeotrope. The composition space is divided by a distillation boundary into two distillation 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.

ponents in the product stream. Also, BVM cannot be applied to mixtures with more than four components. To address these drawbacks, Julka and Doherty (1990) 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. Nevertheless, ZVC is limited to only direct and indirect splits, thereby limiting its applicability and use. Later, Koehler et al. (1991) proposed an empirical minimum angle criterion (MAC) and claimed that it improved the ZVC. Yet, the MAC does not really have 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. (1994) presented an eigenvalue criterion (EC) that can be considered as a hybrid of the BVM and ZVC. However, this approach requires tremendous computational efforts. Finally, Bausa et al. (1998) developed the rectification body method (RBM) which constructs a pinch point curve and calculates the minimum reflux ratio in an iterative manner. Unfortunately, the calculation of pinch point curves is known to be computationally intensive (Liu et al., 2004; Jiang, 2020). Also, the iterative nature of the RBM algorithm leads to computational challenges that hinder it from solving large-scale problems. Thus, an accurate and easy-to-use shortcut method that does not involve rigorous tray-by-tray calculations or tedious iterations is yet to be developed.

Composition Space Decomposition

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 and multicomponent systems (Anderson and Doherty, 1984; Vogel, 1999). Therefore, an azeotrope can be treated as a pseudo-component, which decomposes the original composition space into two or more decomposed composition spaces. In this regard, each distillation compartment is essentially a decomposed composition space. Depending on which decomposed composition space it lies in, any mixture composition can be converted to a new coordinate through a linear transformation T . To illustrate, consider a common ternary system shown in Figure 4a with a binary minimum boiling azeotrope Az between the lightest component A and the intermediate component B. The original composition space can be decomposed into two distinct distillation compartments. Suppose the distillation column feed stream composition lies in the compartment enclosed by Az , B, and C. Through $T : X \rightarrow \bar{X}$, compositions of the distillation compartment of interest are mapped to the new coordinate system $\bar{X} = (\bar{x}_1, \dots, \bar{x}_c)$ (Figure 4b), whose vertices are $(\bar{x}_1, \bar{x}_2, \bar{x}_3) = (0, 0, 1)$ (mapped from azeotrope Az), $(\bar{x}_1, \bar{x}_2, \bar{x}_3) = (0, 1, 0)$ (mapped from component B), and $(\bar{x}_1, \bar{x}_2, \bar{x}_3) = (1, 0, 0)$ (mapped from component C). Of course, in order for such composition space decomposition to be physically feasible for a given c -component azeotropic system, each and every decomposed composition space must contain exactly c singular points with 1 stable node, 1 unstable node, and $c - 2$ saddle points. We point out that most azeotropic systems reported in literature satisfy this rule (Kiva et al., 2003), with only a few exceptions such as the acetone/benzene/n-heptane ternary system (see Figure 2a). In fact, among all of the 1783 published 3-component azeotropic systems summarized by Kiva et al. (2003), more than 80% of them belong to five major topological classes as illustrated in Figures 2b thru f, all of which fulfill this rule.

Minimum reflux calculation using shortcut methods typically assumes every component has a constant relative volatility (CRV). Conventionally, relative volatility of a pure component is defined as the ratio of its equilibrium constant with respect to that of the least volatile component. However, since the temperature varies substantially from top to bottom of a column, relative volatility values vary substantially as well. Furthermore, when azeotrope is present, even the relative volatility order of each pure component and azeotrope can be different from one distillation compartment to another. Thus, we extend the CRV assumption by developing a new procedure to approximate the VLE behavior in each decomposed composition space using constant relative volatilities. For a c -component azeotropic system, once we know in which distillation compartment the feed composition lies, we can generate a series of residue curves via simulation within the compartment. We then solve a minimization problem which identifies the optimal relative volatility set $\{\alpha_i\}_{i=1}^c$

