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# CONCEPTUAL DESIGN OF NON-IDEAL MIXTURE SEPARATION WITH LIGHT ENTRAINERS

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**Abstract** - A method is proposed to study the separation of minimum-, maximum-boiling azeotropic, and low volatility mixtures with a light entrainer, to investigate feasible regions of the key operating parameters reboil ratio (S) and entrainer - feed flowrate ratio ( $F_E/F$ ) for continuous processes. The thermodynamic topological predictions are carried out for 1.0–2, 1.0–1a, and 0.0–1 Serafimov's class diagrams. It relies upon the knowledge of residue curve maps, along with the univolatility line, and it enables the prediction of possible products at the bottom of the column and limiting values of  $F_E/F$ . The profiles of the stripping, extractive, and rectifying sections are calculated by equations considering S and  $F_E/F$ , and they bring information about the location of singular points and possible composition profile separatrices that could impair process feasibility. Providing specified product composition and recovery, the approximate calculations are compared with rigorous simulations of extractive distillation processes. Separating non-ideal mixtures using a light entrainer provides more opportunities for the case when it is not easy to find an appropriate heavy or intermediate entrainer.

**Keywords:** Conceptual design; Feasibility study; Extractive distillation; Azeotropic mixture; Light entrainer.

## INTRODUCTION

In extractive distillation, a suitable entrainer commonly should be a miscible, heavy boiling component. It should form no new azeotrope, and interact differently with the components to be separated, causing the changes of relative volatilities, and thereby ease the separation. However, there are some cases when its use is not recommended, such as for a heat sensitive, high boiling component mixture to be separated. Different entrainers can cause different components to be recovered as bottom product or recovered overhead in extractive distillation. Poten-

tial entrainers are critical since an economically optimal design made with an average design using the best entrainer could be much less costly (Laroche *et al.*, 1991). Theoretically, any candidate entrainer satisfying the feasibility and optimal criteria can be used no matter if it is a heavy, light, or intermediate entrainer. Literature studies on intermediate or light entrainers validate this assumption. Laroche *et al.* (1991) investigated the use of heavy, intermediate, and light boiling entrainers to separate minimum-boiling azeotropes. In a batch operation, a recently published paper reviewed the use of these three kinds of entrainers to separate maximum-boiling azeotropes

and low relative volatility mixtures (Rodriguez-Donis *et al.*, 2009a,b; Rodriguez-Donis *et al.*, 2012a,b; Shen *et al.*, 2013a,b,2015). However, Rodriguez-Donis *et al.* (2012a) mainly focused on thermodynamic topological insight of how knowledge of the location of univolatility lines and residue curve analysis help in assessing the feasibility of batch extractive distillation. It was not further tested for continuous operation.

In this study, we extended our previous work (Shen *et al.*, 2013b) on the design of thermodynamic feasibility insight for a conceptual batch and continuous extractive distillation. The separations of some new ternary systems, including a low relative volatility mixture with light entrainer, are explored. The UNIQUAC Thermodynamic model is used instead of the UNIFAC model to provide more reliable VLE calculations. After a brief analysis of the topological features of the system, profiles of the different sections are calculated. We focus on a sensitivity analysis of key operational parameters: entrainer - feed flow rate ratio and reboil ratio. The influences of the key operational parameters on profiles of different sections are studied. The composition profiles of the stripping, extractive and rectifying sections are calculated. The interaction relationships of key operational parameters have been explored. The rigorous simulation using the UNIQUAC model has been carried out to validate the thermodynamic insights and sensitivity analysis.

## STATE OF THE ART WITH LIGHT ENTRAINER

After studying more than 400 couples of azeotrope - entrainer systems, Laroche *et al.* (1992) concluded that: (1) light entrainers, even though rare in industrial practice, could be as common as heavy entrainers theoretically since it is as easy to find a potential light entrainer as a heavy one; (2) light entrainers often represent the only viable alternative when a heavy entrainer cannot be used; and (3) light entrainers can perform as well or better than heavy entrainers.

Compared to extractive distillation using a heavy entrainer, very few literature studies focus on light entrainers. The minimum-boiling azeotropic mixture ethanol and water with the light entrainer methanol was first tested by Hunek *et al.* (1989) in a pilot-plant experiment; this process is called reverse extractive distillation. Using the light entrainer acetone in the separation of ethanol (A) – water (B), Laroche *et al.* (1991) showed that the univolatility curve location could be used to determine the product. Lang *et*

*al.* (1999) assessed the feasibility of the extractive distillation of ethanol (A)-water (B) with the light entrainer methanol in a batch rectifier and of a mixture of n-butanol (A) - n-butylacetate (B) with n-propylformate and di-propylether as light entrainers in a batch stripper. Concerning a batch rectifier and a batch stripper, Varga *et al.* (2006) studied the separation of three types of mixtures: ethanol-water (minimum-boiling azeotrope) with the light entrainer methanol, water - ethylene diamine (maximum-boiling azeotrope) with the light entrainer methanol, and chlorobenzene - ethylbenzene (close boiling mixture) with the light entrainer 4-methylheptane. More recently, applying thermodynamic insights with the knowledge of the location of univolatility lines and residue curve analysis, Rodriguez-Donis *et al.* (2012a) published a study on the feasibility of extractive distillation for possible separation of azeotropic mixtures with a light entrainer that belongs to Serafimov's class 1.0-2 and 1.0-1a. Some azeotropic and low relative volatility mixture separations using light entrainer studied in the literature are summarized in Table 1. Light entrainer is denoted as E, the higher-boiling component recovered at the bottom is defined as B, the lower-boiling component obtained as top distillate is denoted as A, and azeotropic point are denoted by Az. This paper aims to investigate thermodynamic feasibility insight for the continuous extractive distillation process of three types of typical mixtures with light entrainers.

