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# Extension of Thermodynamic Insights on Batch Extractive Distillation to Continuous Operation. 2. Azeotropic Mixtures with a Light Entrainer

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**ABSTRACT:** We have studied the continuous extractive distillation of minimum- and maximum-boiling azeotropic mixtures with a light entrainer. The ternary mixtures belong to class 1.0-2 and 1.0-1a diagrams, each with two subcases depending on the location of the univolatility line. The feasible product and feasible ranges of the operating parameters reboil ratio ( $S$ ) and entrainer/feed flow rate ratio for the continuous process ( $F_E/F$ ) were assessed. Equations were derived for the composition profiles of the stripping, extractive, and rectifying sections in terms of  $S$  and  $F_E/F$ . Class 1.0-1a processes enable the recovery of only one product because of the location of the univolatility line above a minimum value of the entrainer/feed flow rate ratio for both batch and continuous processes. Given a target purity, a minimum reboil ratio  $S$  also exists; its value is higher for the continuous process than for the batch process, for the continuous process where stricter feasible conditions arise because the composition profile of the rectifying section must intersect that of the extractive section. Class 1.0-2 mixtures allow either A or B to be obtained as a product, depending on the feed location on the composition triangle. Then, the univolatility line location sets limiting values for either the maximum or minimum of the feed ratio  $F_E/F$ .

## 1. INTRODUCTION

Distillation is the most widely used industrial method of separating liquid mixtures in many chemical and other industry fields such as perfumery, medicine, and food processing. In most distillation systems, the predominant nonideality occurs in the liquid phase because of molecular interactions. These interactions can lead to the occurrence of a maximum-boiling azeotrope or a minimum-boiling azeotrope.<sup>1</sup> The separations of azeotropic mixtures and low-relative-volatility mixtures require unconventional distillation processes, among which the three leading processes are pressure-swing distillation<sup>2–5</sup> if the composition of the azeotrope changes significantly with pressure, azeotropic distillation,<sup>1,6,7</sup> and extractive distillation.<sup>1,7,8</sup>

Extractive distillation has been studied for many decades and has a rich literature. Some of the main subjects studied include (1) batch column configurations;<sup>2,10–12</sup> homogeneous<sup>1</sup> and heterogeneous<sup>13,14</sup> column configurations; (2) process operating policies and strategies;<sup>9,15–19</sup> (3) process design, synthesis, and optimization;<sup>20–22</sup> (4) separation sequences;<sup>23,24</sup> (5) entrainer design and selection;<sup>16,25,26</sup> and (6) feasibility studies.<sup>27–30</sup> Assessing process feasibility is important before making design specifications for an extractive distillation process.

Extractive distillation involves the addition of an entrainer, similarly to azeotropic distillation. However, extractive distillation is distinguished from azeotropic distillation in that the entrainer is fed at a different location than the main mixture. Compared to an azeotropic distillation column, there exists an additional extractive section in the column, between the stripping and rectifying sections. The common industrial rule for selecting a suitable entrainer is to choose a miscible,

heavy-boiling compound that forms no new azeotrope. It should interact differently with the components of the mixture, causing their relative volatilities to either increase or decrease, thereby easing the separation. Laroche et al.<sup>31</sup> investigated the use of heavy, intermediate, and light entrainers to separate minimum-boiling azeotropes. For batch operation, Rodríguez-Donis et al. reviewed the use of these three kinds of entrainers to separate minimum- and maximum-boiling azeotropes, as well as low-relative-volatility mixtures.<sup>28,29,32,33</sup> They also showed that entrainers forming azeotropes could also be used in extractive distillation,<sup>34</sup> but that was not further tested for continuous operation.

In this series of articles, we focused on extending the thermodynamic insight on extractive distillation feasibility developed for batch distillation to continuous extractive distillation. According to Laroche et al.,<sup>31</sup> “an economically optimal design made with an average design using the best entrainer can be much less costly”. In the first part of this work,<sup>35</sup> we studied the continuous extractive process with a heavy entrainer. We showed that continuous extractive distillation exhibits a smaller feasible range of entrainer/feed flow rate ratio than batch extractive distillation but otherwise shares the same features: possible products and limiting operating parameter values as predicted by the general feasibility criterion for extractive distillation under an infinite reflux ratio.<sup>28</sup>

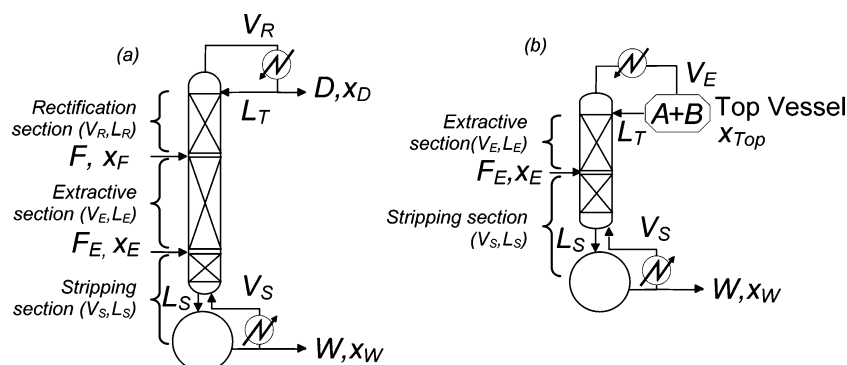


Figure 1. Configurations of extractive distillation columns: (a) continuous process, (b) batch stripper process.

This part of the work investigated the use of a light entrainer for the separation of minimum- and maximum-boiling binary azeotropes. After a brief description of the state of the art, we recall the essential features of the methodology described in part 1.<sup>35</sup> We stress the specificities due to the use of a light entrainer and apply the general feasibility criterion formulation for a light entrainer.<sup>29</sup> Then, we investigate two subcases of process alternatives, depending on the location of the univolatility curve, for the separations of a maximum-boiling azeotrope with a light entrainer (class 1.0-1a) and a minimum-boiling azeotrope with a light entrainer (class 1.0-2). Through a systematic calculation of the composition profiles of the different sections, the feasibility regions for the two key parameters entrainer/feed flow rate ratio and reboil ratio are determined and validated by rigorous simulation.

## 2. STATE OF THE ART

**2.1. Extractive Distillation with a Light Entrainner.** In extractive distillation, an entrainer, E, is added as a third component to interact selectively with the original components of a binary mixture, A and B, to reinforce their relative volatility, thus enhancing the original separation. We consider that A has a lower boiling point than B. The entrainer E is fed continuously at another column position than the feed mixture A–B, either into the still, in the column, or at the column top. The study of entrainer design is rich in the literature. A potential candidate entrainer is often referred to three major property classes: (1) pure solvent properties such as boiling point, vapor pressure, molar volume, and so on;<sup>36,37</sup> (2) process properties such as relative volatility, solvent solubility power, phase stability criterion performance index,<sup>38</sup> and univolatility and undistribution curves;<sup>28,29,32–34,39</sup> and (3) environment-related properties such as LC<sub>50</sub> (standard measure of toxicity of a material that will kill 50% of a sample population in a specified period)<sup>40</sup> and environmental waste, impact, health, and safety issues.<sup>41</sup> In industry, the entrainer is conventionally chosen as a heavy (high-boiling) component.<sup>1,28,42,43</sup> However, there are some cases when use of a heavy entrainer is not recommended, such as if a heat-sensitive or high-boiling component is to be separated, prompting studies with light and intermediate entrainers.

Literature studies on light entrainers for extractive distillation are scarce compared to those on heavy entrainers. Hunek et al.<sup>44</sup> investigated the separation of the minimum-boiling azeotropic mixture ethanol (A)–water (B) with the light entrainer methanol in a pilot-plant experiment, calling this process reverse extractive distillation. Laroche et al.<sup>31</sup> showed

that the location of the univolatility curve could be used to determine the product obtained from extractive distillation of a minimum-boiling azeotrope with a light entrainer: For example, the separation of ethanol (A)–water (B) using acetone as a light entrainer gives water (B) as the bottom product of the extractive column, whereas the separation of methyl ethyl ketone (A)–water (B) with acetone gave methyl ethyl ketone (A) as the bottom product of the extractive column. The general criterion for the feasibility of extractive distillation under an infinite reflux ratio<sup>28</sup> fully corroborates this analysis by simultaneously combining the relationship between the residue curve map and the location of the univolatility line.

Analyzing more than 400 binary azeotrope–entrainer system, for either azeotropic or extractive distillation, Laroche et al.<sup>31</sup> concluded that (1) light entrainers are common, almost as common as heavy entrainers; (2) light entrainers often represent the only viable alternative when a heavy entrainer cannot be used; and (3) light entrainers can perform as well as or better than heavy entrainers. Further works have concerned batch extractive distillation. Lang et al.<sup>45</sup> assessed the feasibility of the extractive distillation of ethanol (A)–water (B) with the light entrainer methanol in a batch rectifier and of *n*-butanol (A)–*n*-butyl acetate (B) with *n*-propyl formate and dipropyl ether as light entrainers in a batch stripper. Considering a batch rectifier and a batch stripper, Varga and co-workers<sup>46,47</sup> studied the separation of three mixtures: minimum-boiling azeotrope ethanol–water with light entrainer methanol, maximum-boiling azeotrope water–ethylene diamine with light entrainer methanol, and close-boiling mixture chlorobenzene–ethyl benzene with light entrainer 4-methylheptane. They assessed the feasibility, operating steps, limiting entrainer flows, limiting reflux ratios, and limiting number of theoretical stages by running a parametric study on profile maps and verified them by rigorous simulation. More recently, with the aid of thermodynamic insights into knowledge of the location of the univolatility line and residue curve analysis,<sup>28</sup> Rodríguez-Donis et al.<sup>29</sup> published a detailed study on the feasibility of homogeneous batch extractive distillation for all possible subcases related to the separation of azeotropic mixtures with a light entrainer belonging to Serafimov's classes 1.0-2 and 1.0-1a. This article aims to use that insight for the study of the continuous extractive distillation process with a light entrainer.