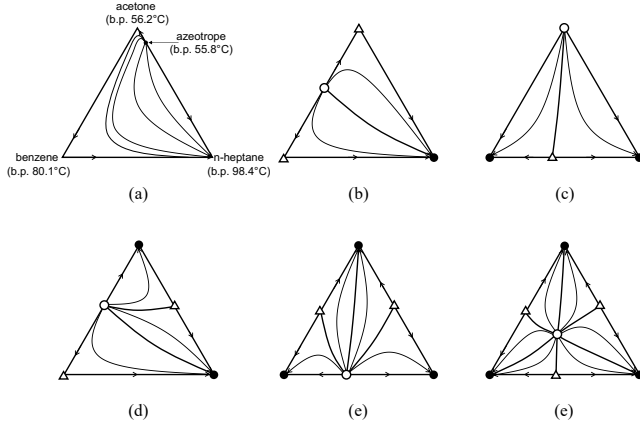


Figure 2: (a) An exception case to the general rule of composition space decomposition. (b)-(f) Topological structures of the five most common ternary azeotropic systems. Here and thereafter, unfilled circles, triangles, and filled circles represent unstable nodes, saddle points, and stable nodes, respectively.

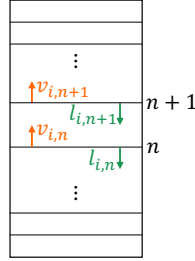


Figure 3: Schematic diagram of the rectifying section, in which the vapor and liquid flow rate for component i leaving stage n based on the transformed composition are respectively given by $v_{i,n}$ and $l_{i,n}$.

for the c pure components and/or azeotropes involved in the distillation compartment of interest, such that the root-mean-square error between simulated residue curves and an ideal VLE surrogate (Equation (1)) is minimized:

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

where \bar{x}_i and \bar{y}_i denote the liquid and vapor composition of pure component or azeotrope i in the new coordinate system for the transformed composition space, respectively. α_i is the relative volatility of i with respect to the least volatile pure component or azeotrope in the distillation compartment. We follow the convention that $\alpha_c > \dots > \alpha_1 = 1$.

Mathematical Modeling

We consider the rectifying section of an azeotropic distillation column (Figure 3). The same analysis approach follows for the stripping section. Under the constant molar overflow (CMO) assumption, which has been extensively validated (Jiang et al., 2022; Madenoor Ramapriya et al., 2018), the total vapor (V) and liquid (L) flow rates inside the section do not change from tray to tray. Thus, the total distillate

flow rate $D := V - L$ is also constant. According to component mass balance, for every $i \in C$, its component distillate flow rate $d_i = v_{i,n} - l_{i,n+1}$ also remains unchanged for all $n = 1, 2, \dots$ in the rectifying section. Here, $v_{i,n} := V \bar{y}_{i,n}$ and $l_{i,n} := L \bar{x}_{i,n}$. Note that in the rectifying (resp. stripping) section, $d_i \geq 0$ (resp. $d_i \leq 0$) for every $i \in C$. Let us consider two adjacent stages, namely $(n+1)$ and n , and substitute Equation (1) into component mass balance:

$$\begin{pmatrix} l_{1,n+1} \\ \vdots \\ l_{c,n+1} \end{pmatrix} = \frac{V}{\sum_{k=1}^c \alpha_k l_{k,n}} \begin{pmatrix} \alpha_1 l_{1,n} \\ \vdots \\ \alpha_c l_{c,n} \end{pmatrix} - \begin{pmatrix} d_1 \\ \vdots \\ d_c \end{pmatrix} = \frac{\mathbf{A}}{\sum_{k=1}^c \alpha_k l_{k,n}} \begin{pmatrix} l_{1,n} \\ \vdots \\ l_{c,n} \end{pmatrix}, \quad (2)$$

where \mathbf{A} is a $c \times c$ matrix defined as:

$$\mathbf{A} := \begin{pmatrix} \alpha_1(V - d_1) & -\alpha_2 d_1 & \dots & -\alpha_c d_1 \\ -\alpha_1 d_2 & \alpha_2(V - d_2) & \dots & -\alpha_c d_2 \\ \vdots & \vdots & \ddots & \vdots \\ -\alpha_1 d_c & -\alpha_2 d_c & \dots & \alpha_c(V - d_c) \end{pmatrix}. \quad (3)$$

