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Feasible separations and entrainer selection rules for heteroazeotropic batch distillation

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Abstract

A feasibility analysis is presented for the separation of close-boiling and azeotropic (minimum- and maximum-boiling) binary mixtures into pure components by the addition of an entrainer introducing a heterogeneous azeotrope. The analysis is done for both the conventional batch rectifier and the multivessel batch column. The analysis is theoretical and based on the assumptions of total reflux/reboil ratios and infinite number of stages. Two feasibility conditions are formulated that make it possible to investigate feasibility based on information coming solely from the distillation line map along with the binodal curve of the ternary mixture. Serafimov's classification is used for classifying the azeotropic phase diagrams. The feasibility analysis provides the necessary background and information for formulating rules for entrainer selection for the process. Two simple rules are then proposed, which make it possible to "screen" entrainers for heteroazeotropic batch distillation with minimum efforts.

Keywords: Distillation; Batch columns; Heterogeneous azeotropic mixtures; Feasibility; Distillation lines; Entrainer selection

1. Introduction

The separation of azeotropic and close-boiling mixtures is often faced in the organic chemical industry. Batch distillation is by far the most common unit operation in the pharmaceutical and fine/specialty chemical industries, where the production quantities are small and the objective and specifications of the separation task are often changing. Thus, investigating the possibilities of separating azeotropic and close-boiling mixtures in batch distillation columns is of great importance.

Distillation of binary azeotropic and close-boiling mixtures (AB) into pure components (light component A and heavy component B) requires the addition of a third component, the so-called entrainer (E), that enhances the separation. When the entrainer is heavy and is added continuously in the top section of the batch column, the process is called extractive batch distillation. When the entrainer forms a homoazeotrope with at least one of the original components and is added batchwise to the original mixture, the process is called homogeneous azeotropic or homoazeotropic batch distillation. When the entrainer forms a binary heteroazeotrope with at least one (and preferably with only one) of the original components or a ternary heteroazeotrope and is added batchwise to the original mixture, the process is called heterogeneous azeotropic or heteroazeotropic batch distillation. The topic of this work is heteroazeotropic batch distillation.

In another paper (Skouras et al., 2005),we presented a detailed analysis of the heteroazeotropic batch distillation process in the batch rectifier and the multivessel column together with simulation results. The two column configurations are shown in Figs. 1a and b, respectively. We mentioned that heteroazeotropic batch distillation, in the wide meaning

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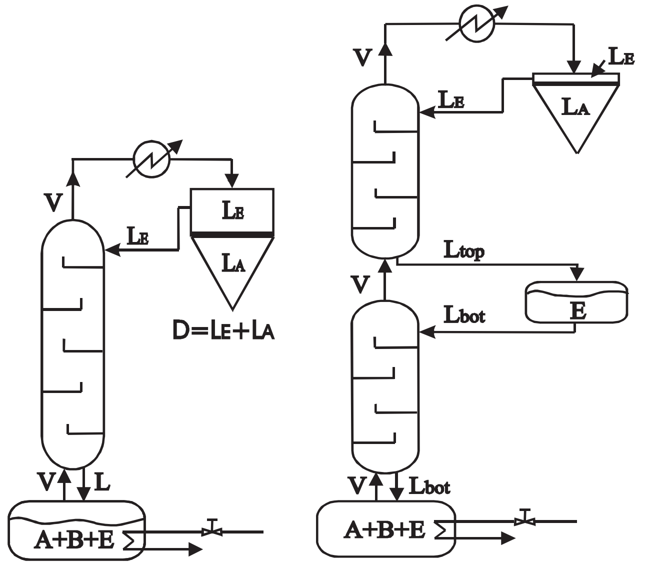


Fig. 1. Heteroazeotropic batch distillation in (a) conventional rectifier column and (b) multivessel column.

of the term, can be performed under two operational modes which we called modes I and II. Mode I is a hybrid process, i.e., a combination of two different separation methods (homogeneous distillation and liquid–liquid split) realised in sequence. The column is refluxed with a mixture of both immiscible phases in the decanter and the liquid–liquid split is not introduced until at the end of the distillation step. Thus, mode I is governed by the rules of homoazeotropic distillation, while the post-operational split of the heteroazeotrope in the decanter gives us the additional possibility to "break" the azeotrope at the column top. On the other hand, mode II is a hybrid process, i.e., a combination of two different separation methods (distillation and liquid–liquid split) realised simultaneously. The liquid–liquid split is performed during the distillation step and we can reflux and withdraw or accumulate any combination of the two decanter phases. Thus, mode II is governed by special laws and is a more flexible process than mode I of heteroazeotropic distillation and homoazeotropic distillation, as was shown by the simulation results. We also analysed different separation strategies, "strategy A" and "strategy B", for mode II of the process that were first mentioned by Koehler et al. (1995).

The studies in entrainer selection for heteroazeotropic batch distillation are limited, but valuable insight can be gained by the related literature for continuous columns. Pham and Doherty (1990a) studied the synthesis of continuous heteroazeotropic distillation and presented some general principles which could be used for distinguishing between feasible and infeasible entrainers for the process. An entrainer was considered to be feasible if the resulting residue curve map provided a feasible column sequence. Furzer (1994) screened entrainers for the process from a different point of view. The UNIFAC group contribution method was used for synthesising efficient entrainers for the heterogeneous dehydration of ethanol. Simple heuristic rules were developed that could be used in a knowledge database of an expert system and limit the extensive search of molecules that could be used as entrainers.

Rodriguez-Donis et al. (2001) were the first to provide entrainer selection rules specifically for batch columns. They pointed out that the rules for continuous columns can be only used as a basis for batch columns as they do not cover all the possible cases. This is because heteroazeotropic batch distillation is more flexible than its continuous counterpart. They studied all possible residue curve maps of heteroazeotropic mixtures under the assumptions of total reflux/total reboil ratios and infinite number of stages. The classification of Matsuyama and Nishimura (1977) with its 113 classes, which was later extended to 125 classes by Foucher et al. (1991), was adopted. The complete set of rules for the feasible entrainers was tabulated in tables.

The feasibility analysis by Rodriguez-Donis et al. (2001) relates to heteroazeotropic batch distillation with reflux of one or both immiscible phases in the decanter. Stripper configurations were also considered in their work. In contrast, the entrainer selection rules formulated in our work relate to reflux of the entrainer-rich phase only and no stripper configurations are considered. We will further comment on these issues later in our paper in order to better illustrate the differences between the two analyses.

Conclusively, our feasibility conditions and entrainer selection rules are a particular case of the more general feasibility analysis by Rodriguez-Donis et al. (2001). On the other hand, Rodriguez-Donis et al. presented many examples of feasible entrainers for the process, but did not formulate well-defined entrainer selection rules that would make it easy for someone to "screen" entrainers. Our objective is to formulate simple and clearly defined entrainer selection rules that can be used for preliminary "screening" of feasible entrainers with minimum efforts.