**2.2. Column Configuration and Operation.** Extractive distillation can be operated in either batch or continuous mode. Aside from conventional batch rectifiers,<sup>11,30,45,46</sup> batch strippers<sup>46</sup> and middle vessel columns<sup>10</sup> have also been suggested and discussed in the literature. The use of a light

entrainer would recommend use of a batch stripper, as the product expected to be a heavy boiler could be removed from the boiler still,<sup>47</sup> but a batch rectifier configuration is also possible.<sup>45</sup> Varga<sup>46</sup> studied four batch rectifying configurations for extractive distillation using a light entrainer premixed with the charge in the still before distillation (SBD) or fed continuously into the still (BED-B), at the top (BED-T), or at an intermediate location BED-I. Varga also studied the four batch stripper configurations with the entrainer fed into the top vessel (SBS), at the column top (BES-T), at a middle tray (BES-I), or at the bottom (BES-B), providing recommendations for separating minimum- and maximum-boiling azeotropes and close-boiling mixtures. In the present article, we consider a continuous column with the entrainer fed at an intermediate location below the main feed (A + B), according to Figure 1a. This gives rise to three column sections: extractive and stripping sections, as in a batch stripper column BES-I (Figure 1b), and a rectifying section above the main feed for the continuous column (Figure 1a).

### 2.3. Extractive Distillation Feasibility Assessment.

According to Serafimov's classification of ternary diagrams,<sup>48</sup> the separation of a minimum-boiling azeotrope with a light entrainer gives rise to a class 1.0-2 diagram (8.5% occurrence among ternary azeotropic mixtures). The separation of a maximum-boiling azeotrope gives rise to a class 1.0-1a diagram (21.6% occurrence).

Part 1 of this work provides an overview of the state of the art on the feasibility assessment of continuous extractive distillation when a heavy entrainer is used.<sup>35</sup> Many classical tools used for azeotropic distillation are valid for extractive distillation, including residue curve map analysis and composition profiles. A key operating parameter in distillation processes is the reflux ratio, which should be as low as possible for economic reasons, because it governs the internal liquid flow into the column. However, the inclusion of an extractive section imposes new challenges for extractive distillation. The ratio of the entrainer flow rate to the main feed flow rate becomes a variable as important as the reflux ratio. In addition, feasibility in terms of composition profiles now requires that all three sections intersect together, as highlighted in the work on double-feed columns by Levy and Doherty.<sup>49</sup> Laroche et al.<sup>31</sup> further brought attention to univolatility curves and volatility order regions for class 1.0-1a with a heavy entrainer. They explained that, when using a heavy entrainer, the distillate product can be either the lightest boiler of the original mixture A or, less intuitively, the heaviest boiler of the original mixture, B, depending on the location of the intersection of the univolatility curve with the A–B–E triangle. Further explanation also came from the study of the composition profile map topology and singular points of the extractive section for class 1.0-1a:<sup>27,28,30,50,51</sup> Feasibility of the extractive distillation process requires that the stable node of the extractive section be near the triangle edge, so as to intersect a rectifying section curve reaching the desired distillate. As the stable node moves along the univolatility curve for class 1.0-1a when the entrainer/feed flow rate ratio increases below a minimum entrainer/feed flow rate ratio value, the process becomes feasible above that limiting value.<sup>30</sup> The existence of a minimum entrainer/feed flow rate ratio value is well-known when computing solvent-free concentration diagrams for the vapor concentration  $y_A^{no S}$  versus the liquid concentration  $x_A^{no S}$ . The minimum entrainer concentration is found when the azeotrope no longer exists in a plot of  $y_A^{no S}$  versus  $x_A^{no S}$ .<sup>1</sup>

Rodríguez-Donis and colleagues systematically extended that analysis for the separation of minimum- or maximum-boiling azeotropes and of low-relative-volatility mixtures, considering light, intermediate, and heavy entrainers, by batch extractive distillation.<sup>28,29,32–34</sup> Combining knowledge of the thermodynamic properties of residue curve maps along with knowledge of the locations of the univolatility and unidistribution curves, they expressed a general feasibility criterion for extractive distillation under an infinite reflux ratio. Serafimov's classes covering up to 53% of azeotropic ternary mixtures can match the criterion and are suited for homogeneous extractive distillation: classes 0.0-1 (low-relative-volatility mixtures),<sup>32</sup> 1.0-1a, 1.0-1b, 1.0-2 (azeotropic mixtures with light, intermediate, or heavy entrainers forming no new azeotrope),<sup>28,29,33</sup> 2.0-1, 2.0-2a, 2.0-2b, and 2.0-2c (azeotropic mixtures with an entrainer forming one new azeotrope).<sup>34</sup> For all suitable classes, the general criterion under infinite-reflux-ratio conditions can explain the product to be recovered and the possible existence of limiting values for the entrainer/feed flow rate ratio for batch operation: a minimum value for class 1.0-1a, a maximum value for class 1.0-2, and so on.

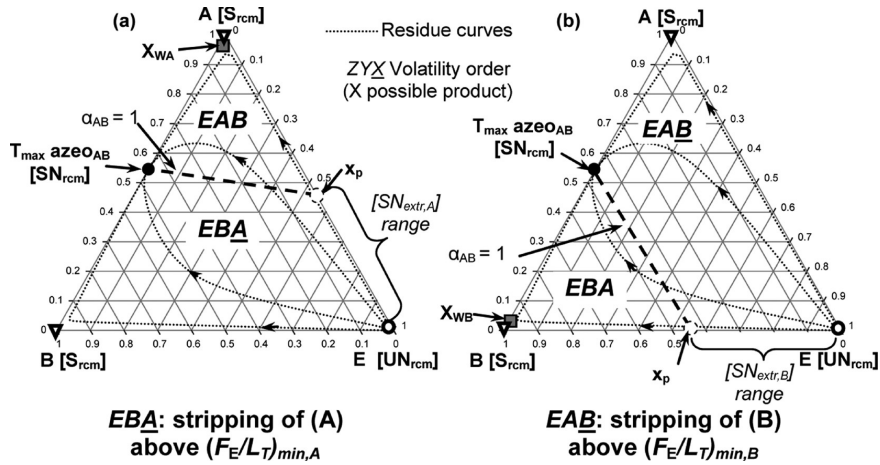
The behavior at finite reflux ratio could be deduced from the infinite-reflux-ratio behavior and properties of the residue curve maps, and some limits on the reflux ratio were found. However, precise determination of the limiting values of the reflux ratio or entrainer/feed flow rate ratio requires other techniques, such as the intersection of composition profiles, either discrete, tray-by-tray profiles<sup>49,52</sup> or continuous profiles from a differential model.<sup>30,43,53</sup> Pinch-point analysis also allows these values to be found, using either algebraic criteria<sup>49</sup> or mathematical approaches, such as bifurcation theory,<sup>27</sup> interval arithmetics,<sup>51</sup> or a combined bifurcation and shortcut rectification body method.<sup>50</sup> Most methods cited have been used to study either batch or continuous extractive distillation processes when using a heavy entrainer. The continuous extractive process with a light entrainer has not been studied in the same detail with such tools. This is the aim of this article.

## 3. FEASIBILITY STUDY METHODOLOGY

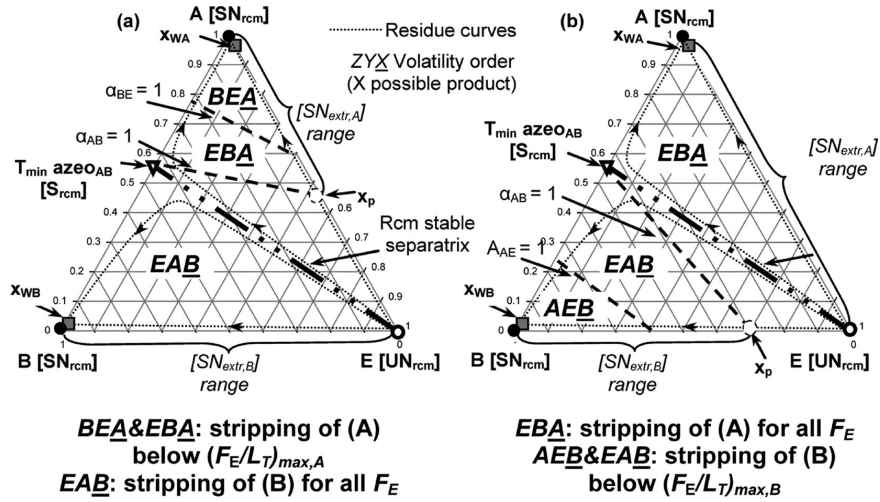
When using a heavy entrainer, the continuous column configuration has an additional stripping section compared to the batch column rectifier configuration.<sup>35</sup> Then, the key operating parameters are the reflux ratio and the entrainer/feed flow rate ratio  $F_E/F$  for continuous operating mode or  $F_E/L_T$  for the batch process with a light entrainer. We refer to the  $F_E/L_T$  ratio because, in a batch stripper (Figure 1b), the original binary mixture (A + B) is initially charged into the column top vessel and fed to the first top tray as a boiling liquid ( $L_T$ ), which is equivalent to  $L_R$  in a continuous column. Partial evaporation of the liquid phase reaching the column bottom gives the vapor flow rate ( $V_S$ ). The remaining liquid is drawn as bottom product ( $W$ ) to maintain the amount of liquid in the boiler. The reboil ratio  $S$  is defined as the ratio of  $V_S$  to  $W$ .