We can linearize Equation (2) by defining a new vector $\mathcal{L}_n := (\mathcal{L}_{1,n}, \dots, \mathcal{L}_{c,n})^T = (l_{1,n}, \dots, l_{c,n})^T \prod_{j=1}^{n-1} \sum_{k=1}^c \alpha_k l_{k,j}$ for every $n \in \mathbb{N}^+$. With this, Equation (2) is successfully linearized as $\mathcal{L}_{n+1} = \mathbf{A} \mathcal{L}_n$ for every $n \in \mathbb{N}^+$. It turns out that matrix \mathbf{A} contains all the information about the composition profile and pinch conditions in the rectifying section. In particular, we are interested in the fixed point solution of the linear system associated with Equation (3), which is given by the eigenvalues and eigenvectors. We determine the characteristic polynomial of \mathbf{A} as:

$$\det(\mathbf{A} - \lambda \mathbf{I}) = \left(1 - \sum_{i=1}^c \frac{\alpha_i d_i}{V \alpha_i - \lambda}\right) \prod_{i=1}^c (V \alpha_i - \lambda), \quad (4)$$

from which one can easily see that the eigenvalues of \mathbf{A} are:

$$\begin{aligned} \lambda_i &= V \alpha_i & \forall i \in C \text{ such that } d_i = 0 \\ \lambda_i &= V \gamma_i & \forall i \in C \text{ such that } d_i \neq 0, \end{aligned} \quad (5)$$

where γ_i represents the i^{th} root of the following equation:

$$\sum_{j=1}^c \frac{\alpha_j d_j}{\alpha_j - \gamma_i} = V, \quad (6)$$

and by convention, $\gamma_c > \dots > \gamma_1$. Equation (6) looks familiar as it resembles the well-known Underwood's distillate equation (Underwood, 1949), except that $\{d_i\}_{i=1}^c$ are now defined in the transformed composition space. Next, for each eigenvalue λ_i , we derive the corresponding eigenvector \mathbf{z}_i :

$$\begin{aligned} \nu_i &= \frac{1}{L} \left(\frac{\alpha_i d_1}{\alpha_1 - \alpha_i}, \dots, \frac{\alpha_i d_{i-1}}{\alpha_{i-1} - \alpha_i}, I_i, \frac{\alpha_i d_{i+1}}{\alpha_{i+1} - \alpha_i}, \dots, \frac{\alpha_i d_c}{\alpha_c - \alpha_i} \right)^T \text{ if } d_i = 0, \\ \nu_i &= \frac{1}{L} \left(\frac{\gamma_i d_1}{\alpha_1 - \gamma_i}, \dots, \frac{\gamma_i d_c}{\alpha_c - \gamma_i} \right)^T \text{ if } d_i \neq 0, \end{aligned} \quad (7)$$

where $I_i = V - \sum_{j \neq i}^c \frac{\alpha_j d_j}{\alpha_j - \alpha_i}$. Essentially, these eigenvectors are c possible liquid pinch zone compositions in the new coordinate system. Recall that a pinch zone is a region in the column section where the liquid or vapor composition remains unchanged from stage to stage. When the section is pinched, there is zero driving force for mass transfer in the pinch zone and an infinite number of stages is required to achieve separation. Furthermore, one can show that these c eigenvectors are affinely independent. Thus, a $c - 1$ -dimensional simplex called the pinch simplex can be constructed, in which every liquid pinch zone composition (*i.e.*, eigenvector) is a vertex of the pinch simplex denoted as Z_i with $i \in C$ (see Figure 4c). We also derive the equations characterizing the facets of pinch simplex as:

$$\begin{aligned} z_i = \bar{x}_i = 0 \quad \forall i \in C \text{ such that } d_i = 0, \\ z_i = \sum_{j=1}^c \frac{\alpha_j \bar{x}_j}{\alpha_j - \gamma_i} = 0 \quad \forall i \in C \text{ such that } d_i \neq 0, \end{aligned} \quad (8)$$

