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THERMODYNAMIC TOPOLOGICAL ANALYSIS OF EXTRACTIVE DISTILLATION OF MAXIMUM BOILING AZEOTROPES

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Abstract - This paper provides a feasibility study of azeotropic mixture separation based on a topological analysis combining thermodynamic knowledge of residue curve maps, univolatility and unidistribution curves, and extractive profiles. Thermodynamic topological features related to process operations for typical ternary diagram classes 1.0-2 are, for the first time, discussed. Separating acetone/chloroform is presented as an illustrative example; different entrainers are investigated: several heavy ones, a light one, and water, covering the Serafimov classes 1.0-2, 1.0-1a and 3.1-4, respectively. The general feasibility criterion that was previously established for ternary mixtures including only one azeotrope (1.0-1a or 1.0-2) is now, for the first time, extended to that including three azeotropes (class 3.1-4).

Keywords: Azeotropic mixtures; Topological analysis; Residue curve map; Extractive distillation; Maximum boiling azeotrope.

INTRODUCTION

In most separation systems, the predominant non-ideality occurs in the liquid phase due to molecular interactions. When chemically dissimilar components are mixed together (e.g., oil molecules and water molecules), there exists repulsion or attraction between dissimilar molecules. If the molecules repel each other, they exert a higher partial pressure than if the mixtures were ideal. In this case, the activity coefficients are greater than unity (called a “positive deviation” from Raoult’s law). If the molecules attract each other, they exert a lower partial pressure than in an ideal mixture. Activity coefficients are less than unity (negative deviations). Activity coefficients are usually calculated from experimental data or from thermodynamic activity coefficient models regressed on experimental data. Azeotropes occur in a number of nonideal systems. An azeotrope exists when the liquid and vapor compositions are the same ($x_i=y_i$) at a given azeotrope temperature. Figure 1 and 2 sketch typical graphical phase representations of the vapor-liquid equilibrium (VLE). The left part of Figures 1 and 2 shows a combined graph of the bubble and dew temperatures, pressure, and the vapor-liquid equilibrium phase mapping, which give a complete representation of the VLE. In addition, the right parts these figures give the equilibrium phase mapping $y$ vs. $x$ alone. Each of these diagrams uniquely characterizes the type of corresponding
mixture. Negative deviations (attraction) can give a higher temperature boiling mixture than the boiling point of the heavier component, called a maximum-boiling azeotrope (Figure 1). Positive deviations (repulsion) can give a lower temperature boiling mixture than the boiling point of the light component, called a minimum boiling azeotrope (Figure 2).

