

# Heterogeneous Entrainer Selection for the Separation of Azeotropic and Close Boiling Temperature Mixtures by Heterogeneous Batch Distillation

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The presence of azeotropes in multicomponent mixtures complicates the design of batch distillation separation processes widely used in pharmaceutical and speciality chemical industries. Most of those processes include the use of homogeneous entrainer to ease the separation. We describe novel methods to break azeotropes using an entrainer that is partially miscible with one of the initial binary mixture components. The core of the paper presents the rules for the selection of a heterogeneous entrainer leading to a feasible process for the separation of a minimum or maximum temperature azeotropic binary mixture or a close boiling binary mixture. Through several illustrating examples, we depict some of the advantages of heterogeneous batch distillation processes: more design alternatives for the separation of an azeotropic binary mixture than with homogeneous batch distillation, simplified distillation sequences as a consequence of fewer distillation tasks, crossing of batch distillation boundaries due to the reflux of either one or both of the decanter phases.

## 1. Introduction

Batch distillation is an important technology because of the operational flexibility that it offers for pharmaceutical and speciality chemical industries where high value-added products are sought in small quantities and multipurpose equipment is needed. It is used in particular for solvent recovery and to help deal with increasing economic incentives and environmental regulations. Equilibrium multicomponent diagrams associated with waste-solvent streams often display azeotropes that complicate both synthesis and design steps of batch distillation processes. Distillation boundaries may arise and outline distillation regions. Hence, the batch distillation product sequence depends on the initial feed in the still, and a binary mixture separation into its pure components may require several batch distillation tasks. The complexity of azeotropic batch distillation synthesis and design steps has prompted many studies but so far restricted the choice of the entrainer added to the azeotropic binary mixture to a homogeneous one. As shown, this bounds the flexibility and the number of process alternatives that we propose to greatly expand.

Heterogeneous batch distillation is a batch unit operation that consists of adding a third component that causes a liquid–liquid phase split with one of the binary mixture components over an extensive range of composition in the ternary system. It will likely increase the process options and even achieve azeotropic separations impossible with homogeneous systems.

Design and synthesis tools for heterogeneous continuous distillation were first formalized and introduced by Pham and Doherty.<sup>1–3</sup> They showed that synthesis of

batch distillation processes for the separation of non-ideal mixtures using a heterogeneous entrainer involves the analysis of a residue curve map as in the homogeneous system case. Residue curve maps can first be used to select the feasible entrainers, and then the related distillation column sequence can be established. Several tools are already available for the synthesis of homogeneous batch distillation processes and can be extended to the heterogeneous case. Batch distillation regions that determine the product sequences may be obtained with the algorithm developed by Ahmad et al.<sup>4</sup> for homogeneous mixtures, whereas the heterogeneous liquid boiling envelope is determined from liquid–liquid–vapor equilibrium data.<sup>1</sup> Then, a state-task network<sup>5</sup> is established, relating product cuts to the column configuration.

The selection of a suitable entrainer for homogeneous batch distillation has been addressed by Bernot et al.<sup>6</sup> and Stichlmair and co-workers.<sup>7,8</sup> Because their rules do not cover all possible cases, we have established recently a complete set of rules for the selection of feasible entrainers for the separation of minimum or maximum temperature azeotropic binary mixtures and close boiling components by homogeneous batch distillation.<sup>9</sup> Those rules emerged from the analysis of ternary residue curve diagrams under the assumption of a high number of trays and total reflux/reboil ratios. 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 an original binary mixture and are made of information about the entrainer and original binary mixture component boiling point order.

Many studies have been carried out to depict the behavior of heteroazeotropic distillation operation in continuous columns. These works addressed issues related to column sequencing and design, column operation and control, and entrainer selection (see a review

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by Widagdo and Seider<sup>10</sup> and, among others, refs 11–14). The scarcity of work on heterogeneous batch distillation found in the literature<sup>7,8,15–17</sup> and industrial interests prompted us to address in this paper the feasibility of batch distillation processes using a heterogeneous entrainer for the separation of azeotropic and close boiling binary mixtures. Pham and Doherty<sup>3</sup> and Fürzer<sup>18</sup> have published on the entrainer screening issue for heteroazeotropic continuous distillation. Pham and Doherty<sup>3</sup> defined some general rules for the selection of entrainers, which provide a feasible continuous column sequence. Fürzer<sup>18</sup> used a group contribution method, the UNIFAC method, to synthesize a heterogeneous entrainer for the separation of the binary mixture ethanol–water. The larger the infinite dilution activity coefficient of the entrainer in ethanol, the easier the separation. Our experience shows that these rules can be applied to batch distillation processes but that they do not cover all of the possible cases. We intend to fill this gap, following a procedure initiated with the definition of universal entrainer screening rules for homogeneous systems in batch distillation.<sup>9</sup>

In this paper we first summarize some key interests of heterogeneous batch distillation. Then, we present the complete set of rules for the selection of entrainers for heterogeneous batch distillation of minimum or maximum temperature azeotropic mixtures or close boiling temperature mixtures. Those rules allow discovery of a feasible batch distillation task sequence. Batch rectifier and stripper column configurations are considered in the batch task sequence, but a middle vessel is not. Assumptions of straight-line boundaries, total reflux/reboil ratios, and an infinite number of trays are made for the synthesis of the process. Most of the rules are illustrated with examples involving real chemical components with which the distillation process is simulated.

Use of the rules could be as follows: “Given a binary mixture, screen among entrainers that induce a liquid–liquid phase split with one of the initial binary components. If one of them obeys the rules given in this paper, then the separation process is feasible.” Similar to homogeneous systems, the defined rules may help set some of the constraints needed by computer-aided molecular design approaches,<sup>19–21</sup> which consist of setting reference property values and finding suitable compounds through the generation of candidate molecules and the evaluation of their properties before testing against the reference set. The list of the residue curve maps generated by the rules is given in Appendix 1 following the common classification of Matsuyama and Nishimura<sup>22</sup> and the one of *Perry’s Chemical Engineer’s Handbook*.<sup>23</sup> Those lists must be used in conjunction with the tables which indicate the proper location of the liquid–liquid demixing zone.

## 2. An Example of Heterogeneous Batch Distillation Process Synthesis

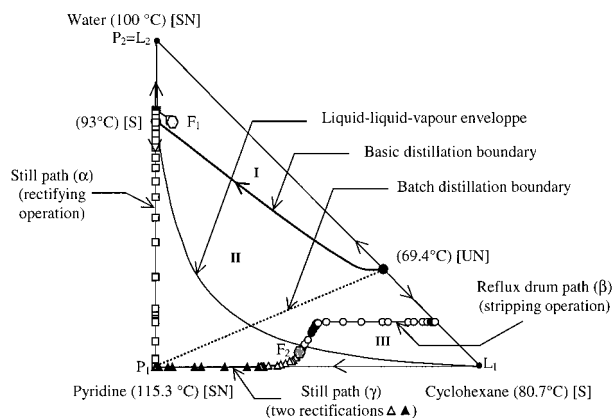
A simple method for the synthesis of homogeneous batch distillation processes was established by Van Dongen and Doherty for a batch rectifier<sup>24</sup> and a batch stripper.<sup>25</sup> Considering large number of trays and reflux/reboil ratios, the sequence of distillate (bottom) fraction is generated from any initial still (reflux drum) composition for a batch rectifier (stripper). The still (reflux drum) composition moves along a straight line until it reaches a stable (unstable) separatrix, and then

it turns and follows the distillation boundary toward the highest (lowest) boiling point of the batch distillation region. At any time, the product cut composition is collinear to the still path tangent. In all cases the product sequence is defined by the fixed points which limit the relevant batch region in decreasing (increasing) order of temperature according to that for a rectifier (stripper). In this way, the unstable (stable) node is the first distillate (bottom) cut, and the following cuts are the saddle points and the stable (unstable) node under the straight-line boundaries approximation.

Those basic concepts and assumptions have been used for the synthesis of multicomponent azeotropic batch distillation. Safrit and Westerberg<sup>5</sup> used a state-task network for the synthesis of batch distillation processes. They considered four different batch column configurations as distillation tasks: rectifier, stripper, middle vessel column, and extractive middle vessel column. Otherwise, Ahmad et al.<sup>4</sup> presented a more complete algorithm to define batch distillation product sequences in the case of multicomponent mixtures using a formulation of the problem as a graph theoretical problem.<sup>26</sup> They showed that the product simplex {P} for a ternary system is formed by three fixed points and can either coincide or be a subset of the relevant batch distillation region.

The use of a heterogeneous entrainer for the separation of an azeotropic mixture by batch distillation was first presented by Düssel and Stichlmair<sup>7</sup> and detailed in Stichlmair and Fair.<sup>8</sup> They presented the heterogeneous rectification of the pyridine–water mixture using toluene as an intermediate entrainer. As in homogeneous batch distillation, they suggested a rectilinear still path which involves a special arrangement of the column top with a reflux of some fraction of the condensed heteroazeotropic vapor to the column, whereas the remaining fraction is sent to a decanter. Notice that the still path could also match the one that would be obtained for a batch cyclic operation<sup>27</sup> with all of the condensed vapor sent to the decanter and with the reflux taken from the decanter. This example shows that homogeneous batch distillation behavior cannot be applied to heterogeneous batch distillation without care.

