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# THERMODYNAMIC INSIGHT ON EXTRACTIVE DISTILLATION WITH ENTRAINER FORMING NEW AZEOTROPES

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#### Abstract

This paper deals with the feasibility analysis of batch extractive distillation taking into account the effect of the univolatility lines  $\alpha_{i,j} = 1$  and the shape of residue curves for ternary mixtures involving two binary azeotropes. A general feasibility criterion previously established for ternary mixtures only including one azeotrope is now extended to Serafimov's classification diagrams: 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c. Application of the feasibility criterion hints at which component goes up or down using a rectifying or stripping column. Preliminary feasibility results are verified by computing the map of extractive liquid profiles using a simplified modelling. Examples including batch rectifier are also corroborated by rigorous simulation using ProSim Batch.

Keywords: homogeneous extractive distillation, univolatility line, batch column

#### 1. Introduction

Batch distillation is preferred in specialty chemical industry, where the amount and the composition of mixtures changes regularly along with the required purity of the products. Over the years, extractive distillation has been considered as an industrial process worth interest, in particular because it was based on only one well established rule for finding a feasible entrainer, namely homogeneous substance that doesn't form azeotropic mixture with the original components. The ternary diagrams concerned when using a light, intermediate or a heavy entrainer belong to four Serafimov's classes, 0.0-1; 1.0-1a; 1.0-1b and 1.0-2, and cover one third of occurring ternary azeotropic mixtures [1].

Besides, the apparent simplicity of this feasible rule is more complex than it appears, because the good performance of extractive distillation depends strongly on the effect of the entrainer on the key components volatility. In particular, the existence of univolatility lines can affect which original component can be drawn as first product cut, the most appropriated column configuration and the existence of limiting values for the entrainer flowrate. Combination of residue curve map analysis along with the unidistribution and univolatility lines has been scarcely considered, except recently to study the use of heavy, intermediate and light entrainers in the separation of azeotropic and low boiling mixtures by using extractive batch rectifying and stripping column configurations encompassing 0.0-1, 1.0-1a; 1.0-1b and 1.0-2 classes [2,3,4]. A general feasibility criterion was then enounced in order to identify which original component will be drawn as first product cut: "*Existence of a residue curve connecting (E) to (A) or (E) to (B) following a decreasing (resp. increasing) temperature direction inside the region where (A) or (B) is the most (resp. least) volatile component of the mixture"*.

In this paper, we demonstrate that this criterion is also applicable when (E) form one additional minimum or maximum boiling azeotrope with (A) or (B) encompassing Serafimov's classes: 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c. Applicability of the general feasibility criterion is checked taking into account the shape of the residue curves and the volatility order between components inside the regions defined by the existence and the position of the univolatility lines.

The map of residue curves along with univolatility lines were computed by using RegSolResidue® [5] and drawn with the freeware TernaryDiagram® [5]. NRTL was the thermodynamic model used for computing the liquid vapour equilibrium. Binary coefficients were taken from literature or determined from UNIFAC-estimated binary data. Ternary mixtures formed by common components found in industry are taken as test mixtures. Validation of the general feasibility criterion is done by computing the map of rectifying (resp. stripping) and extractive liquid profiles using the simplified model proposed

by Lelkes et al. [6]. These models were implemented in excel using Simulis®thermodynamics [5]. Finally, the separation of ternary mixtures by extractive distillation in a batch rectifier was corroborated via rigorous simulation using the commercial program BatchColumn® [5].

#### 2. Thermodynamic and topological features of the ternary diagrams

Figure 1 displays the thermodynamic and topological properties of ternary mixtures involving two binary azeotropic mixtures and no ternary azeotrope. According to Serafimov's classification they correspond to diagrams 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c. The nature occurrence of these ternary diagrams is displayed in Figure 1 [1]. Depending on the stability of singular points, there is only one or several possibilities for the location of the univolatility lines always associated to the position of binary azeotropes following the thermodynamic constrains: (1) univolatility lines intercepts each other only if a ternary azeotrope exits and, (2) no univolatility line crosses a residue curve map boundary. The univolatility lines then define volatility order regions like ACB: A is more volatile than C more volatile than B. From one side of a univolatility line  $\alpha_{AB}$  to the other, the relative volatility between A and B is reversed.