The study of the thermodynamic classification of liquid-vapor phase equilibrium diagrams for ternary mixtures and their topological interpretation has a long history. Considering a ternary diagram A-B-E formed by a binary mixture A-B with the addition of an entrainer E, the classification of azeotropic mixtures into 113 classes was first proposed by Matsuyama et al. (1977). As explained by Hilmen (2000), Serafimov (1996) extended the work of Gurikov (1958) and used the total number of binary azeotropes $M$ and the number of ternary azeotropes $T$ as classification parameters. Serafimov's classification denotes a structural class by the symbol "M.T." where $M$ can take the values 0, 1, 2 or 3, and $T$ can take the values 0 or 1. These classes are further divided into types and subtypes denoted by a number and a letter. As a result of this detailed analysis, 4 more feasible topological structures, not found by Gurikov, were revealed. Thus, Serafimov’s classification includes 26 classes of feasible topological structures of VLE diagrams for ternary mixtures. Both the classifications of Gurikov and Serafimov consider topological structures and thus do not distinguish between antipodal structures since they have the same topology. Thus, the above classifications include ternary mixtures with opposite signs of the singular points and in an opposite direction of the residue curves (antipodal diagrams). Serafimov’s classification is presented graphically in Figure 3. The transition from one antipode to the other (e.g., changing from minimum-to maximum-boiling azeotropes) can be made by simply changing the signs of the nodes and inverting the direction of the arrows. The correspondence between Matsuyama and Serafimov’s classification is detailed in Kiva et al. (2003).
Ternary systems are studied in this research on the basis of Serafimov’s classification, including 26 classes of feasible topological structures of VLE diagrams for ternary mixtures (Serafimov, 1996). The entrainer E is conventionally defined by its boiling temperature with respect to the binary mixture A-B to separate. A heavy entrainer E has a boiling temperature higher than A and B; an intermediate entrainer E has a boiling temperature between the A and B; a light entrainer E has a boiling temperature lower than A and B. In industry, the extractive distillation entrainer is usually chosen as heavy (high boiling) component mixtures (Luyben and Chien, 2010; Lang et al., 1994; Rodriguez-Donis, 2009; Shen 2012; Shen et al., 2013a; Benyounes et al., 2014; Benyahia et al., 2014). Theoretically, any candidate entrainer satisfying the feasibility and optimal criteria can be used, no matter whether it is a heavy, light, or intermediate entrainer. Literature studies on intermediate entrainers or light entrainers validate this assumption (Lelkes et al., 2002; Lang et al., 1999; Rodriguez-Donis et al., 2012; Shen, 2012; Shen and Gerbaud, 2013b; Laroche et al., 1992). Based on the calculation of the still path and possible composition profiles of the column sections, Lang et al. (2000a, b) extended the feasibility of extractive distillation in a batch rectifier for the investigation of the separation of maximum azeotropes, Rodriguez-Donis et al. (2009a, 2012a,b) studied the maximum azeotropic mixture separation. However, extractive distillation studies have always considered a heavy entrainer to split a minimum boiling aze trope which belongs to class 1.0-1a (Knapp and Doherty, 1994a; Luyben, 2008a, 2008b; Brüggemann and Marquardt, 2004). Düssel and Stichlmair (1995) proposed a hybrid method by replacing one distillation step into a decantation or absorption, which is less energy intensive for the separation of minimum azeotropes with a heavy entrainer. These study focus on maximum azeotropic mixture separation and provide a useful guide for the separation of azeotropic mixtures by batch extractive distillation.

SIMPLE THERMODYNAMIC INSIGHT TOOLS

Residue Curve Map

A residue curve map (RCM) is a collection of the liquid residue curves in a simple one-stage batch distillation originating from different initial compositions. The RCM technique is considered to be a powerful tool for flow-sheet development and the preliminary design of conventional multi-component separation processes and has been extensively studied since 1900. Using the theory of differential equations, the studies of the topological properties of the residue curve map (RCM) are summarized in two recent articles (Kiva et al., 2003; Hilmen et al., 2003). The simple RCM was modeled by the set of differential equations.

\[
\frac{dx_i}{dh} = x_i - y_i^* 
\]

where \( h \) is a dimensionless time describing the relative loss of the liquid in the still-pot. \( x_i \) is the mole fraction of species \( i \) in the liquid phase, and \( y_i \) is the mole fraction of species \( i \) in the vapor phase. The \( y_i \) values are related with the \( x_i \) values using equilibrium constants \( K_i \).

The singular points of the differential equation are checked by computing the associated eigenvalues. Within a non-reactive residue curve map, a singular point can be a stable or an unstable node or
a saddle, depending on the sign of the eigenvalues related to the residue curve equation. For non-reactive mixtures, there are 3 stabilities: unstable node, stable node, and saddle point. The residue curves move away from the unstable node to stable node with increasing temperatures. Some residue curves move away from a saddle point with decreasing temperatures and others with increasing temperatures.

**Unidistribution and Relative Volatility**

The distribution coefficient and relative volatility are well-known characteristics of the vapor–liquid equilibrium. The distribution coefficient $K_i$ is defined by:

$$K_i = \frac{y_i}{x_i}$$

(K$_i$ characterizes the distribution of component $i$ between the vapor and liquid phases in equilibrium. $K_i=1$ defines the unidistribution curve. The vapor is enriched with component $i$ if $K_i>1$, and is impoverished with component $i$ if $K_i<1$ compared to the liquid. The higher $K_i$, the greater the driving force ($y_i-x_i$) and the easier the distillation will be. The ratio of the distribution coefficient of components $i$ and $j$ gives the relative volatility. The relative volatility is a very convenient measure of the ease or difficulty of separation in distillation. The volatility of component $j$ relative to component $i$ is defined as:

$$\alpha_{ij} = \frac{y_j/x_j}{y_j/x_j}$$

The relative volatility characterizes the ability of component $i$ to transfer (evaporate) into the vapor phase compared to the ability of component $j$. Component $i$ is more volatile than component $j$ if $\alpha_{ij}>1$, and less volatile if $\alpha_{ij}<1$. For ideal and nearly ideal mixtures, the relative volatilities for all pair of components are nearly constant in the whole composition space. The situation is different for non-ideal and in particular azeotropic mixtures, where the composition dependence can be complex.