As discussed by Franklin and Forsyth (1997), one can directly calculate the liquid composition profile without performing explicit tray-by-tray calculations inside rectifying section using the results derived so far (see Figure 4c and d). We emphasize that, depending on where the starting composition lies with respect to the pinch simplex, the liquid composition profile can exhibit different trajectories and patterns (Figure 4d), and the exact pinch zone composition the column section would observe as the number of stages becomes infinite would also be different.

Following a similar procedure as above, we can also determine the eigenvalues and eigenvectors of matrix \mathbf{A} corresponding to the stripping section, from which a $c - 1$ -dimensional pinch simplex for the stripping section can be constructed given its internal vapor traffic and bottoms product composition and flow rate.

Minimum Reflux Condition for Azeotropic Distillation

To determine the minimum reflux ratio of an azeotropic distillation column, the pinch simplices for both rectifying and stripping sections are constructed using Equation (8) simultaneously. When the distillation column is operated above the minimum reflux, the desired separation can be achieved with finite number of stages. When the column is at minimum reflux, the desired separation can only be achieved using infinite number of stages. Both column sections are pinched at minimum reflux condition. If the column is unable to achieve the desired separation even with infinite stages, it is operated below the minimum reflux ratio.

How is this related to the pinch simplex? It turns out that, in order for a distillation task to be feasible, the rectifying and stripping section pinch simplices must be connected, which allows the composition profile to be continuous from the top to bottom of the column (Franklin and Forsyth, 1997). Furthermore, it can be shown that this geometric condition is equivalent to a set of eigenvalues constraints $\gamma_i^{\text{rec}} \geq \gamma_{i-1}^{\text{strip}}$ for every $i \in C$ whose α_i lies in between the relative volatilities of light and heavy key components (Jiang et al., 2022). And the

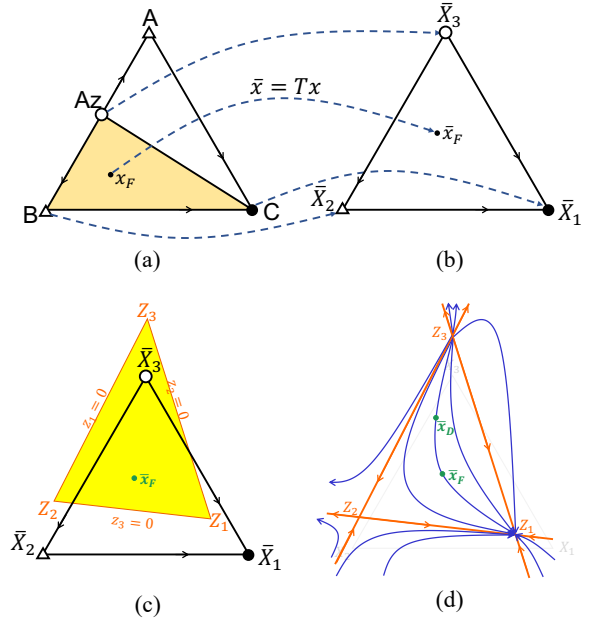


Figure 4: (a) The distillation compartment of interest drawn in the original composition space. (b) Through a linear mapping $T : X \rightarrow \bar{X}$, the original compartment is transformed into a new composition space. (c) A pinch simplex can be constructed under the transformed composition space. (d) The pinch 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 indicate the direction where liquid composition evolves as one moves downward in the column section.