From basic mass balance analysis, feasibility of an extractive distillation under a finite reflux ratio (reboil ratio in reverse extractive distillation) condition requires that the top and bottom product compositions are connected each other through the liquid composition profiles  $x_i$  in each section. The calculation requires choosing a target product composition and depends on many parameters. In azeotropic distillation, or a common distillation process with two column sections, the relevant parameters to be considered are the heat condition of the feed variable  $q$ , the feed stage location, total number of stages, column holdup, flow rates, condenser cooling duty, boiler heat duty, and reflux ratio. Not all are independent because the distillation column model has only two degrees of freedom (Widgado and Seider, 1996). Extractive distillation further adds the entrainer feed flow rate ratio to the list of the parameters as another degree of freedom. We focus only on the influence of the reboil ratio and entrainer - feed flow rate ratio on feasibility. Finding the ranges of reboil ratio and entrainer - feed flow rate ratio values that enable a feasible extractive distillation is the main issue of extractive distillation.

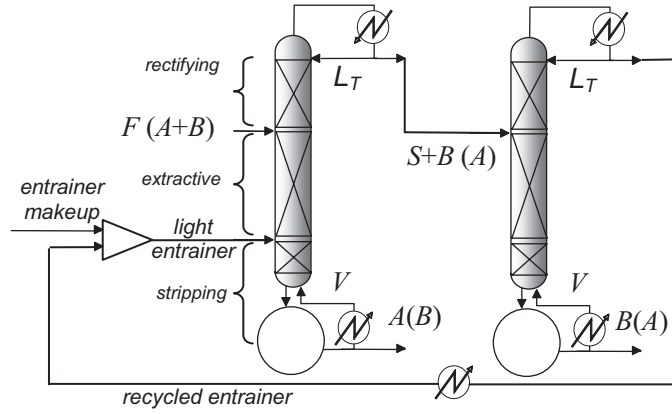
**Table 1: The study case related to extractive distillation separation of azeotropic and low relative volatility mixtures with light entrainers.**

<b>Classification: 1.0-2; Azeotropic type: Minimum; Volatility order: E&gt;Az&gt;A&gt;B</b>				
A	ethanol	ethanol/propanol	MEK	n-butanol
B	water	toluene	benzene	n-butyl-acetate
E	MeOH	acetone	acetone	n-propyl-formate /dipropyl-ether
References	Hunek <i>et al.</i> 1989  Laroche <i>et al.</i> 1992  Lang <i>et al.</i> 1999 Varga <i>et al.</i> 2006b Rodriguez-Donis <i>et al.</i> 2012a Shen and Gerbaud 2013	Laroche <i>et al.</i> 1992  Rodriguez-Donis <i>et al.</i> 2012a	Rodriguez-Donis <i>et al.</i> 2012a Shen and Gerbaud 2013	Lang <i>et al.</i> 1999
<b>Classification: 1.0-1a; Azeotropic type: Maximum; Volatility order: E&gt;A&gt;B&gt;Az</b>				
A	water	acetone	propanoic acid	
B	ethyl-enediamine	chloroform	Dimethyl-formamide	
E	MeOH	Dichloromethane	MIBK	
References	Varga <i>et al.</i> 2006b Rodriguez-Donis <i>et al.</i> 2012a Shen and Gerbaud 2013	Rodriguez-Donis <i>et al.</i> 2012a	Rodriguez-Donis <i>et al.</i> 2012a Shen and Gerbaud 2013	
<b>Classification: 0.0-1; Azeotropic type: low alpha; Volatility order E&gt;A&gt;B</b>				
A	chlorobenzene	ethyl acetate	benzene	
B	ethylbenzene	acetone		
E	4-methylheptane			
References	Varga <i>et al.</i> 2006b	Rodriguez-Donis <i>et al.</i> 2012a		

Applying a light entrainer for separating a maximum-boiling azeotrope, the corresponding ternary diagram belongs to the Serafimov class 1.0-1a (occurrence 21.6%). The separation of a minimum-boiling azeotrope with a light entrainer corresponds to the 1.0-2 class (occurrence 8.5%). The extension of thermodynamic insight to other mixture classes with light entrainers was systematically studied by Rodriguez-Donis *et al.* (2012a), who combined knowledge of the thermodynamic properties of residue curve maps and of the univolatility and unidistribution curve locations. Rodriguez-Donis *et al.* (2012a) explored thermodynamic insights for extractive distillation of non-ideal mixtures with light entrainer, not only for well-studied cases (e.g., 1.0-1a class), but also for other possible feasible classes found in a batch processes study. For suitable classes, the general criterion under infinite reboil ratio could explain the product to be recovered and the possible existence of limiting values for the entrainer - feed flow rate ratio for batch operation: there exists a minimum entrainer feed ratio for the Serafimov class 1.0-1a with univolatility curve  $\alpha_{AB} = 1$  that reaches the A-E (B-E) edge; there exists maximum entrainer flow rate to recover A(B) and no limit for B (A) recovery in the bottom product for the class 1.0-2 with univolatility curve  $\alpha_{AB} = 1$  that reaches the A-E (B-E),

etc. The behavior at finite reboil ratio could be deduced from the infinite behavior and properties of the residue curve maps, and some limits on the reboil ratio were found. However precise determination of the limiting values of reboil ratio or of the entrainer - feed flow rate ratio required other techniques, summarized as follows.

For separating azeotropic mixtures, besides the conventional batch rectifier (Lelkes *et al.*, 1998a; Stéger *et al.*, 2005), both batch stripper (Varga, 2006) and middle vessel columns (Davidyan *et al.*, 1994) have also been suggested and discussed in the literature, even though the use of a light entrainer would be recommend for use at a batch stripper, since the product expected to be a heavy boiler could still be removed from the boiler (Varga *et al.*, 2006). Extractive distillation can be operated either in a batch or in continuous mode. In the present work, we consider a continuous column configuration. Because we consider a light entrainer (boiling temperature below that of both A and B), the entrainer stream is fed below the main feed, these two feeds leading to three column sections: stages above the azeotropic mixture feed are called the rectifying section, stages between the azeotropic mixture feed and entrainer feed named the extractive section, with the stages below the stripping section (Figure 1).



