

Incorporating Pinch Distillation Boundaries into the Conceptual Modeling of Batch Distillations: Ternary Mixtures

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S Supporting Information

ABSTRACT: This contribution explores the influence of curved unstable distillation boundaries on the performance of batch distillations in ternary mixtures and its incorporation into a conceptual modeling framework under the assumption of a batch rectifier with an infinite number of stages. First, the concept of preferred separation in batch distillation is presented. Calculation of “pitchfork” distillation boundaries is then determined using a robust predictor-corrector algorithm based on improved memory method with the purpose of estimating the maximum feasible distillate composition in the preferred separation line. Four highly nonideal systems are studied. Finally, the model is extended to allow simulation of the operation at different reflux policies. Results of a complete simulation performed with the enhanced conceptual model are shown for the system octane/2-ethoxyethanol/ethylbenzene.

1. INTRODUCTION

Characterization of distillation boundaries at total reflux from the calculation of distillation lines (Stichlmair and Fair)¹ or the calculation of residue curves (Doherty and Malone)² had a great impact in process synthesis of highly nonideal mixtures during the nineties. For these authors, if a continuous column is operated at total reflux, it must occur that distillate, bottom, and feed compositions belong to the same distillation region. However, for the purpose of saving energy, it is common to operate columns at a finite value of the reflux ratio close to the minimum one. In this case, boundaries at total reflux can be very different from those at finite reflux, especially in cases in which boundaries at total reflux present a pronounced curvature.^{3–6}

In order to make it clear, Figure 1 shows the adiabatic profiles of rectification and stripping sections of a feasible continuous column for a specific design and an operation reflux close to the minimum one for a ternary system Acetone/Chloroform/Benzene. In this case, while the feed and distillate compositions belong to the distillation region at “total reflux” where the acetone is the light component, the bottom composition belongs to the distillation region where the chloroform is the light component. Accordingly, the residue curve corresponding to the bottom composition begins at the pure chloroform vertex (unstable node, UN), goes near the azeotrope A-C (saddle node, SA) and ends at benzene (stable node, ST) (see Figure 2).

Since the difference between distillation boundaries at total reflux and finite reflux ratios can be relevant in process synthesis, many authors^{3–6} have proposed the use of pinch branches instead of using the approximation at total reflux. Koehler et al.⁷ defined a pinch branch as the concentration profile of a reversible separation (i.e., a separation where an infinite number of intermediate heaters and coolers along the column supply energy such that in total no energy is emitted to the environment). A feasible specification requires that the distillate product and the bottom product are connected by a continuous path of pinch branches departing from their corresponding column products.

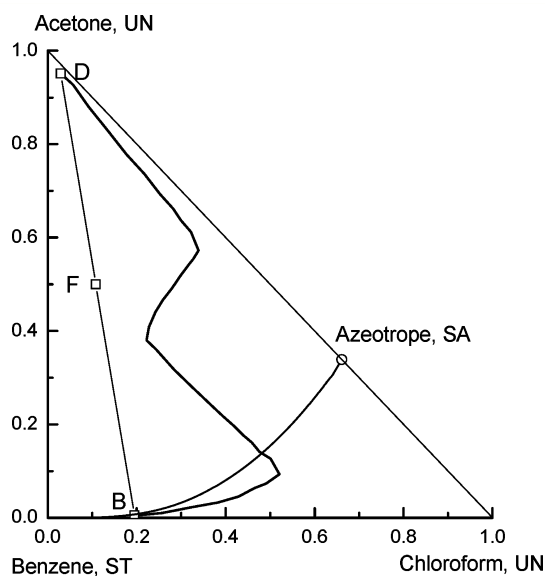


Figure 1. Feasible design for a bottom composition belonging to the lower distillation region, consisting of chloroform (light component), the azeotrope A-C (intermediate component) and benzene (heavy component). The distillate composition belongs to the upper distillation region.

Several authors^{4–6} went further and developed a mathematical description of boundaries at finite reflux ratios in terms of the apparition of pitchfork bifurcations of reversible profiles. Boundaries calculated with the aid of bifurcation theory were named as pinch distillation boundaries (PDB) by Brüggemann and Marquardt.⁶

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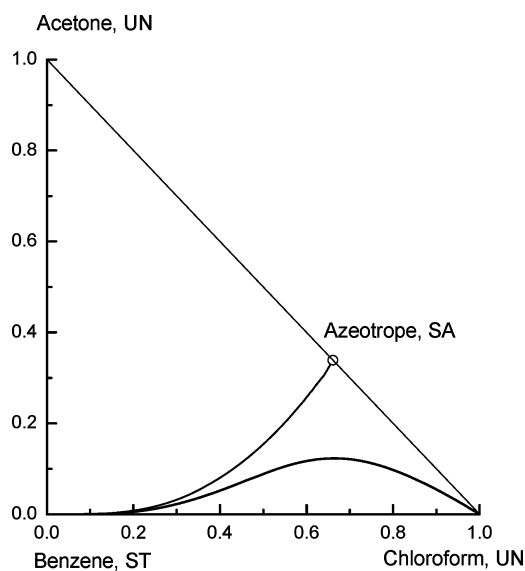


Figure 2. Residue curve corresponding to the bottom composition used in the previous feasible design. The composition belongs to the region situated between the distillation boundary at total reflux and the “pitchfork” distillation boundary.

