### Entrainer Selection Rules for the Separation of Azeotropic and Close-Boiling-Temperature Mixtures by Homogeneous Batch Distillation Process

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Batch distillation of nonideal mixtures usually produces the azeotropes often associated with those mixtures. Among various techniques available to break azeotropes, azeotropic and extractive distillation processes have a place of choice. They rely upon the selection of a suitable entrainer. Entrainer screening is therefore a key step for the synthesis and design of these processes. From an analysis of all ternary residue curve maps under assumptions of a large number of stages and total reflux/reboil ratio, we devise in this paper a complete set of rules for the selection of a suitable entrainer enabling the separation of minimum- and maximum-boiling azeotropic binary mixtures and close-boiling-temperature binary mixtures. These rules complete previously published rules and expand by many times the set of entrainer alternatives previously considered. Feasible batch distillation processes can always be obtained considering two batch task sequences using rectifier and stripper configurations. The effect of distillation boundary curvature on the selection of entrainers is analyzed, and in this case, a sequence of up to a three batch distillation configurations must be used to separate the original mixture components. Several practical examples are shown to illustrate the application of the defined rules in each studied case.

#### **1. Introduction**

Batch distillation is an important separation technique in chemical industries. In particular, it is widely used in pharmaceutical and speciality chemical manufacturing to recover valuable components from wastesolvent mixtures. The frequent presence of multicomponent azeotropes in these streams can delimit distillation regions in which the types of feasible separations are limited. Therefore, products generated by a separation process such as batch distillation are highly dependent on the initial mixture composition. To split a mixture into its pure components, a sequence of batch processes might be required, and several different configurations of columns might have to be used.

The pioneering work of Doherty and Perkins<sup>1</sup> on the structure of residue curve maps for continuous distillation was extended to batch distillation by Van Dongen and Doherty.<sup>2</sup> Bernot et al.<sup>3,4</sup> set the patterns of composition change, feasibility, and product sequences in batch rectifiers or strippers at total reflux or reboil for an infinite number of trays. Recently, a residue-curve-map analysis for the batch distillation of homogeneous mixtures with arbitrary numbers of components led to an algorithm<sup>5–7</sup> that permits the construction of batch distillation regions, first defined by Bernot et al.<sup>3</sup> Each batch distillation region is characterized by a product simplex, which is obtained when an infinite reflux ratio, a large number of trays, and linear pot composition boundaries are considered.

Safrit and Westerberg<sup>7</sup> defined basic distillation regions and presented an algorithm to determine and

break down basic regions into one or more batch regions, whose number depends on the batch distillation column configuration (stripper, rectifier). The initial still composition determines the product sequence and Safrit and Westerberg<sup>8</sup> described as a state-task network the consecutive mixture-batch step sequence that is needed to obtain the desired products from a particular ternary mixture under the assumptions of total reflux/reboil and an infinite number of trays.

The synthesis and design of an azeotropic batch distillation process proceeds in two steps. The first step, process synthesis, involves the selection of one or more candidate entrainers, the determination of the residue curve diagram and of the product cut sequence, and the choice of one or more column configurations. The second step, process design, involves the search for optimal batch process parameter values. The complexity of the second problem depends on the solutions obtained for the first problem because efficiency in azeotropic distillation is largely determined by the choice of a suitable entrainer. Most of the work published on the entrainer screening issue for distillation processes either chooses the entrainer on the basis of its interaction with the mixture components<sup>9-12</sup> or defines guidelines for the selection of entrainers that produce feasible designs in continuous distillation. $^{13-16}$  However, the criteria obtained for continuous distillation processes cannot be applied directly to batch distillation processes because continuous and batch distillation regions differ and the product cut sequences are not alike. As a consequence, some entrainer selection rules specifically suited for homogeneous batch azeotropic distillation have been derived by Bernot et al.<sup>4</sup> and Düssel and Stichlmair.<sup>17</sup>

This paper contains four parts. After a brief introduction, we review and complete the practical literature on

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residue curve maps and their implications for batch distillation in terms of batch distillation regions and product cut sequences. Then, we critically compare the entrainer screening rules that have been published so far, noting their coherence and incompleteness. In the third part, we present a complete set of rules for the selection of entrainers for homogeneous batch distillation. These rules allow for the separation of minimum or maximum azeotropic mixtures or close-boiling-temperature mixtures through a feasible batch distillation task sequence. Batch rectifier and stripper configurations are considered in the batch task sequence, but middle vessels are not. Assumptions of straight line distillation boundaries, infinite reflux (reboil) ratios, and large numbers of trays are made, and the implications of their removal is discussed in the fourth section. Practical examples are given for each case to illustrate the use of the proposed entrainer selection rules.

Use of the rules could be described as follows: "Given a binary mixture, screen entrainers. If one of them obeys the rules given in this paper, then the separation process is feasible". In fact, such rules could help set some of the constraints needed by computer-aided molecular design approaches for the combined design of entrainers and processes.<sup>18–20</sup>

# 2. Definitions and Literature Survey and Contribution

**2.1. Residue Curve Maps and Their Classification.** Residue curve maps have proven to be a very useful topological tool for the analysis of the thermodynamic behavior of ternary mixtures, especially when azeotropes are present.<sup>1,21,22</sup> The distillation of azeotropic or close-boiling- point binary mixtures can be eased by the addition of a separation agent often called entrainer. Residue curve maps reflect multicomponent phase equilibria and can also contain information about the boiling temperatures and stabilities of the fixed points (pure components and azeotropes). Azeotrope existence and composition can be determined either from experimental data<sup>23</sup> or by numerical methods, such as homotopy continuation<sup>24–26</sup> or global optimization,<sup>27</sup> using activity coefficient thermodynamic models with binary interaction parameters.

The classification of residue curve maps and the amount of information necessary to define them has recently been controversial. Matsuyama and Nishimura<sup>21</sup> first assumed that each binary face has no more than one azeotrope and that the ternary system possesses at most one ternary azeotrope. They showed that only 113 different and independent residue curve maps are possible based on topological constrains emerging from index theory. Each ternary system is then labeled by three digits and a letter. The three digits correspond to the presence and stability of binary azeotropes, whereas the letter reveals the presence of a ternary azeotrope.<sup>21</sup> For each ternary diagram, the boiling temperature profile is arranged according to increasing boiling point of the fixed points of the residue curve map.<sup>28</sup> Knowledge of the stability of each fixed point<sup>1</sup>stable, unstable, or saddle-is necessary because some ternary diagrams are consistent with more than one temperature profile and the inverse is also true.<sup>28,29</sup>

Safrit and Westerberg<sup>7</sup> discussed this phenomenon in a ternary system with two binary azeotropes [a maximum-temperature one (A-B) and a minimumtemperature one (B-C)]. Component (A) is an unstable node, component (C) is a stable node, and component (B) is a saddle. The application of topological restrictions between various nodes and saddles in a ternary system shows that one of the two binary azeotropes has to be a saddle and the other has to be a node.<sup>1</sup> Depending on the stability of those binary azeotropes, two ternary diagrams, 410 and 320, can be obtained from the same boiling temperature profile ( $T_A < T_{BC} < T_B < T_{AB} < T_C$ , denoted A/BC/B/AB/C). Therefore, only the full knowledge of the fixed point stability information and of the temperature profile allows for the correct determination of the distillation boundaries.