Figure 1. Residue curve map and univolatility lines for ternary mixtures with two azeotropes

For all ternary diagrams displayed in Figure 1, the general feasibility criterion can be regarded for the duo of zeotropic components in each volatility order region as follow:

- Diagram 2.0-1: only one position for the univolatility lines α<sub>A,B</sub> and α<sub>A,C</sub> dividing the ternary composition space in three volatility order regions. In this case the feasibility criterion is accomplished for the saddle components *B* and *C* (underlined in fig. 1). *B* (resp. *C*) is the most (resp. least) volatile component inside the region wherein there is a residue curve connecting *B* to *C* following a decreasing (resp. increasing) temperature direction. *B* (resp. *C*) can then be separated by using a rectifying (resp. stripping) distillation column.
- Diagram 2.0-2a: two positions for  $\alpha_{A,B}$  are possible. Criterion is always feasible for *C* (least volatil component) no matter the interception of  $\alpha_{A,B}$ . However, *A* accomplishes the criterion as the most volatile compound only under thermodynamic conditions of Figure b.1.
- Diagram 2.0-2b: criterion is always feasible for C as the least volatil component and for B as most volatile compound only if α<sub>A,B</sub> reaches the zeotropic binary side BC (Figure c.1).
- Diagram 2.0–2c: existence of the univolatility line  $\alpha_{B,C}$  sets obligatory location of  $\alpha_{A,B}$  and  $\alpha_{A,C}$ . Feasibility criterion is only accomplished for *C* in a region near to the zeotropic binary side *BC*.

#### 3. Validation of feasibility criterion on practical ternary mixtures

#### 3.1- Diagram 2.0-1

Figure 2 displays the residue curve map and univolatility lines for mixtures showing one minimum and maximum binary azeotrope. Depending of the binary azeotropes position, the resulting ternary diagram corresponds to 103,130 or 031 according to Matsuyama and Nishimura's classification [1] and feasibility criterion accomplishes for *A* or *B* as the most volatile component or for *B* or *C* as the heaviest component. In all cases, all pure components are saddles. Hence, none of them goes to the top or the bottom of the distillation column by using batch conventional or azeotropic distillation. Nevertheless, batch extractive distillation can enable it, if the adequate component is fed continuously at intermediate position of the column with a flow rate higher than the minimum value determined by the interception of  $\alpha_{A,B}$ ,  $\alpha_{A,C}$  or  $\alpha_{B,C}$  depending on the thermodynamic features of the ternary mixture.

Figure 2 displays the thermodynamic properties for the 2.0-1 class ternary mixtures methanol – tetrahydrofuran – n-butylamine and cyclopentane – methyl acetate – chloroform corresponding to the Nishimura diagrams 103 and 130, respectively. Because the  $\alpha_{A,B}$ =1 crosses different diagram side, feasibility criterion is valid for tetrahydrofuran (*B*) as lightest component in Figure 2a but for cyclopentane (*A*) in Figure 2b and there is a residue curve connecting the zeotropic components in both ternary mixture and enabling their recovery as product in a rectifying column configuration. Feasibility criterion also holds for the high boiling component (*C*), n-butylamine and chloroform for each mixture, respectively, enabling their recovery as product in a stripper.



Figure 2. Residue curve map and univolatility lines for mixtures of diagram 2.0-1

Computed extractive liquid profiles for rectifying and stripping batch column is shown in Figure 3 for obtaining tetrahydrofuran THF (B) (Figure 3a) and n-butylamine (C) (Figure 3b) at the top and the bottom of the column, respectively. All extractive liquid profiles were computed using the simplified model proposed by Lelkes et al. (1998) under total reflux condition [6]. In Figure 3a, the extractive liquid profiles map is computed for  $F_E/V=0.2$  under total reflux and all profiles reach the extractive stable node SN<sub>B</sub> intercepting a residue curve acting as rectifying liquid profile towards THF.