minimum reflux is reached in the limiting case when these two pinch simplices only share a common face (see Figure 5b). Algebraically, this is equivalent to $\gamma_i^{\text{rec}} = \gamma_{i-1}^{\text{strip}} := \theta_{i-1}$ for all $i \in C$ whose $\alpha_i \in (\alpha_{\text{HK}}, \alpha_{\text{LK}})$. We can show that all candidate θ roots can be directly calculated using feed stream information:

$$\sum_{j=1}^c \frac{\alpha_j f_j}{\alpha_j - \theta_i} = V_F \quad \forall i \in \{1, \dots, c-1\}, \quad (9)$$

where $\theta_i \in [\alpha_i, \alpha_{i+1}]$ and f_i and V_F denote the component material flow rate and vapor portion flow rate of the feed stream, respectively. Equation (9) is similar to the classic Underwood feed equation (Underwood, 1949), but is now generalized to homogeneous azeotropic distillation. Note that there might be more than one feasible θ root candidate whose value lies within $(\alpha_{\text{HK}}, \alpha_{\text{LK}})$. In this case, the minimum rectifying section vapor flow $V_{\text{min}}^{\text{rec}}$ is given by its largest value determined from Equation (6) after substituting all feasible θ root candidates. And the minimum reflux ratio is simply:

$$R_{\text{min}} = \frac{V_{\text{min}}^{\text{rec}}}{D} - 1 \quad (10)$$

An Illustrative Example

To demonstrate the accuracy and effectiveness of this shortcut method, we study the separation of ace-

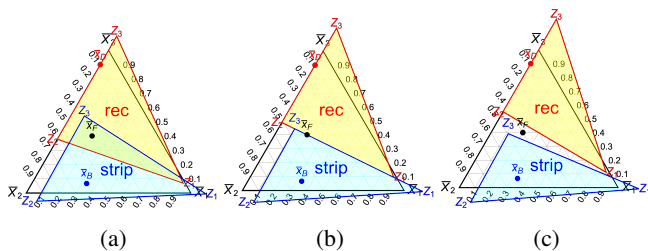


Figure 5: The pinch simplex diagram of a distillation column operated (a) above minimum reflux; (b) at minimum reflux; (c) below minimum reflux. The red and blue pinch simplices describe the rectifying and stripping sections, respectively. The red, green, and black dots represent the liquid composition 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.

tone/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 2c. The residue curve map (Figure 6) is synthesized by rigorous Aspen Plus simulations using the NRTL activity coefficient model. From Figure 6, it is clear that the distillation boundary between acetonitrile and the azeotrope (Az) separates the composition space into two distillation compartments. In this example, we consider a saturated liquid feed (1000 mol/hr) containing 65 mol% acetone, 20 mol% chloroform, and 15 mol% of acetonitrile. Hence, we apply the following linear mapping that transforms this distillation compartment into a new ternary composition space:

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

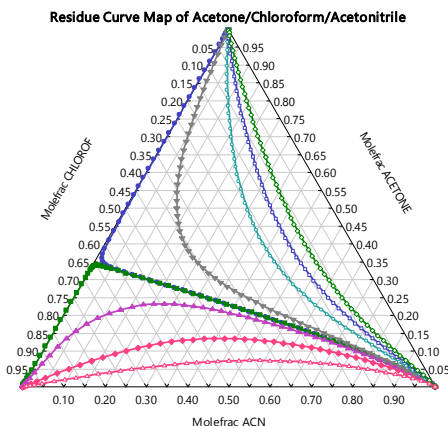


Figure 6: Residue curve map of acetone-chloroform-acetonitrile ternary system, with a binary maximum boiling azeotrope at 34.1 mol% acetone, 65.9 mol% chloroform.