Our contribution lies in the fact that the definition of distillation boundaries is also ambiguous for ternary systems with three binary azeotropic points and has not been fully considered in the literature. For example, the ternary diagram 411 can be obtained from three different temperature profiles (AC/A/BC/B/AB/C, AC/BC/A/ B/AB/C, and BC/AC/A/B/AB/C). The first two can also describe the diagram 321, and the last can be used to obtain the diagram 312. The same behavior is observed for the diagram 323, which can be determined from three different temperature profiles (A/BC/B/C/AC/AB, A/BC/B/AB/C/AC, and A/BC/B/C/AB/AC). The first temperature profile can also be used to obtain the diagram 314, and the last two profiles can define the diagram 413. For a ternary system with a minimum ternary azeotrope, each of the three temperature profiles ABC/ BC/AC/A/B/AB/C, ABC/AC/A/BC/B/AB/C, and ABC/AC/ BC/A/B/AB/C is associated with each of the diagrams 322-m, 412-m, and 421-m. In the case of ternary diagrams with a maximum-temperature ternary azeotrope, the temperature profiles A/BC/B/AB/C/AC/ABC, A/BC/B/C/AB/AC/ABC, and A/BC/BC/AC/AB/ABC describe the ternary systems 414-M, 324-M, and 423-M.

Such an ambiguity is further complicated for a few cases in which the knowledge of the fixed point stability and of the temperature profile must be completed by the integration of the residue curve equation to determine the correct boundary limit sets, as shown by Ahmad et al.<sup>6</sup> Those authors studied six ternary diagrams among the 113 possible ternary diagrams defined by Matsuyama and Nishimura<sup>21</sup> that are globally undetermined (112-s, 121-s, 211-s, 334-s, 343-s, and 433s). They state that a system is globally undetermined if topological requirements for the multicomponent diagram given by the composition, the boiling temperature, and the stability of each fixed point can be met by more than one combination of boundary limit sets. The six diagrams display one ternary saddle azeotrope and three minimum (maximum) binary azeotropes with two among three unstable (stable) nodes and the last binary azeotrope point a saddle. All pure-component vertexes are stable (unstable) nodes of the system. Then, three different topological structures can be obtained from the stability requirements of each fixed point for each diagram. This behavior increased to 125 the total number of diagrams established initially (113) by Matsuyama and Nishimura.<sup>21</sup> The 125 diagrams are listed by Perry and Green,<sup>29</sup> along with a table for the temperature profile-distillation region diagram correspondence.

**2.2. Determination of Batch Distillation Boundaries and Regions.** The presence of azeotropes introduces distillation boundaries that outline distillation regions in which the type of feasible separation is limited. Knowledge of these distillation boundaries and Quoting Ahmad and Barton,<sup>5</sup> we define a batch distillation region as a region that is the set of compositions that lead to the same sequence of product cuts upon distillation (rectification or stripping) under the limiting conditions of infinite reflux/reboil ratio and large number of equilibrium stages. Under those limiting conditions, a product cut sequence is defined as the sequence of pure-component and azeotrope compositions (fixed points).

Van Dongen and Doherty<sup>2</sup> and Bernot et al.<sup>3,4</sup> first studied the still and product paths and batch distillation regions in ternary and quaternary systems for a batch rectifier and stripper. Bernot et al.<sup>3</sup> defined the following heuristic guidelines to determine batch distillation regions for ternary systems: "First the triangular diagram is divided by one stable separatrix or two adjoining separatrices into regions each containing one unstable node. In each region that contains one unstable node, the other batch distillation boundaries are straight lines joining the unstable node with other fixed points (saddle and stable nodes) of the regions. If the stable separatrix is highly curved, the straight line will be tangent to the stable separatrix." Further studies have been performed in this field because these heuristics cannot characterize the multicomponent diagram for all topological configurations, even for ternary systems.

Ahmad and Barton<sup>5</sup> and Ahmad et al.<sup>6</sup> used nonlinear dynamics and topology concepts to set the rigorous framework that enables us to find the batch distillation boundaries for multicomponent systems. They were motivated by the failures noticed with the methodology proposed by Bernot et al.,<sup>3</sup> which cannot be applied to ternary diagrams that involve a stable ternary node and a single unstable node. In these cases, the stable separatrix that constrains the still path does not divide the composition space. The same problem was pointed out by Safrit and Westerberg,<sup>7</sup> who introduced specific rules to determine basic distillation boundaries. We present both the Ahmad et al.<sup>6</sup> and Safrit and Westerberg<sup>7</sup> approaches and highlight the similarities.

Under the assumption of straight distillation boundaries, Safrit and Westerberg<sup>7</sup> established an algorithm to generate basic and batch distillation regions for azeotropic mixtures with *k* components. A basic distillation region is defined as a set of residue curves that start at a specific unstable node and terminate at a particular stable node. First, they say that "if there is a k-dimensional unstable (stable) azeotrope, any path of decreasing (increasing) temperature from a stable (unstable) fixed point that ends in a saddle must be supplemented by the connection of the azeotrope to the saddle", this connection being a stable (unstable) separatrix. After this preprocessing step, they defined a maximum (minimum) residue surface, denoted MaxRS (MinRS), as a manifold that separates a composition space into subregions each containing one unstable (stable) node. The MaxRS (MinRS) is the intersection of the lists of fixed points that can be reached along basic boundaries and edges of the ternary diagram with increasing (decreasing) temperature from each unstable (stable) node up to each stable (unstable) node. Hence, the maximum (minimum) residue surface defines the

stable (unstable) separatrices of the ternary system. The combination of the maximum residue surface and the minimum residue surface determines the basic distillation regions. Basic distillation regions are then divided into one or more batch distillation regions depending on the batch column configuration. For the rectifier (stripper) configuration, batch distillation region boundaries are found by connecting each unstable (stable) node of the basic region to every other fixed point. Batch distillation boundaries for the rectifier and stripper configurations might not be identical. However, connections between unstable and stable nodes in basic regions are the same for both rectifier and stripper configurations if basic distillation boundaries are straight.

The algorithm established by Ahmad et al.<sup>6</sup> demonstrates that the composition simplex for k-component mixtures can be obtained by determining the complete unstable or stable boundary limit sets of each fixed point.<sup>5</sup> New concepts such as the unstable (stable) manifold, stable (unstable) dividing boundary, and unstable (stable) boundary limit set of a fixed point are introduced. The unstable manifold is defined as the region that contains all simple distillation trajectories approaching a fixed point with decreasing time. Hence, the unstable manifold of an unstable node has a dimension equal to k - 1. If the system contains two or more unstable nodes, unstable manifolds will be separated with a (k - 2)-dimensional surface called a stable dividing boundary. These surfaces are similar to the maximum residue surface defined by Safrit and Westerberg.<sup>7</sup> Likewise, the unstable dividing surface is equivalent to the minimum residue surface. The stable dividing boundary is determined from the common unstable boundary limit set, which is obtained by defining an unstable boundary limit set for each unstable node. The unstable boundary limit set of the unstable node involves all fixed points that are limit points to its unstable manifold, except for the unstable node itself.

According to Ahmad et al.,<sup>6</sup> their algorithm can be applied to k-component topological structures that exhibit unstable nodes and less than three stable nodes, assuming that there is only one fixed point involving kcomponents. Systems are classified into 13 categories listed in Table 1 of Ahmad et al.<sup>6</sup> The algorithm does not take into account systems that have no distillation boundary and the six ternary diagrams globally undetermined that were discussed before. However, we show below that the algorithm can also be applied to ternary systems with three unstable (stable) nodes. The methodology for generating the unstable boundary limit set includes the definition of the adjacency matrix  $A_{nc}$ . The individual steps for obtaining the adjacency matrix are described by Ahmad et al.<sup>6</sup> Depending on the k-component system category some of the 14 steps constituting the core of the algorithm (Figures 5 and 6 in Ahmad et al.6) are applied. Ternary systems do not have to be divided in subsystems and can be readily described with the categories 1-9 and 11 of Table 1 presented by Ahmad et al.<sup>6</sup> Only steps 1, 2, 4–7, 10–12, and 14 are required to obtain the adjacency matrix of ternary diagrams.