**Figure 1:** Configurations of typical extractive distillation with light entrainer.

### FEASIBILITY STUDY METHODOLOGIES

Our methodology for the investigation of the extractive process feasibility relies on a short-cut method to compute the extractive distillation liquid column profiles, derived from differential Equation (1) (Lelkes *et al.*, 1998):

$$\frac{dx_i}{dh} = y_i - y_i^* \quad (1)$$

$y_i^*$  and  $y_i$  are the equilibrium composition with  $x_i$  and the operating composition computed from material balance for a given tray, respectively. This

equation is solved as an initial value problem during the feasibility study (Varga *et al.*, 2006). The model calculates the liquid composition profile in each column section based on the following assumptions: (1) theoretical plates; (2) saturated liquid feed of mixture to be separated; (3) saturated vapor entrainer feed; (4) constant molar flow rate ratio of liquid and vapor in the three respective sections of the column; (5) the liquid is an incompressible fluid.

Depending on Equation (1), Shen and Gerbaud (2013) published Equations (2), (3), and (4) for section profiles by considering a boiling liquid main feed  $F$  (feed physical state  $q=0$ ) and defining the reboil ratio  $S$ . The rectifying profile for the saturated vapor entrainer is:

$$\frac{dx_i}{dh} = \frac{S + \frac{F_E}{W}}{(S+1) - \frac{F}{W}} \cdot \left[ \frac{1}{S + \frac{F_E}{W}} \left( \frac{F_E}{W} \cdot x_E + \left( S - \frac{F}{W} + 1 \right) x_i + \frac{F}{W} \cdot x_F - x_W \right) - y_i^* \right] \quad (2)$$

and the extractive profile for the saturated vapor entrainer

$$\frac{dx_i}{dh} = \frac{S + \frac{F_E}{W}}{S+1} * \left[ \left( \frac{1}{S + \frac{F_E}{W}} \right) \left[ (1+S) \cdot x_i + \left( \frac{F_E}{W} \right) \cdot x_E - x_W \right] - y_i^* \right] \quad (3)$$

For the stripping profile:

$$\frac{dx_i}{dh} = \frac{S}{S+1} \cdot \left[ \left( 1 + \frac{1}{S} \right) \cdot x_i - \frac{1}{S} \cdot x_w - y_i^* \right] \quad (4)$$



Under the infinite reboil ratio, the equations are identical whatever the entrainer feed state  $q$  value is, as was recalled by Rodriguez-Donis *et al.* (2012): “the extractive liquid composition maps are similar and the process limiting entrainer - feed flow rate ratio under infinite reboil ratio is identical considering the entrainer as a saturated liquid or vapor”. This will hold for the assessment of the limiting flow rate ratio values. Then, as the entrainer is fed below the main feed (Figure 1), all the entrainer readily goes up into the extractive section. Consequently, we use Equations (2), (3) and (4) to compute each section composition profile. The second section of this work tries to continue validating these equations, and study the influence of the reboil ratios on profiles of different sections. Rigorous simulation validation is then carried out with ProSim Plus software for continuous column.

## RESULTS AND DISCUSSION

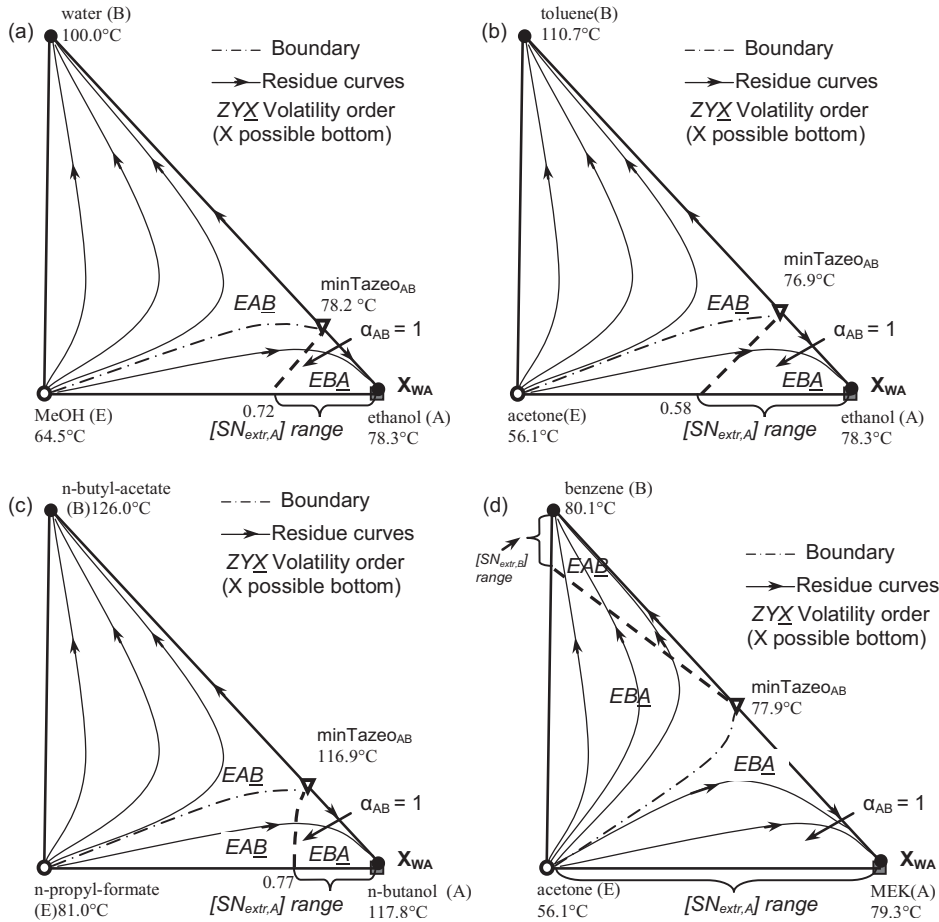
### Thermodynamic Topological Feasibility Insights