This thermodynamic scenario indicates the possibility for separating THF from the minimum azeotrope methanol – THF by continuous feeding of n-butylamine as heavy entrainer that also forms a maximum boiling azeotrope with methanol. This behavior was also corroborated by rigorous simulation with Batchcolumn considering a batch rectifying column having 35 theoretical stages and boiling n-butylamine is fed at tray 12 from the top with a relationship  $F_E/V$  around 0.2. An amount of 16.3 moles of equimolar mixture methanol – tetrahydrofuran ( $x_0$ ) was considered as initial charge. Continuous feeding of n-butylamine during some minutes allows replacing of minimum boiling azeotrope by tetrahydrofuran with 0.95 of molar composition ( $x_T$ ) and the still composition by  $x_\infty$ . Notice in Figure 3a the good agreement between the liquid profiles inside the extractive column section computed by the simplified model and by rigorous simulation. Withdrawal of THF in a subsequent operating step as first distillate product is possible at a fixed reflux ratio. Nevertheless, methanol can be separated as a

second distillate product only if the still path reaches the segment limited by the methanol vertex and the maximum boiling binary azeotrope. Finally, a distinct feature of the process is that the entrainer can not be obtained in a pure form.

Conversely, Figure 3b displays the map of extractive liquid profiles considering a batch stripper for obtaining n-butylamine (C) at the bottom of the column under total reflux and  $F_E/L= 0.25$ . In this case, the light entrainer methanol has to be fed continuously at intermediate column position. As indicated by the thermodynamic scenario of Figure 2a, all extractive liquid profiles are able to reach the zeotropic binary side at SN<sub>c</sub> and they can intercept any residue curve passing near to n-butylamine vertex as indicated in Figure 3b by  $x_N$ .



Figure 3. Map of extractive liquid profiles. (a) Batch rectifier for B. (b) Batch stripper for C

#### 3.2- Diagram 2.0-2a:

Diagram 2.0-2a corresponds to the Matsuyama and Nishimura's classification 023, 320, 401 and 410. It is rarely encountered because of the inclusion of two binary azeotropes of opposite kind (minimum and maximum boiling temperature) as node and saddle. A more frequent topological configuration with a minimum and a maximum boiling temperature binary azeotrope comprises the existence of a saddle ternary azeotrope giving the diagram 2.1-3a (2.7% of occurrence) [1].

#### 3.3- Diagram 2.0-2b:

With a 21% occurrence, diagram 2.0-2b is one of the most frequent ternary diagrams. The 2.0-2b class includes six Matsuyama and Nishimura's classification diagrams: 102, 120, 021, 043, 430, 403 involving two binary azeotropes of the same kind (both minimum or maximum boiling temperature) but being a node and a saddle. As for diagram 2.0-2a, the interception of the univolatility line  $\alpha_{AB}$ =1 is not unique providing two thermodynamic cases (Figure 1b1 1b2 and 1c1 1c2).

Cyclohexane (A) – Methyl Acetate (B) – benzene (C) mixture exhibits a thermodynamic state matching to Figure c.1 as it can be seen in Figure 4a. In this case, the feasibility criterion is valid for *B* and *C* as most and least volatil component, respectively. However when methyl acetate is substituted by ethyl acetate, the thermodynamic scenario corresponds to Figure c.2 according to the Figure 4b. Then, the feasibility criterion is not valid for B anymore because of the changing of the interception location of the univolatility line  $\alpha_{A,B}$ .