Heterogeneous batch distillation behaves in a way similar to that of continuous feeding homogeneous extractive distillation.<sup>28</sup> Feasibility in heterogeneous batch distillation means that at least one liquid profile joining the instantaneous still composition and the liquid overflow leaving the top tray  $x_T$  exists during the whole process. During total reflux operation, a liquid profile connects the initial still composition to the unstable node composition (that can be the binary heteroazeotrope) boiling overhead. When distillation starts, the feasibility condition has to be achieved through the liquid reflux at the column top of a combination of both decanted phases. Depending on the reflux policy, the still path can follow a linear trajectory defined by the position of the distillation composition  $x_W$  or be restricted to move in a vector cone defined as the vectors  $x_S - x_W$  and  $x_R - x_S$  if the refluxed entrainer-rich phase proportion is higher than the one defined by the splitting ratio in the decanter or  $x_S - x_W$  and  $x_S - x_R$  in the opposite case.  $x_S$  is the still path composition,  $x_W$  is the distillate composition, and  $x_R$  is the composition of the entrainer-rich phase. Then an “extractive” liquid profile must join at any time the  $x_S$  composition and a



**Figure 1.** Separation of water–pyridine by heterogeneous batch distillation with cyclohexane. The heterogeneous binary azeotrope case where the still path crosses the distillation boundary.

top liquid composition  $x_T$  whose equilibrium vapor lies in the immiscible region at the decanter temperature. There may exist a minimum overall liquid refluxed phase flow rate for which this is not the case and the separation is not feasible because of operating constraints.

As in heterogeneous continuous distillation, heterogeneous batch distillation enables to cross easily distillation boundaries because of the possibility that an entrainer-rich phase is refluxed. This makes the boundary curvature influence less critical than that for homogeneous batch distillation.<sup>9</sup> Köhler et al.<sup>16</sup> studied experimentally the separation of a binary mixture made of water with a high-boiling-temperature product using a low-boiling-temperature component as the entrainer. The entrainer induces a liquid–liquid-phase split with water. They showed that the still path could cross the distillation boundary because of the reflux of the entrainer at the column top. If the initial ternary composition is introduced in a batch region containing the binary heteroazeotrope, then the still pass moves from its initial position, crosses the distillation boundary, and arrives at the pure-component vertex miscible with the entrainer and located in a different batch region. Figure 1 shows this behavior for the system cyclohexane–water–pyridine. The initial ternary composition is located in batch region I limited by both azeotropes (one of them is heterogeneous) and water. This batch region is different from the batch region limited by pyridine, but pyridine is obtained at the end of the process in the still. At total reflux, the unstable heteroazeotropic node is linked to the initial still composition by the column liquid profile. When distillation begins, the heteroazeotrope evaporates from the column top and is cooled in a decanter where a liquid-phase split takes place. Because of the reflux of the entrainer-rich liquid phase, the liquid profile in the column deviates abruptly from the one established at infinite reflux. Indeed, the liquid reflux total composition  $L_1$  is placed in another batch distillation region. This allows the liquid column profile to cross the distillation boundary and consequently the still path too. As shown in Figure 1, the simulated still path ( $\alpha$ ) moves from the initial point  $F_1$  and later crosses the distillation boundary, and the rectification process finishes when the pure pyridine vertex is reached. Analogous results can be obtained when the ternary system exhibits a heterogeneous ternary azeotrope, as we will present in the next section. Simulation conditions are given in Appendix 2.

In the two heterogeneous batch distillation cases described in the literature, a rectifier was used. However, because pyridine is a stable node and is located in the same batch region as the heterogeneous binary azeotrope, a single batch stripper task can also be employed for the separation of both original mixture components. Pyridine is removed as a bottom product until exhaustion. Then, two liquid phases remain in the reflux drum, one of them with a high water content. The simulated reflux drum path ( $\beta$ ) corresponding to such a stripper operation is shown in Figure 1 for the separation of a water–pyridine mixture with cyclohexane. The initial composition  $F_2$  is located in batch region III limited by cyclohexane, pyridine, and the binary heteroazeotrope. Pure pyridine is obtained as a bottom product during the single batch stripping task and gradually removed from the column trays and from the reflux drum where a liquid-phase split takes place. Notice that, although a single batch task is needed, the stripping operation requires a higher amount of entrainer than the batch rectifying one corresponding to still path ( $\alpha$ ). Finally, the same ternary mixture ( $F_2$ ) can also be separated by rectification [still path ( $\gamma$ ) in Figure 1], but two sequential batch tasks are required: the binary heteroazeotrope is obtained as the distillate, whereas the still path ( $\gamma$ ) moves from the initial point until it reaches the cyclohexane–pyridine binary side (white triangles). In a second batch task (filled triangles), cyclohexane is separated as a second distillate cut and pure pyridine remains in the still. In summary, this example points out that cyclohexane is a perfect entrainer candidate because it leads to a feasible process using only one batch task provided that the amount of entrainer added to the initial binary mixture is low.

This example outlines the flexibility of heterogeneous batch distillation as well as its complexity in terms of the number of parameters that govern its feasibility and its operability. Inherently, heterogeneous batch distillation is significantly more complex than homogeneous batch distillation.<sup>9</sup> We present now the rules for heterogeneous entrainer selection which provide a feasible batch distillation process involving both rectifier and stripper column configurations.

### 3. Entrainment Screening Rules for Heterogeneous Batch Distillation

The definition of residue curves for homogeneous systems has been extended to heterogeneous ones by considering a mean liquid composition.<sup>1</sup> The number of heterogeneous ternary diagrams is inferior to the 125 homogeneous ones because heteroazeotropes can only be unstable nodes or saddles.<sup>29</sup> Besides, the liquid–liquid–vapor boiling envelope has to be introduced in the residue curve map to distinguish between homogeneous and heterogeneous regions. Azeotrope existence and composition can be determined either from experimental data<sup>30</sup> or by numerical methods such as homotopy continuation<sup>31–34</sup> or global optimization<sup>35</sup> using activity coefficient thermodynamic models with binary interaction parameters. Several commercial packages are available to perform routinely those calculations as well as to compute and nicely represent residue curve maps.

As is well-known for homogeneous systems, straight distillation boundaries cannot lead to a feasible process for the separation of components located in different distillation regions. In heterogeneous systems, a total

liquid composition inside the demixing region will split into two liquid phases in equilibrium that often lie in different distillation regions. Through the reflux of a suitable combination of both liquid phases, heterogeneity provides a cheap and efficient method for moving across distillation boundaries caused by the presence of azeotropes. In fact, this will increase process options and even achieve azeotropic separations impossible with homogeneous systems. Besides, it may simplify the entrainer recovery and recycling process. On the other hand, heterogeneous distillation is noteworthy for operability and controllability difficulties.

Pham and Doherty<sup>2,3</sup> performed theoretical studies on the synthesis of continuous heteroazeotropic distillation processes. They pointed out that no guidelines were then available for both selecting feasible entrainers and understanding their relationship with distillation column sequences. They stated as a general principle the following:

*“Any entrainer which induces a liquid-phase heterogeneity over a portion of the composition triangle is a feasible entrainer if (a) it does not introduce a boundary that puts the components into different batch distillation regions or (b) it generates liquid–liquid tie-lines which can cross at least one of the boundaries dividing the two regions containing the two components to be separated.”*

Property a means that any ternary diagram obtained by application of this rule provides a feasible column sequence for both homogeneous and heterogeneous systems. Property b shows the great advantage of heterogeneity which allows separation impossible in homogeneous systems. Then, a broader range of conditions for the selection of separation-suitable entrainers can be established from an analysis of residue curve maps. However, we discuss in the next section that property b is not a general statement for heterogeneous batch distillation and that it is sometimes possible to obtain a feasible batch distillation process when the liquid–liquid–vapor envelope does not traverse the distillation boundary dividing the regions that contain both original components.

The general rules to select a feasible heterogeneous entrainer for the separation of azeotropic and close boiling binary mixtures are based on criteria related to the entrainer boiling temperature and its capability to form binary or ternary azeotropes (heterogeneous or homogeneous) with each of the original mixture components. The rules were established from the analysis of all ternary residue curve diagrams relevant to heterogeneous systems. Total reflux/reboil and infinite tray number are assumed. Total liquid-phase split between the entrainer and one of the original binary mixture components is first considered; this completeness hypothesis removal is discussed afterward. In the case that the ternary diagram involves a minimum-boiling-temperature ternary azeotrope, it is considered as heterogeneous when it is the only possibility to provide a feasible process which allows separation of components A and B located in different regions.

For each ternary diagram, the process feasibility of all possible alternatives is studied. First, the position of components A and B to be separated and their azeotrope is defined on one side of the triangular diagram. Then, we consider the addition of a light, an intermediate, or a heavy entrainer and its immiscibility with either A or B (a type I liquid–liquid ternary diagram is considered). All possible batch task se-

quences for both rectifying and stripping operation are obtained, taking into account the position of the initial feed in each batch region. Finally, only the batch distillation sequence involving the lowest number of batch tasks is retained, and definition of the required entrainer properties is done accordingly, although the smallest number of units or operations does not necessarily mean the lowest cost or the most efficient overall operations. Further purification of the decanted phase rich in the component with finite immiscibility with the entrainer may be required. These supplementary tasks are not considered in the total number of tasks because they are mixture specific and will depend on the stability of this pure-component vertex.

Using this methodology, we have established six general conditions for the selection of heterogeneous entrainer, allowing a feasible separation of minimum-boiling azeotropic binary mixtures, maximum-boiling azeotropic binary mixtures and close boiling binary mixtures. The first four conditions are identical to those defined for homogeneous batch distillation.<sup>9</sup> The six general conditions are as follows:

1. No additional azeotrope is introduced.
2. A minimum temperature binary homoazeotrope exists between E and either A or B.
3. A maximum temperature binary homoazeotrope exists between E and either A or B.
4. E forms either a homogeneous or heterogeneous ternary azeotrope.
5. E is not miscible with one of the components of the original binary mixture.
6. E forms a minimum temperature binary heteroazeotrope with A or B.

A complete set of rules for the selection of feasible entrainers can be established by combining those six thermodynamics conditions with some topological constraints. The rules are established according to the following scheme:

Condition {1, 2, 3, 4, 5, or 6}(component {A or B} [stability {un, sn, or s}])

This condition is to be read as follows for the first case 2 (A[un]): Condition 2 applies to component A that is an unstable node. The double arrow symbol “A ↔ B” means that the condition can be found for A or B. Double arrows can apply to stability as well as to components.