The thermodynamic topological ternary diagram is introduced to illustrate the feasibility of azeotropic mixture separation with light entrainer. Filled circles represent stable node  $SN_{rcm}$ , empty circles represent unstable node  $UN_{rcm}$ , and empty down triangles represent residue curve saddle points  $S_{rcm}$ . For all illustrated mixtures, the diagram is obtained at 1 atm and the UNIQUAC thermodynamic model is used. For simplicity, three component abbreviations are used: A represents the lightest component with lower boiling point than B in the mixture to be separated, B represents the component with higher boiling point in the mixture of A and B, and E represents the entrainer. Based on the general feasibility criterion proposed in Shen and Gerbaud (2013): “Component A or B can be drawn as first bottom product using a stripper configuration if there is a residue curve going from the entrainer E towards A or B and following an increasing temperature in the region in which A or B is the least volatile component of the ternary mixture.” In other words, the general feasibility criterion is valid for either component A or B in the mixtures of 1.0-1a, i.e., either of them can be drawn as first bottom product using a stripper configuration that depends on the univolatility line location at A-E side or B-E side. If the  $\alpha_{AB}=1$  curve intersects the binary side A-E, A is the expected product in the distillate because it is the most volatile in the region ABE where it is connected to E by a residue curve of decreasing temperature from E to A. If the  $\alpha_{AB}=1$

curve intersects the binary side B-E then B is the expected product. Thermodynamic topological feasibility analysis is carried out for the following categories of mixtures.

### Minimum-Boiling Azeotropic Mixture Separation Using Light Entrainer

Four cases of separation of minimum-boiling azeotropic mixtures using light entrainers are illustrated in Figure 2. Using light entrainer, the ternary system belongs to the 1.0-2 class. The volatility order is  $E > A_z > A > B$ . The cases ethanol/water/methanol (Fig. 2a denoted as case a), ethanol/toluene/acetone (Fig. 2b denoted as case b), and n-butanol/n-butyl-acetate/n-propyl-formate (Fig. 2c denoted as case c) belong to the sub-case of class 1.0-2 with a univolatility curve  $\alpha_{AB}=1$  that reaches the A-E edge. In the volatility order region indicated, both A and B are the least volatile in the respective regions, where there exists a residue curve with increasing temperature from E to their locations; either component A or B is a possible bottom product of the extractive distillation process depending on the overall feed composition. When B is the desired bottom product, it can be recovered without any limit for the entrainer feed ratio, whereas when A is the desired bottom product, the entrainer candidates will strongly depend on the extractive stable range  $SN_{extr,A}$ , as there exists a minimum entrainer feed ratio to get A. If the upper limit for the feed flow rate is not a concern for industrial practice of continuous extractive distillation, the lower limit should be as low as possible to keep the energy demand low. The location of the univolatility line is the closest to E for case b, then for case a, and finally for case c. This expands the extractive stable range  $SN_{extr,A}$  range, which also means an increase in the upper limit for the feed flowrate; case b has indeed the highest upper limit for the feed flowrate. Overall, Fig. 2b indicates that acetone exhibits the largest feasible extractive region for the separation of ethanol and toluene, targeting ethanol as product, which can result in a better operational stability. That may become critical at low reflux ratio when the range of feasible feed flowrate is narrowed. For the case of the benzene – MEK (i.e., methyl ethyl ketone) separation using the entrainer acetone (Fig. 2d). The univolatility line  $\alpha_{AB}=1$  ends at the binary B-E side at about 10% benzene and defines two feasible regions. Since the azeotropic components can be distilled only if the boundary is curved enough, however, extractive distillation is a worthy alternative process, as the feeding of the entrainer at an intermediate column tray generates extractive profiles



**Figure 2:** Minimum-boiling azeotropic mixture separations using light entrainer (1.0-2 class).

that are able to cross the distillation boundary of the residue curve map (Bernot et al. 1990). The rectifying stable separatrix is slightly curved, i.e., concave shape, in the region that contains component A, which makes it hardly possible to obtain MEK in azeotropic distillation, but feasible to get MEK as a bottom product in extractive distillation, while the other examples in Figure 2 have the convex shape in the region that contains component A.

### Maximum-Boiling Azeotropic Mixture Separation Using Light Entrainer

The separations of the maximum-boiling azeotropes using light entrainers are illustrated by three cases in Figure 3. From Fig. 3a for separation of water (A) and ED (i.e., ethylenediamine) (B) using the light entrainer MeOH (E), the univolatility line  $\alpha_{AB}=1$  ends at the B - E sides at about 20 mol% ED, defining two different volatility regions. The feasible region  $EBA$  lies above the univolatility line. Water (A) can be recovered as bottom product above a minimum entrainer - feed flow rate ratio, so it can intersect a stripping profile which can reach  $x_{W,A}$ ,

whereas no corresponding flow rate restrictions are placed on recovering B. Fig. 3b shows the acetone (A) and chloroform (B) separation using the light entrainer DCM (i.e., dichloromethane) (E). The point where the univolatility line intercepts the DCM-acetone edge is near to a dichloromethane vertex, located at  $x_E=0.88$  (88% DCM). The stable extractive node  $SN_{ext,A}$  give rise to a minimum entrainer flow rate ratio. Below the minimum values,  $SN_{ext,A}$  is located on the univolatility line; thus, the extractive profile cannot reach a stripping profile that approaches the expected product A. Similarly, Fig. 3c interprets the topological features for the separation of the maximum-boiling azeotropic mixture propionic acid - DMF (i.e., dimethylformamide) using the light entrainer MIBK (i.e., methyl isobutyl ketone). The univolatility line starts at the maximum-boiling azeotrope, intersects one triangle side and divides the composition graph into two volatility order regions,  $EBA$  and  $EAB$ . The point where the univolatility line intercepts the A-E edge is near to a MIBK corner, located at  $x_E=0.97$  (97% MIBK), and decides if apex A can be recovered from the bottom as  $x_{P,A}$  lies on the A-E side (Fig. 3b). A is less vola-



tile than E and B in the region  $E\bar{B}A$  where it is connected to E by a residue curve of increasing temperature from E to A.

The separation of ethyl acetate (131.9 °C) (A) – benzene (136.2 °C) (B) with low relative volatility using the light entrainer acetone (56.5 °C) (E) belong to the 0.0-1 class. Figure 4 displays the thermodynamic features of the second case of ethyl acetate -

benzene using acetone as entrainer. The univolatility line  $\alpha_{AB}=1$  intersects the A-E edge very close to the A apex and the B-E edge closer to the B apex. Then the two components A and B are products in the  $E\bar{B}A$  and  $E\bar{A}B$  volatility order regions, respectively. A requires a minimum entrainer flow rate ratio value, whereas B recovery is limited by a maximum entrainer flow rate ratio value.