Map of extractive liquid profiles is shown in Figure 5a for the mixture Cyclohexane (A) – Methyl Acetate (B) – benzene (C) considering  $F_E/V= 0.3$  at total reflux operation. All extractive profiles reach the extractive stable node  $SN_A$  crossing any residue curve passing near to binary side methyl acetate – benzene. Hence, methyl acetate goes up the column replacing the azeotrope methyl acetate – cyclohexane being the unstable node of the mixture. This behavior was corroborated by rigorous simulation using ProSim Batch. The still was charged with 10.6 moles of equimolar composition of

methyl acetate – cyclohexane ( $x_0$ ). Batch column has 20 equilibrium stages and boiling liquid benzene was fed at stage seven. Methyl acetate of molar composition of 0.944 ( $x_T$ ) stayed at the column top thanks to continuous feeding of benzene under total reflux after 6 minutes of operating time. Figure 5a displays the liquid profile inside the distillation column for the still composition  $x_{\infty}$  showing a good agreement with the map of extractive liquid profiles computed using the simplified modeling.

Figure 5b displays the map of extractive liquid profiles for the stripping configuration column in order to obtain benzene at the bottom of the column for the mixture cyclohexane – benzene – ethyl acetate under total reflux and taking  $F_E/L= 0.2$ . Similarly to Figure 3b, the light entrainer, in this case, ethyl acetate has to be fed continuously at the intermediate position of the column producing that liquid profile inside the extractive section reach the binary side benzene – ethyl acetate intercepting a residue curve which finishes at the benzene vertex.



Figure 4. Residue curve map and univolatility lines for diagram 2.0-2b mixtures



Figure 5. Map of extractive liquid profiles. (a). Batch rectifier for B. (b) Batch stripper for C.

#### 3.4- Diagram 2.0-2c:

Even though ternary diagram 2.0-2c also includes two binary azeotropes having the same nature like diagram 2.0-2b and the corresponding Matsuyama and Nishimura's classification is 201, 210, 012, 034, 304 and 340, they are less frequent because of the topology of the azeotropes. In all cases, the

node minimum (resp. maximum) boiling azeotrope has to be formed between the two heaviest (lightest components). However, commonly used components can exhibit this type of topology as displayed in Figure 6a for the mixture acetonitrile– benzene – ethyl acetate. In this case all three univolatility lines exist and the feasibility criterion is only accomplished by benzene (C) in a region near to the binary side ethyl acetate – benzene. In this case, benzene is the least volatil component inside the region where a residue curve exists and finishes at the vertex of this component. This was corroborated by computing the map of extractive profiles inside the extractive section of a stripping column considering  $F_E/L=0.18$  at infinite reflux (Figure 6b). All extractive profiles go towards the binary side of ethyl acetate – benzene and they are all able to intercept any residue curve ending at benzene vertex. The feasible region also includes the distillation region located on the left of the distillation boundary wherein benzene is not the stable node anymore. Benzene will stay at the bottom of the column while ethyl acetate is fed continuously at intermediate position of the column at total reflux. This analysis is also valid for Figure 5b.



**Figure 6.** (a)Residue curve map and univolatility lines for mixtures of diagrams 2.0-2b. (b) Map of extractive liquid profiles for component B in a batch stripper.

#### 4. Conclusions

A general feasibility criterion considering the effect of the univolatility lines and the shape of the residue curves for ternary mixtures has been validated for the first time to ternary mixtures with two binary azeotropes. Dual azeotropic ternary mixture corresponds to four Serafimov's diagrams classes: 2.0-1, 2.0-2a, 2.0-2b and 2.0-2c.

The general feasibility criterion allows determining which component goes up or down using a rectifying or stripping column for batch extractive distillation process only based on the position of univolatility lines and the respective volatility order among components inside the residue curve map. Application of the criterion was done for several ternary mixtures commonly found in industrial practice. Then, the preliminary synthesis results for batch rectifying or stripping column were well corroborated by computing the map of extractive liquid profiles using a simplified and rigorous simulation. Depending on the position of the univolatility lines, these ternary diagrams could be viable for separating azeotropic mixtures, mainly for the most reported diagram 2.0-2b. However, unlike to the extractive distillation for classes 1.0-1a 1.0-1b and 1.02, the entrainer is not recovered purely, but drawn as an azeotropic mixture with one original component.

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