In a recent work, Brüggemann and Marquardt⁸ have shown the great potential of including a closed form representation of distillation boundaries in the synthesis and design of distillation trains. In the first paper of the series,⁶ they proposed a geometric feasibility test for azeotropic separations based on bifurcation theory. In addition to giving a yes-or-no assessment of the feasibility of the proposed split, it also can be used during the phase of the qualitative design of alternative flowsheets for a given separation task. In the second contribution,⁸ the authors used the feasibility test together with a method to estimate the minimum energy demand of a given separation [Rectification Body Method (RBM), Bausa⁹] to optimize the recycle policy of a distillation train.

For the case of batch distillations, several efforts have been made in the field of minimum energy demand calculation by applying pinch theory. The first attempt to estimate the minimum reflux necessary to achieve a distillate of prefixed composition was done by Düssel.¹⁰ He extended the ideas of Offers et al.¹¹ from continuous to batchwise operation of a rectifier with distillate cuts of constant composition. In his work, Düssel proposed to solve the eigenvalue problem of the Jacobian of the equilibrium function in the instantaneous still composition to obtain a linearization of the adiabatic profile in the neighborhood of the still composition and hence, an estimation of the instantaneous minimum reflux ratio by considering the overall mass balance through a rectifier with an infinite number of stages. On the other hand, Espinosa and Salomone¹² adapted the approach to handle the operation at constant reflux ratio. Depending on the value of the reflux ratio, the conceptual model estimates the value of the instantaneous distillate composition. All the mentioned algorithms have been programmed in Delphi Pascal (CBD Toolkit)¹³ to handle the different operation modes encountered in batch distillation. New releases of the software incorporated both azeotrope^{14,15} and distillation region^{16,17} calculations to take into account linear approximations of distillation boundaries. Recently, the influence of tangent pinch points^{18,19} on the operation performance was also taken into account.

Besides the linearization of the adiabatic profile in the neighborhood of the still composition (Düssel¹⁰ and Offers et al.¹¹

for operation at constant distillate composition; Espinosa and Salomone¹² for operation at constant reflux ratio) there is another approach to calculate the instantaneous rectifier performance, which is based on the calculation of rectification bodies.²⁰ While linearization needs the solution of an eigenvalue problem of the Jacobian of the equilibrium function for any instantaneous still composition, the rectification body method approximates the manifold of all potential profiles by linearly connecting controlling pinch points.²¹ It is noteworthy that both approaches make the assumption that the controlling pinch points are invariant, which is true for ideal mixtures but only an approximation for highly non ideal systems.^{20,21}

In this work, incorporation of curved unstable distillation boundaries into the conceptual modeling framework (CBD Toolkit)¹³ is done for ternary azeotropic mixtures.

First, the concept of preferred separation in batch distillation is presented. The next two sections deal with algorithms designed to calculate both the pinch distillation boundary and the intersection of the preferred separation line with the previously calculated boundary. Finally, results of a complete simulation performed with the enhanced conceptual model are shown. Several highly nonideal mixtures are considered throughout the contribution.

2. PREFERRED SEPARATION IN BATCH DISTILLATION

The concept of preferred separation is the key to understand the algorithms presented in Section 4. The separation of a ternary mixture into two main fractions can serve to introduce this concept. Let us consider the separation by batch distillation of the mixture acetone, methanol, and water. The system shows one unstable node (the azeotrope acetone-methanol), one stable node (water), and two saddles (acetone, methanol). All residue curves depart from the unstable node and end at the water vertex. Therefore, there is only one distillation region without distillation boundaries dividing the composition simplex.

The objective is to distill off the methanol and acetone to produce a solvent mixture with less than 5 wt % water, and also to end up with at least 99 wt % of pure water in the still.

In order to accomplish the objective, the first cut should be free of the heavy component water and must contain almost all the light component acetone. The second cut should be formed by methanol and water to allow the high water purity in the still at the end of the operation.

While the end water specification in the pot could be achieved operating the column at constant reflux, the composition of the main product could be reached implementing a variable reflux policy. Figure 3 shows the evolution of the still path calculated with the aid of CBD Toolkit.¹³ At each instant of time during the first cut, the instantaneous distillate composition is located on the intersection between the equilibrium vector and the binary axis acetone–methanol. This instantaneous separation is named preferred separation and it is characterized by a distillate composition free of the heavy component, while the instantaneous energy demand to achieve the distillate composition is the minimum one. A pinch with the composition of the still controls the separation as the conceptual model assumes a column with an infinite number of equilibrium stages. Figure 4 shows the predicted evolution for the reflux ratio as a function of the rectification advance, which is defined as the ratio between the cumulative amount of product distilled and the initial amount of mixture fed to the still.

The way in which the initial reflux ratio profile of Figure 4 can be used in the optimization of the operation with the aid of Aspen

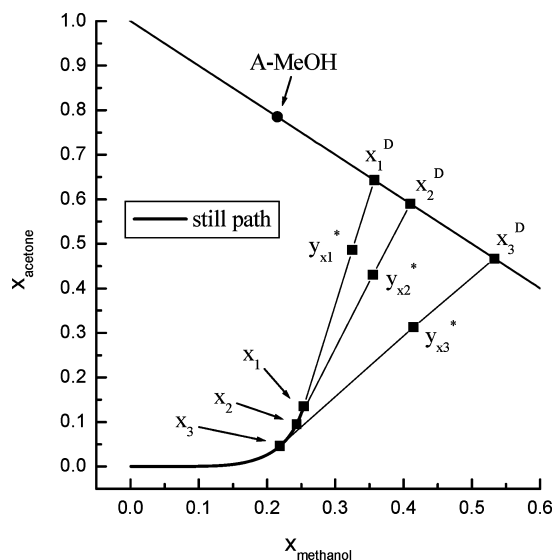


Figure 3. Still path calculated from CBD Toolkit.¹³ The first cut is characterized by instantaneous distillate compositions located on the preferred separation lines.