In a recent paper, Modla et al. (2003) presented results for heteroazeotropic and heteroextractive distillation in a batch rectifier. The separation of a close-boiling mixture by using a heavy entrainer (Serafimov's class 1.0–1b) was investigated. First, the feasibility of the process was addressed and then results from rigorous simulations verified the theoretical findings. The main findings of their feasibility analysis are in agreement with ours, as it will become obvious in the main parts of our paper.

By "feasibility" in this paper, we mean recovering the original component (B or A) miscible with the entrainer in pure form in the still, while the original component (A or B) immiscible with the entrainer and involved in the heteroazeotrope is recovered at the composition of the entrainer-lean phase (L_A or L_B) in the decanter. It is possible that a subsequent distillation task is required in order to recover a pure original component (A or B) from the entrainer-lean phase (L_A or L_B). This issue is discussed in the paper, but it is not covered by the feasibility conditions and entrainer selection rules developed. Moreover, it is usually not required to recover pure entrainer E, since it can be recycled to the next batch. However, cases where pure entrainer E can be recovered are also discussed.

Our objective is to derive simple conditions for feasibility that do not require a detailed analysis. The basis for this simplified analysis is the distillation line map along with the binodal curve of a ternary mixture. We initially use a working example in order to illustrate the principles of our feasibility analysis (Section 2). First, the differences in the feasibility regions for modes I and II of heteroazeotropic distillation are shown. After this we focus on mode II and illustrate the feasibility for separation strategies A and B in the rectifier column and the multivessel column. In Section 3, two general feasibility conditions are formulated that enable us to investigate feasibility based on minimum information coming from the distillation line map along with the binodal curve of the ternary mixture. In Section 4, we present the results from checking feasibility for various ternary diagrams. The original binary mixture (AB) can be (a) close-boiling, (b) minimum homoazeotropic and (c) maximum homoazeotropic and, in each case, the addition of various entrainers is investigated. These results provide the necessary background for the formulation of simple entrainer selection rules that can be used for preliminary "screening" of feasible entrainers for the process. These rules together with some guidelines for entrainer selection are given in Section 5.

2. Feasibility analysis for the working example

In this section, we present the principles of our feasibility analysis. The principles are general and apply to all mixtures studied in this paper. However, a working example is used for illustrative reasons. First, we discuss the feasibility for modes I and II of heteroazeotropic batch distillation mentioned in the introduction. Second, the feasibility for separation strategies A and B in the rectifier column and also in the multivessel column is addressed.

Suppose that an initial close-boiling binary mixture (AB) is to be separated. Components A and B are the so-called original components and the mixture AB is the so-called original mixture. Component A (light) is considered to have a lower boiling point than component B (heavy). To facilitate separation, a light entrainer (E) that forms a binary heteroazeotrope (AzEA) with the original component A is added. The heteroazeotrope AzEA becomes the unstable node (○) of the distillation line map, components E and A become saddles (△) and the original component B becomes the stable node (●), as shown in Fig. 2. This working mixture belongs to Serafimov's class 1.0–1a. No distillation boundary exists but the ternary diagram is divided into two batch distillation regions (a) and (b) by the line B–AzEA running from the heteroazeotrope AzEA to the original component B.

2.1. Feasibility for modes I and II

Both modes of heteroazeotropic batch distillation require an initial start-up period with total reflux in order to establish the composition profile in the column. The differences of the two modes start after this initial start-up period.

When the process is performed under mode I, the column is refluxed with the heteroazeotrope during the whole operation and the distillation step continues until the whole heteroazeotrope AzEA is collected in the decanter. Only when the distillation part is over we introduce the liquid–liquid split that allows us to "break" the azeotrope and recover an entrainer-rich phase L_E and an entrainer-lean (product) phase L_A rich in the original component A. The other original component B is recovered pure in the still. Since the liquid–liquid split happens post-operationally, mode I of the process is governed by the rules of homoazeotropic batch distillation. This is illustrated by the feasibility region shown in Fig. 2a, which indicates that the process is feasible only in area (a). This is the region described in the feasibility rules by Skouras and Skogestad (2004) for the multivessel column. However, their process is actually mode II and, consequently, the feasibility analysis is partially incorrect and applies only to the start-up step of the process. The additional possibilities obtained during the main step (mode II) were not considered.

Duessel and Stichlmair (1995) adopted mode I for the separation of water (A)–pyridine (B) by using toluene (E) as a heteroazeotropic entrainer. The feed F was placed exactly on the straight line B–AzEA and a single rectification step was required since they could reach the pure component B vertex by removing the heteroazeotrope AzEA during the whole process. The main disadvantage of mode I is that large amounts of entrainer E are required.

On the other hand, mode II allows operation also in a part of region (b) where smaller amounts of entrainer E are required. In mode II, the splitting of the heteroazeotrope in the decanter is introduced during the distillation step, which allows us to reflux and withdraw/accumulate any combination of these two phases in the decanter, while the entrainer-lean L_A phase is withdrawn (open operation) or accumulated in the decanter (closed operation). Thus, mode II is a flexible process governed by special laws, and some limitations on the feasible regions for mode I are not valid for mode II. Fig. 2b illustrates these additional possibilities. The process under mode II is feasible also in the part of region (b) limited by the straight line B–L_A connecting the still product *B* and the entrainer-lean phase L_A. Paragraph removed to next page!

The feasibility analysis of Modla et al. (2003) agrees with the above findings even though the terminology used is different. They use the term "total reflux" for indicating mode I and the term "finite reflux" for mode II. The authors mention "it can be stated that the minimum amount of the entrainer decreases if, instead of the heteroazeotrope, the distillate is only withdrawn from the A-rich phase". In mode I, the

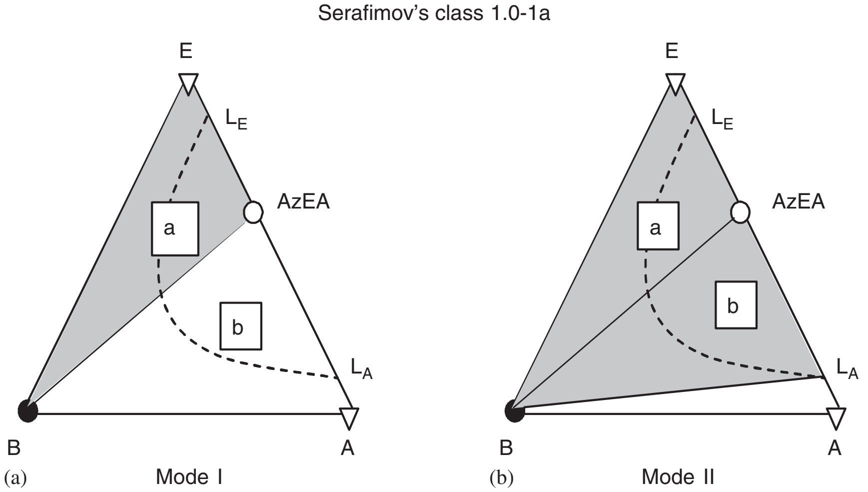


Fig. 2. Feasible regions (shaded) for modes I and II of heteroazeotropic batch distillation.

minimum amount of entrainer lies on the line B–AzEA while in mode II, it lies on the line B–L_A, as illustrated in Fig. 4 in Modla et al.