Unidistribution and univolatility line diagrams can be used to sketch VLE diagrams and represent topological features of the simple phase transformation trajectories. The qualitative characteristics of the distribution coefficient and relative volatility functions are typical approaches for thermodynamic topological analysis. Kiva et al., (2003) considered the behavior of these functions for binary mixtures. The composition dependencies of the distribution coefficients are qualitative and quantitative characteristics of the VLE for the given mixture. In a similar way to the distribution coefficient, the relative volatility features can be represented by isovolatility lines and the system of univolatility lines when $\alpha_{ij}=1$ proposed. It is evident that the point of a binary azeotrope gives rise to univolatility line and then the point of a ternary azeotrope gives rise to the three univolatility lines. These features are represented in Figure 4 for the most probable classes. The main aim of their work (Kiva et al., 2003) was to consider feasible structures of the residue curve maps in more detail, and in fact this study helped to popularize more refined classification of the ternary diagrams. The diagrams of unidistribution lines were used as a main tool for analysis of tangential azeotropes.

![Figure 4: Unidistribution and univolatility line diagrams for the most probable classes of ternary mixtures according to Reshetov’s statistics. Reproduced from Kiva et al. (2003), with permission from Elsevier.](https://example.com/image.png)

Recently, Rodriguez-Donis et al., (2009a, 2009b, 2010, 2012a, 2012b) studied how univolatility lines split the composition triangle into regions of a certain order of volatility of components and defined a general feasibility criterion for extractive distillation under an infinite reflux ratio: “Homogeneous extractive distillation of a A-B mixture with entrainer E feeding is feasible if there exists a residue curve connecting E to A or B following a decreasing (a) or
increasing (b) temperature direction inside the region where A or B are the most volatile (a) or the heaviest (b) component of the mixture. In this work, we consider unidistribution and univolatility line diagrams for the purpose of sketching the volatility order region and thus of assessing the feasible structures that will obtain possible products and offer information of possible limitations of entrainer feed.

APPLICATION OF TOPOLOGIC ANALYSIS FOR SEPARATING ACETONE/CHLOROFORM

The separation of the maximum-boiling azeotrope acetone/chloroform using 7 different candidate solvents was employed as case study. The azeotropic behaviors in multicomponent mixtures with solvents are shown in Table 1. Separation of the azeotropic mixture A-B with heavy entrainers DMSO (E1), chlorobenzene (E2), EG (E3), o-xylene (E4) or benzene (E5) has same type of singular properties, as they exhibits the same 1.0-2 classification, while using water (E6) introduces two more azeotropes, which makes the separation more complicated. The light entrainer dichloromethane (E7) has another type of singular character. The separation of the maximum-boiling mixture acetone/chloroform with the proposed solvents exhibit class 1.0-1a, 1.0-2, and 3.1-4. The thermodynamic insights published in previous work (Shen et al., 2013a; Benyounes et al., 2014; Benyahia et al., 2014; Lelkes et al., 2002; Lang et al., 1999; Rodriguez-Donis et al., 2012; Shen et al., Gerbaud, 2013b) and validated for the 1.0-1a and 1.0-2 ternary mixture class are applied here, and the general feasibility criterion previously established for ternary mixtures including only one azeotrope (1.0-1a or 1.0-2) is now, for the first time, extended to that including three azeotropes (class 3.1–4).