When using a light entrainer, Figure 1a shows that the additional section for the continuous column configuration is a rectifying section compared to the batch column stripper configuration. In addition, the key parameters are now the reboil ratio  $S$ , as we focus on a bottom product, and again the entrainer/feed flow rate ratio  $F_E/F$ . Other key parameters, such as the number of trays and the holdup, are not considered in this article.

The methodology proceeds in three steps: Step 1 assumes that the possible products identified from the thermodynamic



**Figure 2.** Thermodynamic features of class 1.0-1a mixtures with respect to batch extractive distillation: separation of a maximum-boiling azeotrope with a light entrainer.



**Figure 3.** Thermodynamic features of class 1.0-2 mixtures with respect to batch extractive distillation: separation of a minimum-boiling azeotrope with a light entrainer.

insight for batch extractive distillation are valid for the continuous process. It also transforms the limiting values of the entrainer/feed flow rate ratio  $F_E/L_T$  found for the batch process into an entrainer/feed flow rate ratio value  $F_E/F$  for the continuous process. Step 2 aims at finding the feasible range of operating parameters reboil ratio  $S$  and entrainer/feed flow rate ratio  $F_E/F$  and at comparing the feasibility of the batch and extractive processes. In step 3, rigorous simulation is used to confirm step 2.

**3.1. Step 1. Thermodynamic Feasibility Criterion for 1.0-1a and 1.0-2 Ternary Diagram Classes with a Light Entrainer.** 3.1.1. *Influence of the Univolatility Line  $\alpha_{AB} = 1$  on the Feasible Product and Limiting Operating Parameter Value.* We use the general criterion for extractive distillation reformulated for light entrainers:<sup>29</sup> Component A or B can be drawn as the first bottom product using a stripper configuration if there is a residue curve going from the entrainer E toward 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. This suggests the expected product and the possible occurrence of limiting values for the reflux ratio and the entrainer flow rate ratio  $F_E/L_T$ .

Figures 2 and 3 summarize the topological features (singular points, univolatility line  $\alpha_{AB} = 1$ , and volatility order regions) and the products achievable for class 1.0-1a (maximum-boiling azeotrope with a light entrainer) and class 1.0-2 (minimum-boiling azeotrope with a light entrainer) diagrams.

For the class 1.0-1a ternary diagram (Figure 2), the entrainer is the residue curve unstable node  $UN_{rcm}$  (open circle), apex A and apex B are residue-curve saddle points  $S_{rcm}$  (open downward-pointing triangle), and the maximum-boiling azeotrope is a stable node  $SN_{rcm}$  (solid circle). By using azeotropic distillation, it is impossible to recover A or B but rather the unstable node maximum-temperature azeotrope at the column bottom in a batch stripper or in the continuous column bottom. By using extractive distillation, either A or B can be removed as the product depending on the location of the univolatility line  $\alpha_{AB} = 1$ . The univolatility line starts at the maximum-boiling azeotrope, intersects one triangle side at  $x_p$  and divides the composition graph into two volatility order regions EBA and EAB. The location of  $x_p$  determines which possible product, A or B, can be recovered from the bottom, namely, A when  $x_p$  lies on the A–E side (Figure 2a) and B otherwise (Figure 2b), because the general criterion is fulfilled: A in Figure 2a (B in

Figure 2b) is the most volatile in the region  $EBA$  ( $EAB$ ) where it is connected to E by a residue curve of increasing temperature from E to A (B), equivalent to the stripping section profile under an infinite reboil ratio.

For the class 1.0-2 ternary diagram (Figure 3), the entrainer is the residue curve unstable node  $UN_{rcm}$ , apexes A and B are stable nodes  $SN_{rcm}$ , and the minimum-boiling azeotrope is a residue curve saddle point  $S_{rcm}$ .

Both A and B are rcm stable nodes, and they lie in two different distillation regions. Therefore, unless the distillation boundary is highly curved, they cannot be recovered sequentially in a batch stripper by azeotropic distillation or in a sequence of continuous distillation columns.<sup>6</sup> Extractive distillation is an interesting alternative process, as the feeding of the entrainer at an intermediate column tray enables extractive profiles that can cross the distillation boundary. The univolatility lines  $\alpha_{AB} = 1$  starts at the minimum-boiling azeotrope and intersects one triangle side at  $x_p$ . According to the general feasibility criterion, both components A and B can be recovered as bottom products. In volatility order regions  $BEA$  and  $EBA$ , A is the least volatile component and is connected to entrainer E by a residue curve of increasing temperature and is a bottom product (denoted in Figure 3 as  $\underline{A}$ ). In volatility order regions  $AEB$  and  $EAB$ , the same occurs for B, which is the bottom product. Univolatility curves  $\alpha_{EA}$  and  $\alpha_{EB}$  do not affect the A versus B volatility order and, therefore, the expected product. More details about the topology changes of the extractive section composition profile map with the reboil ratio and the entrainer/feed flow rate ratio in the case of a light entrainer are discussed in Rodríguez-Donis et al.<sup>29</sup>

We expect the general criterion for batch mode to explain the feasible conditions under which the extractive and stripping sections can intersect for the continuous process (Figure 1a), as these two sections already exist for the batch process (Figure 1b).

**3.1.2. From Batch to Continuous Limiting Operating Parameter Value.** Knowledge of the existence of limiting values for the entrainer/feed flow rate ratio in batch mode, namely, a minimum value for  $F_E/L_T$  for class 1.0-1a and a maximum for class 1.0-2, is transformed into a limiting entrainer/feed flow rate ratio for continuous-mode  $F_E/F$  by means of an equation derived from mass balances

$$\left(\frac{F_E}{F}\right) = \left(\frac{F_E}{L_T}\right) \left[ \frac{(S+1)\frac{W}{F} - q'}{1 + q\left(\frac{F_E}{L_T}\right)} \right] \quad (1)$$

where we use the notation given in Figure 1a for the continuous extractive column. We have considered the general case of partially vaporized feeds  $F$  ( $q' = 1$  for boiling liquid,  $q' = 0$  for saturated vapor) and  $F_E$  ( $q = 1$  for boiling liquid,  $q = 0$  for saturated vapor). This equation shows that the limiting value for  $F_E$  depends on  $S$  and  $W$  when using a light entrainer. As the bottom product composition  $x_W$  is chosen to compute the composition profiles, the setting of a product recovery enables  $W$  to be computed from mass balances, once the main and entrainer feed compositions and flow rate ratios are known. Table 1 summarizes these data for all of the mixtures.

**3.2. Step 2. Calculation of the Feasible Range of Reboil Ratio and Entrainer/Feed Flow Rate Ratio.** The feasibility of extractive distillation is determined by computing continuous composition profiles maps for all three sections, namely, rectifying, extractive, and stripping, and visually

**Table 1. Operating Parameters<sup>a,b</sup> for All Mixtures Studied**

product		A	B	E		
Class 1.0-1a Case a: A (Propanoic Acid)–B (DMF) + E (MIBK) or A (Acetone)–B (Chloroform) + E (Dichloromethane)						
A (propanoic acid or acetone)	$x_F$	0.9	0.1	0	$D$	1.1
	$x_E$	0	0	1	$W$	0.9
	$x_W$	0.98	0.01	0.01	$F$	1
	$x_D$	0.0164	0.0827	0.9009	$F_E/F$	1
	$\eta_b$	0.98	0	0	$S$	10
	$x_F + x_E$	0.45	0.05	0.50	$R$	8.09
Class 1.0-1a Case b: A (Water)–B (EDA) + E (Acetone)						
B (EDA)	$x_F$	0.1	0.9	0	$D$	10.02
	$x_E$	0	0	1	$W$	0.98
	$x_W$	0.01	0.98	0.01	$F$	1
	$x_D$	0.002	0.980	0.018	$F_E/F$	10
	$\eta_b$	0	0.98	0	$S$	15
	$x_F + x_E$	0.0818	0.0091	0.9091	$R$	1.47
Class 1.0-2 Case a: A (Ethanol)–B (Water) + E (Methanol)						
A (ethanol)	$x_F$	0.9	0.1	0	$D$	10.1
	$x_E$	0	0	1	$W$	0.9
	$x_W$	0.990	0.005	0.005	$F$	1
	$x_D$	0.0018	0.0094	0.9888	$F_E/F$	10
	$\eta_b$	0.98	0	0	$S$	10
	$x_F + x_E$	0.0818	0.0091	0.9091	$R$	0.88
B (water)	$x_F$	0.1	0.9	0	$D$	10.1
	$x_E$	0	0	1	$W$	0.9
	$x_W$	0.005	0.990	0.005	$F$	1
	$x_D$	0.0094	0.0018	0.9888	$F_E/F$	10
	$\eta_b$	0	0.98	0	$S$	10
	$x_F + x_E$	0.0091	0.0818	0.9091	$R$	0.88
Class 1.0-2 Case b: A (MEK)–B (Benzene) + E (Acetone)						
A (MEK)	$x_F$	0.9	0.1	0	$D$	5.1
	$x_E$	0	0	1	$W$	0.9
	$x_W$	0.98	0.01	0.01	$F$	1
	$x_D$	0.0035	0.0179	0.9786	$F_E/F$	5
	$\eta_b$	0.98	0	0	$S$	5
	$x_F + x_E$	0.1500	0.0167	0.8333	$R$	0.86
B (benzene)	$x_F$	0.1	0.9	0	$D$	5.1
	$x_E$	0	0	1	$W$	0.9
	$x_W$	0.01	0.98	0.01	$F$	1
	$x_D$	0.0179	0.0035	0.9786	$F_E/F$	5
	$\eta_b$	0	0.98	0	$S$	5
	$x_F + x_E$	0.0167	0.1500	0.8333	$R$	0.86

<sup>a</sup> $x_F$ , mole fraction in the main feed;  $x_E$ , mole fraction in the entrainer feed;  $x_W$ , bottom composition;  $x_D$ , top composition;  $\eta_b$ , product recovery;  $x_F + x_E$ , global mole fraction in the feed;  $D$ , distillate flow rate;  $W$ , bottom flow rate;  $F$ , feed flow rate;  $F_E/F$ , entrainer/feed ratio;  $S$ , reboil ratio;  $R$ , reflux ratio. <sup>b</sup>Molar units used.

checking their intersection. The feasibility of the batch extractive distillation process requires that the extractive and stripping section profiles intersect. The continuous process requires the intersection of the rectifying and extractive profiles as well.