To complete the analysis of Ahmad et al.,<sup>6</sup> we remove some of their restrictions with respect to a maximum of two stable nodes and two unstable nodes for globally determined ternary diagrams 122, 212, 221, 222-m, 344, 443, 434, and 444-M as follows: For the systems with three stables nodes and one unstable node (binary or ternary azeotrope), we can perform an analysis equivalent to that done on categories 4 (systems with one binary or ternary azeotropic unstable node) and 5 (systems with two stable nodes) of Ahmad et al.<sup>6</sup> In this case, step 4 can be applied to determine the complete unstable boundary set of the unstable node. Systems with three unstable nodes and a binary or ternary azeotropic stable node can be included in category 7 or 9, respectively (systems with one binary or ternary azeotrope stable node and two unstable nodes). The complete unstable boundary sets of the unstable nodes are determined using steps 6 and 11 for categories 7 and 9, respectively. Ternary diagrams with four stable nodes do not exist.

At the end of the batch distillation boundary and region analysis with the algorithm of Ahmad et al.,<sup>6</sup> the adjacency matrix  $A_k$  is obtained where every element has a 1 or 0 value. Each batch distillation region of the ternary diagram is defined through the completed boundary limit sets.  $A_k$  also enables us to define all of the product cuts that can be achieved by batch distillation. This is discussed in the next part.

**2.3. Use of Residue Curve Maps for Batch Distil-lation Task Sequencing.** Addition of an entrainer to a binary azeotropic mixture results in the formation of a more favorable azeotropic pattern for the desired separation that is either too expensive or impossible by simple distillation. For close-boiling or pinched feed mixtures, the addition of an entrainer allows for the separation to occur along a less pinched path. For an azeotropic mixture, once the batch distillation region is defined, the set of products obtained from a feed located in a given batch region can be predicted from the distillate path.

Van Dongen and Doherty<sup>2</sup> and Bernot et al.<sup>3,4</sup> found the still and product paths and batch distillation regions for batch rectifier and stripper for three- and fourcomponent systems. They reported that, for a rectifier (stripper) under conditions of infinite reflux and high number of stages, the composition of the pot will move along a straight line until it reaches a stable (unstable) separatrix; then, it will turn and follow the distillation boundary toward the highest-boiling-point vertex of the batch distillation region. For each batch distillation residue curve, there will be a corresponding distillate curve that denotes the locus of the distillate composition as it changes during the course of the distillation process. The aforementioned authors showed that the relationship between the still and distillate paths is the same as the relationship between a simple distillation residue curve and its vapor boil-off curve.

Safrit and Westerberg used their own methodology for finding the batch distillation regions<sup>7</sup> to assess the synthesis of batch column sequences needed to separate the binary mixture into its pure components.<sup>8</sup> These sequences depend on the initial feed composition, which is represented using the vector system earlier developed by Ahmad and Barton.<sup>30</sup> The batch column network is then determined using a state–task network, in which the states are mixtures and the tasks are various distillation column configurations applied to the states. Under the assumptions of total reflux/reboil ratio and infinite number of trays, Safrit and Westerberg<sup>8</sup> considered four different batch column configurations: rectifier, stripper, middle vessel column, and extractive middle vessel column as distillation tasks. A task sequence is a combination of those four batch column configurations. The state-task network algorithm was tested on the ternary mixture acetone-chloroform-methanol.

Ahmad et al.<sup>6</sup> presented a more complete algorithm to define the batch distillation product cut sequence in the case of multicomponent mixtures. Considering linear pot composition boundaries, the product cut sequence is enumerated from the adjacency matrix  $A_k$ using a formulation of the problem as a graph theoretical problem.<sup>31</sup> This formulation provides a set  $\{D\}$  of k points that starts at a batch region unstable node and contains the remaining batch region fixed points in increasing order of boiling temperature. The authors defined four categories to describe all possible characteristics of {D} that can be found in ternary diagrams. They established necessary and sufficient conditions for determining the *k* feasible product simplex {P} depending on the {D} category. They showed that the product simplex {P} formed by the *k* fixed points can either coincide with or be a subset of the respective batch distillation region. Moreover, these conditions permit the cases in which the batch region determined from the adjacency matrix provides an unfeasible product sequence using batch distillation to be discarded.

To complete the analysis of Ahmad et al.,<sup>6</sup> systems with a ternary azeotrope can also exhibit such behavior, provided that the unstable (stable) node (pure component or binary azeotrope) is linked to another fixed point included in the same batch region. In these cases, the unstable (stable) separatrix might intercept a stable (unstable) separatrix depending on the location of ternary azeotrope in triangular diagram. It is then possible to obtain a batch region whose product simplex {P} cannot be considered as a feasible product sequence, because there is no initial composition point that gives rise to this product sequence. Although Ahmad et al.<sup>6</sup> studied only a batch rectifier configuration, the methodology presented can include a set of specific rules associated with other alternative batch distillation technologies.

Removing the assumptions of total reflux/reboil and infinite number of stages would prevent the product cuts from always coinciding with the fixed points (pure components or azeotropes). Also, the switching between product cuts would not be instantaneous, and intermediate cuts would have to be recycled or processed further, hence increasing the number of tasks in the batch distillation sequence required to separate the original mixture into its pure components. On the other hand, removing these assumptions might produce curved separatrices that have some advantages. As pointed out by Bernot et al.,<sup>3,4</sup> the curvature of stable or unstable separatrices can allow a product path to move into a batch region other than the region in which the initial pot composition remains. Several works have studied the advantages of a curved separatrix, because it is possible to design feasible batch column sequences that would be impossible if only straight line distillation boundaries were considered. In particular, the separation of components situated in different batch distillation regions can be carried out using such alternatives.<sup>3,4,6-8</sup> Distillation boundary crossing can also be achieved by mixing any of the fixed points that belong to a region other than the initial still composition region.<sup>8</sup> The effect of distillation boundary curvature on the selection of entrainers is analyzed later in this paper.

**2.4. Previously Published Entrainer Selection Criteria.** Over the years, several authors have studied the following problem: given a binary mixture to be separated into pure components through batch distillation, find the simple conditions that the entrainer must satisfy for a feasible separation to be obtained.<sup>4,17,32</sup> Various techniques are currently used to break azeotropes that involve the addition of a third component when pressure-swing distillation cannot be used. These techniques can be classified into four basic groups, namely, homogeneous azeotropic distillation, heterogeneous azeotropic distillation, reactive distillation, and "salted" distillation, depending on the physicochemical properties of the selected entrainers.

Bernot et al.<sup>4</sup> described methods for breaking azeotropes using a homogeneous entrainer in a batch stripper or in a rectifier. Several schemes emerged from an analysis of the batch distillation regions. They proposed the following criteria for selecting of entrainers depending on the type of azeotropic mixture A-B involved in the process. The following conventions to describe the ternary diagram for a given mixture are used: (1) A is the lowest-boiling-point compound of the binary azeotropic or close-boiling mixture, B is the highest, and E is the entrainer. (2) The entrainer E can have the lowest (L), an intermediate (I), or the highest boiling temperature (H) of the ternary mixture. A and B are then attributed the remaining letters. (3) In the ternary diagram, the lower right (upper left, lower left, respectively) corresponds to the lighter component (medium, heavier, respectively) of the ternary mixture.