Topological Features Related to Process Operation

The general feasibility criterion holds for infinite reflux ratio operations. In this section we take a class 1.0-2 diagram to display the qualitative topological features of the ternary system related to process operation. Under infinite R and FE/V=0+, Figures. 5(a) and 5(b) show the typical feature for a residue curve map (Figure 5(a)) and an extractive map (Figure 5(b)). The column has a single rectifying section, and the composition profile of the rectifying section in a tray column follows strictly a residue curve assuming the constant molar overflow hypothesis and infinite number of trays (Jobson et al., 1995; Krolikowski, 2002). The rcm analysis states that both original components A and B are unstable nodes; the entrainer (E) is the stable node, while the maximum boiling azeotrope between AB is a saddle point. The rcm stable separatrix, which is also called the basic distillation region boundary, links the azeotrope to E. Separation of components A and B is theoretically impossible by conventional azeotropic distillation adding E initially into the still, because components A and B are located in different distillation regions, separated by the rcm stable separatrix. Under infinite R and FE/V=0+ (Figure 5(b)), the maximum boiling azeotrope azeo AB is a saddle Sextr and A and B are stable extractive nodes (SN A,extr and SN B,extr, respectively), whereas E is an unstable extractive node (UNextr). There will always be an unstable extractive separatrix between UNextr (vertex E) and Sextr (T max azeotrope AB). All the general features of the topology of the extractive composition profile map and its difference relative to class 1.0-1a are now discussed as follows, depending on the intersection of the αAB=1 curve with the triangle edges. Figure 5(c) shows the extractive composition profile maps for a higher value of FE/V but lower than (FE/V)max while R is infinite. Sextr moves inside the ternary composition space, precisely along the univolatility line αAB=1. Furthermore, the stable extractive nodes SN A,extr and SN B,extr move toward E over the binary edges A-E and B-E, respectively. Therefore, there exist a stable extractive separatrix SN B,extr-Sextr-SNA,extr and an unstable extractive separatrix UNextr-Sextr-UN'extr. Logically, under finite reflux ratio, the unstable extractive separatrix UNextr-Sextr-UN’ will move toward the selected distillate product (A or B), reducing the size of their respective feasible regions. Further increases in FE/V allow the fusion of Sextr and SN A,extr. All extractive composition profiles then reach the unstable node SN B,extr (Figure 5(d)).

Table 1: Types of single points of extractive distillation entrainers.

<table>
<thead>
<tr>
<th>Ezeotropes introduced by E</th>
<th>A-E</th>
<th>B-E</th>
<th>A-B-E</th>
<th>E</th>
<th>A</th>
<th>B</th>
<th>AZEO_AB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy entrainers (E1-E5)</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>Stable</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Saddle</td>
</tr>
<tr>
<td>Light entrainer (E6)</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>Unstable</td>
<td>Saddle</td>
<td>Saddle</td>
<td>Stable</td>
</tr>
<tr>
<td>Water (E7)</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Saddle</td>
<td>Stable</td>
<td>Saddle</td>
<td>Saddle</td>
<td>Stable</td>
</tr>
</tbody>
</table>
Figure 5: Topological features related to the extractive distillation process operation of class 1.0-2 when using a heavy entrainer.
The above observation shows the significance of the univolatility line in the synthesis of the homogeneous extractive distillation process, because it sets limiting values of $(F_{E/V})_{\text{max}}$. Here, the $\alpha_{AB}=1$ line sets a maximum value $(F_{E/V})_{\text{max},B,R}$ to recover component A. Under finite reflux ratio, extractive profiles are dependent on the distillate composition. Therefore, rectifying and extractive composition profile maps must be computed for both possible distillates $x_{DA}$ and $x_{DB}$ for different $F_{E/V}$ and R conditions (Figures 5(e) and 5(g) for product A and Figure 5(f) and 5(h) for product B). For Figure 5(e), the ternary saddle $S_{\text{extr}}$ moves toward vertex B while for Figure 5(g) $S_{\text{extr}}$ moves toward the B-E edge inside the composition triangle and the stable node $S_{N_B,\text{extr}}$ is located outside the composition triangle. The rectifying reflux ratio allows one to set the extractive separatrix on the left of the rectifying separatrix, and an optimal reflux ratio exists for a given $F_{E/V}$. The occurrence of an unstable extractive separatrix prevents complete recovery of the distillate, because an unfeasible region of growing size arises as R decreases. In contrast, for Figures 5(f) and 5(h), the ternary saddle $S_{\text{extr}}$ moves toward the A-E edge inside the composition triangle and the stable node $S_{N_A,\text{extr}}$ is located outside the composition triangle.