Once the product purity and recovery are fixed and the entrainer and feed stream compositions and flow rates are given (see Table 1), all of the needed parameter values can be obtained from the mass balances.

The results are displayed in plots of reboil ratio  $S$  versus entrainer/feed flow rate ratio  $F_E/F$ , where the feasible parameter ranges for the batch and continuous processes are sketched. Notice that these results are dependent on the target purity and recovery and on the choice of the thermodynamic

model used to compute  $y_i^*$ . This last point should first be validated carefully against experimental data for any industrial use of the methodology.

We next derive the general liquid composition profile equations in each column section by using the differential model first published by Van Dongen and Doherty<sup>53</sup> and popularized by Lelkes et al.<sup>30</sup> with the assumption of constant molar overflow once a composition of the bottom product  $x_W$  has been chosen

$$\frac{dx_i}{dh} = \frac{V}{L}(y_i - y_i^*) \quad (2)$$

Assuming constant molar overflow, one can write the vapor internal flow rates as

$$V_S = SW \quad (3)$$

$$V_E = V_S + (1 - q)F_E = SW + (1 - q)F_E \quad (4)$$

$$\begin{aligned} V_R &= V_E + (1 - q')F \\ &= SW + (1 - q)F_E + (1 - q')F \\ &= L_T + D \end{aligned} \quad (5)$$

and the internal liquid flow rates as

$$L_R = L_T \quad (6)$$

$$L_E = L_R + q'F = L_T + q'F \quad (7)$$

$$\begin{aligned} L_S &= V_S + W = (S + 1)W = L_E + qF_E \\ &= L_T + q'F + qF_E \end{aligned} \quad (8)$$

Then, the expressions for  $y$  are obtained from partial mass balances in each section.

The general expressions for  $y$  and  $V/L$  in the rectifying section are

$$\begin{aligned} y_i &= \frac{1}{S + (1 - q)\frac{F_E}{W} + (1 - q')\frac{F}{W}} \\ &\times \left[ \frac{F_E}{W}x_{i,E} + \left( S - q'\frac{F}{W} - q\frac{F_E}{W} + 1 \right)x_i + \right. \\ &\quad \left. \frac{F}{W}x_{i,F} - x_{i,W} \right] \end{aligned} \quad (9)$$

$$\frac{V_R}{L_R} = \frac{SW + (1 - q)F_E + (1 - q')F}{(S + 1)W - qF_E - q'F} \quad (10)$$

To obtain the equations relevant to the extractive section, one should set  $F = 0$  in eqs 9 and 10. To obtain the relevant equation for the stripping section, one should set  $F_E = 0$  and  $F = 0$  in eqs 9 and 10.

For a continuous column, supposing a boiling liquid main feed  $F$ , for  $q = 0$  (saturated vapor entrainer), the rectifying profile becomes

$$\begin{aligned} \frac{dx_i}{dh} &= \frac{S + \frac{F_E}{W}}{(S + 1) - \frac{F}{W}} \left\{ \frac{1}{S + \frac{F_E}{W}} \left[ \frac{F_E}{W}x_E + \left( S - \frac{F}{W} + 1 \right)x_i + \right. \right. \\ &\quad \left. \left. + \frac{F}{W}x_F - x_W \right] - y_i^* \right\} \end{aligned} \quad (11)$$

For  $q = 1$  (boiling liquid entrainer), the rectifying profile is

$$\begin{aligned} \frac{dx_i}{dh} &= \frac{S}{(S + 1) - \frac{F_E}{W} - \frac{F}{W}} \\ &\left\{ \frac{1}{S} \left[ \frac{F_E}{W}x_E + \left( S - \frac{F}{W} - \frac{F_E}{W} + 1 \right)x_i + \right. \right. \\ &\quad \left. \left. \frac{F}{W}x_F - x_W \right] - y_i^* \right\} \end{aligned} \quad (12)$$

The extractive section profile for  $q = 0$  (saturated vapor entrainer) is

$$\begin{aligned} \frac{dx_i}{dh} &= \frac{S + \frac{F_E}{W}}{S + 1} \left\{ \left[ \frac{1}{S + \frac{F_E}{W}} \right] \left[ (1 + S)x_i + \right. \right. \\ &\quad \left. \left. \left( \frac{F_E}{W} \right)x_E - x_W \right] - y_i^* \right\} \end{aligned} \quad (13)$$

and for  $q = 1$  (boiling liquid entrainer), it is

$$\begin{aligned} \frac{dx_i}{dh} &= \frac{S}{(S + 1) - \frac{F_E}{W}} \left\{ \frac{1}{S} \left[ \frac{F_E}{W}x_E + \right. \right. \\ &\quad \left. \left. \left( 1 + S - \frac{F_E}{W} \right)x_i - x_W \right] - y_i^* \right\} \end{aligned} \quad (14)$$

Finally, for the stripping section profile

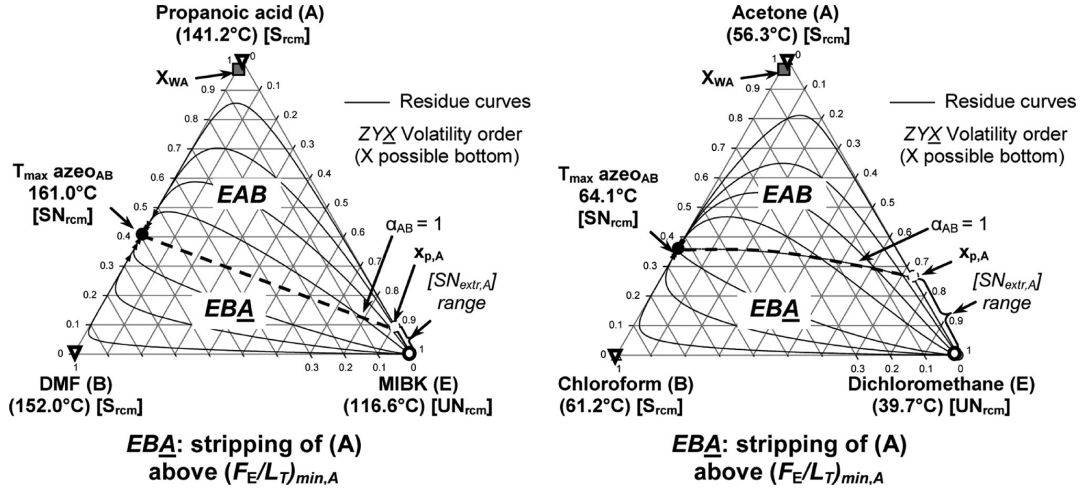
$$\frac{dx_i}{dh} = \frac{S}{S + 1} \left[ \left( 1 + \frac{1}{S} \right)x_i - \frac{1}{S}x_W - y_i^* \right] s \quad (15)$$

Under an infinite reboil ratio, the equations are identical regardless of the entrainer feed state  $q$ , as was recalled by Rodríguez-Donis et al.:<sup>29</sup> “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 holds for the assessment of the limiting flow rate values in step 1. For step 2, small differences might arise, but we consider hereafter that the entrainer is fed as a saturated vapor only ( $q = 0$ ). Then, because the entrainer is fed below the main feed (Figure 1a), all of the entrainer readily goes up into the extractive section. Consequently, we use eqs 11, 13, and 15 to compute the composition profiles of the rectifying, extractive, and stripping sections, respectively.