(a) Maximum-Boiling Binary Azeotrope. A maximumboiling azeotrope A–B can be broken by adding an entrainer that has a boiling point intermediate between those of A and B, or it can also form a minimum-boiling azeotrope with the B component. The state–task network includes two tasks of batch rectification, creating two new states (A and E or B–E) and leaving component B as a transformed state in the still at the end.

(b) Minimum-Boiling Binary Azeotrope. A minimumboiling azeotrope A–B can be broken by adding an entrainer with a boiling temperature intermediate between those of A and B, or it can form a maximum azeotrope with the A component. The state–task network includes two tasks of batch stripping, producing two new states (B and E or A–E) and the component A as a transformed state at the end in the reflux drum.

Taking into account these criteria, they stated that any feasible scheme found for separating a maximumboiling azeotrope in a batch rectifier can also be applied to break a minimum-boiling azeotrope in a batch stripper by reversing the trajectories in the original simple residue curve. They demonstrated this by using an intermediate entrainer. However, we discuss below that it is also true when light or heavy entrainers are used to separate minimum- or maximum-boiling azeotropes, respectively. Finally, as discussed above, Bernot et al.<sup>4</sup> found that the curvature of distillation boundaries changes the batch distillation regions and the product cut sequences for both stripper and rectifier batches.

*(c) Close-Boiling Azeotropic Components.* For closeboiling azeotropic components, the azeotrope A–B can be broken by adding an entrainer that forms a new azeotrope that is easier to break than the original binary azeotrope. In this case, it is not possible to perform the separation with an intermediate-boiling-temperature entrainer. Bernot et al.<sup>4</sup> also analyzed the separation of a minimum-boiling azeotrope with a heavy boiling entrainer that forms a minimum azeotrope with component A. The advantages of the introduction of an entrainer that is partially miscible with one of the components (heterogeneous batch distillation) was also pointed out for this particular case.

*(d) Ternary Azeotropes.* In most cases, the ternary azeotrope can be separated into binary azeotropes and pure components by changing the quantity of one of the mixture components until the total ternary composition lies in the adequate batch distillation region.

Stichlmair and co-workers proposed three classes of processes for separating azeotropic mixtures by batch distillation.<sup>17,32</sup> The first class includes processes carried out with a single distillation task. The entrainer must not introduce any distillation boundary between the components to be separated. In this case, the entrainer has to be a medium boiler or a low boiler that forms a medium-boiling azeotrope with the lowest-boiling original component (minimum azeotrope separation case) or a high boiler that forms a medium-boiling azeotrope with the highest-boiling original component (maximum azeotrope separation case). These results are in agreement with the rules defined by Bernot et al.<sup>4</sup> The second class consists of processes that require two distillation tasks. The entrainer selected is such that the two components to be separated are situated in different batch distillation regions. The batch distillation process is feasible if the components of the initial binary mixture are either origins or termini of distillation lines and if the distillation boundaries are curved. The separation of mixtures with minimum azeotropes requires a high boiler or an entrainer that forms new maximum azeotropes. The third class consists of hybrid processes in which one distillation step is replaced by a decanter or an absorption operation for economic improvements.

We have found that any entrainer that satisfies the criteria mentioned above always makes separation feasible by batch distillation. However, our conclusion is that these criteria are incomplete because they reject a significant fraction of suitable entrainers for homogeneous systems. In this work, we address the entrainer selection issue for the separation of both minimum and maximum azeotropic and close-boiling binary mixtures. We define a complete set of screening rules for homogeneous ternary systems.

# **3. Selection of Entrainer for Homogeneous Batch Distillation**

The screening of entrainers consists of comparing the structures of the residue curve maps describing the ternary mixture obtained by adding the entrainer to the binary azeotropic or close-boiling mixture. Screening rules are defined from the analysis of the ternary diagrams that enable a feasible batch distillation process. Simple rules are preferred because components that do not satisfy them can be immediately discarded. Restrictions on the entrainer boiling point and its ability to form azeotrope(s) with the binary mixture components are such efficient criteria.

The classification of residue curve maps follows the rules of Matsuyama and Nishimura.<sup>21</sup> Straight line distillation boundaries are assumed. They ensure that product cuts are sharp in composition. The effects of

| Table 1. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of                    |
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| Minimum-Boiling-Temperature Azeotropic Binary Mixture by Homogeneous Batch Distillation. Straight Boundaries |
|  |

|   | HOMOGENEOUS BATCH<br>DISTILLATION  | Straight boundaries MINIMUM BOILING AZEOTROPIC<br>BINARY MIXTURE |  |
|---|--|--|--|
|   |  | ENTRAINER  | _  |
| _ | Low boiling  | Intermediate boiling   | High boiling   |
| 1 | The state of the second st | 1  | and the second   |
| 2 |  | 4[un]  | a second for the second for  |
| 3 | 3 (A)[s]   |  |  |
| 4 | 2(B) + 3(A)[s]   |  | and the second   |
| 5 | 3 (A) +  | 4[un]  | the analysis of the part of th |
| 6 | $2(B)[un\leftrightarrow s]+3$  | (A)[s] + 4[un]   |  |

curvature are discussed below, and its impact on entrainer screening rules and batch task sequences is assessed. Azeotrope location in the composition triangle has been set centrally on the graphs for ease of understanding. Given an azeotropic or a close-boilingpoint binary mixture and a candidate entrainer E, we establish that A–B separation is feasible if there exists at least one separation sequence with an arbitrary number of batch processes (tasks) and recycles that produces both A and B as pure components. Recycled cuts can be either pure E, a binary azeotrope between E and either A or B, or a ternary azeotrope.

Once the entrainer has been chosen, batch distillation regions for the two column configurations are found using the tool developed by Ahmad et al.<sup>6</sup> All possible feasible batch task sequences for each batch distillation region are obtained using the state—task network of Safrit and Westerberg.<sup>8</sup> Batch rectifier and stripper configurations are considered, excluding middle vessel configurations. Among all of the batch task sequences that can be devised for a given ternary diagram to guarantee a feasible batch separation process, we choose the network that involves the lowest number of tasks.

The structure of a particular batch task sequence depends on the residue curve map topology for the ternary mixture formed by the addition of entrainer to the binary feed mixture. Two general approaches can be used for selecting an entrainer in homogeneous batch distillation: (1) selection of an entrainer such that all of the desired products lie within the same batch distillation region and (2) selection of an entrainer such that the desired products lie in different batch distillation regions and the curvature of distillation boundaries is exploited.

Among the 125 different residue curve maps representing ternary mixtures, only a few can be used to obtain feasible batch task sequences using the first approach. Indeed, the basic requirements are defined in the literature as follows:<sup>4,17,32</sup> no distillation boundary is connected to the binary A–B azeotrope if present, and the initial composition must lie in the same region as these two pure components. We complete this statement by adding that either A or B is a stable or an unstable node of a batch distillation region.

Application of the feasibility criteria defined above on all diagrams allows us to define four general conditions for selecting candidate entrainers that can be used for the separation of minimum-boiling azeotropic binary mixtures, maximum-boiling azeotropic binary mixtures, and close-boiling binary mixtures by homogeneous batch distillation. (1) No additional azeotrope is introduced. (2) A minimum-temperature binary azeotrope exists between E and either A or B. (3) A maximum-temperature binary azeotrope exists between E and either A or B. (4) There might be a ternary azeotrope.