2.2. Feasibility in the rectifier column

The rest of the paper focuses at mode II of heteroazeotropic batch distillation with reflux of the entrainer-rich phase (L_E) only. Koehler et al. (1995) presented two separation strategies A and B for the rectifier column, which were analysed in more detail by Skouras et al. (2005). Both strategies can be realised in the open or closed rectifier. We address now feasibility issues and illustrate feasible regions for both strategies. The same working example (Serafimov's class 1.0-1a) as before is used.

2.2.1. Strategy A

This strategy requires output/accumulation of one phase at the decanter at a time. Generally, with an arbitrary amount of entrainer E, the process requires two steps; product recovery step (first step) and entrainer recovery step (second step).

In the first "product recovery" step, component A is recovered with total reflux of the entrainer-rich phase L_E. A binary mixture S_1 of components B and E remains in the still at the end of this step while the entrainer-lean phase L_A is recovered in the decanter. Feasibility during this first step requires that (see Fig. 3a):

Mass balance line: The final still composition (S_1) is connected with the feed composition (F) and the composition of the entrainer-lean phase (L_A) by a straight line.

Composition profile: The final still composition (S_1) is connected with the composition of the reflux (L_E) by a distillation line.

In the second "entrainer recovery" step, pure entrainer E is recovered in the decanter and pure component B is recovered in the still. Reflux of pure entrainer E is applied during this step. Feasibility during this first step requires that (see Fig. 3b):

Mass balance line: The final still composition (B) is connected with the feed composition (S_1) and the composition of the pure entrainer (E) by a straight line.

Composition profile: The final still composition (B) is connected with the composition of the reflux (E) by a distillation line.

In the limiting case, strategy A can be implemented in one single step (product recovery step) and no need for the entrainer recovery step exists. Such cases were described by Rodriguez-Donis et al. (2002) with the feed F placed exactly on the straight line B–L_A. The process was then feasible with one rectification step since the pure component B vertex could be reached by removing the entrainer-lean phase L_A during the whole process.

2.2.2. Strategy B

Strategy B uses partial reflux of the entrainer-rich phase L_E and output/accumulation of both the entrainer-lean L_A and the entrainer-rich phase L_E. Pure original component B is recovered in the still at the end of the process. Feasibility for strategy B requires that (see Fig. 4):

Mass balance line: The final still composition (B) is connected with the feed composition (F) and the final total composition (D) of the entrainer-lean (L_A) and entrainer-rich phase withdrawn/accumulated in the decanter by a straight line.

Composition profile: The final still composition (B) is connected with the composition of the reflux (L_E) by a distillation line.

Skouras et al. (2005) pointed out that strategy A has the advantage that it allows the recovery of pure entrainer E during the second step. Fig. 5a illustrates the feasibility region when strategy A is implemented. The whole BL_AE triangle, that is, the whole feasibility region under mode II, is avail-

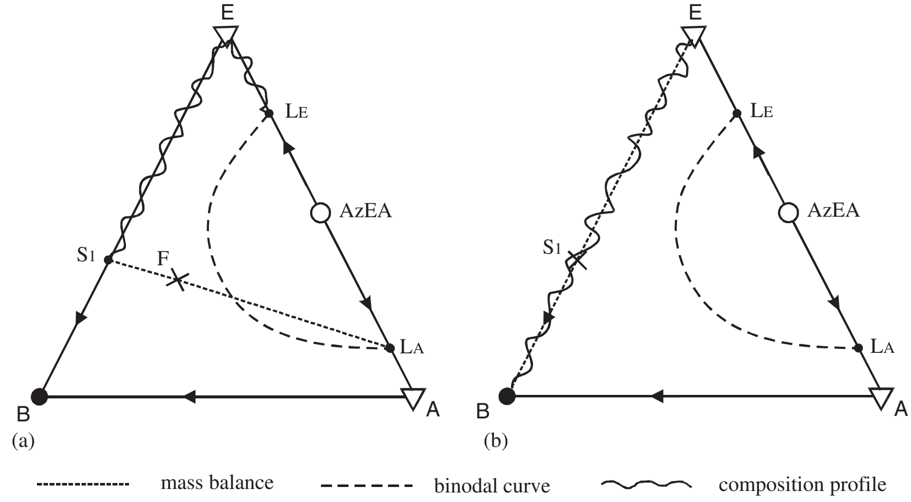


Fig. 3. Feasibility for strategy A in the rectifier column (a) product recovery step (first step) and (b) entrainer recovery step (second step).

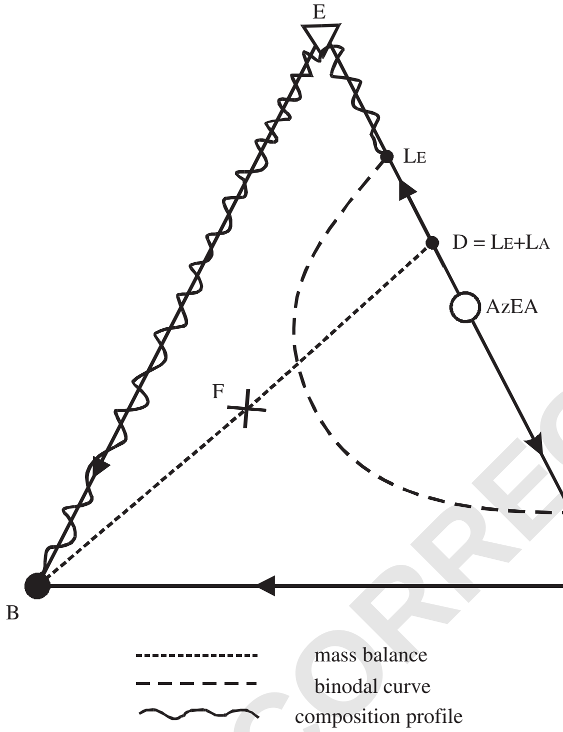


Fig. 4. Feasibility for strategy B in the rectifier column.

able under strategy A. Strategy A should be adopted when we want to recover all three components from a ternary heteroazeotropic mixture.