Through this transformation, acetone (original coordinate (0, 0, 1)), azeotrope (original coordinate (0, 0.659, 0.341)),

and acetonitrile (original coordinate (1, 0, 0)) are 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, the relative volatilities of acetone (*i.e.*, α_3) and azeotrope Az (*i.e.*, α_2) with respect to acetonitrile (*i.e.*, $\alpha_1 = 1$) are estimated to be 2.1 and 1.2, respectively. The distillate product (300 mol/hr) contains 99.50 mol% of acetone, 0.50 mol% of chloroform, and negligible quantity of acetonitrile. And the bottoms product (700 mol/hr) contains 50.21 mol% of acetone, 28.36 mol% of chloroform, and 21.43 mol% of acetonitrile. The component flow rates of distillate and bottoms streams in the transformed space are calculated to be $(d_1, d_2, d_3) = 300 \times (0.9924, 0.0076, 0)$ mol/hr and $(b_1, b_2, b_3) = 700 \times (0.2143, 0.4303, 0.3554)$ mol/hr, respectively. Based on this information, the active root of Equation (9) is $\theta_2 = 1.4527$, which is substituted to Equations (6) and (10) to give $R_{\min} = 2.183$.

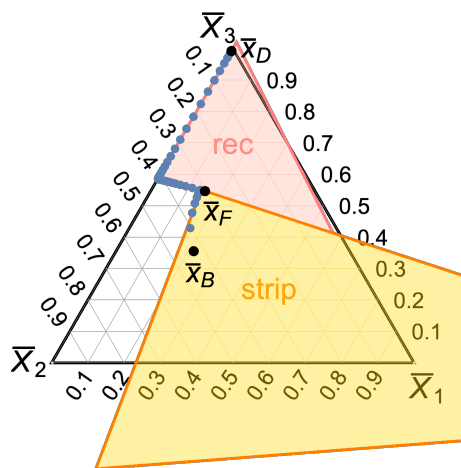


Figure 7: The pinch simplex diagram in the new coordinate system at minimum reflux. The rectifying and stripping section pinch simplices share a common edge in which the feed composition lies. The blue dots correspond to the actual liquid composition profile obtained from rigorous Aspen Plus simulation.

Figure 7 shows the pinch simplex diagram at minimum reflux operation. The two pinch simplices share a common edge, during which $\gamma_3^{\text{rec}} = \phi_2^{\text{strip}} = \theta_2$. We validate this minimum reflux ratio result by simulating the distillation column in Aspen Plus. Both sections are given 50 theoretical stages (Figure 8). The minimum reflux ratio determined from Aspen Plus simulation is 2.174, which is only 0.46% different compared to our shortcut calculation result. The simulated liquid composition profile is also mapped to the new composition space and drawn in Figure 7.

Conclusion

In this article, we develop a shortcut model for multicomponent homogeneous azeotropic distillation and derive minimum reflux condition. This shortcut model can be applied to most common homogeneous azeotropic systems. We first discuss composition space decomposition technique to transform a distillation region into a new multicomponent sys-

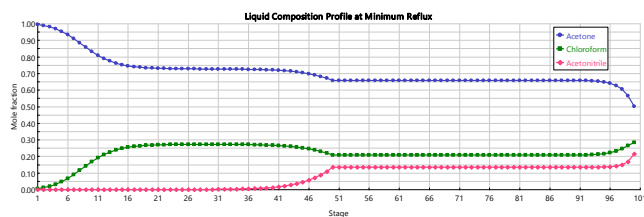


Figure 8: The actual liquid composition profile within the column at minimum reflux. Both column sections are given sufficient number of stages to ensure that the true minimum reflux is achieved.

tem, in which the azeotrope becomes a pseudo-component in the decomposed composition space. We outline an effective procedure for determining the relative volatility parameters for the resulting new multicomponent system, thereby allowing us to adopt an ideal VLE surrogate model while ensuring accuracy. We utilize these techniques and methodologies to develop the shortcut model, which generalizes the classic Underwood method (Underwood, 1949) that was developed for ideal multicomponent systems. Compared with existing approaches, our proposed method is simple, accurate, and easy-to-use. Furthermore, similar to the classic Underwood method, our model can be easily incorporated into an optimization framework to synthesize and design energy-efficient azeotropic distillation systems.

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