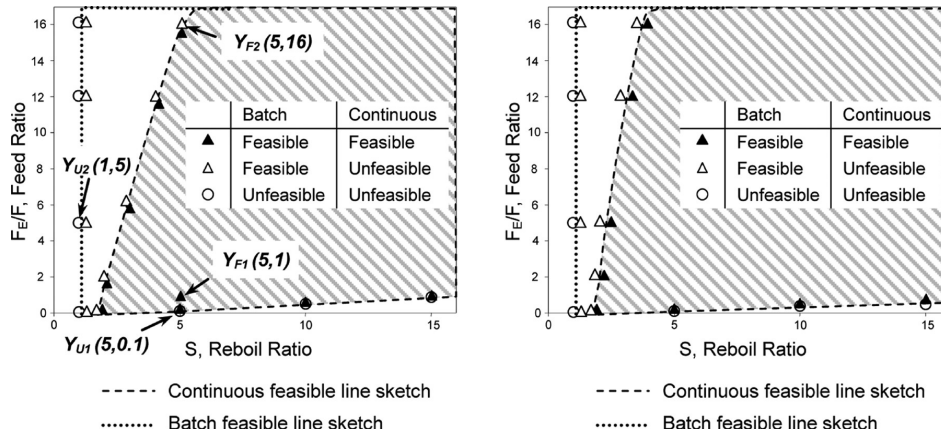
**3.3. Step 3. Rigorous Simulation.** Rigorous simulation with a MESH (mass, equilibrium, summation, and heat) equilibrium distillation column model using either ProSimPlus 3.1<sup>54</sup> or Aspen 11.1<sup>55</sup> software was run to check the feasibility predicted by step 2. Considering the reboil ratio, entrainer/feed flow rate ratio, and entrainer composition, these simulations provide the exact distillate and bottom compositions, along with the stage compositions, flows of liquid and vapor, and temperatures. Additionally, these simulations consider energy balances, which do not play a significant role in feasibility. The step 3 simulation is not aimed at optimizing the separation, in particular, with respect to the reflux ratio, energy demand, entrainer/feed flow rate ratio, or number of trays in each section. Such an optimization is outside our scope and should be done for a column sequence with both the extractive distillation and entrainer regeneration column.<sup>1</sup> The number of

**Table 2. Column Operating Specifications for Rigorous Simulation**

parameter	class 1.0-1a (Figure 7)	class 1.0-2 (Figure 15a–c)	class 1.0-2 (Figure 15d–f)	class 1.0-2 (Figure 15g–i)
number of trays, $N$	65	50	100	50
entrainer tray, $N_{FE}$	60	30	60	30
feed tray, $N_F$	20	15	10	15
$x_F$ (A, B, E)	(0.7, 0.3, 0.0)	(0.9, 0.1, 0.0)	(0.45, 0.55, 0.0)	(0.1, 0.9, 0.0)
$x_E$ (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)



**Figure 4.** Class 1.0-1a residue curve map and extractive distillation process insights into (a) propanoic acid–DMF maximum-boiling azeotrope separation using light entrainer MIBK and (b) acetone–chloroform separation using dichloromethane.



**Figure 5.** Entrainer/feed flow rate ratio  $F_E/F$  as a function of the reboil ratio  $S$ : (a) propanoic acid–MIBK separation using DMF to recover 98% propanoic acid, (b) acetone–chloroform separation using dichloromethane to recover 98% acetone.

trays in the extractive section is set at a proper value so that the terminal point of the extractive section composition profile can reach the region around the extractive section stable node. For all illustrated mixtures, the modified (Dortmund) UNIFAC thermodynamic model (1993) is used.<sup>56,57</sup> Table 2 lists the specifications of the extractive distillation column.

## 4. RESULTS AND DISCUSSION

**4.1. Separation of Maximum-Boiling Temperature Azeotropes with Light Entrainers (Class 1.0-1a).** The separation of the maximum-boiling azeotrope propanoic acid (A, 141.2 °C)–dimethyl formamide (DMF; B, 152.0 °C) ( $x_{azeo,A} = 0.4$  at 161.0 °C, 1 atm) using methyl isobutyl ketone (MIBK; E, 116.6 °C) as a light entrainer and the separation of

acetone (A, 56.3 °C)–chloroform (B, 61.2 °C) ( $x_{azeo,A} = 0.37$  at 64.1 °C, 1 atm) using light entrainer dichloromethane (E, 39.7 °C) illustrate class 1.0-1a case a when  $\alpha_{AB} = 1$  intersects binary side A–E (Figure 2a). The separation of the maximum-boiling azeotrope water (A, 100.0 °C)–ethylene diamine (EDA; B, 117.2 °C) ( $x_{azeo,A} = 0.35$  at 119.9 °C) with acetone (E, 56.3 °C) as a light entrainer illustrates class 1.0-1a case b when the  $\alpha_{AB} = 1$  curve intersects binary side B–E (Figure 2b). All of these ternary diagrams belong to class 1.0-1a. However, because E is now a light entrainer and the azeotrope Azeo<sub>AB</sub> is a maximum-boiling azeotrope, it is the antipodal diagram of the class 1.0-1a diagram<sup>48</sup> referring to the separation of a minimum-boiling azeotrope using a heavy entrainer, described in part 1.<sup>35</sup>

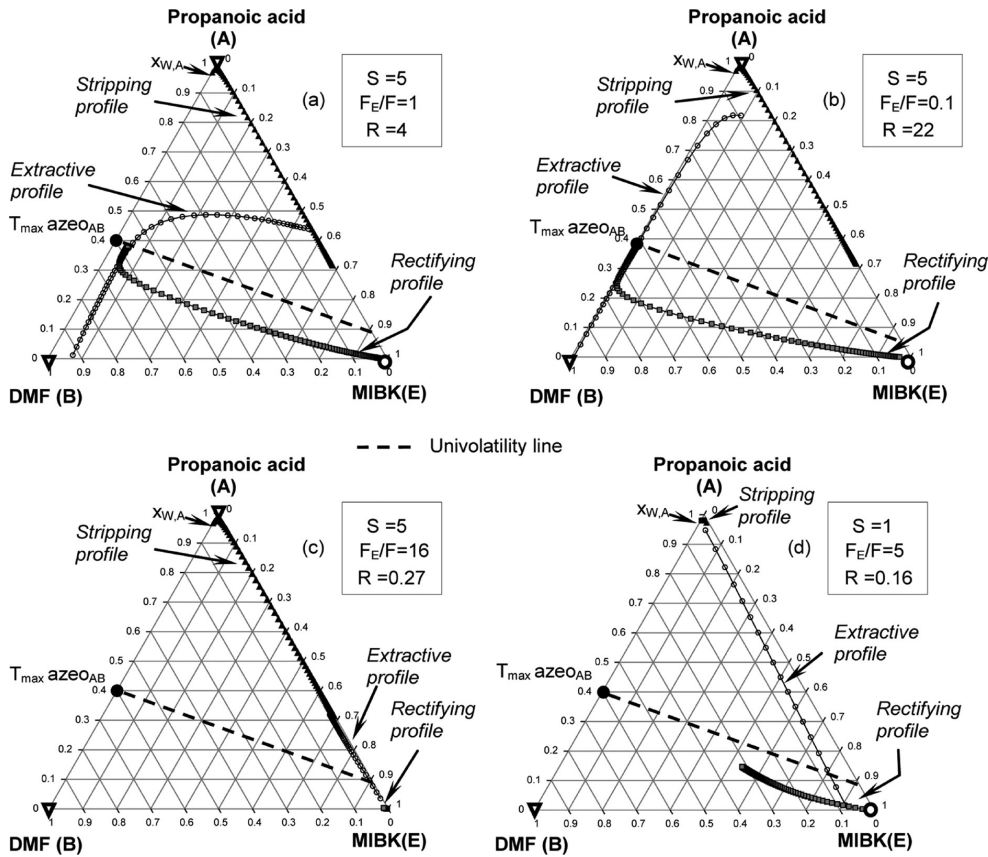


Figure 6. Rectifying, extractive, and stripping section composition profiles for four operating parameter points taken from Figure 5: (a) point  $Y_{F1}$ , (b) point  $Y_{U1}$ , (c) point  $Y_{F2}$ , and (d) point  $Y_{U2}$ .

4.1.1. Class 1.0-1a Case a:  $\alpha_{AB} = 1$  Line Reaches Binary Side A–E. The univolatility line  $\alpha_{AB} = 1$  ends at the A–E side near 90 mol % MIBK (Figure 4a) and about 73 mol % dichloromethane (Figure 4b), defining the two different volatile regions EBA and EAB.

Regarding step 1, the insight into batch extractive distillation at an infinite reboil ratio<sup>29</sup> states that propanoic acid (A) (Figure 4a) or acetone (A) (Figure 4b) can be recovered as a bottom product for an entrainer flow rate ratio  $F_E/L_T$  above a minimum value, so that  $SN_{ext,A}$  lies near the A–E edge, where it can intersect a stripping profile that can reach  $x_{W,A}$ . Recovering acetone (A) in the second example might seem easier, as the volatility order region EBA is larger in Figure 4b than in Figure 4a and the concentration of the entrainer at point  $x_p$  is smaller, hinting at a lower entrainer minimum value. One can use eq 1 to translate the  $F_E/L_T$  limit value into a limiting entrainer/feed flow rate ratio value  $F_E/F$ .

For step 2, when considering a continuous column, the process feasibility requires the intersection of the extractive and rectifying profiles, in addition to the intersection of the stripping and extractive sections as for the batch process. The  $F_E/F$  versus  $S$  diagram in Figure 5 shows the range of feasible operating conditions (triangle symbols) to obtain a bottom product with a 98 mol % purity and a 98 mol % recovery.

First, the minimum entrainer/feed flow rate ratio value exists for both the batch and continuous process under a finite reboil ratio. It also decreases as the reboil ratio decreases. There exists a minimum reboil ratio. Switching the  $x$  and  $y$  axes, we can state that the desired product specification can be maintained over a

wider range of reboil ratio as the entrainer/feed flow rate ratio increases. Second, a maximum entrainer/feed flow rate ratio exists for the continuous process.

The minimum entrainer/feed flow rate ratio is the same for both the batch and continuous processes, as it comes from the intersection condition between the stripping and extractive profiles that the two processes share. Figure 6a,b illustrates that, for point  $Y_{F1}$ , all three profiles intersect, whereas for point  $Y_{U1}$ , which is below the minimum entrainer/feed flow rate ratio, the composition profile of the stripping section cannot intersect the extractive section profile, leading to an unfeasible process for both the batch and continuous processes. Figure 6c (point  $Y_{F2}$ ) illustrates the occurrence of a maximum entrainer/feed flow rate ratio case for the continuous process, above the minimum values the batch process is feasible whereas the continuous process is not (open triangle) because the rectifying profile does not intersect the extractive profile. At very low reboil ratio (point  $Y_{U2}$  in Figure 6d), neither process is feasible because the stripping profile is too short. Similar results were obtained for batch distillation.<sup>41</sup>

Figure 6 also shows that the stripping profile gets shorter as the reboil ratio decreases. This affects the feasibility because a smaller stripping section profile might not intersect the extractive section profile.