In strategy B the original component A is recovered at the composition of the entrainer-lean phase L_A, as in strategy A. However, the entrainer E can only be recovered at the composition of the entrainer-rich phase L_E and not pure entrainer as in strategy A. This limitation of strategy B is illustrated in Fig. 5b, where we see that the feasibility region is limited to the triangle BL_AL_E. A feed F inside the triangle BL_EE cannot be separated by strategy B, but it can be separated by strategy A. Strategy B, should be adopted when separating a binary original mixture AB by adding a heteroazeotropic entrainer E because in this case we are, most likely, not interested in recovering pure entrainer.

2.3. *Feasibility in the multivessel column*

The separation in the multivessel column as described by Skouras et al. (2005) is illustrated in Fig. 1b. The entrainer-rich phase L_E is totally refluxed and only the entrainer-lean phase L_A is withdrawn/accumulated in the decanter. For our working example, pure entrainer E is recovered in the middle vessel and pure original component B in the still. This operation of the column is shown in Fig. 1b.

Feasibility in the multivessel column requires that (see Fig. 6):

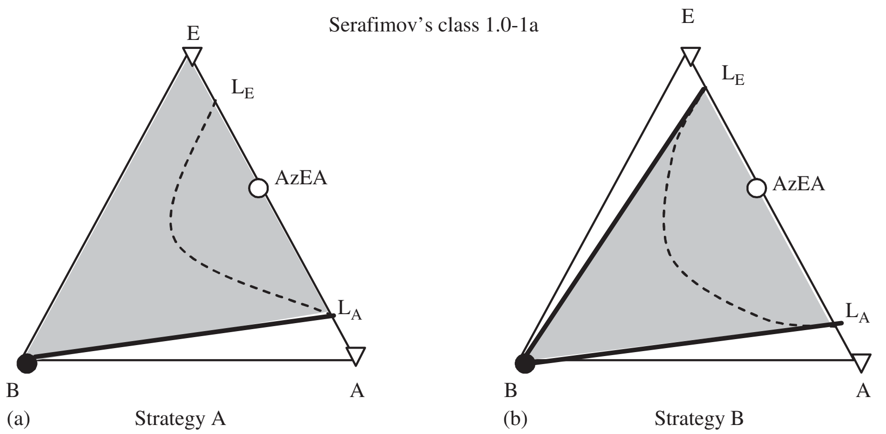
Mass balance triangle: The feed composition (F) lies in the triangle spanned by the final still composition (B), the middle vessel composition (E) and the entrainer-lean composition (L_A) withdrawn/accumulated in the decanter.

Composition profile: The final still composition (B) is connected with the composition of the reflux (L_E) by a distillation line.

The described separation in the multivessel column resembles strategy A in the rectifier column. Strategy A performs the separation in two steps sequentially in time, while the multivessel performs the two steps simultaneously in the rectifying and stripping section of the column. The products are the same for both processes; entrainer-lean phase L_A, pure entrainer E and pure original component B. Consequently, the feasible region for the multivessel column is the same as for strategy A, which was shown in Fig. 5a.

3. General feasibility conditions

In this section we attempt to address the question: "Given a distillation line map along with the binodal curve of


Serafimov's class 1.0-1a

(a) Strategy A (b) Strategy B

Fig. 5. Feasible regions (shaded) for separation strategies A and B in the rectifier column.

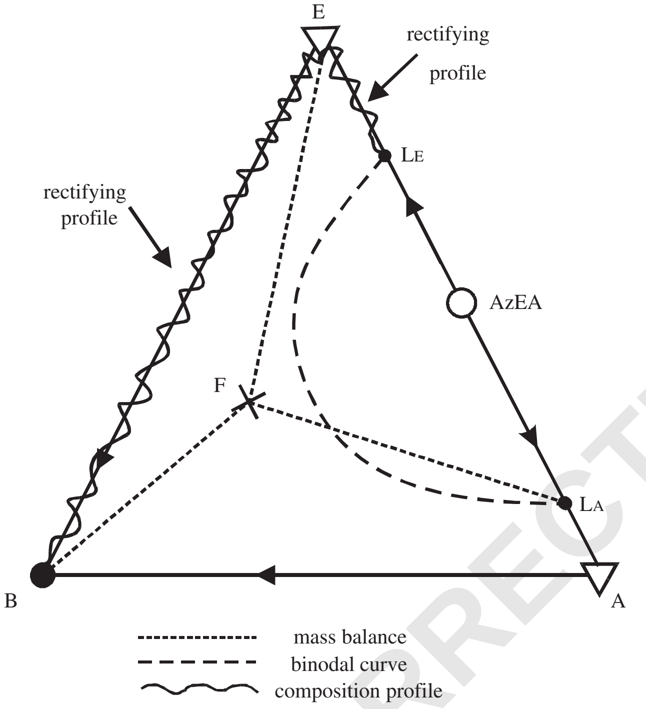


Fig. 6. Feasibility in the multivessel column.

a ternary mixture, how can we check if the separation is feasible"? We want to know, at a preliminary stage, if a separation is feasible without doing all the detailed feasibility analysis. Of course, if the separation is feasible, the detailed analysis should be done, in a later stage, in order to identify feasible regions, initial feed location, minimum amount of added entrainer, etc. Thus, we summarise the findings from the previous section and formulate two general conditions which are valid for both the rectifier and the multivessel column. These conditions enable us to investigate feasibility based on minimum information coming from the distillation line map along with the binodal curve of the ternary mixture.

In order to develop such feasibility conditions based on minimum information, the assumptions of total reflux/total reboil ratios and infinite number of stages are necessary. Under these assumptions, the distillation line map and the binodal curve of the mixture provide all the necessary information for checking feasibility. These working assumptions are tools that allow us to address feasibility theoretically and relaxing them is not affecting the results of the feasibility analysis. We will come back to this issue later.

Let us assume that we want to separate a binary azeotropic or close-boiling mixture (AB) by the addition of a heteroazeotropic entrainer (E). The resulting ternary mixture (A+B+E) is introduced into the still of the rectifier or the multivessel column equipped with a decanter for accommodating the phase splitting at the top, as shown in Fig. 1.

An initial start-up period is needed in order to build up the composition profile in the column and collect some of the heteroazeotrope in the decanter. This period is run under total reflux and the entire mixed phases in the decanter are refluxed. The only feasibility requirement during the start-up period is that the initial feed has to be located in a region where the heteroazeotrope is the unstable node, so it will boil overhead.