Rules are then defined by combining the thermodynamic conditions and topological stability constraints. In the case of straight line boundaries, Tables 1–3 summarize all of the conditions that a suitable entrainer must fulfill to enable feasibility of homogeneous batch distillation for the separation of minimum-temperature azeotropic binary mixtures, maximum-temperature azeotropic binary mixtures, and close-boiling binary mixtures, respectively. A list of the residue curve maps defined by the rules is given in Appendix 1. The rules are established according to the following code:

### condition 1, 2, 3, or 4

#### (component A or B [stability un, sn, or s])

This condition is to be read for the first case 1(A[un]): condition 1 applies to component A, which is an unstable node. The comma "A, B" means that the rules applies to both A and B. The symbol "A  $\leftrightarrow$  B" means that the condition can be found for A or B. Both commas and double arrows can apply to stability as well as to components.

Completing these rules, the equation of topological indexes for ternary systems<sup>1,33</sup> can be used for the determination of the stability of the fixed points that have not defined. The notations N and S stand for node and saddle, respectively. The subscript numbers 1, 2, and 3 refer to pure components, binary mixtures, and ternary mixtures, respectively.

$$2N_3 - 2S_3 + N_2 - S_2 + N_1 = 2$$
 (1)

As an application example, the rule defined as 2(B) + 3(A) + 4[un] means that the entrainer must form a minimum-boiling-temperature azeotrope with component B, a maximum-boiling-temperature azeotrope with component A, and a minimum-boiling-temperature ternary azeotrope. Application of the stability eq 1 says that both binary azeotropes are saddles. For an entrainer with a boiling point intermediate between those



**Figure 1.** Separation of a minimum-boiling-temperature azeotropic binary mixture by homogeneous batch distillation. Dichloromethane–ethanol–acetone case.

of the binary components, the described rule defines the ternary diagram classified as 420-m. Likewise, the rule 2(A, B) describes a ternary mixture in which the entrainer forms a minimum-boiling azeotrope with each component. The rule  $2(A \leftrightarrow B)$  describes two unlike ternary diagrams in which the entrainer introduces a minimum-boiling azeotrope with either A or B. If two ternary diagrams exhibit two maximum-boiling azeotropes between the entrainer and both components and if the difference between their topological structures depends on the stability of the fixed points, then, the rule is defined as  $3(A[sn \leftrightarrow s], B[s \leftrightarrow sn])$  and includes some stability information.

**3.1. Minimum-Boiling Azeotropes.** Ninety-three different ternary topological structures out of 125 contain at least one minimum-boiling azeotrope. Only the nine ternary diagrams defined by the rules summarized in Table 1, however, can be used for the separation of minimum-temperature azeotropic binary mixtures by homogeneous batch distillation. Shaded regions indicate that the rule does not exist for the low-, intermediate-, or high-boiling entrainer. In all nine cases, the high-boiling original component is a stable node of the batch region that involves the two compo-



**Figure 2.** Separation of a maximum-boiling-temperature azeotropic binary mixture by homogeneous batch distillation. Propanoic acid-pyridine-cyclopentanone case.

nents to be separated. The initial composition of the ternary mixture must be situated in this particular batch region and the heavy component, B, can be removed as a bottom product of a batch stripper. The batch distillation task sequence includes two tasks of the stripper batch column configuration.

Bernot et al.<sup>4</sup> presented several theoretical examples in which an intermediate entrainer is used for the separation of a binary minimum azeotropic mixture. This entrainer can be described by rules 1 and 3 of Table 1. A practical example is the separation of the minimumboiling water-valeric acid azeotrope using formic acid as an intermediate entrainer and is shown by Perry and Green.<sup>29</sup> This entrainer follows rule 3 of Table 1. Two batch distillation tasks allow for the separation of the two components.

The separation of dichloromethane-ethanol with acetone as an intermediate entrainer is illustrated in Figure 1. Acetone was selected applying rule 1 in Table 1. The binary and ternary azeotropic data were obtained from the literature.<sup>23</sup> The ternary diagram exhibits a single batch region. The ethanol vertex is a stable node and can be obtained as a bottom product  $P_1$  in a batch stripper. At the end of the first task, the reflux drum

 Table 2. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of

 Maximum-Boiling-Temperature Azeotropic Binary Mixture by Homogeneous Batch Distillation. Straight Boundaries

 Case

|   | HOMOGENEOUS BATCH<br>DISTILLATION | Straight boundaries MAXIMUM BOILING AZEOTROPIC<br>BINARY MIXTURE |                | DILING AZEOTROPIC<br>RY MIXTURE |
|---|-----------------------------------|--|----------------|---------------------------------|
|   |                                   | ENTRAINER  |                |                                 |
|   | Low boiling                       | Intermediate boiling   | hig            | h boiling                       |
| 1 |                                   | 1  | and the second |                                 |
| 2 |                                   | 4[sn]  |                |                                 |
| 3 |                                   | 2(B)[s]  |                |                                 |
| 4 |                                   | 2 (B)[s  | ] + 3 (A)      |                                 |
| 5 |                                   | 2(B)[s] + 4[sn]  |                |                                 |
| 6 |                                   | $2 (B)[s] + 3 (A)[sn \leftrightarrow s] + 4[sn]$                 |                |                                 |

| Table 3. C | Complete Set of Rules for | r the Selection of I | Entrainers En | abling the Separat | tion of Close-Boilir | ig Binary i | Mixture |
|------------|---------------------------|----------------------|---------------|--------------------|----------------------|-------------|---------|
| by Homog   | eneous Batch Distillatio  | n. Straight Bound    | aries Case    |                    |                      |             |         |

|    | HOMOGENEOUS BATCH<br>DISTILLATION       | Straight boundaries CLOSE BOILING BINARY MIXTURI            |   |  |  |
|----|---|---|---|--|--|
|    |   | ENTRAINER   | •                                       |  |  |
|    | Low boiling                             | Intermediate boiling  | High boiling                            |  |  |
| 1  |   | 1   |   |  |  |
| 2  |   | $2 (A[un \leftrightarrow s], B)$                            |   |  |  |
| 3  |   | $2(A,B) + 4[un \leftrightarrow s]$                          |   |  |  |
| 4  |   | $3 (A[sn \leftrightarrow s], B)$                            |   |  |  |
| 5  |   | $3(A,B) + 4[sn \leftrightarrow s]$                          |   |  |  |
| 6  | 3(A) + 4[s]                             | 3(A) + 4[s]  or  3(B) + 4[sn]                               | $3(A \leftrightarrow B) + 4[sn]$        |  |  |
| 7  | 2 (A↔B) [un]                            | $2(A[un]\leftrightarrow B[s])$                              | 2 (B[s])                                |  |  |
| 8  | $2(A\leftrightarrow B) + 4[un]$         | 2(A) + 4[un]or 2(B) + 4[s]                                  | 2(B) + 4[s]                             |  |  |
| 9  | 2(B) + 3(A[s])                          | $2 (B[un \leftrightarrow s]) + 3 (A[s \leftrightarrow sn])$ | 2(B) + 3(A[sn])                         |  |  |
| 10 | 3 (A)                                   | 3 (A↔B)   |   |  |  |
| 11 | $2(B) + 3(A) + 4[un \leftrightarrow s]$ | $2(B) + 3(A) + 4[sn \leftrightarrow un \leftrightarrow s]$  | $2(B) + 3(A) + 4[sn \leftrightarrow s]$ |  |  |

contains only the dichloromethane–acetone binary mixture  $P_2$ , which can be separated by another batch stripper process into products  $P_3$  and  $P_4$ .

Table 1 does not include heavy<sup>34</sup> and light entrainer<sup>35</sup> selection rules for extractive batch distillation processes with continuous feeding of the entrainer. In both cases, a batch extractive distillation with continuous feeding of the entrainer is performed and allows for the crossing of the batch distillation boundary between the binary azeotrope and the entrainer.