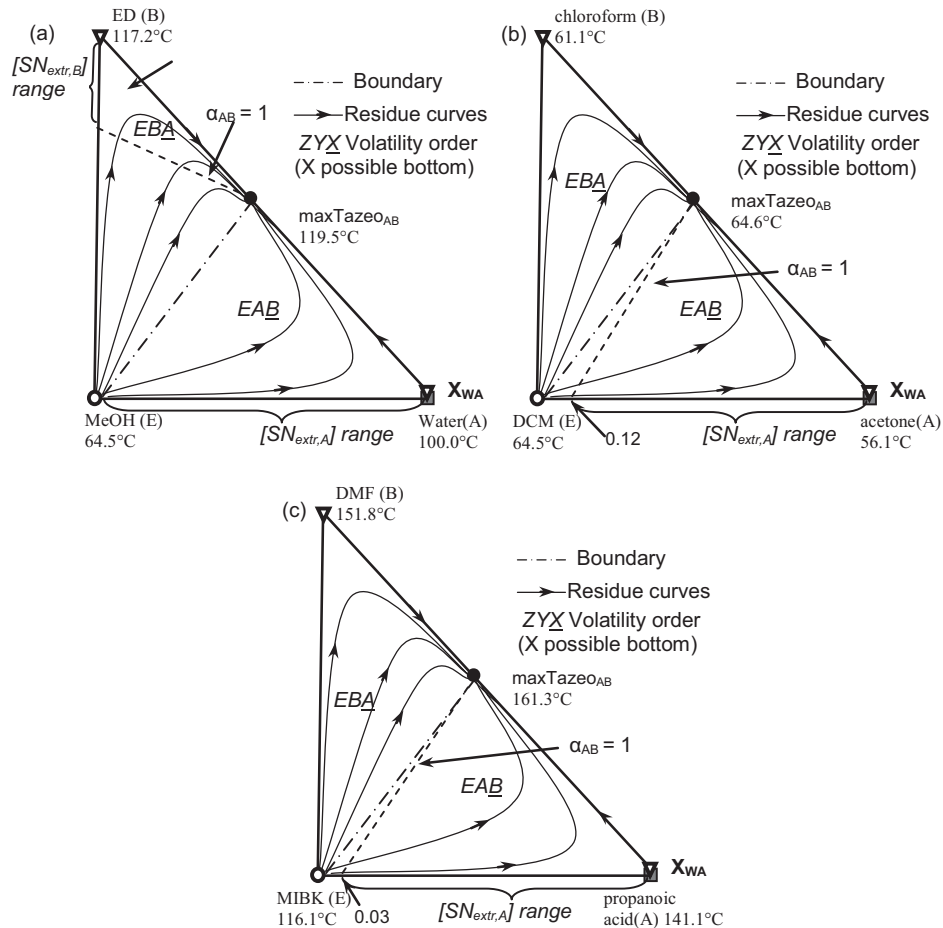


Figure 3: Maximum-boiling azeotropic mixture separations using light entrainer (1.0-1a class).

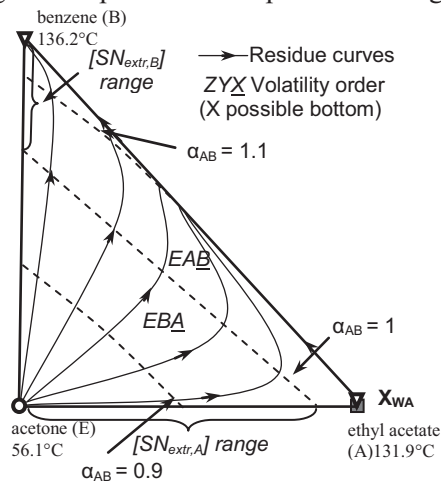


Figure 4: Low relative volatility mixture separation with light entrainer (0.0-1 class).

## The Influence of the Reboil Ratio on Composition Profiles of Different Sections

A detailed calculation of the profile map shows that when the reboil ratio gets smaller the feasible region of the stripping profiles gets smaller until the stripping profiles can no longer intersect the extractive profile region. This is shown in Figure 5. For  $x_{WA} = \{A, B, E\} = \{\text{vary, vary, 0.01}\}$ , where the composition of component E is kept constant at the value 0.01 while varying the composition of components A and B, Fig 5a displays three stripping profiles computed as the result of varying the expected purity in component A from 0.98 to 0.7. The shape of the stripping profiles follows that of the residue curves typical for a 1.0-1a mixture. For an A content of 98 mol % or 70 mol %, the profiles are near the AE edge. For an A content of 30 mole%, it goes to the BE edge. Fig. 5b shows the evolution of the stripping profile computed from  $x_{WA}$  with a purity of 98% in A, while changing the other component concentrations under various reboil ratios. Under an entrainer - feed flow rate ratio  $F_E/F=1$ , the shaded region in Figure 5b shows all the possible stripping profiles while varying the composition of B and E. Accordingly, the three different parts of these shaded regions are obtained by changing reboil ratios. Figure 5b also indicates that the stripping profile gets shorter in length as the reboil ratio decreases from 10 to 1. This will affect the feasibility because a smaller stripping profile may not intersect an extractive profile. In other words, changing the reboil ratio with

the entrainer - feed flow rate ratio, we can state that the desired product specification can be maintained over a wider range of reboil ratios as the entrainer - feed flow rate ratio increases.

Figure 6a, b, c, concerning the separation of MEK (i.e., methyl ethyl ketone) and benzene using acetone as entrainer, illustrates the evolution of the fixed points and separatice locations as the reboil ratio  $S$  decreases. The extractive unstable node  $UN_{\text{extr}}$  moves toward apex A parallel to the binary edge AB. The saddle node  $S_{\text{extr}}$  moves toward the  $SN_{\text{extr,A}}$  on the extractive separatrix, which results in the shrinking of the extractive feasible region when the boilup ratio  $S$  decreases from 30 to 1. The extractive separatrix location remains the same. At the boilup ratio  $S=1$ , this stresses the need for a large reboil ratio for the process to be feasible, whose consequence is a large heat duty.