When some of the heteroazeotrope is collected in the decanter, the main period of the process can start. The entrainer-rich phase (L_E) is refluxed to the column. As mentioned before, the reflux can be total (strategy A in the rectifier or the multivessel column) or partial (strategy B in the rectifier column) and the immiscible phases in the decanter can be either withdrawn (open operation) or accumulated (closed operation). The feasibility requirement during the main period is that there exists a column profile connecting the still composition to that of the reflux composition L_E at the top of the column. At total reflux the column composition profile is represented by a distillation line.

As a consequence of the above, two feasibility conditions are formulated:

Feasibility condition 1: There should exist a feed region where the heteroazeotrope is the unstable node such that it boils overhead and starts accumulating in the decanter.

Feasibility condition 2: There should, at steady state, exist a distillation line connecting the reflux composition L_E with the still product composition B or A in the direction of increasing temperature from L_E to B or L_E to A.

The feasibility conditions formulated above relate to mode II of heteroazeotropic batch distillation with reflux of the entrainer-rich phase only. Consequently, they differ from the rules proposed by Rodriguez-Donis et al. (2001) which apply to mode II with reflux of both the entrainer-rich and entrainer-lean phase. Moreover, the conditions are valid for both the rectifier and the multivessel column. This is dictated by the fact that the separation in the multivessel column resembles the separation strategy A in the rectifier column. Finally, they are valid for both strategies A and B since reflux of the entrainer-rich phase only is applied in both strategies.

The assumption of infinite number of stages is used in order to secure that the stationary points of the distillation line map are achieved in the column, e.g. the heteroazeotrope is collected in the decanter, pure component B or A is recovered in the still, etc. This assumption can be relaxed, since we can always use the finite number of stages assuring the desired product specifications.

The assumption of total reflux/reboil ratios enables us to use the distillation lines instead of calculating the exact column profile. In simple words, this assumption implies that the final column profile lies on the edge between the still composition B and the reflux composition L_E, as shown for example in Figs. 4 and 6. Of course, the real separation is performed at finite reflux, which means that the final column profile would lie near the edge B–L_E depending on the reflux and the number of stages. Thus, this assumption can be also relaxed without loss of the validity of our analysis.

4. Feasibility results for various cases

In this section, the validity of feasibility conditions 1 and 2 is checked for the distillation line maps of various mixtures. If the conditions are satisfied, the separation is feasible.

The following three general cases were studied:

Case a: The original mixture (AB) is close-boiling. Ten cases were analysed and the results are shown in Table 1.

Table 1
Feasibility results for close-boiling original mixtures (AB)

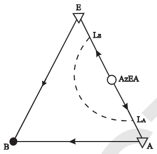
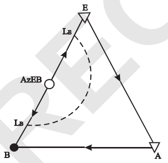
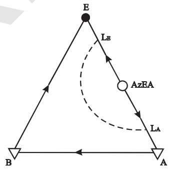
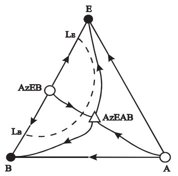
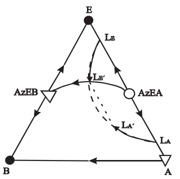
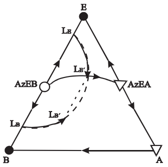
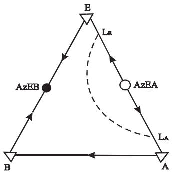
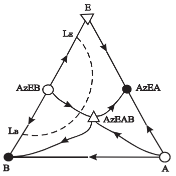
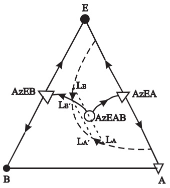
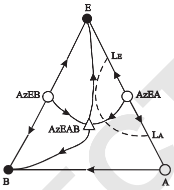
Entrainer description	Distillation line map	Class	Feasibility	Pure components
Case a1: Light entrainer (E) forms heteroazeotrope (AzEA) with light original component (A)		1.0-1a	YES	YES
Case a2: Light entrainer (E) forms heteroazeotrope (AzEB) with heavy original component (B)		1.0-1b	YES	YES
Case a3: Heavy entrainer (E) forms heteroazeotrope (AzEA) with light original component (A)		1.0-1b	NO	—
Case a4: Heavy entrainer (E) forms heteroazeotrope (AzEB) with heavy original component (B) and ternary saddle (AzEAB)		1.1-2	NO	—
Case a5: Entrainer (E) forms a heteroazeotrope (AzEA) with light original component (A) and min. homoazeotrope (AzEB) with heavy original component (B)		2.0-2b	YES	NO

Table 1
(*Continued*)

Entrainer description	Distillation line map	Class	Feasibility	Pure components
Case a6: Entrainer (E) forms heteroazeotrope (AzEB) with heavy original component (B) and min. homoazeotrope (AzEA) with light original component (A)		2.0-2c	YES	NO
Case a7: Entrainer (E) forms heteroazeotrope (AzEA) with light original component (A) and max. homoazeotrope (AzEB) with heavy original component (B)		2.0-1	NO	—
Case a8: Entrainer (E) forms heteroazeotrope (AzEB) with heavy original component (B), max. homoazeotrope (AzEA) with light original component (A) and ternary saddle (AzEAB)		2.1-3a	NO	—
Case a9: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), min. homoazeotrope (AzEB or AzEA) with the other (B or A) and ternary heteroazeotrope (AzEAB)		2.1-2b	YES	NO
Case a10: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), min. homoazeotrope (AzEB or AzEA) with the other (B or A) and ternary saddle (AzEAB)		2.1-3b	NO	—

Case b: The original mixture (AB) has a minimum-boiling homoazeotrope (AzAB). Nine cases were analysed and the results are shown in Table 2.

Case c: The original mixture (AB) has a maximum-boiling homoazeotrope (AzAB). Seven cases were analysed and the results are shown in Table 3.

We did not analyse mixtures where:

N1. The formed heteroazeotrope after the addition of the entrainer is not an unstable node of the distillation line map. In such a case, it is impossible to recover the heteroazeotrope in the top of the column by a rectification process.

N2. The original mixture (AB) is heteroazeotropic. In such a case, we can always perform a binary heteroazeotropic distillation and recover the original components.

N3. The entrainer has a boiling point between the boiling points of the original components (intermediate entrainer). The possibilities of finding such entrainers are rather limited since close-boiling and azeotropic mixtures do not usually differ by more than about 30 °C in their boiling points (Perry et al., 1997).

N4. Mixtures that are unlikely to occur in practice. All mixtures are classified under one of the 26 Serafimov's classes. Hilmen et al. (2002) and Kiva et al. (2003) pointed out that 10 of these classes have not been reported in the literature. In addition, one class applies only to zeotropic mixtures (Class 0.0-1) and one requires that the heteroazeotrope is a saddle (Class 1.0-2), thus excluded from our analysis (exception N1). Consequently, a total of 15 classes are included in this study.