**3.2. Maximum-Boiling Azeotropes.** Ninety-seven ternary diagrams exhibit at least one maximum-temperature binary azeotrope. The rules summarized in Table 2 concern only the nine diagrams that provide a feasible homogeneous batch task sequence. In all nine cases, the low-boiling original component is an unstable node of the batch distillation region that includes both components. The feed ternary mixture must be situated in this particular region. The batch distillation network includes two tasks of batch rectification, which allows for the separation of components A and B with the desired purity.

Theoretical examples of feasible homogeneous batch distillation for the separation of maximum-boiling azeotropes are presented by Bernot et al.<sup>4</sup> The described entrainers follow the first and third rules defined for intermediate entrainers in Table 2. The process sequence is composed of two batch rectifier tasks for the separation of the two original components. Figure 2 presents such a practical example for the separation of a pyridine-propanoic acid mixture using cyclopentanone as an intermediate entrainer selected according to the first rule in Table 2. Cyclopentanone forms no binary azeotrope with either original component. A ternary azeotrope is neither reported<sup>23</sup> nor predicted using the UNIFAC model. The pyridine vertex is an unstable node, so it can be separated through a batch rectifier process. Pyridine is removed as distillate P<sub>1</sub>. After its exhaustion from the still, the entrainer is

obtained as the second distillate cut  $P_3$ . At the end of the process, propanoic acid with a high purity is retained in the still (product  $P_4$ ). Therefore, two sequential batch rectifier tasks provide a feasible process for separating the two components from the original binary mixture.

Table 2 does not include light entrainer<sup>36,37</sup> selection rules for extractive batch distillation processes with continuous feeding of the entrainer.

In summary, new rules have been established for the selection of candidate entrainers that guarantee the feasibility of the separation of minimum- or maximumboiling binary azeotropic mixtures under the assumptions of straight distillation boundaries. We have shown that, unlike previous works (continuous feeding cases excluded), which considered mostly intermediate-boiling-temperature entrainers, light- and heavy-boilingtemperature components can be used for the separation of minimum and maximum azeotropic binary mixtures, respectively. This considerably extends the alternatives of homogeneous batch distillation. In addition, the old "intermediate entrainer only making a maximum azeotrope with one of the component of the minimum-boiling azeotrope mixture to be separated" rule<sup>4</sup> is difficult to fulfill when binary mixture components have close boiling-temperature values. The new alternative rules are obviously easier to satisfy.

All feasible diagrams for maximum-boiling azeotropes (intermediate and heavy entrainers) can be obtained from those found for minimum-boiling azeotropes considering light and intermediate entrainers. The following changes have to be performed to obtain feasible ternary diagrams for the separation of maximum-boiling azeotropic mixtures (Table 2) from those established for the separation of minimum-boiling-temperature azeotropes (Table 1). The light entrainer defined in Table 1 transforms into a heavy entrainer (Table 2), but the intermediate entrainer stays invariable. The pure entrainer vertex stability changes from stable to unstable

 Table 4. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of

 Minimum-Boiling-Temperature Azeotropic Binary Mixture by Homogeneous Batch Distillation. Effect of Distillation

 Boundary Curvature

|    | HOMOGENEOUS BATCH<br>DISTILLATION                               | Curved boundaries  | MINIMUM BOILING AZEOTROPIC<br>BINARY MIXTURE                     |  |
|----|---|--|--|--|
|    |   | ENTRAINER  |  |  |
|    | Low boiling   | Intermediate boiling   | High boiling   |  |
| 1  | 1   |  |  |  |
| 2  | 3 (A↔B)[sn]   |  |  |  |
| 3  |   | 4 [un]   |  |  |
| 4  | 3 (A)+  | -4[un]   |  |  |
| 5  |   | $2(A \leftrightarrow B)[un]$                                   |  |  |
| 6  | $2 (A[un \leftrightarrow s], B[s \leftrightarrow un])$          |  |  |  |
| 7  | $2 (A \leftrightarrow B)[un] + 3 (B \leftrightarrow A)[sn]$     |  |  |  |
| 8  |   | $2(A \leftrightarrow B) + 4[un]$                               |  |  |
| 9  | $3(A \leftrightarrow B) + 4[sn]$                                |  |  |  |
| 10 |   | 2(B) + 4[s]  | $2(A \leftrightarrow B) + 4[s]$                                  |  |
| 11 | $2 (A,B) [un \leftrightarrow s] + 4 [s^{1} \leftrightarrow un]$ | $2 (A,B) + 4 [s^2 \leftrightarrow un]$                         | $2 (A,B) + 4 [s^3 \leftrightarrow un]$                           |  |
| 12 | $2(A[s] \leftrightarrow B[un \leftrightarrow s]) + 3(B)$        | $B[sn] \leftrightarrow A[s \leftrightarrow sn]) + 4 [un]$      | $2 (A \leftrightarrow B) + 3 (B \leftrightarrow A)[sn] + 4 [un]$ |  |
| 13 |   | $2 (A \leftrightarrow B)[un] + 3(B \leftrightarrow A) + 4[sn]$ |  |  |

<sup>1-3</sup> Ternary diagrams undetermined topologically 121-s, 112-s, and 211-s, respectively.

and vice versa, except when it is a saddle. The stabilities of pure original component vertexes A and B change also. If component A (B) is a saddle (stable node) in the ternary diagrams defined in Table 1, then this component will become an unstable node (saddle) in the diagrams described by the Table 2 rules and by eq 1. The binary and ternary azeotropic points included in the feasible diagrams established for the separation of minimum-boiling-temperature azeotropes change both their boiling temperature classification and their stability, except when they are a saddle, as follows: minimumboiling azeotropic points transform into maximumboiling azeotropic points and vice versa. Then, the stability of these fixed points shift from unstable to stable and vice versa. Figure 3 shows an example of the application of this approach that transforms ternary diagram 412-m defined in Table 1 into ternary system 324-M established in Table 2.

**3.3. Close-Boiling-Temperature Component Zeotropic Binary Mixtures.** For the separation of binary mixtures with close-boiling components, a total of 57 diagrams that display no binary azeotrope on the edge A–B must be considered. For nine diagrams, the still path ends on the edge A–B. Hence, the addition of an entrainer does not offer a more favorable azeotropic pattern for the desired zeotropic separation. The remaining 48 diagrams provide feasible batch task sequences. In this case, components A and B are in the same batch region as the initial ternary feed. The state– task network includes two batch processes, either two rectifier or two stripper configurations depending on whether one of the component is a stable node or an unstable node of the batch region. Rules for the selection of entrainers enabling the separation of close-boiling binary mixture by homogeneous batch distillation are displayed in Table 3. Figure 4 shows an example for the separation of a water-acetic acid mixture with 1-propanol, a low-boiling entrainer selected from rule 7 of Table 3.

The binary thermodynamic data used in Fugure 4 were obtained from the literature.<sup>23</sup> Using the NRTL model, no ternary azeotrope was predicted. The acetic acid vertex is a stable node, so acetic acid can be obtained as the bottom product  $P_1$  using a batch stripper process. When acetic acid is removed from the column, the second batch stripper task provides water as the bottom product  $P_3$  until the composition of the 1-propanol–water azeotropic mixture  $P_4$  is achieved in the reflux drum and is recycled to a further batch cycle to be added to a water–acetic acid mixture to give feed F.