**Topological Feasibility Criterion**

Figure 6 displays the general thermodynamic principles of the 1.0-2 class corresponding to extractive distillation of a maximum-boiling azeotropic mixture A-B with heavy entrainer benzene. While using heavy entrainers DMSO, chlorobenzene, EG or xylen, the ternary systems bear the same features as benzene. The $\alpha_{AB}=1$ reaches the binary side B-E when using these heavy entrainers. Figure 6(a) shows that a rectifying stable separatrix divides the composition space into two distillation regions. Both components A and B are rcm unstable nodes. The size of the volatility order regions BAE (and BEA eventually) and ABE (and AEB eventually) depends on the $\alpha_{AB}=1$ univolatility curve location. The other univolatility curve ($\alpha_{BE}=1$ in Figure 6(a)) may exist, but does not affect the process feasibility and the product targeting. Both A and B are connected by a residue curve of decreasing temperature to E, which nears the triangle edge in the ternary diagram. Therefore, they can both be distillate products, depending on the location of the global feed composition, either in BAE (B product) or in ABE and AEB (A product).

The extractive profile map analysis enables identification of feasible and unfeasible regions for the composition in the extractive section of the column. Those regions are bounded by extractive stable and unstable separatrices crossing at saddle extractive singular points (Knapp and Doherty, 1994). The rcm singular points become the singular points of the extractive profile map with an opposite stability for the heavy entrainer case. Then for the 1.0-2 class, increasing the entrainer flowrate, the extractive profile singular points $S_{\text{extr},A}$ and $S_{\text{extr},B}$ originating from A and B move toward the entrainer vertex. In Figure 6(a), $S_{\text{extr},A}$ can go up to E and there is no limiting flowrate. But $S_{\text{extr},B}$ disappears at point $x_P$ when it merges with the saddle extractive $S_{\text{extr}}$ originating at the $T_{\text{max}, \text{azeo}_{AB}}$. So, there is a maximum flowrate ratio $F_{E/V,\text{max}}$ to obtain A as product by extractive distillation. That behavior is directly related to the volatility order regions, which explains how the general criterion is established. The above criterion indicates that A can be distilled without any limit for the entrainer feed ratio, whereas there exists a maximum entrainer feed ratio to get B. Depending on the overall feed composition, either A or B can be distilled: from $x_{F1}$ B is the distillate product; from $x_{F2}$ below the extractive separatrix, A is the distillate product.

![Figure 6: Thermodynamic feasibility criterion for 1.0–2 case b with heavy entrainer benzene (DMSO; chlorobenzene; EG or o-xylene).](image)
Figure 7(a) summarizes the topological features and the products achievable for the class 1.0–1a (maximum boiling azeotrope with a light entrainer). The point of entrainer dichloromethane is the residue curve unstable node UNrcm (open circle); apex A and B are residue curve saddle points Srcm (open triangle down), while the maximum boiling azeotrope is a stable node SNrcm (filled circle). By using extractive distillation, either A or B can be recovered as product depending on the univolatility line αAB=1 location. The univolatility line starts at the maximum boiling azeotrope, intersects one triangle side at x_{pA}, and divides the composition graph into two volatility order regions, EBA and EAB. The x_{pA} location decides that A can be recovered from the bottom as x_{pA} lies on the A-E side (Figure 7(a)). A is the most difficult volatile in the region EBA where it is connected to E by a residue curve of increasing temperature from E to A. Figure 7c presents the extractive profiles under the condition of infinite reflux and FE/V = 0.5; all the extractive profiles start from the unstable node point, depend on the overall feed composition, and either product can be distilled correspondingly. Figure 7(b) displays the thermodynamic properties for the ternary mixtures of acetone – chloroform – water where the entrainer water forms two additional binary minimum-boiling azeotropes. According to Serafimov’s classification they correspond to the diagrams class 3.1-4. Depending on the stability of singular points, there is only one or several possibilities for the location of the univolatility lines always associated with the position of azeotropes. Univolatility lines intercept each other at the ternary azeotrope, and part of univolatility lines overlap with the residue curve map boundary. The univolatility lines then define volatility order regions like AEB: A is more volatile than E, and E is more volatile than B. From one side of a univolatility line αAB to the
other, the relative volatility between A and B is reversed. Because $\alpha_{A,B}=1$ crosses the diagram binary A-E side, the feasibility criterion is valid for acetone (A) as the lightest component, and there is a residue curve connecting the azeotropic components, enabling recovery of acetone as product in a very small region AEB. The feasibility criterion also holds for the high-boiling component water (E), enabling its recovery as product in a stripper. Besides, the separation using the entrainer water, which is immiscible with chloroform (see Figure 7(d)), makes the separation process harder than it should be. Even though water as a solvent has a high economic and environmental advantage, the thermodynamic insight indicates that it is a limited efficiency solvent for separating the acetone/chloroform system.