The results for cases a–c are summarised in Tables 1–3, respectively. The first column refers to the properties of the added entrainer E and presents all the specific cases analysed. In the second column the distillation line map along with the binodal curve of the ternary mixture is shown. The arrows in the maps indicate the direction of increasing temperature. The third column classifies the mixture according to Serafimov's classification. In the fifth column a "YES" indicates feasibility and the entrainer is acceptable, while a "NO" indicates infeasibility. In the last column, we reply to the question of whether or not it is possible to recover pure original component A or B from the entrainer-lean phase L_A or L_B by subsequent batch distillation steps. A "YES" under the last column titled "pure components" means that we can recover pure A or B and a "NO" means that we cannot recover pure components in subsequent steps. In cases where the separation is infeasible, we just put the sign (—) in the last column. Additional information about the expected final products in the vessels is given in Table 4.

To illustrate the use of these diagrams, we will look closer at some subcases of cases a–c.

4.1. *Case a : Original mixture (AB) is close-boiling*

Separation of close-boiling mixtures into pure products requires high reflux ratios and high number of stages and the process often becomes uneconomical. Ten different cases, not excluded by N1–N4, were investigated (Cases a1–a10) and the results are shown in Table 1. The mixtures are classified under nine of Serafimov's classes. Five of the studied cases lead to feasible separations. Case a1 was used as the working example (Figs. 3–6) and is not further discussed. We will look closer to case a5 since it has some interesting features.

Case a5: The added entrainer forms a heteroazeotrope AzEA with the light original component A and a minimum-boiling homoazeotrope AzEB with the heavy component B and the mixture is of Serafimov's class 2.0-2b. There exist two distillation regions that are separated by

Table 2
Feasibility results for minimum homoazeotropic original mixtures (AB)

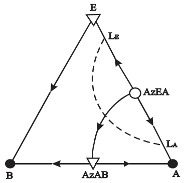
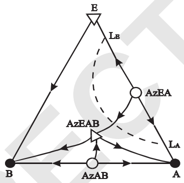
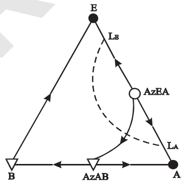
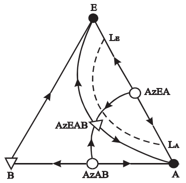
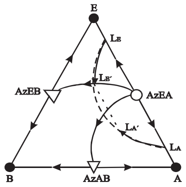
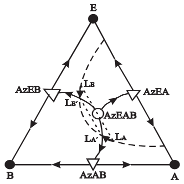
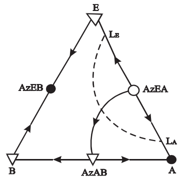
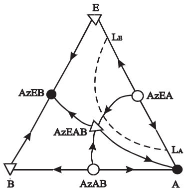
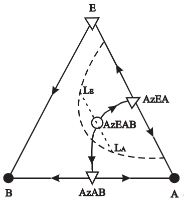
Entrainer description	Distillation line map	Class	Feasibility	Pure components
Case b1: Light entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B)		2.0-2b	YES	YES
Case b2: Light entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and ternary saddle (AzEAB)		2.1-3b	YES	YES
Case b3: Heavy entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B)		2.0-2c	NO	—
Case b4: Heavy entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and ternary saddle (AzEAB)		2.1-3b	NO	—
Case b5: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and min. homoazeotrope with the other (AzEB or AzEA)		3.0-2	YES	YES

Table 2
(*Continued*)

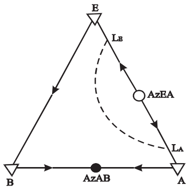
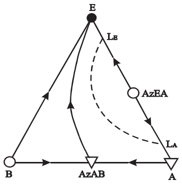
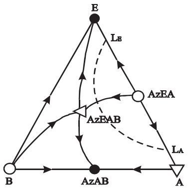
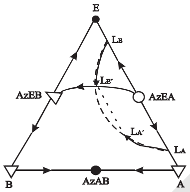
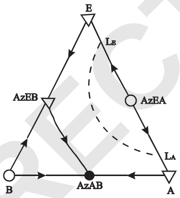
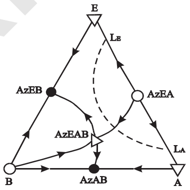
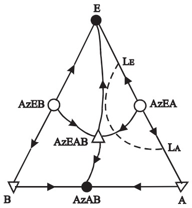
Entrainer description	Distillation line map	Class	Feasibility	Pure components
Case b6: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), min. homoazeotrope with the other (AzEB or AzEA) and ternary heteroazeotrope (AzEAB)		3.1-2	YES	YES
Case b7: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and max. homoazeotrope with the other (AzEB or AzEA)		3.0-1b	NO	—
Case b8: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), max. homoazeotrope with the other (AzEB or AzEA) and ternary saddle (AzEAB)		3.1-4	NO	—
Case b9: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and ternary heteroazeotrope (AzEAB)		2.1-2b	NO	—

a distillation boundary (unstable separatrix) running from the heteroazeotrope AzEA to the homoazeotrope AZEB.

If we look at the distillation line map for case a5 in Table 1 and we check if feasibility condition 2 is fulfilled, we can easily reach the conclusion that the condition is violated. There is no distillation line connecting the desired still product B and the entrainer-rich phase L_E, and the separation should be infeasible. Such a conclusion is however wrong. Condition 2 requires that such a connection should exist at steady state. In Table 1, we see that the reflux path (the path of the entrainer-rich phase L_E) moves along the binodal curve from point L_E to point $L_{E'}$, which is the intersection point of the binodal curve and the distillation boundary. This means that the points $L_{E'}$ and B are connected by a distillation line in the direction of increasing temperature from $L_{E'}$ to B and, thus, condition 2 is fulfilled at steady state. In addition, it is easy to check that condition 1 is also fulfilled and therefore the separation is feasible. The figure in Table 1 shows also the path of the entrainer-lean phase from L_A to $L_{A'}$. The steady-state point $L_{A'}$ is in equilibrium with the point $L_{E'}$ and consequently they belong to the same tie-line.