#### 4. Curved Distillation Boundaries

Bernot et al.<sup>3,4</sup> studied the effects of curved boundaries on the product cut sequences in batch distillation. The still (reflux drum) path follows the stable (unstable) separatrix for the batch rectifier (stripper). When the still or reflux drum path moves on a curved separatrix from the concave side of the separatrix, the column profile switches into another region to follow the residue curves, and the product compositions are defined by the fixed points of the new region. In particular, the curvature of the distillation boundaries is responsible for the peculiar behavior obtained experimentally and by simulation in batch rectification where the distillate temperature decreases for a while and then increases



**Figure 3.** Transformation of the ternary diagram 324-M enabling the separation of maximum-boiling-temperature azeotrope A–B from the ternary diagram 412-m enabling the separation of the minimum-boiling-temperature azeotrope A–B.



**Figure 4.** Separation of a close-boiling-temperature binary mixture by homogeneous batch distillation. Acetic acid-water-1-propanol case.

again as expected in the straight distillation boundary case.<sup>38</sup> Bernot et al.<sup>4</sup> showed that a decrease in the distillate temperature can actually be observed during batch rectification if the still path follows a curved stable separatrix. In a similar way, the bottom temperature can increase during a batch stripper process if the reflux drum path follows a curved unstable separatrix.

As in the case of continuous distillation, the curvature of the distillation boundaries enhances the feasibility of batch distillation schemes by allowing for the separation of components located in different batch regions.<sup>4,8,17,32</sup> As mentioned above, Stichlmair and coworkers<sup>17,32</sup> established incomplete rules for the selection of entrainers when the components to be separated are situated in different batch regions and the boundaries are curved. We show below that far more ternary diagrams with curved distillation boundaries allow for feasible homogeneous batch task sequences than those with straight boundaries.

**4.1. Minimum-Boiling Azeotropes with Curved Distillation Boundaries.** Rules are established for the selection of candidate entrainers enabling the separation of minimum-boiling-temperature binary azeotropes in the presence of curved distillation boundaries (Table 4). The same four entrainer choice conditions defined

for homogeneous batch distillation with straight lines boundaries are considered. Seventy-three ternary diagrams with at least one minimum azeotropic point and with the two original components located in different basic distillation regions were analyzed. Fifty ternary diagrams can be used to obtain a feasible batch distillation process for the three types of entrainers (low, intermediate, and high boiling temperature).

Comparing Tables 1 and 4 to assess the effect of the curvature of distillation boundaries, we notice that the number of rules defining suitable topological structures has increased because the components A and B can be now situated in different distillation regions. Moreover, high-boiling entrainers are now available for the separation of minimum-boiling-temperature azeotropic binary mixtures even without continuous entrainer feeding. Twenty of the feasible ternary diagrams can be described by rules previously given in the literature.<sup>17,32</sup> For the 30 remaining diagrams, one of the initial binary mixture components must be a stable node, and usually the A–B azeotrope is a saddle node of the batch region. For all diagrams, the initial mixture must be located on the concave side of the curved boundary where the initial binary mixture component is a node. The statetask network includes a sequence of three batch stripper tasks. Superscripts 1-3 in Table 4 correspond to the topologically undetermined ternary diagrams 121-s, 112-s, and 211-s, respectively, and rule 11 takes into account all three topological configurations. In these cases, the A-B azeotrope is always a saddle, and the two others binary azeotropic points are unstable nodes.

We also found three diagrams (101-s, 110-s, and 011-s) in which the A–B azeotrope is an unstable node and that enable a feasible separation process by homogeneous batch distillation. In these diagrams, only one of the components is a stable node, and the other component does not form a binary azeotrope with the entrainer. A sequence of three stripper batch tasks is needed, with the third column performing the separation of the mixture A–E (or B–E) to recover the saddle pure component.

An example of an entrainer obeying the fourth rule defined in Table 4 for a low boiler is given by Düssel and Stichlmair<sup>17</sup> for the separation of the binary mixture propanol-water using ethanol as the entrainer. Bernot et al.<sup>4</sup> studied the separation of the mixture methyl acetate-methanol with methyl formate. They selected a low-boiling entrainer obeying the first rule

 Table 5. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of

 Maximum-Boiling-Temperature Azeotropic Binary Mixture by Homogeneous Batch Distillation. Effect of Distillation

 Boundary Curvature

|    | HOMOGENEOUS BATCH<br>DISTILLATION   | S BATCH Curved boundaries MAXIMUM BOILING AZEOTROPIC BINARY MIXTURE |  |  |  |
|----|---|---|--|--|--|
|    |   | ENTRAINER   |  |  |  |
|    | Low boiling   | Intermediate boiling  | High boiling   |  |  |
| 1  |   |   | 1  |  |  |
| 2  |   |   | 2 (A↔B)[un]  |  |  |
| 3  |   |   | 2 (A↔B)+4[un]  |  |  |
| 4  | and the second second second  | 4 [sn]  |  |  |  |
| 5  |   | 2 (B)-  | +4[sn]   |  |  |
| 6  |   | 3 (A↔B)[sn]   |  |  |  |
| 7  | $3 (A[sn \leftrightarrow s], B[s \leftrightarrow sn])$  |   |  |  |  |
| 8  |   | $2(A \leftrightarrow B)[un] + 3(B \leftrightarrow A)[sn]$           |  |  |  |
| 9  |   | $3(A \leftrightarrow B) + 4[sn]$                                    |  |  |  |
| 10 | $3 (A \leftrightarrow B) + 4[s]$  | 3 (A )+ 4[s]  |  |  |  |
| 11 | $3 (A, B[sn \leftrightarrow s]) + 4 [s^1 \leftrightarrow sn]$   | $3 (A, B [sn \leftrightarrow s]) + 4 [s^2 \leftrightarrow sn]$      | $3 (A, B [sn \leftrightarrow s]) + 4 [s^3 \leftrightarrow sn]$ |  |  |
| 12 |   | $2(A \leftrightarrow B) + 3(B \leftrightarrow A)[sn] + 4[un]$       |  |  |  |
| 13 | $2(A \leftrightarrow B)[un] + 3(B \leftrightarrow A) + 4[sn] \qquad 2(A[un] \leftrightarrow B[un \leftrightarrow s]) + 3(B[s] \leftrightarrow A[s \leftrightarrow sn]) + 4[sn]$ |   |  |  |  |

<sup>1-3</sup> Ternary diagrams undetermined topologically 343-s, 334-s, and 433-s, respectively.

of Table 4. Both components of the original mixture are stable nodes, and the azeotropic point is a saddle. As defined above, a sequence of three batch stripper tasks allows for the separation of the desired components.

4.2. Maximum-Boiling Azeotropes with Curved **Distillation Boundaries.** Rules for the selection of entrainers enabling the separation of maximum-boiling azeotropes in the presence of curved distillation boundaries are shown in Table 5. The total number of analyzed ternary diagrams (73) and the number of obtained feasible diagrams are identical to the minimumboiling azeotrope case. As in the previous case, feasible ternary diagrams exhibit at least one pure-component vertex A or B as an unstable node, and generally, the A–B azeotrope is a saddle of the system. The initial composition of the ternary mixture must be located on the concave side of the curved boundary where component A (or B) is an unstable node of the batch region. Separation of the components can be performed by a sequence of three batch rectifiers, as shown in an example in Figure 5. Benzene is the heavy entrainer used for the separation of the methyl acetate-chloroform azeotrope. Benzene obeys the first rule of Table 5. The stable distillation boundary is curved, and the two original components can be separated with a sequence of three batch rectifier tasks. Figure 5 shows the sequence of the process and the position of the initial ternary feed, as well as the distillate drum and bottom products obtained in each batch tasks. The distillation boundary curvature between the benzene vertex and the chloroform-methyl acetate maximum-temperature azeotrope was computed by interpolation between residue



**Figure 5.** Separation of a maximum-boiling-temperature azeotropic binary mixture by homogeneous batch distillation. Exploitation of the curvature of distillation boundaries. Methyl acetatechloroform-benzene case.

curves linked to different unstable nodes with the NRTL thermodynamic model.