The equation of topological index for the ternary system developed by Doherty and Perkins<sup>36</sup> can be used for the determination of the stability of the fixed points that have not been defined. Notations N and S stand for node and saddle, respectively. Subscripts 1, 2, and 3 refer to pure-component, binary, and ternary mixtures, respectively. This equation is

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

As an application example, the rule defined as 2 (A ↔ B) + 4 [un] + 6 (B ↔ A) for the separation of a minimum temperature A–B azeotrope means that the entrainer must form a minimum-boiling-temperature homoazeotrope with component A (or, respectively, B), a minimum-boiling-temperature unstable ternary azeotrope, and a minimum-boiling-temperature heteroazeotrope with component B (or, respectively, A). Application of the stability equation (1) says that both binary azeotropes are saddles. When any entrainer (low, intermediate, or high-boiling) is chosen, the described rule defines the ternary diagram classified as 222-m. The rule 3 (A[sn ↔ s] ↔ B[sn]) + 6 (B ↔ A)[un] describes

**Table 1. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Minimum-Boiling-Temperature Azeotropic Binary Mixtures by Heterogeneous Batch Distillation<sup>a</sup>**

no.	entrainer		
	low boiling	intermediate boiling	high boiling
1	6 (A↔B)[un]		
2	2 (A↔B) + 6 (B↔A)[un]		
3	3 (A[sn↔s]↔B[sn]) + 6 (B↔A)[un]		3 (A↔B)[sn] + 6 (B↔A)[un]
4		4 [un] + 5 (A↔B)	
5	4 [un↔s] + 6 (A↔B)		
6	2 (A↔B) + 4 [un] + 5 (B↔A)		
7	3 (A) + 4 [un] + 5 (B)	3 (A[s]↔B[sn]) + 4 [un] + 5 (B↔A)	3 (A↔B)[sn] + 4 [un] + 5 (B↔A)
8	2 (A↔B) + 4 [un] + 6 (B↔A)		
9	2 (A[un <sup>2</sup> ↔s <sup>3</sup> ]↔B[un <sup>2</sup> ↔s <sup>1</sup> ]) + 4 [s] + 6 (B↔A)[un]	2 (A[un <sup>1</sup> ↔s <sup>3</sup> ]↔B[un <sup>1</sup> ↔s <sup>2</sup> ]) + 4 [s] + 6 (B↔A)[un]	2 (A[un <sup>3</sup> ↔s <sup>1</sup> ]↔B[un <sup>3</sup> ↔s <sup>2</sup> ]) + 4 [s] + 6 (B↔A)[un]
10	3 (A)[s] + 4 [un] + 6 (B)[un↔s]		
11	3 (A↔B)[sn] + 4 [un] + 6 (B↔A)		
12	3 (A↔B)[s↔sn] + 4 [sn↔s] + 6 (B↔A)[un]		

<sup>a</sup> The first batch task in the process sequence is a rectification. Superscripts 1, 2, and 3 are relevant to diagrams 112-S, 121-S, and 211-S, respectively.

three unlike ternary diagrams: (i) 3 (A)[sn] + 6 (B)-[un], stable maximum-boiling azeotrope with A and unstable minimum-boiling azeotrope with B; (ii) 3 (A)-[s] + 6 (B)[un], saddle maximum-boiling azeotrope with A and unstable minimum-boiling azeotrope with B; (iii)-3 (B)[sn] + 6 (A)[un], stable maximum-boiling azeotrope with B and unstable minimum-boiling azeotrope with A. The three corresponding ternary diagrams for a low-boiling entrainer are 321, 411, and 123, respectively. Similarly, for the complex rule 2 (A ↔ B)[un ↔ s] + 4 [s ↔ un] + 6 (B ↔ A)[un ↔ s], when E forms a minimum temperature azeotrope with A (or, respectively, B) which is an unstable node, E forms a ternary azeotrope that is not unstable but a saddle, and E forms a minimum temperature heteroazeotrope with B (or, respectively, A) that is unstable and not a saddle. The other stability statements [s] specified for the conditions 2 and 6 respectively are taken into account when E forms a ternary azeotrope, which is a unstable node.

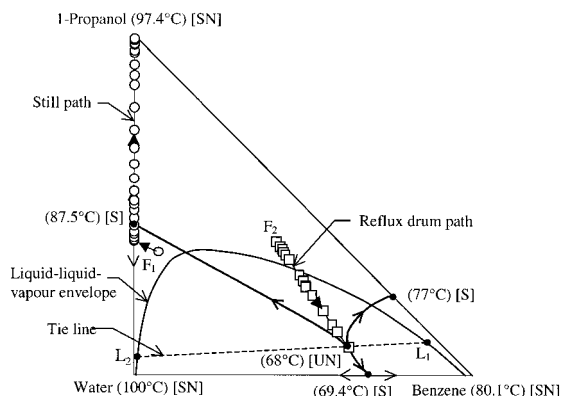
### 3.1. Separation of Minimum-Boiling Azeotropes.

A total of 93 different ternary topological structures out of 125 contain at least one minimum-boiling azeotrope, but only 72 ternary diagrams contain heteroazeotropes with the mandatory unstable or saddle characteristic mentioned before. The remaining 21 ternary diagrams display three binary azeotropes, two of them are maximum-boiling. A feasible entrainer provides a ternary diagram where the two original components are or are not in the same batch distillation region and either the heteroazeotrope or one of the original components is a node. When the heteroazeotrope is an unstable node, a batch rectifier as the first batch task is the preferred choice because it leads to the lowest number of batch tasks needed to obtain a sequence of high-purity products. Conversely, a stripper (rectifier) can be used when the original component is a stable (unstable) node. We first present the rules leading to ternary diagrams where a rectification must be performed as the first batch task of the sequence. Stripping at first is discussed afterward.

**3.1.1. Rectifier as the First Batch Task.** The entrainer properties defined in Table 1 lead to 53 ternary diagrams that exhibit an unstable binary or a ternary heteroazeotrope. Hence, a rectification is first performed and distillates overhead this particular azeotrope. The total number of batch tasks depends on the distillation region where the initial ternary mixture is placed, on the immiscibility degree between the entrainer and one of the original components, and on the still composition after the first batch rectification. The rule defined in row nine of Table 1 describes all topological structures leading to the undetermined diagrams 112-S, 121-S, and 211-S.<sup>23,37</sup> Superscripts 1, 2, and 3 give the relevant stability conditions for diagrams 112-S, 121-S, and 211-S, respectively. For instance, superscript 3 for an intermediate entrainer leads to the rule 2 (A[s] + 4 [s] + 6 (B)[un]) and corresponds to the ternary diagram 211-S.

Three subcases are distinguished below for the separation of minimum azeotropic binary mixtures, namely, (i-m) the unstable binary heteroazeotrope is situated in the same batch region as the binary homoazeotrope A–B to be separated and then either A or B, (ii-m) a ternary unstable heteroazeotrope is placed in the same distillation region as the original homoazeotrope, and (iii-m) the unstable binary heteroazeotrope is not located in the same batch region as the homoazeotrope.

Subcase i-m includes ternary diagrams where the binary heteroazeotrope is an unstable node and is situated in one of the two batch regions that contains the binary homoazeotrope A–B and either A or B. The initial feed must be located in one of these batch regions. A single batch rectifier task is needed to separate both original components if the initial quantity of entrainer added and the column reflux ratio are carefully monitored. As illustrated in Figure 1 (path α), very little entrainer is added to the original binary mixture. In this way, after a total reflux operation, the heteroazeotrope moves up to the column top and the small amount of entrainer remains mainly on the column top trays and

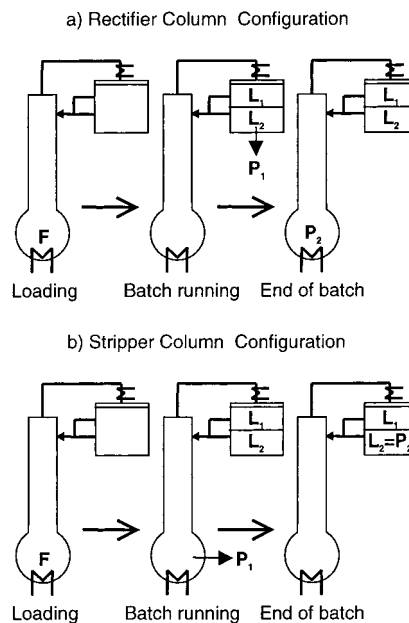


**Figure 2.** Separation of a 1-propanol–water azeotropic mixture by heterogeneous batch distillation with benzene. The heterogeneous ternary azeotrope case where the still path crosses the distillation boundary.

in the decanter, leaving the still composition on the entrainer-free side of the diagram. The entrainer-rich phase in the decanter is refluxed, and the other phase rich in A (or B) is removed as distillate and thus progressively exhausts A (B) from the still and from the column. At the end of the process, the component miscible B (A) with the entrainer is obtained with a high purity in the still. The entrainer-rich liquid-phase remaining in the decanter can be recycled to the next batch process. An example of a ternary system included in Table 1 is shown in Figure 1. Cyclohexane is a light entrainer that obeys the rule 1 defined in Table 1. Rodriguez-Donis et al.<sup>15</sup> reported simulated and experimental results in very good agreement for the separation of the mixture acetonitrile–water using acrylonitrile as an entrainer. Acrylonitrile was selected by applying rule 1, and a little amount of entrainer was added to the original mixture. A 91.8% water-rich phase was recovered as distillate, and a 99.85% acetonitrile-rich phase was left in the still at the end of the process.