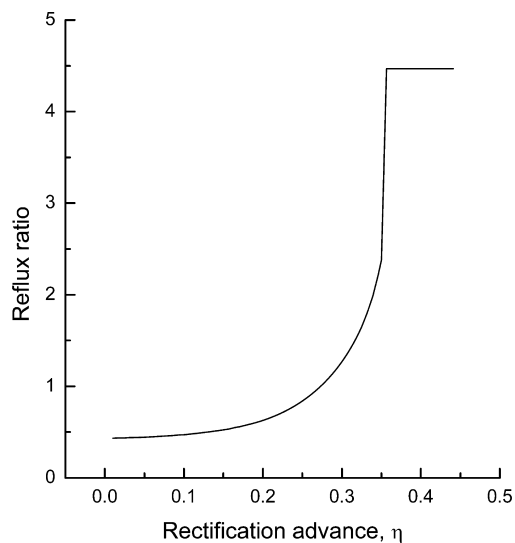


Figure 4. Reflux ratio versus the rectification advance. Results obtained from pinch theory (CBD Toolkit¹³).

Batch Distillation²² can be found in the Supporting Information section of this manuscript.

It is noteworthy that the concept of preferred separation was first developed by Offers et al.¹¹ In the context of batch distillation it can be defined as a separation in which the instantaneous distillate composition is located on the equilibrium line corresponding to the instantaneous still composition. The above concept can be easily extended when distillation boundaries limit the distillate compositions that can be achieved by distillation. While the concept of preferred separation remains the same, the maximum instantaneous feasible composition in the line of preferred separation will be located at the intersection of the equilibrium vector with the pinch distillation boundary.

3. CALCULATION OF THE "PITCHFORK" SOLUTIONS CURVE AND THE "PITCHFORK" DISTILLATION BOUNDARY

3.1. Theoretical Basics. The mass balance for a given column and the corresponding equilibrium equations at the pinch point

give rise to eqs 1 and 2. Both of them are associated with rectification and stripping profiles, respectively:

$$-y(x) + \frac{r}{r+1}x + \frac{1}{r+1}z_D = 0 \quad (1)$$

$$y(x) - \frac{s}{s+1}x + \frac{1}{s+1}z_B = 0 \quad (2)$$

In these equations, x is the vector of liquid compositions, $y(x)$ is its vapor in equilibrium, r is the reflux ratio, s is the reboil ratio and z_D, y, z_B are the vectors of molar fractions of product, whether corresponding to the distillate (D) or to the "bottom" (B). More generally, eqs 1 and 2 can be rearranged in one expression as follows:

$$\tau x + (1 - \tau)y(x) = z_p \quad (3)$$

where $\tau = -r$ and $z_p = z_D$ for the rectification profile or $\tau = s + 1$ and $z_p = z_B$ for the "stripping" profile. From eq 3, it is possible to obtain the pinch points curve, varying the value of τ between $-\infty$ and $+\infty$. For systems showing an unstable distillation boundary which limits the compositions that can be achieved in the distillate, a distillate composition belonging to the boundary is characterized by a pinch curve having two branches: one that contains the product ("pinch" product branch) and the other that does not contain it (disjoint pinch branch). When the product branch crosses the disjoint branch, the intersection is called a "pitchfork solution" or a "pitchfork bifurcation".

A set of pitchfork solutions is obtained, as the value of τ is changed, by applying the implicit function theorem in eq 3.^{4,5}

$$\tau I(x - y) + (1 - \tau)\det(Y)Y^{-1}(x - y) = 0 \quad (4)$$

where I is the identity matrix and Y is the Jacobian matrix of equilibrium ($(\partial y_k)/(\partial x_i)$). Elements of Y are analytically calculated from analytical derivatives with respect to the composition and temperature of properties like vapor pressures and activity coefficients.^{2,23}

Note that for each value of τ in eq 4, we can obtain a "pitchfork" solution x and the corresponding value of z_p (i.e., a point on the pinch distillation boundary) from eq 3.

3.2. Numerical Resolution of Eq 4. In order to calculate the entire pinch distillation boundary, a robust algorithm of secant homotopic continuation is proposed. The method is similar to the one developed by Aguirre and Espinosa²⁴ for the calculation of reversible profiles. In this case, the continuation method solves eq 4 in the correction step using the improved memory method developed by Shacham²⁵ for the solution of a nonlinear equation or error function.

Focusing our attention on the numerical solution of eq 4 at the correction step of the continuation method, the improved memory method is used to solve nonlinear equations of the form $f(x) = 0$ by approximating the inverse function of $f(x)$; namely $x = \Psi(f)$, through inverse interpolation with continued fractions and evaluating the inverse function for $f = 0$. The x found value is the root of the nonlinear equation; i.e., $x^* = \Psi(0)$.

The algorithm requires the evaluation of a series of points $(x_{0f_0}), (x_{1f_1}), \dots, (x_{nf_n})$ and it demands the smallest number of function evaluations in comparison with other methods as a consequence of using the information from previous iterations to generate greater order estimations of the inverse function (lineal, quadratic, etc.). Two initial points $(x_{0f_0}), (x_{1f_1})$ must be calculated to start the algorithm in such a way that $f(x_1) \cdot f(x_2) < 0$. More details can be found elsewhere.²⁵

Note that eq 4 represents a system of equations in vectorial form and its unknown variables are x and τ ; that is, four unknown variables and three equations. Hence, it is necessary to fix one of the variables to guarantee existence and uniqueness of the solution. In this case, we choose one of the components of the vector of molar fractions as pivot. Moreover, if we consider the fact that the sum of molar fractions must be equal to one, equation system (4) is reduced to two equations with two unknown variables: x_i , $i = 1, 2$, or 3 (depending on which is the fixed component), and τ . This system can then be solved in an iterative way by selecting one of the remaining mole fractions as iterative variable.