## Rigorous Simulation

In this section, rigorous simulation is performed with ProSim Plus 3.1. For all illustrated mixtures, the thermodynamic UNIQUAC model is used. These simulations provide compositions and temperatures profiles for different entrainer-feed ratio, reboil ratio, and composition. Table 2 displays the corresponding extractive distillation column specifications. The number of trays in the extractive section is set at a proper value so that the terminal point of the extractive section composition profile reaches near to the extractive section stable node.

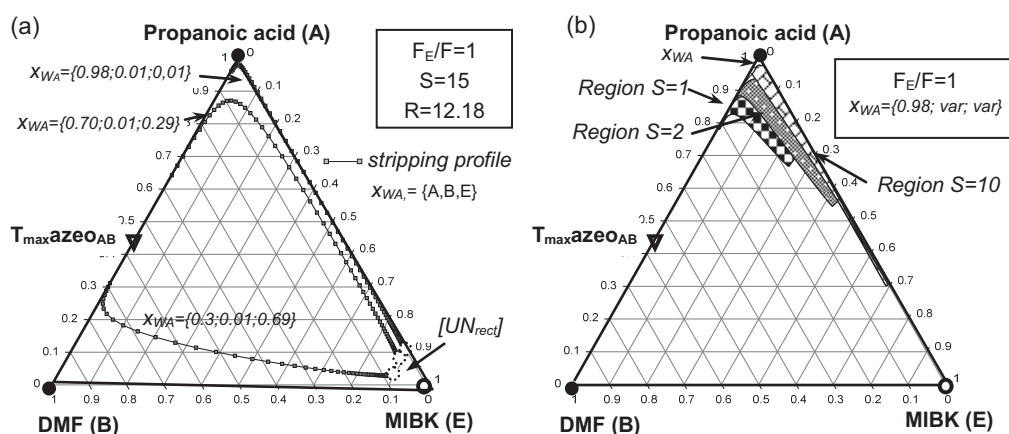


Figure 5: Influences of the reboil ratio on composition profiles of the stripping section.

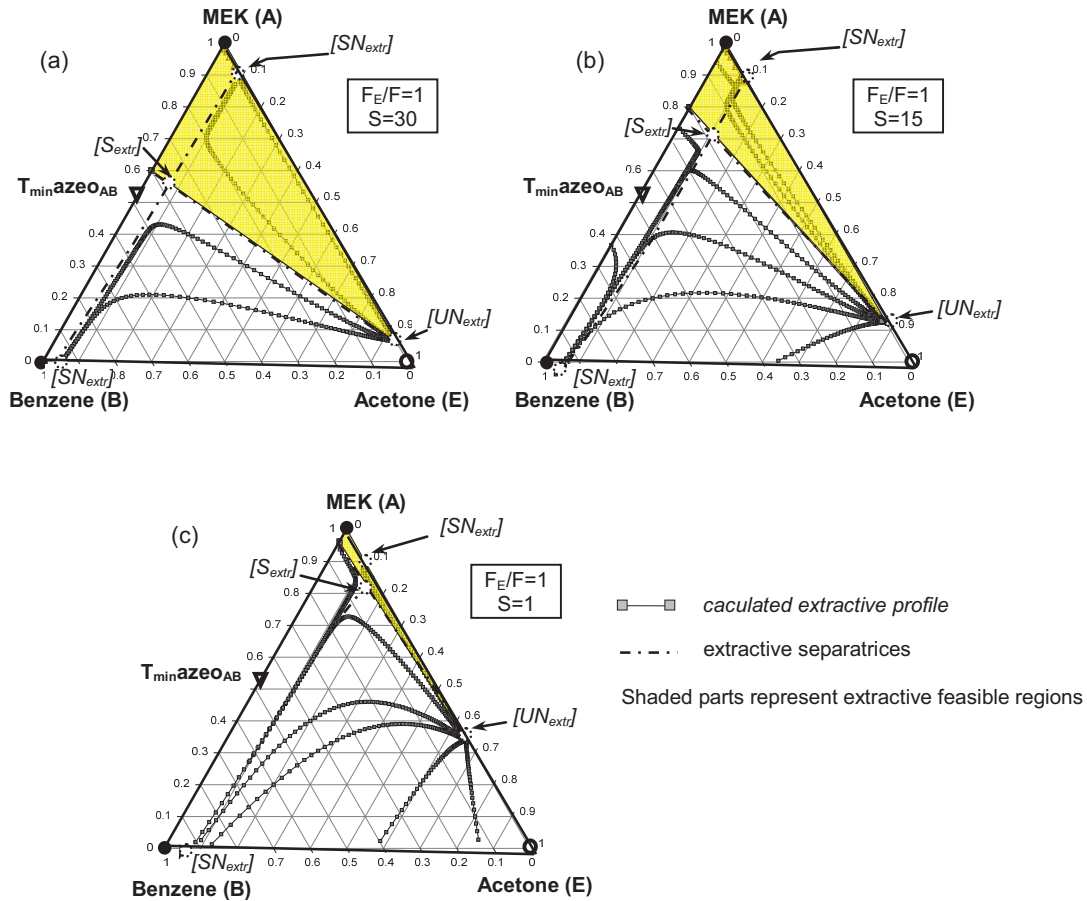


Figure 6: Influences of the reboil ratio on composition profiles of the extractive section.

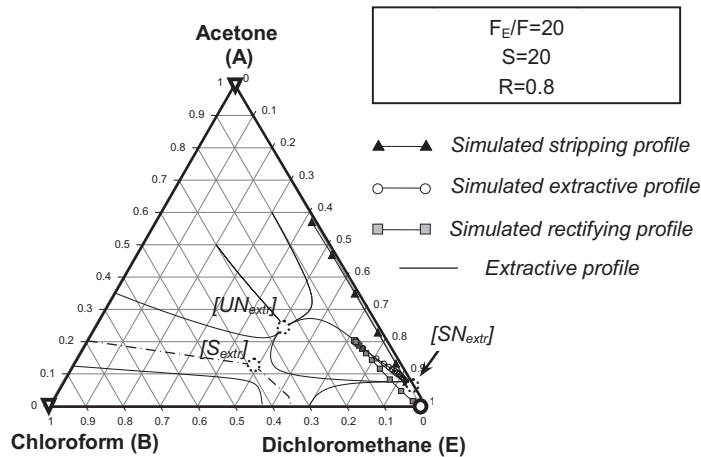
Table 2: Column operating specifications for rigorous simulation.