Subcase ii-m includes ternary systems that exhibit a ternary unstable heteroazeotrope placed in the same distillation region as the original binary homoazeotrope. Therefore, the binary heteroazeotrope is a saddle if it exists. For a rectifying operation, similar to the example of Figure 1, the heterogeneous unstable node moves up the column after a total reflux step, the entrainer-rich phase is refluxed, the other phase is removed as a distillate cut, and the still path can reach the miscible original component vertex at the end of the process by control of both the initial amount of entrainer and the reflux of the entrainer-rich phase. This rectification process is illustrated in Figure 2 with the separation of 1-propanol–water using benzene. Benzene obeys rule 8 for light entrainers in Table 1.

Figure 3a shows the sequence of the heterogeneous batch rectification displayed in Figure 2. The unstable ternary heteroazeotrope boils overhead. A liquid-phase split takes place into the decanter, and the water-rich phase  $L_2$  ( $x \approx 0.95$ ) is removed as the distillate  $P_1$ . The liquid-phase split depends on the 1-propanol mole fraction of the ternary heteroazeotrope. Although very little benzene is added to original binary mixture, the separation is possible due to the reflux of  $L_1$ , the entrainer-rich phase ( $x \approx 0.672$ ). The still path goes from the initial ternary composition  $F_1$  toward the pure 1-propanol vertex ( $P_2$ ). It crosses the distillation boundary between the 1-propanol–water binary homoazeotrope and the ternary heteroazeotrope. The simulated

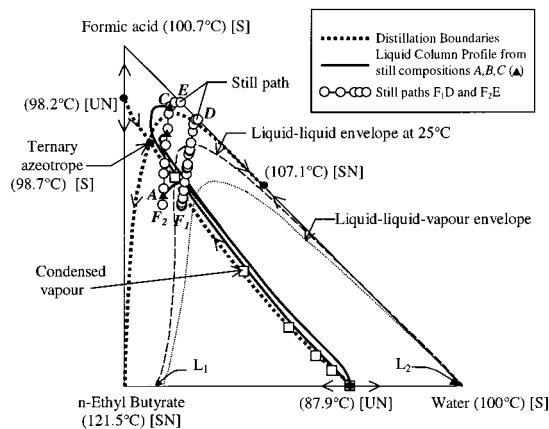


**Figure 3.** Operation sequence of one batch distillation task for different column configurations.

still path is shown in Figure 2. Simulation conditions are given in Appendix 2. A single batch rectification task allows the separation of pure 1-propanol, but several supplementary batch distillation tasks may be required if a water purity higher than that of  $L_2$  (here  $x \approx 0.95$ ) is sought. Because water is a stable node, a single additional stripper will here allow one to obtain pure water from the  $L_2$  mixture.

The separation of 1-propanol can also be performed with one batch stripper because 1-propanol is a stable node. Figure 2 shows the simulation results of the reflux drum path, and the batch task sequence appears in Figure 3b. Because the initial ternary mixture  $F_2$  has to be located in the batch region including the 1-propanol vertex, more entrainer is required than in the previous rectifier case. From the entrainer consumption point of view, the optimum feed location lies, in fact, on the batch distillation boundary between the 1-propanol–water homoazeotrope and the ternary heteroazeotrope. During stripping, 1-propanol is removed from the bottom as product  $P_1$ , while the reflux drum departs from  $F_2$  and ends at the ternary heteroazeotrope. A liquid-phase split takes place in the reflux drum. The process finishes when the reflux drum reaches the ternary heteroazeotrope. The aqueous phase  $L_2$  is removed as product  $P_2$ , whereas the entrainer-rich phase  $L_1$  can be recycled to the next batch task.

Subcase iii-m includes ternary diagrams where the unstable binary heteroazeotrope is not located in the same batch region as the binary homoazeotrope to be separated. In this case, the initial ternary composition has to be placed in the distillation region that contains the binary heteroazeotrope. Besides, a larger quantity of entrainer than the two previous subcases has to be added to the original binary mixture. Figure 4 presents the separation of *n*-ethyl butyrate–formic acid with water as a light entrainer. Water obeys rule 12 of Table 1 and forms a maximum azeotrope with formic acid. The ternary system has a saddle ternary homoazeotrope, and the diagram is divided into four basic distillation regions by curved separatrices. Simulation results are presented in Figure 4 for two initial compositions in the



**Figure 4.** Separation of a *n*-ethyl butyrate–formic acid azeotropic mixture by heterogeneous batch distillation with water. The heterogeneous ternary azeotrope case where the still path crosses the distillation boundary.

still  $F_1$  and  $F_2$  placed in the basic distillation region that contains the heterogeneous azeotrope and the distillate product  $L_1$ . Therefore, the still path moves away from the *n*-ethyl butyrate-rich phase  $L_1$ . For the  $F_1$  case, the still path trajectory is almost linear and ends on the formic acid–water edge with a formic acid composition higher than that of the binary azeotropic point (point D in Figure 4). One batch rectification stage allows the separation of the binary heteroazeotrope in which the organic phase  $L_1$  contains mainly *n*-ethyl butyrate and is obtained as a distillate cut  $P_1$  with a molar purity of 90.8%. The aqueous entrainer phase  $L_2$  is refluxed at the top of the column until *n*-ethyl butyrate is completely removed from the still. Later, a second batch rectification stage is needed to separate the water–formic acid azeotropic mixture (D), and the heavy-component formic acid is obtained as a second distillate cut while the maximum-boiling-temperature azeotrope water–formic acid is recycled to the next process sequence. The simulated still path is shown in Figure 4. Simulation conditions are given in Appendix 2. The process feasibility is highly dependent on the stable separatrix curvature between the ternary azeotrope and the maximum-boiling binary azeotrope because the still composition is always placed in the basic regions limited by the unstable heterogeneous azeotrope.

A similar and curious behavior was obtained by simulation for the initial mixture  $F_2$ . In this case, a lower amount of entrainer than that for  $F_1$  is added to the original mixture. At first, like case  $F_1$ , the still path trajectory is rectilinear while the still composition stays in the basic region where the heteroazeotrope is the unstable node. Two column liquid profiles are displayed for two instantaneous still compositions A and B, and both reach the unstable heteroazeotrope as expected. When the still composition crosses the stable separatrix, it is now located in a basic region where the original homoazeotrope is the unstable node. In this case, the formic acid composition increases in the condensed vapor, but as seen in Figure 4, it stays in the heterogeneous regions until the process finishes. Consequences on the still path are noteworthy: the still path deviates from its rectilinear trajectory and follows a new direction which is determined by the position of the homogeneous unstable node and the direction of the stable separatrix. In this case the whole process feasibility is determined by the existence of a column liquid profile that links the punctual still composition with the

heterogeneous condensed vapor. The illustrative column liquid profile for still composition C is shown in Figure 4. Similar to the previous case, the still path reaches the binary side at point E and the subsequent separation of formic acid is possible.

We are well aware that the feasibility of such a process depends on a proper combination of the heterogeneous region shape and size, of the azeotrope location and distillation boundary curvatures, of the initial amount of entrainer, and of operation parameters such as the number of trays in the column and the reflux ratio. The ternary diagrams included in case iii-m exhibit several basic distillation regions that are limited by unstable homogeneous and heterogeneous azeotropes. With all of these factors properly combined, the still path will cross several boundaries and achieve the desired separation.

Subcase iii-m also highlights an important difference between batch and continuous distillation processes: contrary to what was enounced for heterogeneous continuous distillation,<sup>2,3</sup> the liquid–liquid–vapor envelope is not obliged to cross the boundaries dividing the two regions containing the two components A and B to be separated. Therefore, whether the ternary azeotrope is homogeneous (Figure 4) or heterogeneous, the same batch distillation sequence is obtained.

**3.1.2. Stripper as the First Batch Task.** Among the ternary diagrams mentioned above, several contain a stable component not only miscible with the entrainer but also situated in the same batch region as the heterogeneous binary azeotrope. For these diagrams, a batch stripper can be used for the separation of both components as shown in Figure 1 (path  $\beta$ ). The stable original component is completely separated as a bottom product  $P_1$  (see Figure 3b), and two liquid phases are obtained in the reflux drum. At the end of the stripper task, the component-rich liquid phase  $L_2$  is removed as product  $P_2$  for further purification. The entrainer-rich liquid phase  $L_1$  can be recycled to the next batch distillation sequence. As said before, this column configuration requires more entrainer added to the initial binary mixture than the batch rectification operation analyzed above.

Table 2 shows the entrainer properties that enable a batch distillation sequence involving the stripping operation as a first task in order to separate the two binary azeotropic components. Rule 10 describes all topological structures of the undetermined diagrams 112-S, 121-S, and 211-S.<sup>23,37</sup> Similar to Table 1, the superscripts 1, 2, and 3 refer to the ternary diagrams 112-S, 121-S, and 211-S, respectively. Notice that rules 2 and 4 generate basically the same ternary diagrams that only differ in the position of the liquid–liquid demixing zone. In the 39 ternary diagrams generated by Table 2, batch rectification cannot be used as the first task because both binary and ternary heteroazeotropes are saddle points. The number of batch tasks needed to separate both original mixture components depends on the locations of the binary heteroazeotrope and of the stable original component vertex. If both belong to the same batch distillation region, then a single batch stripper is needed as shown in Figure 3b. Otherwise, if both fixed points are not in the same batch distillation region, then the first stripper task must be followed by several other batch tasks. The first batch stripper takes the stable component out of the column bottom, while two liquid phases are obtained in the decanter.