As an example, assume we fix the variable x_3 (pivot) and select x_2 as the iterative variable of the method, hence both $x_1 = 1 - x_2 - x_3$ and the inverse of the Jacobian matrix of equilibrium

$$Y^{-1} = \begin{bmatrix} \tilde{y}_{11} & \tilde{y}_{12} \\ \tilde{y}_{21} & \tilde{y}_{22} \end{bmatrix} \text{ can be calculated. Equation system (4) can then}$$

be rearranged as follows:

$$\tau(x_1 - y_1) + (1 - \tau)\det(Y)[\tilde{y}_{11}(x_1 - y_1) + \tilde{y}_{12}(x_2 - y_2)] = 0 \quad (5)$$

$$\tau(x_2 - y_2) + (1 - \tau)\det(Y)[\tilde{y}_{21}(x_1 - y_1) + \tilde{y}_{22}(x_2 - y_2)] = 0 \quad (6)$$

Note that while τ can be calculated from eq 6, this value can be used in eq 5 to define the error function for the improved memory method.

Having explained the algorithm at the correction step, main steps for the secant homotopic continuation algorithm can then be presented:

Step 0. (Initialization) As the composition of the azeotrope verifies $x = y(x)$, this is the first point in the “path” of “pitchfork” solutions, since $x = y(x)$ is a trivial solution of the system of eqs 4. From this initial solution it is possible to obtain another solution from an initial stage of prediction and correction:

- i. **Initial Prediction Stage:** Predict a new “pitchfork” solution solving the eigenvalue problem at the azeotrope, and executing an infinitesimal movement in the direction of the eigenvalue that is not parallel to the binary axis of the simplex of compositions. That is, choose an initial solution a_0 in the neighborhood of the azeotrope and over the unique direction d_0 that comes into the simplex. The fixed component is the one that varies more along the direction of the eigenvector. Additionally, as the method requires an initial search interval, we can generate b_0 from modifying the known initial solution a_0 . Hence, we have an initial interval $[a_0, b_0]$ for the improved memory method.
- ii. **Initial Correction Step:** Given the initial interval $[a_0, b_0]$, calculate the Jacobian of equilibrium in each composition. Therefore, we can obtain the corresponding value of τ from one of the equations presented in equation system (4). Using the remainder equation, calculate the error function for a_0 and b_0 in order to initialize the improved memory method. In this first implementation, solving equations system (4) using the improved memory method provides a “pitchfork” solution x_{bif}^0 . From eq 3, calculate z_p^0 .

Step 1. (Prediction) Determine the new search direction $d_i = x_{\text{bif}}^{i-1} - x_{\text{bif}}^{i-2}$. The estimate of the solution a_i must be situated along the direction d_i , from x_{bif}^{i-1} . Fix as pivot the component that varies more along the direction d_i and determine b_i .

Step 2. (Correction) Implement the improved memory method to obtain x_{bif}^i and z_p^i .

Step 3. (Stop Criterion) The algorithm ends when some of the compositions, (bifurcation compositions x_{bif}^i or distillate compositions z_p^i) do not belong to the simplex of compositions.

Figure 5(a)–(d) shows the results of implementing the previous algorithm in the case of four ternary systems: (i) Acetone/Chloroform/Benzene, (ii) Octane/2-Ethoxyethanol/Ethylbenzene, (iii) Acetone/Chloroform/Methanol, and (iv) Methanol/Ethanol/Water. Molar volume, Antoine equation coefficients for each component and Wilson parameters were extracted from Aspen Hysys database²² and are shown in the Supporting Information Section. Topologic information is also given.

4. CALCULATION OF THE MAXIMUM FEASIBLE SEPARATION IN THE LINE OF PREFERRED SEPARATION AND DIFFERENT OPERATING MODES

4.1. Maximum Feasible Separation in the Preferred Line. Given an instantaneous still composition, it is possible to calculate the composition of the maximum feasible distillate in the preferred line direction onto the unstable boundary. To this end, the system octane/2-ethoxyethanol/ethylbenzene, which presents an unstable boundary, has been studied. This system has two binary azeotropes: one between octane and 2-ethoxyethanol, with composition [0.6003 0.3997 0], and the other between 2-ethoxyethanol and ethylbenzene, with composition [0 0.4697 0.5303]. Figure 5(b) shows the pitchfork solutions curve and the corresponding “pitchfork” distillation boundary, together with the boiling temperatures corresponding to the azeotropic mixtures.

As explained above, a distillate composition that belongs to the distillation boundary must obey eqs 7 and 8:

$$\tau_B x_{\text{Bif}} + (1 - \tau_B)y(x_{\text{Bif}}) = x_D^* = x_D^{*1} \quad (7)$$

$$\tau_B I(x_{\text{Bif}} - y_{\text{Bif}}) + (1 - \tau_B)\det(Y)Y^{-1}(x_{\text{Bif}} - y_{\text{Bif}}) = 0 \quad (8)$$