The same behaviour with the reflux path moving along the binodal curve is encountered in cases a6, a9, b5, b6 and c4 (Tables 1–3). Skouras et al. (2005) presented rigorous simulation results for a mixture classified under Serafimov's class 3.1-2 (case b6 in Table 2) and discussed this issue. However, we should note here that the reflux cannot always move freely along the binodal curve. The critical point of the binodal curve, that is the point where the distinction between coexisting liquid phases vanishes (Pham and Doherty, 1990b), limits the reflux on its movement. If the reflux "meets" the critical point before it reaches the intersection point of the binodal curve with the distillation boundary, then no liquid–liquid split is available anymore and thus the process is infeasible. Consequently, the feasibility in cases a5, a6, a9, b5, b6 and c4 depends also on the interposition of the critical point with the intersection point of the binodal curve with the distillation boundary. A brief introduction on the intersection of the distillation boundaries and the binodal curve is given by Kiva et al. (2003), where it seems that the distillation boundaries never go through the critical point. However, based on this analysis, a general statement about where exactly the critical point is

Table 3
Feasibility results for maximum homoazeotropic original mixtures (AB)

Entrainer description	Distillation line map	Class	Feasibility	Pure components
Case c1: Light entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B)		2.0-1	YES	YES
Case c2: Heavy entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B)		2.0-2a	NO	—
Case c3: Heavy entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and ternary saddle (AzEAB)		2.1-3a	NO	—
Case c4: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and min. homoazeotrope with the other (AzEB or AzEA)		3.0-1b	YES	YES
Case c5: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B) and max. homoazeotrope with the other (AzEB or AzEA)		3.0-1b	NO	—
Case c6: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), max. homoazeotrope with the other (AzEB or AzEA) and ternary saddle (AzEAB)		3.1-4	NO	—
Case c7: Entrainer (E) forms heteroazeotrope (AzEA or AzEB) with one original component (A or B), min. homoazeotrope with the other (AzEB or AzEA) and ternary saddle (AzEAB)		3.1-4	NO	—

placed in comparison to the distillation boundaries cannot be made.

One important difference between case a5 and our working example (case a1) is that it is not possible to recover pure entrainer E in case a5. This is because the binary edge EB in case a5 exhibits an additional stationary point, which is the homoazeotrope AzEB. This homoazeotrope is then recovered in the rectifier column during the second (entrainer recovery) step or in the middle vessel of the multivessel column. In Table 4, we give the final products in the vessels for all cases both for the rectifier and the multivessel column.

Case a3: This is the case of a close-boiling mixture (AB) to be separated by the addition of a heavy entrainer (E) that forms a heteroazeotrope (AzEA) with the light original component (A). Case a3 is, according to our analysis, infeasible. This is because the steady state still product B is not connected with the reflux composition L_E in the direction of increasing temperature from L_E to B. The arrows in Case a3 indicate that the temperature increases from B to E along the BE edge. Thus, no rectifier column can recover component B in the still with reflux of the entrainer-rich phase L_E, as required by strategy A (during the entrainer recovery step) or strategy B.

Modla et al. (2003) studied feasibility for the same class of mixtures (class 1.0-1b) in case of one-phase and two-phase reflux. In the former case they reached the conclusion: "If only one phase reflux is applied, the specified distillate composition cannot be reached from anywhere and the whole area of the triangle will be infeasible", which is in agreement with our findings. In the latter case, they found out that the process is feasible and, thus, component A can be recovered in the composition of the entrainer-lean phase L_A if two-phase reflux is applied. Note that Rodriguez-Donis et al. (2001), who also studied two-phase reflux, showed that such an entrainer is feasible (see Table 5, set of rules no. 1 in their article). This situation is repeated in cases a7, b3, b7 and b9 (Tables 1 and 2), which are infeasible according to our analysis (one-phase reflux) but feasible according to Rodriguez-Donis et al. (2001) (two-phase reflux).

4.2. *Case b: Original mixture (AB) is minimum-boiling homoazeotropic*

When the original mixture (AB) is azeotropic, there are two general cases that have to be studied. The first one is when the original mixture exhibits a minimum-boiling (min) homoazeotrope (case b), and the second is when the original mixture exhibits a maximum-boiling (max) homoazeotrope (case c).

We look at case b first. Nine different cases, not excluded by N1–N4, were identified and are given in Table 2. The corresponding distillation line maps were classified under eight of Serafimov's classes and four of them proved to be feasible. We further discuss case b2.

Case b2: A light entrainer E is added to the original mixture AB that forms a heteroazeotrope AzEA with the light original component A. In addition, a ternary saddle homoazeotrope AzEAB exists. There exist four distillation regions divided by four distillation boundaries. Two boundaries (stable separatrices) are running from the saddle ternary homoazeotrope AzEAB to the two original components A and B, while two boundaries (unstable separatrices) are running from the binary azeotropes AzEA and AzAB to the ternary saddle AzEAB. The mixture is of Serafimov's class 2.1-3b and is interesting because of the ternary saddle homoazeotrope.

It is easy to check that both feasibility conditions 1 and 2 are fulfilled. Indeed, the corresponding distillation line map in Table 2 shows that there exists a region in which the heteroazeotrope AzEA is the unstable node. Moreover, we can see that a distillation line exists that connects the reflux L_E with the desired still product B in the direction of increasing temperature (see the arrows) from L_E to B. Therefore, the separation and, consequently, the added entrainer are feasible.

However, we have to point out that even if the separation B2 is feasible, this is the only case where an entrainer that leads to the formation of a ternary saddle homoazeotrope makes the process feasible. Tables 1–3 indicate that in all other cases where a ternary saddle is formed by the addition of an entrainer, like in cases a4, a8, a10, b4, b8, c3, c6 and c7, the separation is infeasible. Thus, our general advice is to avoid entrainers that lead to the formation of ternary saddle azeotropes.

4.3. *Case c: Original mixture (AB) is maximum-boiling homoazeotropic*

The task of separating an original mixture AB that exhibits a maximum-boiling (max) homoazeotrope AzAB is faced less often in azeotropic distillation, because maximum azeotropes are less probable than minimum ones. Seven different cases of heterogeneous entrainers were analysed and two of them fulfilled the criteria of feasibility, as Table 3 indicates. The seven cases studied belong to five different azeotropic classes. We will now look to a case where the separation is infeasible.

Case c5: The added entrainer forms a heteroazeotrope AzEA with the light original component A and a maximum-boiling homoazeotrope with the heavy original component B. The distillation line map of the mixture is shown in Table 3 and it represents Serafimov's class 3.0-1b. There is one distillation boundary (stable separatrix) running from the homoazeotrope AzEB to the maximum homoazeotrope AzAB and the composition space is divided into two distillation regions.

A check of the distillation line map leads to the conclusion that the separation is infeasible. There exists a rather large region (AzEB-AzEAB-AzAB-A-AzEA-E-AzEB) in which the heteroazeotrope (AzEA) can be obtained at the top of the column, thus satisfying feasibility condition 1. However, in this area it is not possible to recover the original component B in the still, but the homoazeotrope AzEB instead. There exists no distillation line connecting the reflux L_E and the desired still product B and feasibility condition 2 is not satisfied. Consequently, the separation is infeasible and the entrainer is rejected.