**Table 2. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Minimum-Boiling-Temperature Azeotropic Binary Mixtures by Heterogeneous Batch Distillation<sup>a</sup>**

no.	entrainer		
	low boiling	intermediate boiling	high boiling
1	1 + 5 (A↔B)	1 + 5 (A)	
2		6 (A↔B)[s]	
3	4 [s] + 5 (A↔B)		
4		2 (A↔B)[un↔s] + 5 (B↔A)	
5		2 (A↔B)[un↔s] + 6 (B↔A)[s]	
6		2 (A↔B) + 4 [s] + 5 (B↔A)	
7		3 (A↔B) + 6 (B↔A)[s]	
8	3 (A[sn↔s]↔B[sn]) + 5 (B↔A)	3 (A)[s] + 5 (B)	
9	3 (A↔B) + 4 [sn↔s] + 5 (B↔A)	3 (A) + 4 [s] + 5 (B)	
10	2 (A <sup>1</sup> ↔B <sup>3</sup> ) + 4 [s] + 6 (B↔A)[s]	2 (A <sup>2</sup> ↔B <sup>3</sup> ) + 4 [s] + 6 (B <sup>2</sup> ↔A <sup>3</sup> )[s]	2 (A <sup>2</sup> ↔B <sup>1</sup> ) + 4 [s] + 6 (B <sup>2</sup> ↔A <sup>1</sup> )[s]

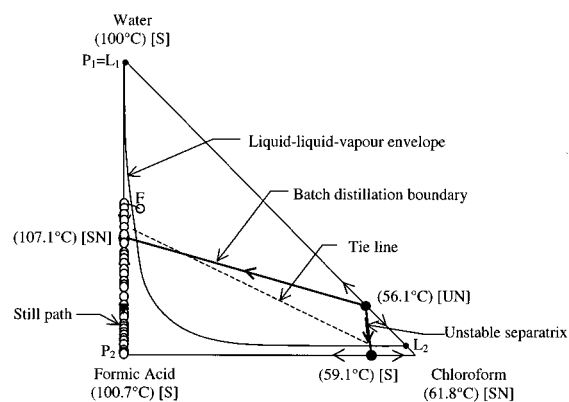
<sup>a</sup> The first batch task in the process sequence is a stripper. Superscripts 1, 2, and 3 are relevant to diagrams 112-S, 121-S, and 211-S, respectively.

We have noticed that the liquid–liquid–vapor envelope must cross the distillation boundary between the original mixture components. It comes from the fact that the composition of the immiscible decanter phase with a high content of the immiscible original component must be located in the batch region containing this component.

In the case of a ternary system that involves a saddle ternary heteroazeotrope, a batch stripper can be the first task in the process sequence in the same way as the one shown in Figure 2 for an unstable ternary azeotrope. At the time when the stable original component is removed as a bottom product, the reflux drum contains the ternary heteroazeotrope. In a second batch task, the component that is not miscible with the entrainer must be separated if the liquid phase containing it in the reflux drum is not pure enough. The column configuration to be used then depends on the stability of fixed points that limit the particular batch region. For the example shown in Figure 2, a stripper is used as a second batch task because both original components are stable nodes.

Entrainer properties defined in Tables 1 and 2 generate overall 65 ternary diagrams, some in both tables, among the 72 relevant diagrams for a heterogeneous ternary diagram with a minimum-boiling azeotropic original mixture. All of these diagrams provide a feasible batch distillation sequence to separate the original binary mixture, either with a rectifier or a stripper as a first task. This number is far greater than the nine feasible ternary diagrams found in the homogeneous batch distillation case under the same assumptions of straight-line boundaries and very high reflux.<sup>9</sup> It clearly demonstrates the flexibility in terms of more process alternatives brought by heterogeneous batch distillation. Finally, as in the homogeneous case, we could not find a feasible process for seven ternary systems (100, 130, 103, 031, 140-M, 104-M, and 041-M) with one basic distillation region where both original components are saddles and are situated in different batch regions. In these latter systems, homoazeotropes (binary or ternary) give both the unstable and stable nodes. Therefore, they will be obtained by either rectification or stripping in place of the wanted pure components.

**3.2. Maximum-Boiling Azeotropes.** A total of 93 ternary residue curve maps out of 125 involve at least



**Figure 5.** Separation of a water–formic acid azeotropic mixture by heterogeneous batch distillation with chloroform. The heterogeneous ternary azeotrope case where the still path crosses the distillation boundary.

one maximum-boiling azeotrope, but all are not usable. Because of thermodynamic and stability constraints, maximum-boiling azeotropes cannot be heterogeneous.<sup>29</sup> Therefore, ternary diagrams that show three binary maximum-boiling-temperature azeotropes are discarded, leaving 80 diagrams. Finally, eight ternary diagrams (030, 040-M, 404-M, 044-M, 440-M, 144-M, 414-M, and 441-M) do not provide a feasible process because both original components are saddles and are situated in different batch regions. Besides, in these systems homoazeotropes (binary or ternary) give both the unstable and stable nodes.

For homogeneous ternary diagrams, we derived a transformation pattern to obtain any feasible ternary diagram for a maximum-boiling azeotrope from any feasible ternary diagram for a minimum-boiling azeotrope. The stability constraint for a heteroazeotrope and the discrepancy between the number of feasible diagrams for minimum-boiling azeotropes (65) and for maximum-boiling azeotropes (72) suggest that such a pattern does not exist for the heterogeneous ternary diagram. We confirm this claim below, in particular with the example illustrated in Figure 5.

We derive two sets of rules for the selection of an entrainer that provides a feasible batch distillation process for the separation of a maximum-boiling-tem-

**Table 3. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Maximum-Boiling-Temperature Azeotropic Binary Mixtures by Heterogeneous Batch Distillation<sup>a</sup>**

no.	entrainer		
	low boiling	intermediate boiling	high boiling
1	6 (A↔B)	6 (A)	
2	2 (A↔B) + 6 (B↔A) [un]		2 (A↔B)[un↔s] + 6 (B↔A)[un]
3	4 [sn↔un] + 6 (A↔B)[un↔s]	4 [sn↔un] + 6 (A)[un↔s]	
4	2 (A↔B)[s] + 4 [un] + 5 (B↔A)	2 (A)[s] + 4 [un] + 5 (B)	2 (B) + 4 [un] + 5 (A)
5	2 (A↔B)[s] + 4 [un] + 6 (B↔A)[s]		2 (A↔B)[s↔un↔s] + 4 [un] + 6 (B↔A)[un↔s↔s]
6	2 (A↔B)[s↔un] + 4 [sn↔s] + 6 (B↔A)[un]		

<sup>a</sup>The first batch task in the process sequence is a rectification of the heteroazeotrope.

**Table 4. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Maximum-Boiling-Temperature Azeotropic Binary Mixtures by Heterogeneous Batch Distillation<sup>a</sup>**

no.	entrainer		
	low boiling	intermediate boiling	high boiling
1		1 + 5 (A↔B)	
2		6 (B)[s]	6 (A[un]↔B[un↔s])
3		2 (B)[s] + 5 (A)	2 (A[un]↔B[un↔s]) + 5 (B↔A)
4		3 (A↔B)[sn↔s] + 5 (B↔A)	
5		3 (A↔B)[sn↔s] + 6 (B↔A)[un]	
6		3 (A) + 6 (B)[s]	
7		4 [sn] + 5 (A↔B)	4 [s] + 5 (A↔B)
8		4 [sn↔s] + 6 (B)[s↔un]	4 [sn] + 6 (B)
9			4 [un] + 6 (A)[s]
10			4 [s] + 6 (A↔B)[un]
11		2 (B)[un↔s] + 4 [s↔sn] + 5 (A)	2 (B) + 4 [sn] + 5 (A)
12			2 (A↔B) + 4 [s] + 5 (B↔A)
13		3 (A)[sn↔s] + 4 [sn] + 6 (B)[s]	
14		3 (A↔B) + 4 [s] + 5 (B↔A)	
15		3 (A↔B)[sn↔s] + 4 [un] + 6 (B↔A)[s]	
16		3 (A↔B) + 4 [s] + 6 (B↔A)	

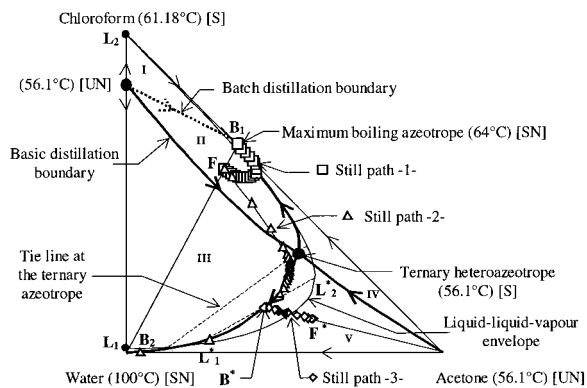
<sup>a</sup>The first batch task in the process sequence is a batch rectification of one of the original component.

perature azeotropic binary mixture. The 31 cases when the original mixture components are not unstable nodes and the corresponding diagram includes a binary or a ternary unstable heteroazeotrope are treated by the rules in Table 3. The 41 cases when one of the original mixture components is an unstable node and the relevant diagram includes a binary or a ternary heteroazeotrope that is either unstable or a saddle are treated by the rules in Table 4.

The two subcases i-M and ii-M, parallel to cases i-m and iii-m of Table 1, are distinguished in Table 3. No equivalence to Table 1 subcase ii-m is found here because this corresponds to ternary diagrams with minimum-boiling-temperature-only azeotropes. Subcases i-M and ii-M include all ternary systems with a binary or ternary unstable heteroazeotrope, and unlike the minimum-boiling azeotrope subcases i-m and iii-m, this fixed point is always located in the same batch region as the original binary azeotrope to be separated. A batch rectifier can be used to obtain in the still the

saddle or stable original mixture component, while the heteroazeotrope demixes in the decanter (see Figure 3a).