In the equations above, the bifurcation reflux R_B is given by $\tau_B = -R_B$, x_{Bif} is the pitchfork composition, $y(x_{\text{Bif}})$ is the vapor in equilibrium with x_{Bif} , x_D^{*1} is the distillate composition belonging to the distillation boundary, I is the identity matrix, and Y is the Jacobian matrix of equilibrium $((\partial y_k)/(\partial x_i))$. Clearly, eq 7 represents the mass balance around the rectification column and eq 8 follows from applying the implicit function theorem to eq 7 and allows the calculation of the set of pitchfork solutions. For each of these solutions, there is a corresponding distillate composition that can be obtained from eq 7. Indeed, the composition of the maximum feasible distillate in the preferred line, given an instantaneous still composition x_s and its vapor in equilibrium $y^*(x_s)$, satisfies the following equation:

$$\tau_S x_S + (1 - \tau_S)y^*(x_S) = x_D^* = x_D^{*2} \quad (9)$$

where $\tau_S = -R^*$, R^* is the limiting reflux ratio and x_D^{*2} is the composition of the maximum feasible distillate in the preferred line. As the distillate belongs to the preferred line, eq 9 can be rewritten as follows:

$$\frac{x_D^{*2} - y^*(x_s)}{y^*(x_s) - x_s} = \frac{x_{D,1}^{*2} - y^*(x_{s,1})}{y^*(x_{s,1}) - x_{s,1}} = \frac{x_{D,2}^{*2} - y^*(x_{s,2})}{y^*(x_{s,2}) - x_{s,2}} \quad (10)$$

Hence, it is possible to write:

$$x_{D,1}^{*2} = \frac{x_{D,2}^{*2} - y^*(x_{s,2})}{y^*(x_{s,2}) - x_{s,2}}(y^*(x_{s,1}) - x_{s,1}) + y^*(x_{s,1}) \quad (11)$$

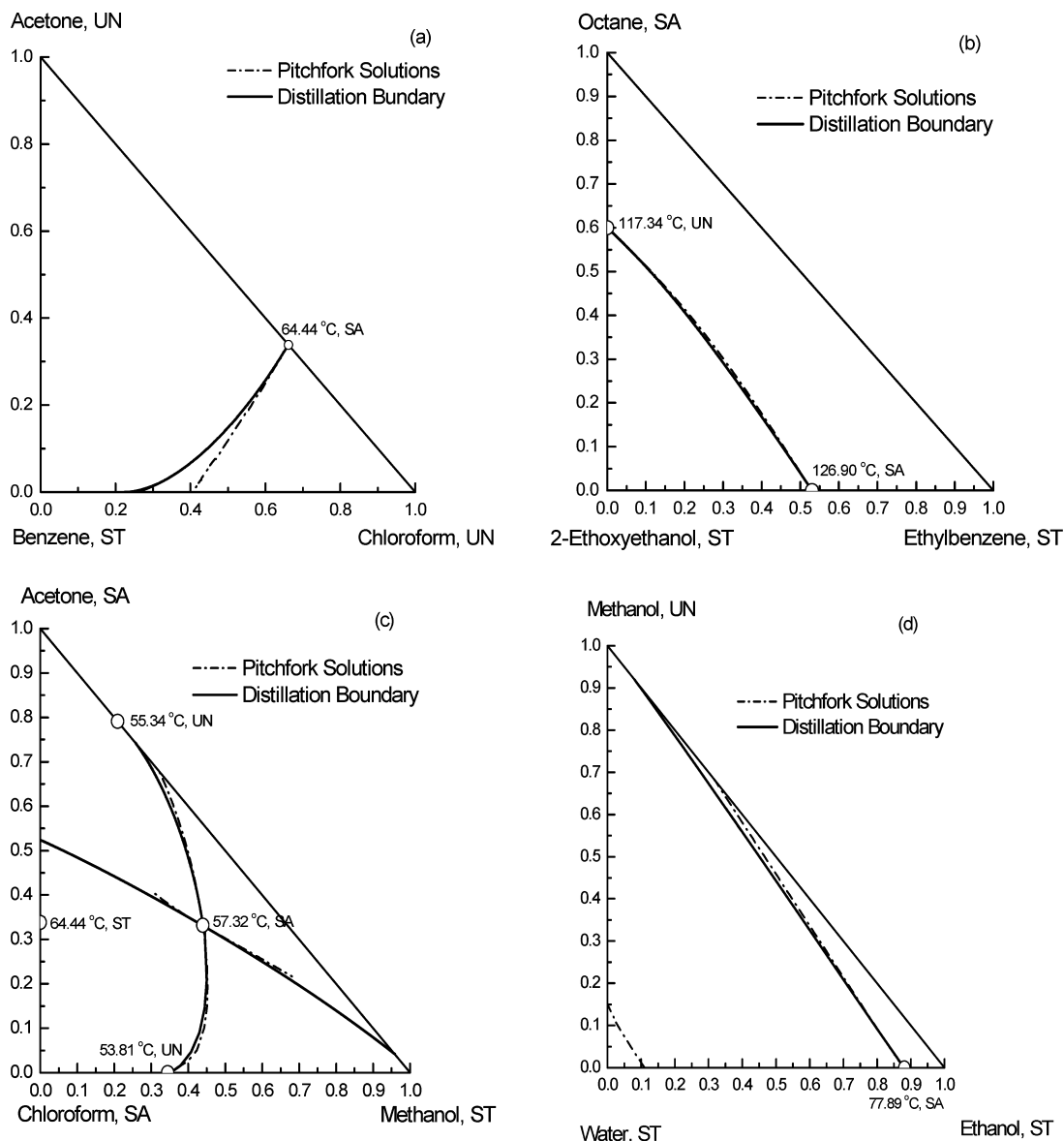


Figure 5. “Pitchfork” distillation boundary and curve of “pitchfork” solutions for the systems: (a) Acetone/Chloroform/Benzene; (b) Octane/2-Ethoxyethanol/Ethylbenzene; (c) Acetone/Chloroform/Methanol; and (d) Methanol/Ethanol/Water.