In step 3, to verify the predictions of step 2, a rigorous simulation was performed for the acetone–chloroform–dichloromethane mixture with the parameter values reported in Tables 1 and 2, but for  $S = 20$  and  $F_E/F = 20$ . The rigorous composition profile is shown in Figure 7 along with the

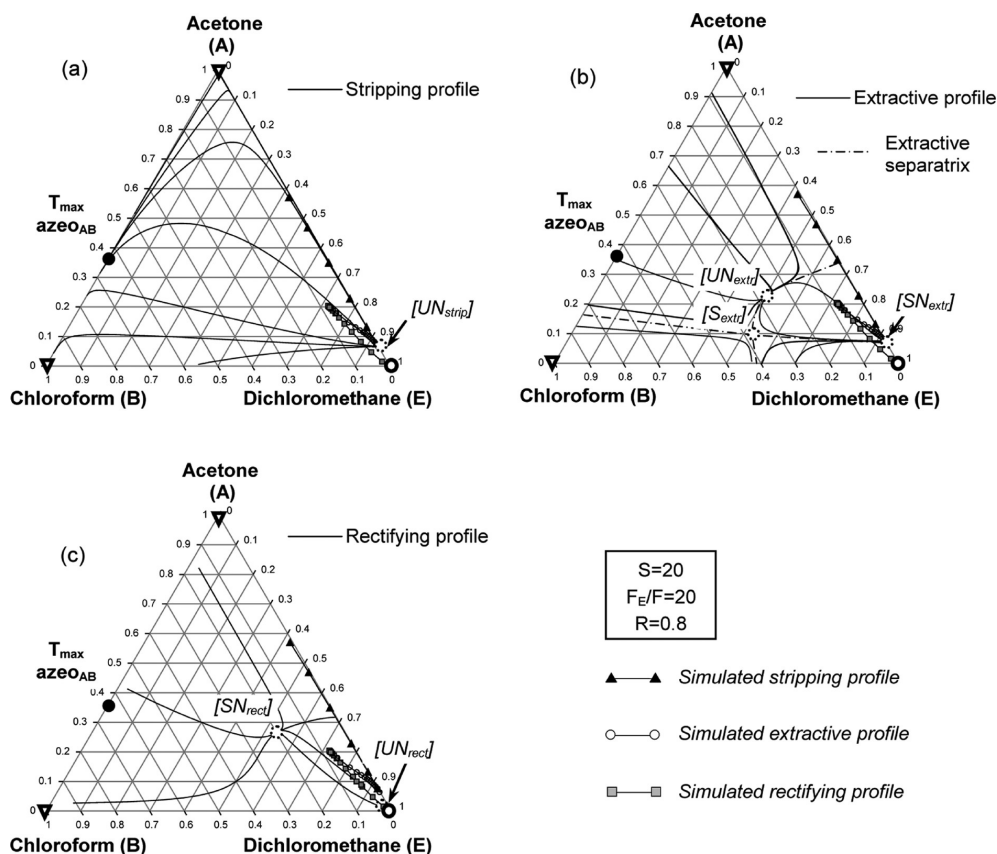


Figure 7. Rigorous simulation results to recover A (acetone) at  $F_E/F = 20$ ,  $S = 20$ , compared with calculated profiles: (a) stripping section, (b) extractive section, and (c) rectifying section.

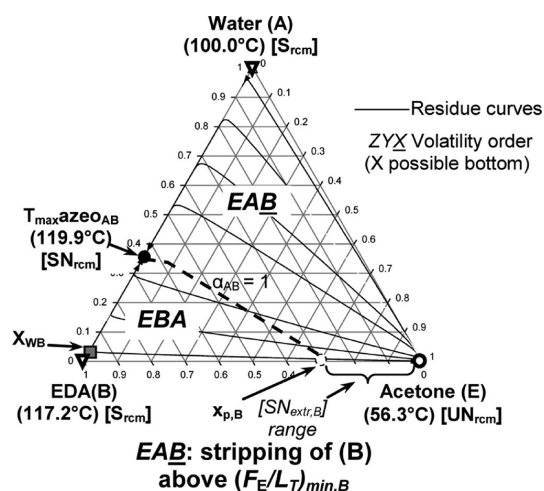


Figure 8. Water–ethylene diamine maximum-boiling azeotrope separation using light entrainer acetone: class 1.0-1a residue curve map and extractive distillation process insights.

simplified profile maps for the rectifying, extractive, and stripping sections from eqs 11, 13, and 15, respectively. The feed mixture was fed as a boiling liquid state, and the entrainer was fed as a saturated vapor.

According to the simulation, the process is able to separate A from B starting from the charge of given composition  $x_F = (0.7, 0.3, 0.0)$ . At such a high entrainer/feed flow rate ratio, both the

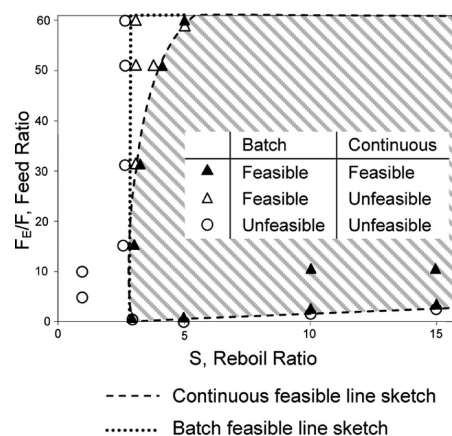


Figure 9. Entrainer/feed flow rate ratio  $F_E/F$  as a function of the reboil ratio  $S$ . Water–EDA separation with acetone to recover 98 mol % EDA as bottom product.

top and bottom products are heavily polluted with the entrainer. No process optimization was done to improve the recovery and purity, and we did not verify the 98 mol % high purity in step 2 but verified the 98 mol % recovery requirement. At the least, the bottom product is almost free of A, and the top product is almost free of B, thus enabling an effective separation of A and B. The simulated and simplified profiles agree well each other. In particular, the extractive section profile reaches  $SN_{ext}$  located as expected on the A–E edge. There, it can

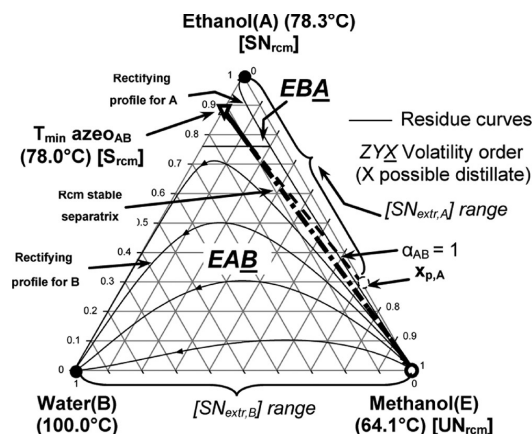


Figure 10. Ethanol–water minimum-boiling azeotrope separation using light entrainer methanol: class 1.0-2 residue curve map and extractive distillation process insights.

intersect a stripping section profile going toward A near the A–E edge.

**4.1.2. Class 1.0-1a Case b:  $\alpha_{AB} = 1$  Curve Reaches Binary Side B–E.** The ternary diagram for the system water (A)–ethylene diamine (B)–acetone (E) belongs to class 1.0-1a, but in this case, the univolatility curve  $\alpha_{AB} = 1$  intersects binary side B–E near 70 mol % acetone (Figure 8).

The case when the univolatility line  $\alpha_{AB} = 1$  reaches binary side B–E to recover B as the bottom product shows results similar to those obtained in the previous case in which  $\alpha_{AB} = 1$  reaches binary side A–E to recover A, except that A and B are switched.

Again, the step 1 thermodynamic insight states that B (EDA) is recovered as a bottom product above a minimum value for the batch entrainer flow rate ratio  $F_E/L_T$  so that the extractive section stable node  $SN_{extr,B}$  lies near the B–E edge. Then, the extractive profile can reach  $SN_{extr,B}$  and cross a stripping section profile near apex B (EDA).

Computation of the approximate composition profile in each column section (step 2) gives the  $F_E/F$  versus  $S$  reboil ratio diagram in Figure 9, which displays the feasible operating range to obtain a residue with 98 mol % purity.

Figure 9 shows the same qualitative features as Figure 5. The same discussion points hold and are not repeated here.

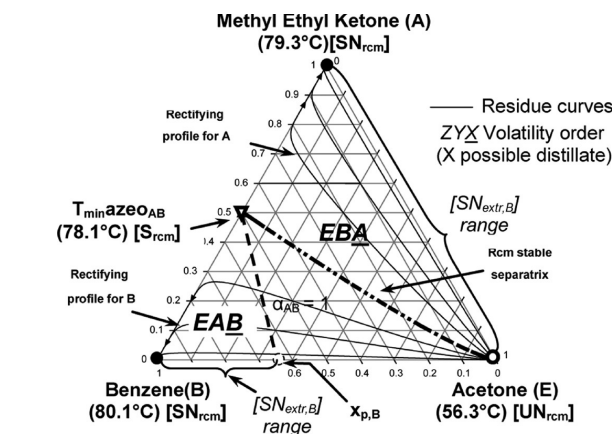
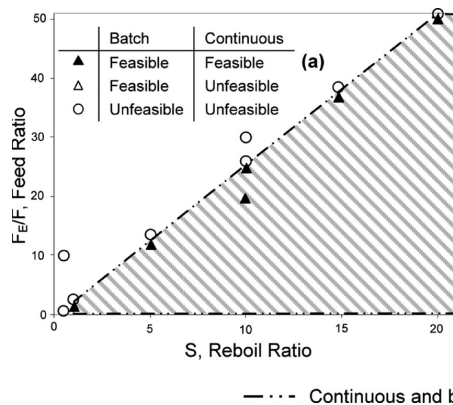


Figure 12. MEK–benzene minimum-boiling azeotrope separation using light entrainer acetone. Class 1.0-2 residue curve map and extractive distillation process insights.