Figure 5 shows an example of the separation of a maximum-boiling azeotrope when the entrainer leads to a ternary diagram involving an unstable heterogeneous binary azeotrope. The separation of water-formic acid using chloroform as a light entrainer is presented. Chloroform fulfills the second rule in Table 3 for low-boiling entrainers. The separation requires a small amount of entrainer, and a single batch rectifier performs. The initial ternary mixture (F) is located in the batch region that does not contain the formic acid vertex. Simulation conditions are given in Appendix 2. Results show that water with a mean molar composition of 99.7% ( $L_1$ ) is obtained as distillate ( $P_1$ ) from the decanter during the operation. The still path moves from its initial point (F), crosses the batch distillation boundary that divides the batch region where the components to be separated are situated, and ends at the formic acid. Rectification is stopped when  $x_{\text{formic acid}} > 0.995$  in the

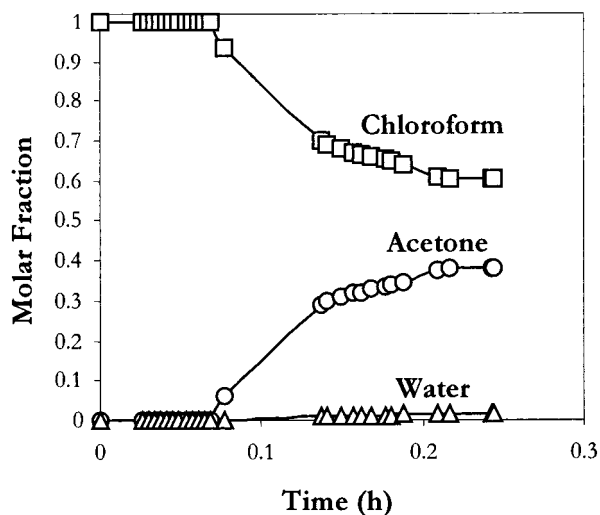


**Figure 6.** Separation of an acetone–chloroform azeotropic mixture by heterogeneous batch distillation with water as the heavy entrainer: (□) still path 1: rectification with reflux of a combination of both decanter phases; (△) still path 2: rectification with reflux of a combination of both decanter phases; (◇) still path 3: rectification to obtain pure acetone distillate.

still ( $P_2$ ). Rodriguez-Donis et al.<sup>15</sup> also reported the use of propyl formate for the separation of the water–formic acid maximum-boiling azeotrope. Propyl formate was selected using rule 1 of Table 3 for light entrainers. Simulation results showed that the distillate product was the water-rich phase (molar composition = 0.9943), while the acetonitrile was retained in the still with a molar fraction of 0.9947.

Table 4 presents the rules for the selection of entrainers that provide a ternary diagram where one of the original components is an unstable node. Therefore, this component can be removed as distillate using a rectification process. Some ternary diagrams described in the first six rows of Table 4 exhibit saddle heterogeneous binary azeotropes, while others have an unstable binary or ternary heteroazeotrope. In this latter case, when a rectification is performed, the stability of the miscible original component forbids the still path to arrive at the vertex of this component. This particular behavior is shown in Figure 6 with the separation of maximum-boiling azeotrope acetone–chloroform with water. Water obeys rule 9 defined for heavy entrainers in Table 4. The ternary diagram exhibits an unstable chloroform–water heteroazeotrope. The acetone vertex is also unstable, whereas the ternary heteroazeotrope is a saddle. The system has two stable separatrices and two unstable separatrices, dividing the triangle diagram into four basic distillation regions. Notice the curvature of those separatrices. A batch distillation boundary joins both binary azeotropes, resulting in five batch regions. The binary heteroazeotrope can be obtained as a distillate in the same way as all systems included in the minimum-boiling-temperature subcase i-m if the initial composition is placed in any distillation region limited by this fixed point. However, this example bears some striking features that we did not expect at first. For instance, a feed, located in region I in Figure 6 to use a very small amount of entrainer, will end up at the stable maximum-boiling azeotrope and will not cross the boundary to reach the acetone vertex like what we first thought by comparison with Figure 5. The reason is that the acetone vertex is an unstable node.

Besides, this restriction on the acetone holds even when the reflux policy allows the control of the still path. Two simulated still paths are shown in Figure 6, from a same initial ternary composition F but with a different reflux policy that combines both decanter phases in various proportions. Simulation conditions are given in



**Figure 7.** Evolution of distillate composition with time. Separation of an acetone–chloroform azeotropic mixture by heterogeneous batch distillation with water as the heavy entrainer.

Appendix 2. More aqueous phase is refluxed for still path 1 than for still path 2. As can be seen, both still paths cross distillation boundaries, but unlike the example of Figure 5, the miscible component, acetone, is not obtained at the end in the still. Actually, it even poisons in some way the distillate: first the water–chloroform heteroazeotrope is condensed at the column top and the chloroform-rich phase  $L_1$  is carefully removed because chlorinated products can be quite harmful. However, when the still path from F crosses a boundary to move into a region where acetone is the unstable node (region IV or V), the acetone moves rapidly to the column top where a ternary mixture is now condensed. Consequently, some acetone is found in the two liquid phases in equilibrium. The still path cannot arrive at the acetone vertex and changes its initial trajectory direction to finish at the stable node of the system (maximum-boiling azeotrope or water vertex). The chloroform-rich distillate composition is comparable for both paths and is displayed in Figure 7 for still path 1. Still path 1 obtained with a reflux of only the lighter aqueous phase  $L_1$  is nonsense in a way that we end up in the still at the maximum-boiling-temperature binary mixture chloroform–acetone  $B_1$  that we want to separate. Still path 2 goes to  $B_2$  near the water vertex thanks to control of the reflux ratio between both decanter phases  $L_1$  and  $L_2$ . It does not though allow obtainment of pure acetone. Notice that, thanks to this reflux policy, the still path 2 initial direction is almost aligned with the  $L_2$  phase that is removed, behaving much like a homogeneous system. Any feed in region III will behave like still path 2, whatever the reflux policy used.

Such a phenomenon cannot be obtained when separating a minimum-boiling azeotrope. Indeed, all ternary diagrams described in cases i-m, ii-m, and iii-m have a miscible component that is either a saddle or a stable node. In these cases, the heteroazeotrope is obtained at the column top after the still path crosses the distillation boundary and a high-purity miscible component is retained in the still at the process end.

To obtain the unstable miscible node, acetone, the feed must be located in region IV or V. It will then behave as described by Van Dongen and Doherty:<sup>24</sup> first the acetone is obtained in the distillate, and when the still

**Table 5. Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Binary Mixtures Involving Close Boiling Components by Heterogeneous Batch Distillation<sup>a</sup>**

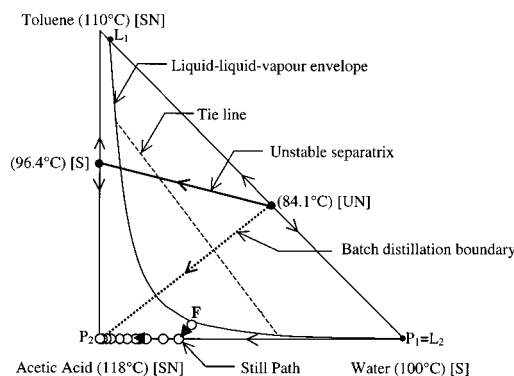
no.	entrainer		
	low boiling	intermediate boiling	high boiling
1	6 (A↔B)	6 (A) [un]	
2	2 (A↔B) + 6 (B↔A)[un]		
3	3 (B) + 6 (A)		
4	4 [un] + 6 (A↔B)	4 [un] + 6 (A)	
5	2 (A↔B) + 4 [un] + 5 (B↔A)	2 (A) + 4 [un] + 5 (B)	
6	2 (A↔B)[un↔s] + 4 [s↔un] + 6 (B↔A)[un↔s]		
7	3 (B)[sn↔s] + 4 [un↔sn] + 6 (A)[s↔un]		

<sup>a</sup> A batch rectifier is used as the first task for the separation of the unstable heteroazeotrope.

path reaches a curved boundary, the distillate composition moves onto the boundary, joining the acetone and the ternary heteroazeotrope, tangent at any time to the still path. An example is shown in Figure 6 for a feed in region V: the still path starts from  $F^*$  and reaches a distillation boundary at  $B^*$  where a liquid-phase split occurs ( $L^*_1$  and  $L^*_2$ ). As noticed by Pham and Doherty,<sup>1</sup> in this system the tie line at the ternary heteroazeotrope does not cross the distillation boundary that divides the distillation region where acetone and chloroform are located. Therefore, we cannot find a process using a rectifier or a stripper that will allow recovery of both original components with a high purity for some time during the operation. However, unlike what is shown in Figure 6, if either  $L^*_1$  or  $L^*_2$  were located in the batch distillation containing the heterogeneous binary azeotrope, then a second batch rectifier task would allow splitting of this fixed point and consequently recovery of the immiscible component. Unfortunately, we could not find such a practical example.

The separation of maximum-boiling azeotropic mixtures using a batch rectifier involving a homogeneous entrainer was presented in a previous work.<sup>9</sup> However, an essential difference exists between the homogeneous and heterogeneous cases. In the heterogeneous case, the process is feasible for a higher number of entrainers because the envelope liquid–liquid–vapor crosses the distillation boundary that divides the distillation region where both desired components are situated.

**3.3. Zeotropic Binary Mixture with Closed Boiling Components.** Separation of close boiling point binary mixtures can be as tedious as azeotropic binary mixture separation. Indeed, pinches on the liquid–vapor equilibrium curve can cause a direct distillation process to become uneconomical because a number of trays are too large. The use of an entrainer that forms a new azeotrope that is easier to break than the original pinched binary mixture is a typical solution for this problem. Rules for the selection of a feasible homogeneous entrainer were published in a previous work.<sup>9</sup> Among the 57 diagrams that displayed no binary azeotrope on the edge A–B, ternary diagrams involving two maximum-boiling azeotropes cannot be considered for the heterogeneous entrainer case because these fixed points must be homogeneous. The 45 remaining ternary diagrams enable a feasible heterogeneous batch distillation process and include cases when (i) it is impossible in the homogeneous entrainer case, (ii) the use of a heterogeneous entrainer allows the separation of both original components using less batch distillation tasks

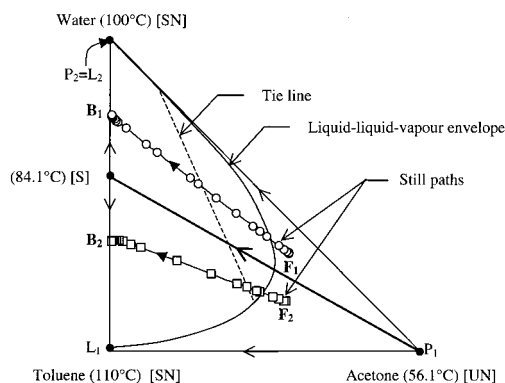


**Figure 8.** Separation of acetic acid–water by heterogeneous batch rectification using toluene as an intermediate entrainer.

than with a homogeneous entrainer, or (iii) the obtained process involves the same number of batch distillation tasks as with a homogeneous entrainer.