**CONCLUSIONS**

A topological insight methodology has been proposed to assess the feasibility of the separation of azeotropic mixture by using different kinds of entrainer. The possible products in the distillation column and the existence of a limiting entrainer/feed flow rate ratio are predicted using general feasibility criteria. The separation of the maximum-boiling azeotropic acetone/chloroform is used as a case study, using 7 candidate solvents, the ternary system can be classified into diagrams class 1.0–1a (using light entrainer), class 1.0–2 (using heavy entrainer), and class 3.1-4 (using water). The conceptual design of the feasibility study of the three classes is developed by the analysis of the residue curve map and product regions.

For the class 1.0–2 (separation of acetone/chloroform by adding heavy entrainer $E_1-E_4$), the univolatility line $\alpha_{AB}=1$ can intersect the B-E edge. The general criterion states that, under infinite reflux ratio, both A and B can be obtained at the top, depending on the overall feed composition location. There also exists a maximum value for $F_e/F$ when component A is the distillate. For the class 1.0–1a, corresponding to the separation of a maximum boiling azeotropic mixture A-B using a light entrainer $E_7$, the process is feasible above a minimal limit entrainer/feed flow rate ratio value, so that the extractive stable node $[SN_{extr}]$ is located in the region where it can intersect a stripping profile which can reach the expected product A. The possible advantage of using a light entrainer is to offer more opportunities for separating minT and maxT azeotropic mixtures when it may not be easy to find a heavy or intermediate entrainer. The thermodynamic insight indicates that using solvent water corresponds to diagrams class 3.1-4 and, even though it has a high economic and environmental advantage, it is a limited efficiency solvent for separating the acetone/chloroform system. Application of the thermodynamic criterion hints at product feasibility, in which the product goes up or down using a rectifying or stripping column, operating parameter values and solvent efficiency.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>light original component</td>
</tr>
<tr>
<td>ABE</td>
<td>volatility orders, A is possible distillate</td>
</tr>
<tr>
<td>B</td>
<td>heavy original component</td>
</tr>
<tr>
<td>E</td>
<td>entrainer</td>
</tr>
<tr>
<td>$F_e/F$</td>
<td>entrainer - feed flow rate ratio, continuous process</td>
</tr>
<tr>
<td>$F_e/V$</td>
<td>entrainer - feed flow rate ratio, batch process</td>
</tr>
<tr>
<td>$(F_e/V)_{\text{min}}$</td>
<td>minimum entrainer - feed flow rate ratio, batch process</td>
</tr>
<tr>
<td>$(F_e/V)_{\text{max}}$</td>
<td>maximum entrainer - feed flow rate ratio, batch process</td>
</tr>
<tr>
<td>$K_i$</td>
<td>distribution coefficient</td>
</tr>
<tr>
<td>RCM</td>
<td>Residue Curve Map</td>
</tr>
<tr>
<td>$[SN_{\text{extr}}]$</td>
<td>extractive node feasible range</td>
</tr>
<tr>
<td>$T_{\text{maxa}z e_{AB}}$</td>
<td>the maximum azeotrope point of mixture AB</td>
</tr>
<tr>
<td>$T_{\text{mina}z e_{AB}}$</td>
<td>the minimum azeotrope point of mixture AB</td>
</tr>
<tr>
<td>maxT</td>
<td>the maximum boiling temperature</td>
</tr>
<tr>
<td>minT</td>
<td>the minimum boiling temperature</td>
</tr>
<tr>
<td>UN</td>
<td>unstable node originating at the entrainer vertex</td>
</tr>
<tr>
<td>UN’</td>
<td>unstable node originating outside the composition simplex</td>
</tr>
<tr>
<td>$x_p$</td>
<td>intersection point between univolatility curve and residue curve passing through the distillate product</td>
</tr>
</tbody>
</table>

**REFERENCES**


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