Note that the equation system of (7), (8), and (9) is consistent and it has a unique solution because there are six unknown variables: τ_B , τ_s , $x_{D,1}^{*1}$, $x_{D,2}^{*1}$, $x_{D,1}^{*2}$, and $x_{D,2}^{*2}$, and six equations (two for each equation, considering summation of mole fractions). Given an instantaneous still composition x_s we can solve eqs 7, 8, and 9 following the next steps:

Step 1. Choose a value for the guess variable $x_{Bif,1}$ (light component of bifurcation composition).

Step 2. Solve subsystem (8) for $x_{Bif,2}$, $x_{Bif,3}$, and τ_B .

Step 3. Solve subsystem (7) for $x_{D,1}^{*1}$, $x_{D,2}^{*1}$, and $x_{D,3}^{*1}$. This distillate composition belongs to the distillation boundary.

Step 4. Estimate the distillate composition belonging to the preferred line (light component) from eq 11 and the value of $x_{D,2}^{*2}$ obtained from the previous step. That is, we fix $x_{D,2}^{*1} = x_{D,2}^{*2}$ and we find the value of $x_{D,1}^{*1}$.

Step 5. If $x_{D,1}^{*1}$ (light component of distillate composition belonging to the distillation boundary, obtained from Step 3) coincides with $x_{D,1}^{*2}$ (light component of distillate composition on the preferred line, obtained from Step 4),

calculate the value of τ_s from eq 9 and stop. In other case, go to Step 1.

The algorithm of resolution is based on two nested improved memory algorithms. Both of them iterate over x_{Bif} but in a different way. The outer loop iterates over the light component of x_{Bif} and the error function is defined as $\Delta x_{D,1} = x_{D,1}^{*1} - x_{D,1}^{*2}$, in order to satisfy eq 11. The inner loop iterates over the intermediate component of x_{Bif} (once the light component has already been fixed in the outer loop) until finding the pitchfork composition, the corresponding distillate composition and the value of τ_B . In this way, the subsystem comprised by equations 7 and 8 is solved by taking eq 8 as the error function. The initial values for the inner loop, $x_{Bif,2}^1$ and $x_{Bif,2}^2$ are chosen from the same initial vector used in the outer loop but considering the intermediate component. Table 1 shows the results obtained from the implementation of the algorithm. Figure 6 emphasizes the graphical interpretation of the algorithm: distillate compositions $x_{D,i}^*$ must be located on both the unstable boundary and the preferred line.

Table 1. Compositions of $y_{x_B}^*$, x_{Bif}^* and x_D^* , Given an Instantaneous Still Composition x_B^a

x_B	$y_{x_B}^*$	x_{Bif}^*	x_D^*
[0.1 0.8 0.1]	[0.2865 0.5885 0.1249]	[0.3593 0.3903 0.2504]	[0.4628 0.3887 0.1485]
[0.15 0.7 0.15]	[0.3236 0.5195 0.1569]	[0.3374 0.3931 0.2695]	[0.4489 0.3893 0.1619]
[0.2 0.2 0.6]	[0.2421 0.2981 0.3713]	[0.1548 0.4297 0.4155]	[0.289 0.4086 0.3025]
[0.3 0.2 0.5]	[0.3357 0.2957 0.3686]	[0.2366 0.4108 0.3525]	[0.3731 0.3960 0.2308]
[0.4 0.2 0.4]	[0.4177 0.2953 0.287]	[0.3172 0.3960 0.2868]	[0.4353 0.39 0.1746]
[0.7 0.2 0.1]	[0.6236 0.3066 0.0698]	[0.5324 0.3890 0.0786]	[0.5615 0.3933 0.0452]

^aSystem Octane/2- Ethoxyethanol/Ethylbenzene.

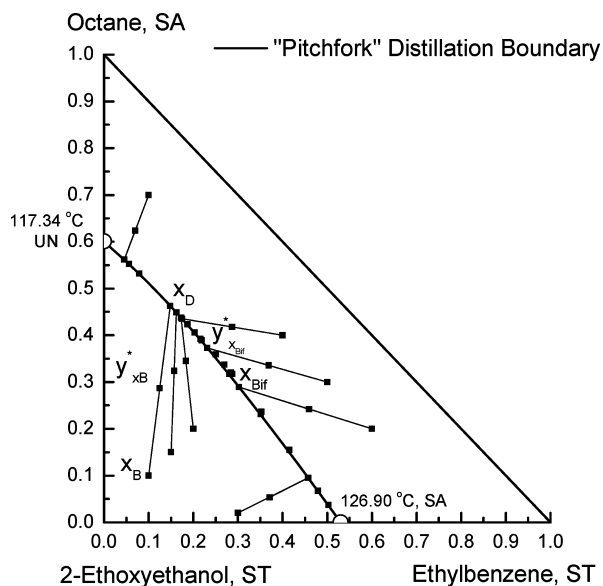


Figure 6. Maximum feasible separations in the preferred line corresponding to instantaneous still compositions given in Table 1. System Octane/2-Ethoxyethanol/Ethylbenzene.

To enhance algorithm convergence, we used a limited number of data points (i.e., ten points) corresponding to the pitchfork distillation boundary obtained with the aid of the secant homotopic algorithm explained in Section 3.2. In order to narrow the search interval for the light component mole fraction of x_{Bif} in the outer loop, two initial values $x_{Bif,1}^1$ and $x_{Bif,1}^2$ are chosen from the previously calculated data points by detecting a variation in the sign of the values of the error function $\Delta x_{D,1} = x_{D,1}^{*1} - x_{D,1}^{*2}$.