Every process sequence established in the previous sections for the separation of minimum- or maximum-boiling azeotropes was found viable for the separation of a binary mixture involving close boiling components. Therefore, a batch rectifier can be used for the separation of an unstable heteroazeotrope (subcases i-m, ii-m, and iii-m) or a batch stripper for the separation of the stable original component. Similar to the maximum-boiling azeotropic mixture case, a batch rectifier can be used to obtain the unstable original component as the first distillate cut. Table 5 displays the entrainer selection rules enabling the separation of close boiling binary mixture using first a batch rectifier to remove the heteroazeotrope in the first distillate cut. They generate 25 ternary diagrams.

The separation of the close boiling components acetic acid–water using toluene as an intermediate entrainer is shown in Figure 7. This entrainer obeys rule 2 in Table 5 because toluene forms an unstable heteroazeotrope with water and a homogeneous minimum-boiling azeotrope with acetic acid. Simulation results are displayed in Figure 8, and the rectification sequence is shown in Figure 3a. Simulation conditions are given in Appendix 2. The initial ternary mixture  $F$  is homogeneous and contains a small amount of entrainer. After the infinite reflux operation, the entrainer stays mainly on the column trays and in the decanter. A single batch rectifier allows the separation of water ( $x > 0.995$ ;  $P_1 = L_2$ ). Acetic acid ( $x = 0.998$ ) is obtained in the still ( $P_2$ ) at the process end.



**Figure 9.** Separation of an acetone–water mixture by heterogeneous batch distillation using toluene as the heavy entrainer.

Because the acetic acid vertex is a stable node, it can also be separated using a batch stripper. Besides, a batch rectifier can be used when the miscible original component is an unstable node, similar to what we established for the maximum-boiling-temperature azeotropic mixture case. Rodriguez-Donis et al.<sup>15</sup> presented similar simulated results for the separation of this binary mixture using vinyl acetate as a light entrainer.

Table 6 displays the rules for the selection of entrainers which make possible the separation of a close boiling binary mixture when one of the two original components is either a stable or an unstable node. A few of the 28 diagrams were also fit for the rules in Table 5. In almost all diagrams derived from Table 6, the heteroazeotrope is a saddle. However, we have also included cases where this fixed point and the miscible component are unstable nodes. In these cases, the arrival of the still path to this component vertex is prohibited, as we have explained in the previous section and illustrated in Figure 6.

Figure 8 displays an example of rule 1 from Table 6 with the separation of acetone–water using toluene as an entrainer. Very high purity acetone is difficult to separate from its mixture with water because the binary system has a relative volatility close to unity when the molar fraction of acetone is higher than 0.95. The use of toluene as an entrainer simplifies the problem and

permits one to draw pure acetone using one single heterogeneous batch distillation task (see Figure 3a). Toluene obeys rule 1 defined for heavy entrainers in Table 6 because this component only forms a saddle heterogeneous binary azeotrope with water. Hence, the acetone vertex is an unstable node, and this component can be removed by batch rectification. Simulation results are shown in Figure 8, considering two initial ternary feeds ( $F_1$  and  $F_2$ ) located in different basic distillation regions. In both cases, the still path finishes at the water–toluene edge ( $B_1$  and  $B_2$ ). Hence, the residue in the still is composed of two liquid phases, where each one has a high concentration of two liquid phases, where each one has a high concentration of water ( $L_2$ ) and toluene ( $L_1$ ), respectively. Simulation conditions are given in Appendix 2. Acetone is obtained as distillate  $P_1$  with a molar purity higher than 99.5% during the whole operation that lasts 1.4 h. The water-rich phase ( $L_2 = P_2$ ) left in the still at the end of the process has a molar concentration near 99.8%.

#### 4. Conclusion

The presence of azeotropes in multicomponent mixtures complicates the design of batch distillation separation processes widely used in pharmaceutical and specialty chemical industries. Most of those processes include the use of a homogeneous entrainer to ease the separation. We have described novel methods to break azeotropes using an entrainer that is partially miscible with one of the initial binary mixture components. The core of the paper presents the complete set of rules for the selection of a heterogeneous entrainer, leading to a feasible rectifier or stripper process for the separation of minimum- or maximum-temperature azeotropic binary mixtures or close boiling binary mixtures. The rules have been established from the analysis of all ternary residue curve diagrams relevant to heterogeneous systems. Assumptions of the total reflux and infinite tray number were made. Several examples were given to show how the rules applied. They depict a few advantages of heterogeneous batch distillation processes: more design alternatives for the separation of an azeotropic binary mixture than with homogeneous

**Table 6.** Complete Set of Rules for the Selection of Entrainers Enabling the Separation of Binary Mixtures Involving Close Boiling Components by Heterogeneous Batch Distillation<sup>a</sup>

no.	entrainer		
	low boiling	intermediate boiling	high boiling
1			6 (B)[s]
2		1+5 (A↔B)	
3	2 (A↔B) + 5 (B↔A)	2 (A[un]↔B[s]) + 5 (B↔A)	2 (B)[s] + 5 (A)
4		2 (A↔B)[un] + 6 (B↔A)	
5	3 (A)[s] + 5 (B)	3 (A[s]↔B[sn]) + 5 (B↔A)	3 (A↔B)[sn] + 5 (B↔A)
6	3 (A) + 6 (B)[un]	3 (A)[s↔sn] + 6 (B)	3 (A)[sn] + 6 (B)
7			4 [s] + 6 (B)
8			2 (B) + 4 [s] + 5 (A)
9	3 (A) + 4 [s] + 5 (B)	3 (A) + 4 [s] + 5 (B) 3 (B) + 4 [sn] + 5 (A)	3 (A↔B) + 4 [sn] + 5 (B↔A)
10	3 (A) + 4 [un↔s] + 6 (B)	3 (A) + 4 [s↔un↔sn] + 6 (B)	3 (A) + 4 [s↔sn] + 6 (B)

<sup>a</sup> A batch rectifier and batch stripper can be used as the first task for the separation of unstable and stable original components, respectively.

**Table 7. Heterogenous Batch Distillation Simulation Parameters for Several Examples<sup>a</sup>**

System A–B–C (Water–Pyridine with Cyclohexane; Figure 1)						
Thermodynamic Parameters						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	1779.180	416.162	0.6932			
A–C	5523.060	4079.050	0.2000			
B–C	319.922	445.833	0.2966			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
$\alpha$	(0.750/0.200/0.050)	0.6754	17	0.096	0.0019	> 2.4
$\beta$	(0.055/0.500/0.445)	0.3980	27	0.233	0.0060	cyclic
$\gamma$	(0.055/0.500/0.445)	0.6240	27	0.064	0.0060	> 2.4
System A–B–C (1-Propanol–Water with Benzene; Figure 2)						
Thermodynamic Parameters						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	-403.15	1945.32	0.19			
A–C	285.777	874.242	0.2899			
B–C	2424.03	2380.02	0.281			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
still path	(0.37/0.56/0.07)	0.600	32	0.1	0.0010	> 3.9
reflux drum path	(0.40/0.18/0.42)	0.200	17	0.3	0.0025	cyclic
System A–B–C ( <i>n</i> -Ethyl Butyrate–Formic Acid with Water; Figure 4)						
Thermodynamic Parameters (Vapor-Phase Association Is Used)						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	1396.55	1014.73	0.7389			
A–C	505.62	3491.63	0.2			
B–C	499.616	-592.069	0.3022			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
still path (F <sub>1</sub> )	(0.30/0.50/0.20)	0.500	52	0.02	0.0001	> 12
still path (F <sub>2</sub> )	(0.35/0.50/0.15)	0.500	52	0.02	0.0001	> 12
System A–B–C (Water–Formic Acid with Chloroform; Figure 5)						
Thermodynamic Parameters (Vapor-Phase Association Is Used)						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	-592.069	499.616	0.3022			
A–C	2762.25	1102.34	0.2			
B–C	1070.89	1023.46	0.4514			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
still path	(0.50/0.45/0.05)	0.600	62	0.05	0.0009	> 34
System A–B–C (Acetone–Chloroform with Water; Figure 6)						
Thermodynamic Parameters						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	-960.782	786.384	0.3025			
A–C	-559.73	1839.46	0.1211			
B–C	1102.34	2762.25	0.2			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
1	(0.24/0.63/0.13)	0.500	102	0.06	0.0010	> 0.5
2	(0.24/0.63/0.13)	0.500	102	0.06	0.0010	> 10.9
3	(0.60/0.10/0.30)	0.600	62	0.01	0.0001	> 50

Table 7. (Continued)