**4.2. Separation of Minimum-Boiling Temperature Azeotropes with Light Entrainers (Class 1.0-2).** The separation of the minimum-boiling azeotrope ethanol (A, 78.3 °C)–water (B, 100.0 °C) ( $x_{azeo,A} = 0.88$  at 78.0 °C) with light entrainer methanol (E, 64.1 °C) illustrates class 1.0-2 case a when the  $\alpha_{AB} = 1$  curve intersects binary side A–E (Figure 3a).

The separation of the minimum-boiling azeotrope methyl ethyl ketone (A, 79.3 °C)–benzene (B, 80.1 °C) ( $x_{azeo,A} = 0.50$  at 78.1 °C) with acetone (E, 56.3 °C) illustrates class 1.0-2 case b when the  $\alpha_{AB} = 1$  curve intersects binary side B–E (Figure 3b). The azeotrope is a saddle point of the residue curve map and is connected to the unstable node of the light entrainer by a distillation boundary. Both A and B are stable nodes, and each can thus be obtained as a bottom product by azeotropic distillation in its respective distillation region. By using extractive distillation, one obtains an enlarged feasible region to recover the bottom product, as was noticed by Lang et al.<sup>45</sup> Depending on the location of the univolatility curve and intersection with either the A–E or B–E side, two subcases arise.

**4.2.1. Class 1.0-2 Case a:  $\alpha_{AB} = 1$  Curve Reaches Binary Side A–E.** The univolatility line  $\alpha_{AB} = 1$  reaches the A–E edge near 70 mol % methanol (Figure 10). In step 1, both A ethanol and B water can be recovered as bottom products. Ethanol (A)

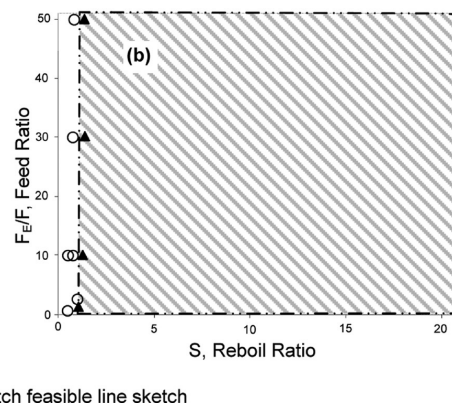


Figure 11. Entrainers/feed flow rate ratio  $F_E/F$  as a function of the reboil ratio  $S$ . Ethanol–water–methanol separation to recover 98 mol % (a) ethanol (A) and (b) water (B).

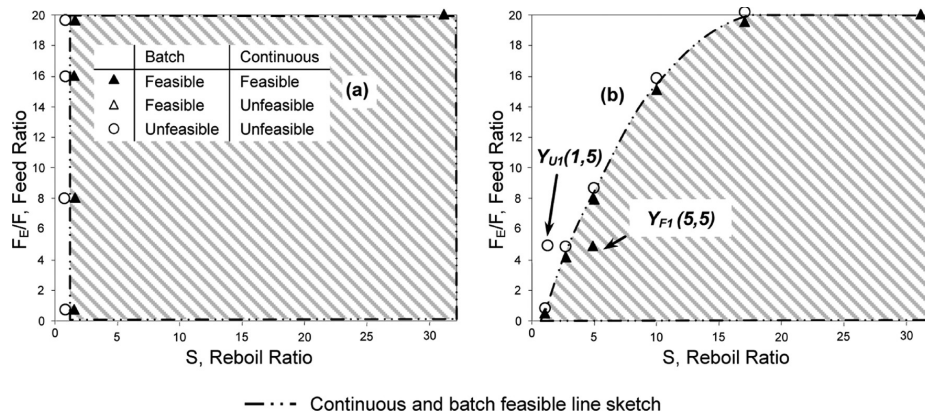


Figure 13. Entrainer/feed flow rate ratio  $F_E/F$  as a function of the reboil ratio  $S$ . MEK–benzene–acetone separation to recover 98 mol % (a) MEK (A) and (b) benzene (B).

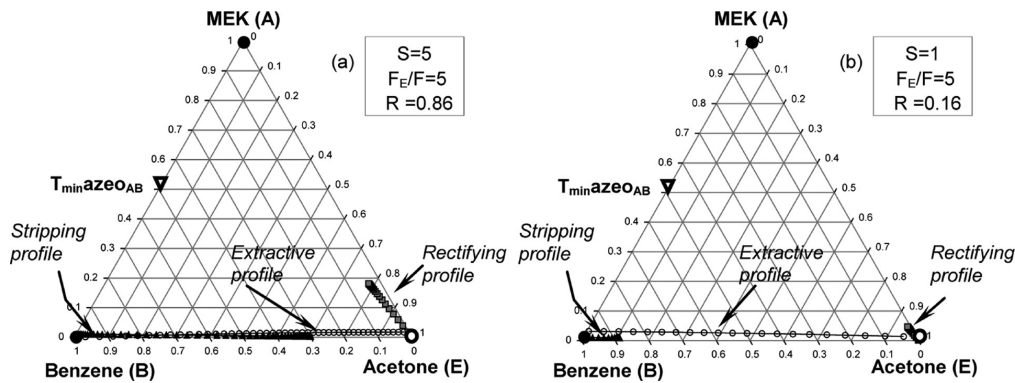


Figure 14. Operating parameter scene explanation. Points taken from Figure 13b: (a) point  $Y_{F1}$ , (b) point  $Y_{U1}$ .

can be recovered only in the small volatility order region EBA, providing that the entrainer flow rate ratio value  $F_E/L_T$  stays below a maximum limit. Water (B) can be recovered by batch extractive stripping under an infinite reboil ratio in region EAB. In that volatility order region, extractive section composition profiles reach  $SN_{extr,B}$ , which connects to the stripping liquid profile running from E to B near edge E–B. Temperature increases along the extractive section profile.

In step 2, we check the feasibility and display the feasible parameter ranges to recover either 98 mol % ethanol (A) (Figure 11a) or 98 mol % water (B) Figure 11b) in terms of the entrainer/feed flow rate ratio  $F_E/F$  versus the reboil ratio  $S$ .

As expected from the batch thermodynamic insight, there exists a maximum value for  $F_E/L_T$  to recover ethanol, which translates for the continuous process into  $F_E/F$ , above which the process is unfeasible. This maximum gradually decreases as the reboil ratio gets smaller, until it reaches a minimum value. A detailed calculation of the profile map<sup>58</sup> showed that the region of feasible stripping section profiles gets smaller until it can no longer intersect the extractive section profile region.

When the bottom product is water (B), Figure 11b shows no limit for the entrainer/feed flow rate ratio in batch mode, as expected from step 1, which persists in continuous mode as well. There exists a minimum reboil ratio as an unstable extractive separatrix reduces the feasible region.

**4.2.2. Class 1.0-2 Case b:  $\alpha_{AB} = 1$  Curve Reaches Binary Side B–E.** The separation of the minimum-boiling azeotrope methyl ethyl ketone (A, 79.3 °C)–benzene (B, 80.1 °C) ( $x_{azeo,A} = 0.50$  at 78.1 °C) with acetone (E, 56.3 °C) illustrates the

subcase for class 1.0-2 with a univolatility curve  $\alpha_{AB} = 1$  that reaches the B–E edge around 36 mol % acetone (Figure 12).

The extractive process behaves as in the previous class 1.0-2 subcase, but in this case, the maximum entrainer/feed flow rate ratio exists to recover benzene (B) as a bottom product. There is no limit to recover A (MEK) as a bottom product. This is verified in step 2 in terms of the entrainer/feed flow rate ratio versus reboil ratio feasible ranges (Figure 13).

Figure 14 shows the simplified profiles for a feasible point and an unfeasible point taken from Figure 13b. Under conditions  $S = 5$  and  $F_E/F = 5$ , the process to obtain benzene is feasible, as the composition profiles of all three column sections intersect. For  $S = 1$  and  $F_E/F = 5$ , the process is unfeasible because the profiles of the stripping and rectifying sections are too short, and neither one intersects the extractive section profile.

Step 3 of the methodology relies on rigorous simulation. Figure 15 displays three simulations for  $F_E/F = 1$  and  $S = 15$ , starting from three different A–B mixtures and compares the rigorous profiles to the simplified composition profile maps for the stripping, extractive, and rectifying sections. The shapes of the rigorous and simplified profiles match well, as observed in other examples.