Specifications	Class 1.0-1a (Fig. 7)	Class 1.0.2 (Fig. 8a)	Class 1.0-2 (Fig. 8b)	Class 1.0.2 (Fig. 8c)
Tray number, N	65	50	50	100
Entrainer tray, $N_{FE}$	60	30	30	60
Feed tray, $N_F$	20	15	15	10
$x_F$ , mole fraction (A,B,E)	{0.7; 0.3; 0.0}	{0.4; 0.1; 0.5}	{0.225; 0.7; 0.075}	{0.225; 0.275; 0.5}
$x_E$ , mole fraction (A,B,E)	{0.0; 0.0; 1.0}	{0.0; 0.0; 1.0}	{0.0; 0.0; 1.0}	{0.0; 0.0; 1.0}

The rigorous simulation operation specifications for the acetone – chloroform – dichloromethane mixture are summarized in Table 2. Under conditions of  $S=20$  and  $F_E/F=20$ , Figure 7, concerning acetone – chloroform mixture separation using dichloromethane as light entrainer, displays the rigorous composition profile, along with the simplified extractive profile from Equations (3). The feed mixture is assumed to be in a boiling liquid state and the entrainer in a saturated vapor. In the physical states (e.g., saturated vapor, saturated liquid, etc) and properties (e.g., temperature, and pressure) of the feed mixture settings, we set the operating saturated liquid temperature to 423 K for the feed mixture and the saturated vapor temperature to 389.3 K for the entrainer at 1 atm. The specification for this column is somewhat unusual, as the reboil ratio is fixed instead of the

common tray using reflux ratio and distillate rate.

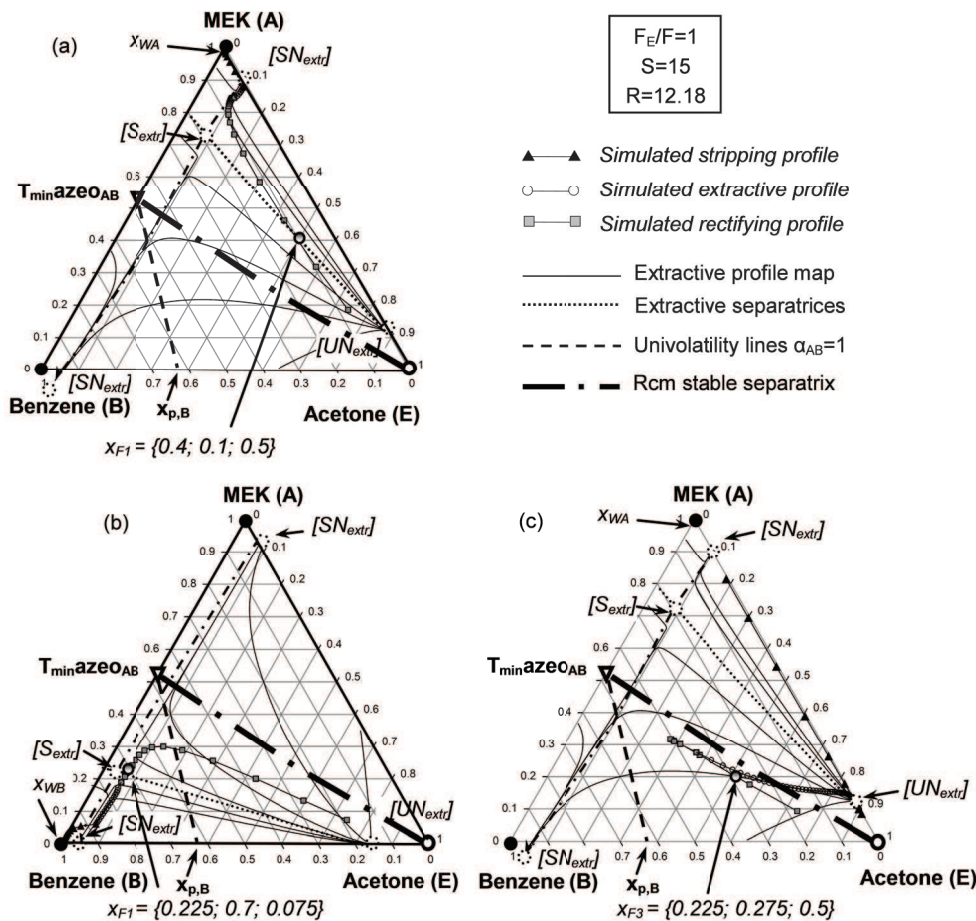
The extractive column has two design degrees of freedom left once the total number of stages and feed plate location are fixed: reboil ratio and entrainer - feed flow rate ratio. Given a composition of  $x_F = \{A; B; E\} = \{0.7; 0.3; 0.0\}$ , it is feasible to recover A from the azeotropic mixture. With  $F_E/F = 20$ , both the top and bottom of column are heavily polluted by the entrainer. However, the bottom of column is almost absent of B and, at the top of column, is almost free of A, thus enabling an effective separation of A and B in the next simple distillation column. The simulated extractive profiles agree well with simplified calculated profiles. Most important, by the extractive section profile reaches the  $SN_{ext}$ , which is located as expected on the A-E edge. Therefore, it can intersect a stripping profile moving towards A near the A-E edge.



**Figure 7:** Rigorous simulation result to recover A (acetone) at  $F_E/F=20$ ,  $S=20$ , compared with calculated composition profiles of the extractive section.