4.2. Different Operation Modes at a Given Reflux Ratio R.

Calculation of the maximum feasible distillate composition in the line of preferred separation z_D^* for a given instantaneous still composition x_B is the key ingredient to estimate the instantaneous performance of a rectifier having an infinite number of stages. The corresponding limiting reflux ratio is named R^* (Espinosa and Salomone)¹² and is calculated from the lever arm rule as follows:

$$R^* = \frac{z_D^* - y_{x_B}^*}{y_{x_B}^* - x_B}$$

This limiting distillate composition is located either on the binary axis corresponding to the more volatile components for systems

which do not show distillation boundaries or on a pitchfork distillation boundary (see Figure 7).

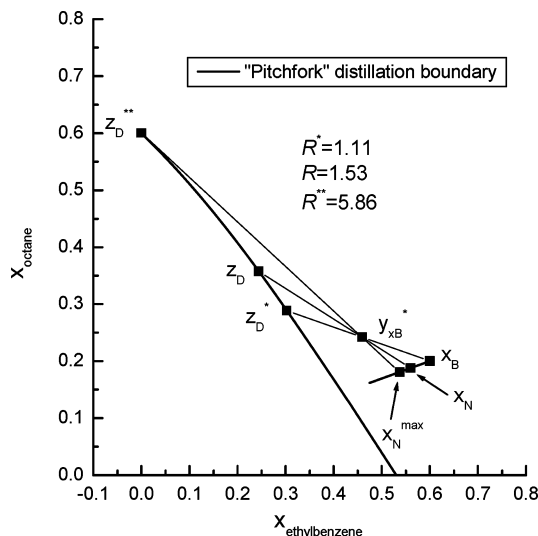


Figure 7. Instantaneous performance of a batch rectifier for a given reflux ratio $R^* < R < R^{**}$. Note that feasible values for x_N belongs to the interval $[x_B, x_{N,max}]$.

Figure 7 also shows the maximum feasible composition on the pitchfork distillation boundary; i.e., the unstable node of the system z_D^{**} . In order to calculate R^{**} , which is the minimum reflux ratio for which it is possible to obtain the unstable node as instantaneous distillate composition, it is necessary to estimate the maximum composition of the liquid leaving the rectifier lower end $x_{N,max}$. This composition is calculated from the intersection between $z_D^{**} - y_{x_B}^*$ (mass balance around the rectifier) and the linearization of the adiabatic profile in the neighborhood of the still composition x_B (named “eigenline” after Duessel¹⁰). Duessel¹⁰ proposed to solve the eigenvalue problem of the Jacobian of the equilibrium function in the instantaneous still composition x_B to obtain the mentioned line.

Once the composition of $x_{N,max}$ is known, the reflux ratio R^{**} can be obtained applying the lever arm rule as follows:

$$R^{**} = \frac{z_D^{**} - y_{x_B}^*}{y_{x_B}^* - x_{N,max}}$$

Having calculated the two limiting reflux ratios corresponding to instantaneous still composition x_B , the estimation of the instantaneous distillate composition z_D depends on the value of the operation reflux R:

- For $R \leq R^*$, the distillate composition is aligned with the equilibrium vector $y_{x_B}^* - x_B$ or “preferred separation line”, starting from $y_{x_B}^*$. Use the lever arm rule to calculate the distillate mole fractions:

$$z_D = y_{x_B}^* + R^*(y_{x_B}^* - x_B)$$

- For $R^* < R < R^{**}$, the distillate composition is located on the pitchfork distillation boundary. The distillate composition z_D is iteratively found for different values of x_N (see Figure 7) as the intersection between the pitchfork distillation boundary and the vector $y_{x_B}^* - x_N$ (mass balance around the rectifier). Convergence is achieved when the