Under these operating conditions, one notices that most profile maps display separatrices inside the triangle and singular points that are no longer pure components or azeotropes, as was the case for infinite-reboil-ratio conditions (residue curve map). In particular, the extractive profile maps depend on the targeted bottom product and the feed composition, as shown in

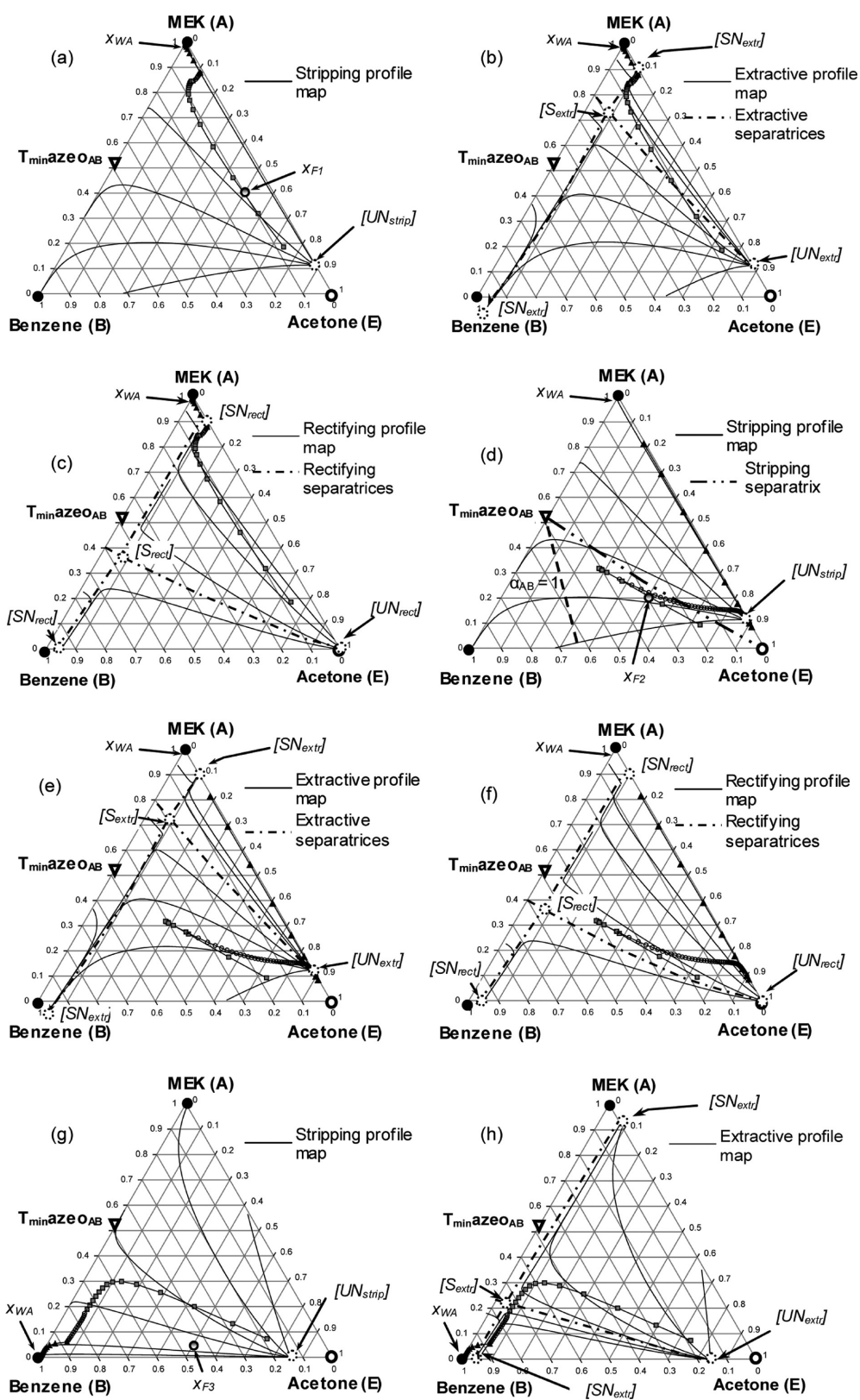
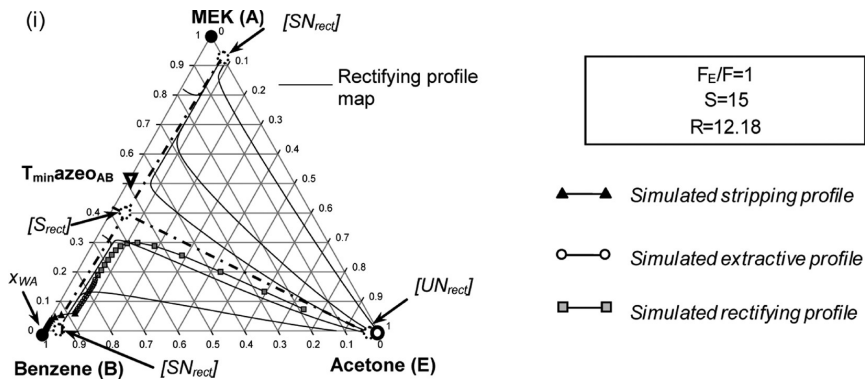


Figure 15. continued



**Figure 15.** Rigorous simulation result to recover (a–f) MEK or (g–i) benzene at  $S = 15$ ,  $F_E/F = 1$ , compared with simplified composition profiles: (a,d,g) stripping section, (b,e,h) extractive section, and (c,f,i) rectifying section.

Figure 15b,e to recover A (product  $x_{WA}$  from  $x_{F1}$  and  $x_{F2}$ ) and Figure 15h to recover B (product  $x_{WB}$  from  $x_{F3}$ ): The locations of the stable nodes and the saddle point are different.

The simulated process enables either MEK or benzene to be recovered with a purity of 99.9 mol %, from the initial average feed points  $x_{F1}$  and  $x_{F3}$ , respectively. One notices that the extractive section profile is not necessary to reach that product purity. Indeed, both MEK and benzene are stable nodes of the residue curve map and can be obtained by azeotropic distillation, the column configuration of which has no extractive section. For both simulations, the extractive profile is merely an extension of the rectifying profile. One notices that the locations of the rectifying and extractive separatrices are close. However, the composition profiles in these two sections have different curvatures. 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  $x_{F2} = (0.225, 0.275, 0.5)$ , located between the boundary and the univolatility line, one would expect to obtain benzene as a bottom product by using azeotropic distillation. However, by using the extractive distillation process, one can recover a bottom product whose composition lies in the neighborhood of the MEK vertex.

## 5. CONCLUSIONS

A methodology has been proposed to assess the feasibility of the continuous extractive distillation process for the separation of minimum- or maximum-boiling azeotrope binary mixtures using a light entrainer fed at an intermediate tray below the main azeotropic feed. It proceeds in three steps: First, the possible products in the distillation column and the existence of a limiting entrainer/feed flow rate ratio are predicted through the general feasibility criterion reported by Rodríguez-Donis et al.<sup>29</sup> Second, the process operation is investigated under finite-reboil-ratio conditions through the computation of approximate composition profiles and the identification of the feasible range of limiting entrainer/feed flow rate ratio versus reboil ratio for given target product composition and recovery. The feasibility regions of the batch and continuous extractive distillation processes are compared, and pinch points and possible composition profiles separatrices that could impair the process feasibility are examined. Third, rigorous simulations of continuous extractive distillation processes provide rigorous values of the product composition and recovery.

Design equations for the columns of the three sections of the extractive distillation process were derived based on bottom product recovery and composition, azeotropic mixture feed composition, and reboil ratio and entrainer/feed flow rate ratio. Both feeds state (boiling liquid and saturated vapor) were considered, but the application of the methodology assumed that the mixture is fed as a boiling liquid and the entrainer is fed as a saturated vapor.

For class 1.0-1a, corresponding to the separation of a maximum-boiling azeotropic mixture A–B using a light entrainer E, two subcases arise, depending on whether the univolatility line  $\alpha_{AB} = 1$  intersects the A–E edge (case a) or the B–E edge (case b). Step 1 shows that the process is feasible above a minimum limiting entrainer/feed flow rate ratio value so that the extractive stable node  $SN_{extr,A}$  ( $SN_{extr,B}$  for case b) is located in the region where it can intersect a stripping profile that can reach expected product A for class 1.0-1a case a (expected product B for class 1.0-1a case b). Applying step 2, there exist a minimum and maximum reboil ratio for each entrainer/feed flow rate ratio for both the batch and continuous processes. The main difference between the two processes lies in the fact that the profile of the rectifying section of the continuous column is too short and cannot intersect the composition profile of the extractive section. This results in the occurrence of an additional maximum entrainer/feed flow rate ratio for the continuous process. Finally, below a minimum reboil ratio, neither of the processes is feasible because the stripping profile is too short.

Two examples were considered for class 1.0-2 corresponding to the separation of a minimum-boiling temperature with a light entrainer: In case a, univolatility curve  $\alpha_{AB} = 1$  reaches the A–E side, whereas in case b, univolatility curve  $\alpha_{AB} = 1$  intersects the B–E edge. Step 1 shows that the continuous extractive distillation process enables either A or B to be obtained as a bottom product, depending on the starting composition. Depending on the location of the univolatility line  $\alpha_{AB} = 1$ , for case a (case b), component B (component A) can be obtained as a bottom product, provided that the entrainer/feed flow rate ratio lies below a maximum value at a given reboil ratio. Under a finite reboil ratio, an extractive unstable separatrix moves inside the diagram and impacts the feasible composition region. The maximum value of  $F_E/F$  decreases as the reboil ratio decreases, and there also exists a minimum reboil ratio  $S$ . There is no limit on the entrainer/feed flow rate ratio to recover the other product, A for case a, B for case b, but the minimum reboil ratio limit also exists.

The possible advantage of using a light entrainer is to provide more opportunities for separating minimum-temperature and maximum-temperature azeotropic mixtures when it might not be easy to find a heavy or intermediate entrainer. In perspective, it could be interesting to evaluate the possible energy gain of the overall process, the extractive distillation column and the regeneration column, compared to that for the use of a heavy entrainer.

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### Notes

The authors declare no competing financial interest.

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