Under conditions  $F_E/F=1$  and  $S=15$ , with other specifications as summarized in Table 2, it can be seen that the singular points are no longer located at pure component points in the extractive profile maps, unlike the case for the residue curve map in infinite conditions. The thermodynamic UNIQUAC model is

used instead of that in our previous work (Shen *et al.* 2013b) for these rigorous simulation results. Depending on the targeted bottom product and the feed composition, Figure 8a shows the case of separation of MEK (i.e., methyl ethyl ketone, A) and benzene (B) using the entrainer acetone to recover MEK (A)



**Figure 8:** Rigorous simulation result to recover MEK or Benzene at  $S=15$ ,  $F_E/F=1$  compared with simplified composition profiles of the extractive section.

(product  $x_{WA}$  from  $x_{F1}=\{A; B; E\} = \{0.40; 0.10; 0.50\}$ ), and Fig. 8b shows the cases of separation of MEA (A) and benzene using the entrainer acetone to recover benzene (B) (product  $x_{WB}$  from  $x_{F2}=\{A; B; E\} = \{0.225; 0.70; 0.075\}$ ). Each section of the rigorous profiles matches well with the simplified profiles. The process enables the recovery of MEK with a purity of 0.99901 or benzene with a purity of 0.99903. For both simulations, the rectifying and the extractive separatrixes have close locations, and extractive profiles are only an extension of rectifying profiles. However, the profiles of these two sections have different curvature. For both cases, the rectifying profile is bounded on its left by the rectifying separatrix. Then the extractive section profile is bounded on its right by the extractive separatrix.

From the initial average feed point  $x_{F3} = \{A; B; E\} = \{0.225; 0.275; 0.500\}$  (see Fig. 8c), located between the boundary and the univolatility line, one would expect to obtain benzene as a bottom product by using azeotropic distillation. However by the extractive distillation process we recover a bottom product whose composition lies in the neighborhood of the MEK vertex.

## CONCLUSIONS

A method to study the separation with a light boiling entrainer E of minimum-azeotropic (Serafimov class 1.0-2), and maximum- azeotropic (Serafimov class 1.0-1a), as well as low-volatility (Serafimov class 0.0-1) mixtures has been proposed, so as to investigate the potential feasible region of the operating parameters: reboil ratio (S) and entrainer - feed flow rate ratio ( $F_E/F$ ) for continuous processes. First, prediction under infinite reboil ratio conditions is illustrated. It relies on the knowledge of the residue curve map topology and classification, along with the computation of the univolatility line, and enables the prediction of possible products at the bottom of the column and the limiting values of the entrainer - feed flow rate ratio. Second, the approximate composition profiles also bring information about the location of pinch points and possible composition profile separatrixes that could impair the process feasibility. We have considered for the continuous process a column configuration with the entrainer fed below the main azeotropic mixture feed, giving rise to three column sections: stripping, extractive and rectifying. Third, the approximate calculations are validated with rigorous simulations of continuous extractive distillation processes at specified values of product composition and recovery.

Under the infinite reboil ratio, the univolatility line  $\alpha_{AB}=1$  ends at the binary sides. This determines two different volatility order regions. We conclude that for maximum boiling azeotrope using light entrainer, class 1.0-1a with univolatility curve  $\alpha_{AB} = 1$  that reaches the A-E (B-E) edge, there exists a minimum entrainer feed ratio which corresponds to  $SN_{ext,A}$  ( $SN_{ext,B}$ ) to get A(B). The  $SN_{ext,A}$  ( $SN_{ext,B}$ ) lies near A-E (B-E) edge where it can intersect the stripping profile which reaches A (B) in the bottom product. For a minimum boiling azeotrope using light entrainer, class 1.0-2 with univolatility curve  $\alpha_{AB} = 1$  that reaches the A-E (B-E), there exists a maximum entrainer flow rate to recover A(B) and no limit for B (A) recovery in the bottom product. This can be explained by the fact that  $SN_{ext,B}$  ( $SN_{ext,A}$ ) to get B (A) can be situated in any location on the edge B-E (A-E). For the separation of low relative volatility mixtures using light entrainers (0.0-1 diagram), feasibility depends on the univolatility line  $\alpha_{AB}$  existence. When it does not exist, B is the unique possible product at the bottom of the column. When it exists, both original components A and B can be recovered, B below a maximum value of the entrainer feed flow rate and A above a minimum value. In perspective, using a light entrainer could provide more appropriate and economic alternatives to a heavy or intermediate entrainer for separating non-ideal mixtures.

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## APPENDIX

The UNIQUAC model is used to calculate vapor

liquid equilibrium (VLE) properties. The binary parameters have been taken from DECHEMA. The model parameters are listed in Table A1.

**Table A1: Thermodynamic UNIQUAC model parameters.**

$i-j$	$A_{ij}$	$A_{ji}$
ethanol(A) -water (B)	232.00	50.88
ethanol(A)-MeOH(E)	791.80	-482.30
water (B)- MeOH(E)	95.26	-10.38
ethanol(A) -toluene (B)	927.40	-167.20

*Continuation Table A1*



**Table A1: Thermodynamic UNIQUAC model parameters.**

<b>i-j</b>	<b>A<sub>ij</sub></b>	<b>A<sub>ji</sub></b>
ethanol(A)-acetone(E)	98.75	94.24
toluene (B)-acetone(E)	-315.30	555.70
butanol(A)-n-butyl acetate (B)	-111.10	279.00
butanol(A)-di-n-propyl-ether(E)	511.70	-203.10
n-butyl acetate (B)-di-n-propyl-ether(E)	-240.20	317.50
MEK(A) -benzene(B)	337.90	-268.10
MEK(A)-acetone(E)	-42.27	12.67
benzene(B)-acetone(E)	-299.80	510.00
water(A) -ED(B)	-798.30	16.43
water(A) -MeOH(E)	95.26	-10.38
ED(B)- MeOH(E)	-121.80	-416.50
acetone(A)-chloroform(B)	-781.60	1566.00
acetone(A)-DCM(E)	-28.34	-135.30
chloroform(B)-DCM(E)	-615.80	1134.00
ethylacetate(A)-benzene(B)	-202.00	204.80
ethylacetate(A)-acetone(E)	-220.70	321.80
benzene(B)-acetone(E)	-299.80	510.60