System A–B–C (Acetic Acid–Water with Toluene; Figure 8)						
Thermodynamic Parameters (NRTL 6 and Vapor-Phase Association Are Used)						
binary param	$A_{ij}$ ( $A_{ij}(T)$ ) (cal·mol <sup>-1</sup> )	$A_{ji}$ ( $A_{ji}(T)$ ) (cal·mol <sup>-1</sup> )	$\alpha_{ij}$ ( $\alpha_{ij}(T)$ )			
A–B	-72.97 (-0.1417)	703.912 (0.527)	0.4158 (0.0)			
A–C	943.047 (0.0)	1242.83 (0.0)	0.7125 (0.0)			
B–C	3510.69 (0.0)	1277.94 (0.0)	0.2 (0.0)			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
still path	(0.65/0.30/0.05)	0.500	15	0.05	0.001	>0.8
System A–B–C (Acetone–Water with Toluene; Figure 9)						
Thermodynamic Parameters						
binary param	$A_{ij}$ (cal·mol <sup>-1</sup> )	$A_{ji}$ (cal·mol <sup>-1</sup> )	$\alpha_{ij}$			
A–B	-559.73	1839.46	0.1211			
A–C	-247.949	727.51	0.295			
B–C	3809.1	2767.3	0.2			
Column Operation Parameters						
path label	$x_F$	$m_F$ (kg)	$N_T$	$H_c$ (kg)	$H_T$ (kg)	$R$
1	(0.60/0.30/0.10)	0.500	22	0.01	0.001	5
2	(0.60/0.15/0.25)	0.500	27	0.01	0.001	5

<sup>a</sup>  $x_F$ : molar initial feed composition.  $m_F$ : initial feed mass.  $N_T$ : column tray number (including boiler and condenser–decanter).  $H_c$ : mass condenser–decanter holdup.  $H_T$ : mass liquid tray holdup.  $R$ : reflux ratio.

batch distillation, simplified distillation sequences as a consequence of fewer distillation tasks, and flexible crossing of batch distillation boundaries due to a versatile reflux policy of either one or both phases in the decanter.

It has been shown that, unlike homogeneous batch distillation, any feasible ternary diagram for a maximum-boiling azeotrope could not be inferred from any feasible ternary diagram for a minimum-boiling azeotrope. This is due to the stability constraint that holds for any heteroazeotrope and to the discrepancy between the number of feasible diagrams for minimum-boiling azeotropes and for maximum-boiling azeotropes.

Finally, heterogeneous batch distillation's flexibility also implies that operation and control policies that more sophisticated than those for homogeneous batch distillation should be devised out, for example, to monitor the reflux combination of the decanter phases in the case of a rectification.

### Appendix 1: Feasible Ternary Diagrams

A list of residue curve maps relative to feasible entrainers for the separation of azeotropic and close boiling temperature mixtures is given. Two classifications are used, namely, the common three digit + letter classification of Matsuyama and Nishimura<sup>22</sup> and the numbering of *Perry's Chemical Engineering Handbook*<sup>23</sup> readily available on any shelves of chemical engineers. Those lists should be used in conjunction with the rules in the tables to properly place the two liquid-phase zones.

1. Separation of a minimum-boiling azeotrope. The first batch task in the process sequence is a rectification of a heteroazeotropic mixture (refers to Table 1).

Matsuyama and Nishimura:<sup>22</sup> 012, 021, 102, 201, 120, 210, 122, 212, 221, 411, 321, 312, 231, 132, 213, 123, 200-m, 022-m, 202-m, 203-m, 402-m, 022-m, 220-m, 032-m, 230-m, 420-m, 232-m, 222-m, 322-m, 412-m, 421-m,

223-m, 214-M, 142-M, 421-M, 412-M, 241-M, 124-M, 101-S, 110-S, 011-S, 112-S, 121-S, 211-S, 113-S; 131-S, 311-S, 112-S, 112-S, 121-S, 121-S, 211-S, 211-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #005, #006, #007, #008, #009, #010, #011, #012, #013, #040, #041, #042, #043, #044, #045, #046, #047, #048, #049, #050, #051, #052, #053, #054, #055, #056, #057, #058, #059, #060, #061, #062, #082, #083, #085, #086, #087, #090, #095, #096, #098, #102, #103, #104, #105, #106, #107, #114, #115, #118, #119, #122, #123.

2. Separation of a minimum-boiling azeotrope. The first batch task in the process sequence is a batch stripper of one of the original components (refers to Table 2).

Matsuyama and Nishimura:<sup>22</sup> 001, 020, 012, 021, 102, 201, 120, 210, 122, 212, 221, 410, 320, 401, 023, 321, 312, 231, 132, 213, 123, 024-M, 420-M, 010-S, 101-S, 110-S, 310-S, 011-S, 013-S, 301-S, 112-S, 121-S, 211-S, 112-S, 112-S, 121-S, 121-S, 211-S, 211-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #002, #004, #005, #006, #007, #008, #009, #010, #011, #012, #013, #027, #028, #030, #031, #041, #042, #043, #044, #045, #046, #073, #078, #091, #093, #094, #095, #096, #097, #098, #102, #103, #104, #114, #115, #118, #119, #122, #123.

3. Separation of a maximum-boiling azeotrope. The first batch task in the process sequence is a rectification of the heteroazeotrope (refers to Table 3).

Matsuyama and Nishimura:<sup>22</sup> 130, 103, 031, 411, 321, 312, 231, 132, 213, 123, 203-m, 032-m, 230-m, 420-m, 232-m, 322-m, 412-m, 421-m, 223-m, 140-M, 104-M, 041-M, 214-M, 142-M, 421-M, 412-M, 241-M, 124-M, 113-S, 131-S, 311-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #026, #029, #032, #040, #041, #042, #043, #044, #045, #046, #050, #054, #055, #056, #057, #059, #060, #061, #062, #072, #076, #077, #082, #083, #085, #086, #087, #090, #105, #106, #107.

4. Separation of a maximum-boiling azeotrope. The first batch task in the process sequence is a batch rectification of one of the original components (refers to Table 4).

Matsuyama and Nishimura:<sup>22</sup> 400, 003, 430, 340, 403, 304, 043, 034, 410, 320, 401, 023, 134, 143, 323, 413, 314, 431, 341, 402-m, 234-m, 243-m, 324-m, 423-m, 342-m, 432-m, 004-M, 024-M, 420-M, 423-M, 324-M, 300-S, 013-S, 301-S, 310-S, 330-S, 303-S, 033-S, 133-S, 313-S, 331-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #014, #016, #017, #018, #019, #020, #021, #022, #027, #028, #030, #031, #033, #034, #035, #036, #037, #038, #039, #051, #063, #064, #065, #066, #067, #068, #070, #073, #078, #088, #089, #092, #093, #094, #097, #099, #100, #101, #108, #109, #110.

5. Separation of a close boiling temperature binary mixture. The first batch task in the process sequence is a rectification of the heteroazeotropic mixture (refers to Table 5).

Matsuyama and Nishimura:<sup>22</sup> 001, 100, 012, 021, 102, 201, 120, 210, 130, 103, 031, 200-m, 002-m, 202-m, 203-m, 022-m, 220-m, 032-m, 230-m, 140-M, 104-M, 041-M, 101-S, 110-S, 011-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #002, #003, #005, #006, #007, #008, #009, #010, #026, #029, #032, #047, #048, #049, #050, #052, #053, #054, #055, #072, #076, #077, #095, #096, #098.

6. Separation of a close boiling temperature binary mixture. A batch rectifier or batch stripper can be used as first task for the separation of one of the original components (refers to Table 6).

Matsuyama and Nishimura:<sup>22</sup> 000, 001, 100, 020, 012, 021, 102, 201, 120, 210, 400, 030, 003, 410, 320, 401, 023, 402-m, 420-m, 040-M, 004-M, 024-M, 420-M, 010-S, 300-S, 013-S, 301-S, 310-S.

*Perry's Chemical Engineering Handbook*:<sup>23</sup> #001, #002, #003, #004, #005, #006, #007, #008, #009, #010, #014, #015, #016, #027, #028, #030, #031, #051, #056, #069, #070, #073, #078, #091, #092, #093, #094, #097.

## Appendix 2: Simulation Conditions

Simulation of heterogeneous batch distillation is carried out with ProPhyPlus (properties server) and ProSimBatch (batch process simulator).<sup>38</sup> Column technological features and operating conditions described above are input in the simulator. The classical NRTL thermodynamic model is used to represent phase equilibrium with binary parameters taken from the DECHEMA tables.<sup>39</sup> Antoine's law was used for the vapor pressure with parameters taken from the DECHEMA tables.<sup>39</sup> The vapor-phase association model is also described in DECHEMA.<sup>39</sup> Calculated equilibrium consistency is checked with ProPhyPlus against experimental data available in the literature.<sup>39</sup> Boundary curvature information is given only when necessary to the discussion (see Figure 6); otherwise, straight-line boundaries are represented. The liquid-liquid envelope at 25 °C applies for the subcooled condenser and for the decanter. The column model consists of the usual plate-by-plate MESH (material balance, equilibrium, summation of fractions, and heat balance) equations which are solved for the whole column, decanter included, and taking into account the liquid-liquid demixion.<sup>38</sup> Numerical treatment of the differential algebraic equation (DAE) system and discrete events handling is performed

with DISCO, a numerical package for hybrid systems with DAE solver based on Gear's method.<sup>40</sup>

Operation parameters vary from one example to another and may be quite unrealistic in practice because the purpose of the simulation is not to evaluate the performance of heterogeneous batch distillation separations but rather to illustrate their thermodynamic feasibility. Common parameters are as follows: distillation starts after a total reflux period lasting 1 h; 205 W boiler duty; atmospheric pressure with a pressure drop uniformly distributed over the column of 0.05 atm; unity tray efficiency. Examples of specific parameters are given in Table 7 and are the reflux ratios that are set up to keep a constant overall level in the decanter. The reflux is equal to the flow-rate ratio over all liquid reflux/distillates, the binary parameters, tray number, column, and still or reflux drum holdup. Several commercial tools are available to compute residue curve maps and determine curved distillation boundaries. In this paper and when needed (see Figure 6), a proprietary tool was used where the distillation boundary curvature was computed by interpolation between residue curves linked to different stable and unstable nodes.

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