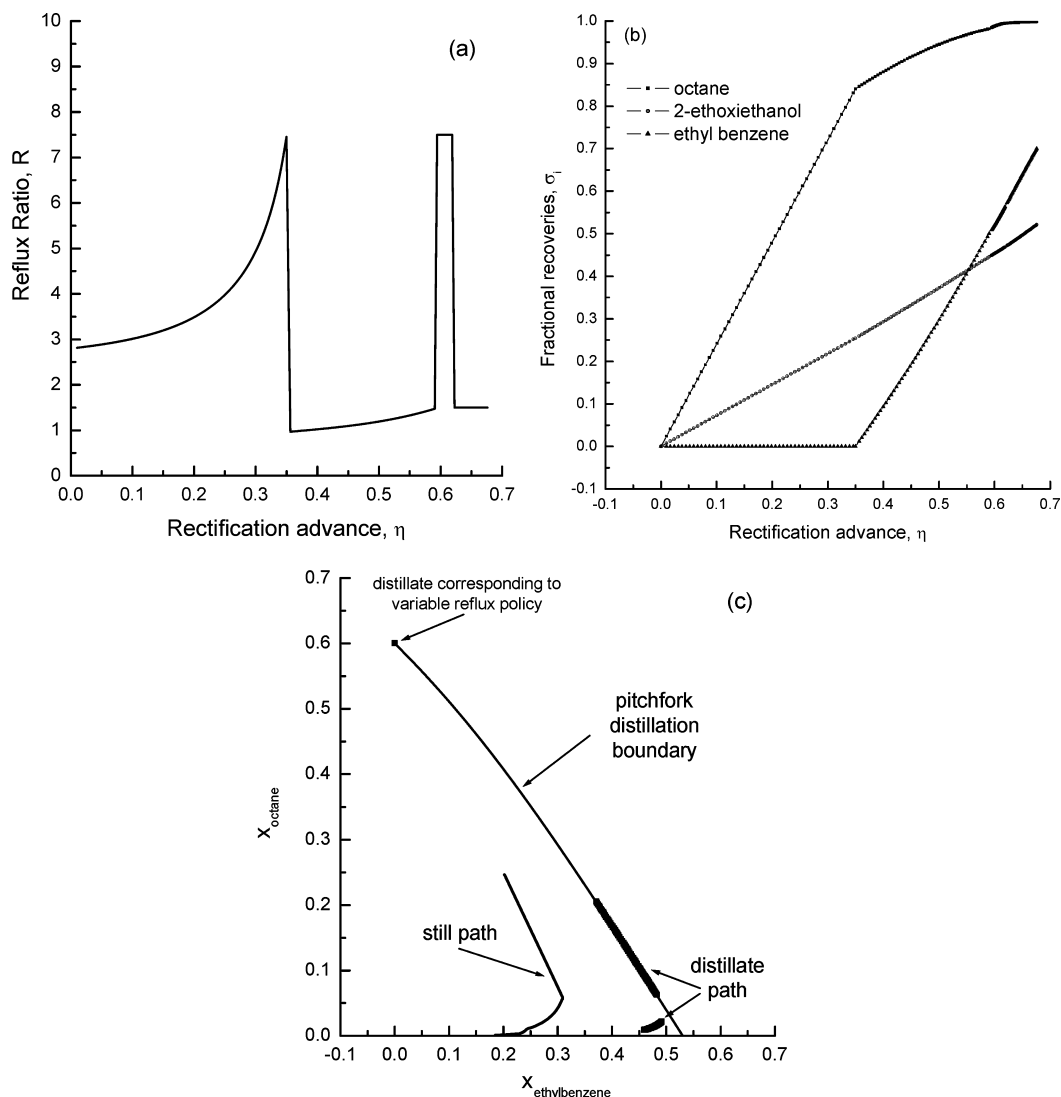


Figure 8. Simulation using the conceptual model including curved unstable distillation boundaries: (a) reflux policy, (b) rectification advance vs fractional recoveries, and (c) still path and distillate path.

reflux ratio calculated from the lever arm rule equals the operation reflux ratio:

$$R = \frac{z_D - y_{x_B}^*}{y_{x_B}^* - x_N}$$

- For values of the operation reflux ratio $R \geq R^{**}$, the distillate composition equals z_D^{**} .

5. OVERALL COLUMN MODEL

In order to model different operation modes of a batch rectifier in terms of component recoveries and rectification advance the following set of algebraic and differential equations were proposed by Salomone:²⁶

$$\frac{d\sigma_i^D}{d\eta} = \frac{x_i^D}{x_{i0}^B}, x_i^B = x_{i0}^B \frac{(1 - \sigma_i^D)}{(1 - \eta)}$$

where σ_i^D is the fractional recovery of component i in the distillate, η is the rectification advance, x_i^D is the mole fraction of component i in the distillate, and x_{i0}^B is the initial mole fraction of component i in the still. A detailed description of the model is

given elsewhere (Espinosa and Marchetti²⁷). Once a new value for the instantaneous still composition is calculated in terms of fractional recoveries and rectification advance from the second equation, either the instantaneous distillate composition (operation at constant reflux ratio) or the instantaneous reflux ratio (operation at constant distillate composition) needs to be estimated with the methods developed in Section 4.2. The incorporation of curved unstable distillation boundaries into the conceptual modeling framework (CBD Toolkit)¹³ notably enhances its predictive potential. Results obtained for an example problem are shown in Figure 8.

Figure 8(a) shows the different reflux policies that were used along the simulation. Note that the batch rectifier is operated at a variable reflux policy (constant distillate composition) until a rectification advance $\eta_1 = 35\%$, at variable reflux (preferred separation) for values of the rectification advance between $\eta_1 = 35\%$ and $\eta_2 = 59\%$, at constant reflux $R = 7.5$ between $\eta_2 = 59\%$ and $\eta_3 = 62\%$ and, at constant reflux $R = 1.5$ from $\eta_3 = 62\%$ to $\eta_4 = 68\%$. Figure 8(b) corresponds to the evolution of fractional recoveries of each component of the mixture in terms of rectification advance. Finally, Figure 8(c) shows the still path and distillate path. For the case of the first operation policy, the still

path (which represents the path followed by still compositions) follows a “straight line” since the distillate is the azeotrope Octane/2-Ethoxyethanol which is the unstable node of the system. Note that distillate compositions are located in the “pitchfork distillation boundary” for both variable reflux policies (constant distillate composition and preferred separation). When the batch rectifier is operated under preferred operation, the instantaneous reflux is the minimum one for which the distillate composition “reach” the unstable boundary. For operation at a constant value of reflux ratio of 7.5, the distillate compositions are also located in the unstable boundary because operation reflux is greater than the instantaneous values R^* . In the end, operation at a constant reflux ratio of 1.5 provides distillate compositions in the “preferred line” which do not reach the distillation boundary because operation reflux is lesser than instantaneous R^* .

6. CONCLUSIONS

On the basis of bifurcation theory, this contribution proposes a conceptual model for the instantaneous rectifier performance to deal with the appearance of curved unstable distillation boundaries also named pitchfork distillation boundaries. The main objective of this research work was to enhance the previously developed conceptual model where unstable distillation boundaries were taken into account from piecewise linear approximations. A simulation of a batch rectifier under different operation modes is presented, incorporating the described algorithms. The results found encourage future research efforts in order to extend the conceptual modeling approach to hybrid processes.

■ ASSOCIATED CONTENT

● Supporting Information

Results of the optimization of the separation given in Section 2 by using both CBD Toolkit¹³ and Aspen Batch Distillation²² are analyzed. Physicochemical data together with the type of residue curve map for all studied systems are also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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