In Table 5, superscripts 1–3 correspond to the topologically undetermined ternary diagrams 343-s, 334-s,

and 433-s, respectively, and rule 11 involves the three topological configurations. In these cases, the A-B azeotrope is always a saddle, and the remaining maximum-boiling binary azeotropes are stables nodes. There are also three diagrams (303-s, 330-s, 033-s) in which the A-B azeotrope is a stable node, one of the components of original binary mixture A (or B) is a unstable node, and the other component B (or A) does not form a binary azeotrope with the entrainer. It is then possible to obtain a feasible separation process made up of the same batch task sequence in which the separation of the mixture B-E (or A-E) is carried out in the last batch rectifier.

Finally, the recycling of intermediate cuts (azeotropes or pure components) has often been used to increase the separation schemes that are possible for a particular mixture. Safrit and Westerberg<sup>8</sup> showed that only the new mixture formed by adding fixed points of another region to the original mixture will lie in a different batch distillation region. A feasible separation process with recycling can be obtained if the distillation boundaries are curved. These authors also showed that a process with recycling is also feasible when the distillation boundaries are straight, depending on the position of the ternary azeotropic point. We add that, more generally, this peculiar behavior exists for all of the ternary diagrams defined in Tables 4 and 5, provided that the pure entrainer vertex is common to the two batch regions where components A and B are located.

#### 5. Conclusion

Azeotropic mixtures often limit the product purity one can obtain using batch distillation. These azeotropes can create batch distillation regions in which the sequence of the products is established by the particular batch region in which the initial mixture is located. In the first part of the paper, we reviewed the thermodynamic and topological properties of residue curve maps and their use for entrainer selection and batch distillation process synthesis. Deficiencies found in previous works on ternary systems have been removed to include all possible cases. In the second part, we established a complete set of rules for the selection of feasible entrainers for the separation of minimum- or maximumtemperature azeotropic binary mixtures or close-boiling components from the analysis of ternary residue curve diagrams under the assumptions of a large number of trays and an infinite reflux/reboil ratio. Those rules include all previously published rules and greatly increase the number of entrainer choice alternatives. Rules are made of a combination of four general conditions related to the entrainer ability to form binary and ternary azeotropes with the components of the original binary mixture and to information about the entrainer boiling point classification relative to the original mixture components boiling points. The rules cover all possible cases of homogeneous batch distillation and handle the influence of the distillation boundary curvature. We have noticed that up to three batch distillation tasks consisting of rectifier or stripper configurations are required to separate the mixture into its pure components. Practical and theoretical examples are given to show how the rules apply. The rules described in this paper might help set some of the constraints needed by computer-aided molecular design approaches for the combined design of entrainers and processes.

#### Appendix 1. List of Residue Curve Maps Relative to Feasible Entrainers for the Separation of Azeotropic and Close-Boiling-Temperature Mixtures<sup>a</sup>

| 1. Separation of minimum-boiling azeotrope. Straight  |
|---|
| boundary case (refers to Table 1)   |
| Matsuyma and Nishimura: <sup>21</sup><br>001, 410, 401, 411, 002-m, 420-m, 402-m, 412-m, 421-m<br>Perry's Chemical Engineering Handbook: <sup>29</sup><br>#002, #027, #030, #040, #048, #051, #056, #060, #061  |
| 2. Separation of maximum-boiling azeotrope. Straight boundary case (refers to Table 2)  |
| Matsuyma and Nishimura: <sup>21</sup><br>003, 320, 023, 323, 004-M, 024-M, 420-M, 423-M, 324-M<br>Perry's Chemical Engineering Handbook: <sup>29</sup><br>#016, #028, #031, #035, #070, #073, #078, #088, #089  |
| 3. Separation of close-boiling-temperature binary mixture.<br>Straight boundary case (refers to Table 3)  |
| Matsuyma and Nishimura: <sup>21</sup><br>000, 001, 100, 020, 012, 021, 102, 201, 120, 210, 400,<br>030, 003, 430, 340, 403, 304, 043, 034, 410, 320, 401,<br>023, 200-m, 002-m, 202-m, 402-m, 022-m, 220-m,<br>420-m, 040-M, 004-M, 404-M, 024-M, 044-M, 440-M,<br>420-M, 010-s, 300-s, 013-s, 301-s, 101-s, 110-s, 310-s,<br>011-s, 330-s, 303-s<br>Perry's Chemical Engineering Handbook: <sup>29</sup><br>#001, #002, #003, #004, #005, #006, #007, #008, #009,<br>#010, #014, #015, #016, #017, #018, #019, #020, #021,<br>#022, #027, #028, #030, #031, #047, #048, #049, #051,<br>#052, #053, #056, #069, #070, #071, #073, #074, #075,<br>#078, #091, #092, #093, #094, #095, #096, #097, #098,<br>#099, #100, #101  |
| 4. Separation of minimum-boiling azeotrope. Curved boundary case (refers to Table 4)  |
| Matsuyma and Nishimura: <sup>21</sup><br>020, 012, 021, 102, 201, 120, 210, 122, 212, 221, 320,<br>023, 321, 312, 231, 132, 213, 123, 002-m, 202-m, 402-m,<br>022-m, 220-m, 420-m, 232-m, 222-m, 322-m, 412-m,<br>421-m, 223-m, 024-M, 420-M, 214-M, 142-M, 421-M,<br>412-M, 241-M, 124-M, 101-s, 110-s, 011-s, 112-s,<br>121-s, 211-s, 112-s, 12-s, 121-s, 211-s, 211-s<br>Perry's Chemical Engineering Handbook: <sup>29</sup><br>#004, #005, #006, #007, #008, #009, #010, #011, #012,<br>#013, #028, #031, #041, #042, #043, #044, #045, #046,<br>#048, #049, #051, #052, #053, #056, #057, #058, #059,<br>#060, #061, #062, #073, #078, #082, #083, #085, #086,<br>#087, #090, #095, #096, #098, #102, #103, #104, #114,<br>#115, #118, #119, #122, #123     |
| 5. Separation of maximum-boiling azeotrope. Curved boundary case (refers to Table 5)  |
| Matsuyma and Nishimura: <sup>21</sup><br>400, 430, 340, 403, 304, 043, 034, 344, 443, 434, 410,<br>401, 134, 143, 413, 314, 431, 341, 402-m, 420-m, 234-m,<br>243-m, 324-m, 423-m, 342-m, 432-m, 004-M, 404-M,<br>024-M, 044-M, 440-M, 420-M, 144-M, 444-M, 414-M,<br>441-M, 423-M, 324-M, 330-s, 303-s, 033-s, 433-s,<br>343-s, 334-s, 334-s, 334-s, 343-s, 343-s, 433-s,<br>9 Perry's Chemical Engineering Handbook: <sup>29</sup><br>#014, #017, #018, #019, #020, #021, #022, #023, #024,<br>#025, #027, #030, #033, #034, #036, #037, #038, #039,<br>#051, #056, #063, #064, #065, #066, #067, #068, #070,<br>#071, #073, #074, #075, #079, #079, #080, #081, #084,<br>#088, #089, #099, #100, #101, #111, #112, #113, #116,<br>#117, #120, #121, #124, #125 |

<sup>*a*</sup> Two classifications are used, namely, the common three digit + letter classification of Matsuyama and Nishimura<sup>21</sup> and the numbering of Perry's Chemical Engineering Handbood,<sup>29</sup> readily available on any shelves of chemical engineers.

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