4.4. *Pure original component from the entrainer-lean phase*

As mentioned already, the original component A or B immiscible with the entrainer E and forming the heteroazeotrope is recovered at the composition of the liquid–liquid split L_A or L_B. The original component B or A miscible with the entrainer is recovered pure in the still. Our feasibility analysis did not cover the possibility of further purification of the entrainer-lean phase. In the last column of Tables 1–3 (under the title “pure components”), we consider this issue for all feasible separations.

Case a1: This case served as the working example in this paper. As can be seen in Table 4, where we give the steady-state products for both the rectifier and the multivessel column, the entrainer-lean phase L_A, rich in the original component A, is recovered in the decanter. The other original component B is recovered pure in the still. The entrainer-lean phase L_A is on the binary edge AE (see Table 1) and, thus, it can be easily separated in a subsequent rectification step. The heteroazeotrope AzEA will then be the top product and pure component A will be the still product. Thus, case a1 is not only feasible but also both original components can be recovered pure. The last column in Table 1 indicates whether the original component (A or B) can be recovered in pure form from the entrainer-lean phase (L_A or L_B) in subsequent distillation steps.

Case a5: As seen in Table 4, pure component B is recovered in the still, while the entrainer-lean phase $L_{A'}$ is recovered in the decanter. A subsequent rectification step for the ternary fraction $L_{A'}$ (Table 1) will lead to the heteroazeotrope AzEA in the decanter, while the still path will end up in the binary edge AB. This means that we return to the close-boiling mixture AB that we wanted to separate initially. Thus, the process is feasible (we can recover B and $L_{A'}$), but we cannot recover pure original component A from the entrainer-lean phase $L_{A'}$ in the decanter. The ternary fraction $L_{A'}$ has to be recycled to the next batch. Therefore, we have a “NO” in the last column of Table 1. The same happens with case a9 in Table 1. We cannot recover pure A from the ternary fraction $L_{A'}$.

Case a6: As we can see in Table 4, pure component A is recovered in the still and an entrainer-lean phase $L_{B'}$ in the decanter. It is not possible to recover pure component B from the entrainer-lean phase $L_{B'}$ with a subsequent rectification step, since this will lead back to the original close-boiling mixture AB (see Table 1). However, it would be possible to recover pure component B from the fraction $L_{B'}$ in a batch stripper since component B is a stable node in the region where the fraction $L_{B'}$ is located. Since batch strippers are not considered in this study, we have a “NO” in the last column of Table 1.

Case b2: In Table 4, we see that pure component B is recovered in the still, while an entrainer-lean phase L_A in the binary edge EA (Table 1) is recovered in the decanter. A subsequent rectification step of the binary fraction L_A can be used for recovering pure component A. Thus, further purification of the entrainer-lean phase is possible.

Generally speaking, in all cases where the entrainer-lean phase L_A or L_B is a binary mixture, it is possible to recover a pure component from this fraction. This happens in cases a1, a2, b1, b2 and c1. The situation is more complicated when the entrainer-lean phase is ternary, as cases a5, a6 and a9 indicated. Let us look at cases b5, b6 and c4. In these cases, the entrainer-lean phase $L_{A'}$ is ternary and we want to check if it is possible to recover pure component A from such a fraction. Remember that this was not possible in cases a5, a6 and a9. In contrast, such a further purification of the entrainer-lean phase $L_{A'}$ is feasible in cases b5, b6 and c4. A subsequent rectification step will provide the heteroazeotrope in the top and a fraction in the binary edge AB in the bottom. This binary fraction AB can then be separated by a third rectification step in the original homoazeotrope AzAB and the pure original component A. In cases b5 and b6, the pure component A is recovered in the still, while in case c4 is recovered at the top.

5. Entrainer selection rules

The objective of this section is to address the following issue: “Formulate some simple rules that enable us to screen entrainers for the process with minimum effort”. Based on the feasibility conditions 1 and 2 in Section 2 and the feasibility results in Tables 1–3, the following rules were formulated:

Entrainer selection rule 1: The entrainer (E) should form a heteroazeotrope (AzEA or AzEB) with one of the original components (A or B) and/or a ternary heteroazeotrope (AzEAB).

Entrainer selection rule 2: The vertex of the original component to be obtained in the still at steady-state (A or B) should be connected with the steady-state reflux point of the entrainer-rich phase (L_E), with a distillation line in the direction of increasing temperature from the top of the column to the bottom ($L_E \rightarrow A$ or $L_E \rightarrow B$).

Among the two rules given above, rule 2 is the most important for the feasibility of the separation task. Whenever a separation is infeasible, this rule is violated. Rule 1 is a necessary starting point for any heteroazeotropic batch distillation process.

These rules refer to the feasibility of the separation in a rectifier or multivessel column (but not in column sequences) in order to recover one of the original components A or B with the entrainer-lean phase and the other component B or A pure in the still. The possibility of recovering pure original component from the entrainer-lean phase is not included in these rules. Moreover, the rules are valid for heteroazeotropic distillation under mode II in the rectifier and the multivessel column with reflux of the entrainer-rich phase L_E only, and are independent of the separation strategy A or B employed. Different reflux policies at the top of the column, e.g. two-phase reflux, are governed by different feasibility rules, as those presented by Rodriguez-Donis et al. (2001).

The entrainer selection rules are necessary but not sufficient conditions for the feasibility of the process. The successful realisation of a theoretically feasible separation always depends on the specific characteristics of the mixture, such as relative volatilities, azeotropic compositions, position of the binodal curve, curvature of the distillation boundaries, etc.

The results in Tables 1–3 helped us to formulate, in addition to the entrainer selection rules, two guidelines that can be used in order to “screen out” infeasible entrainers.

Guideline 1: The entrainer (E) must not lead to the formation of maximum azeotropes with any of the original components (A or B).

Guideline 2: The entrainer (E) should preferably not lead to the formation of a ternary saddle homoazeotrope.

Guideline 1 is a consequence of the infeasibility of cases a7, a8, b7, b8 and c6. In all these cases, the entrainer (E) forms a maximum homoazeotrope (AzEA or AzEB) with one of the original components (A or B) and the separation is infeasible. Thus, such entrainers should be rejected.

Guideline 2 is a consequence of the analysis for cases a4, a8, a10, b2, b4, b8, c3, c6 and c7. In all these cases a ternary saddle homoazeotrope exists, but the process is feasible only in case b2. Thus, it seems reasonable to avoid such entrainers unless we make sure that the entrainer is like the one described in case b2.

6. Conclusions

A feasibility analysis for heteroazeotropic batch distillation with reflux of the entrainer-rich phase only is provided for the rectifier and the multivessel column. The analysis is theoretical and based on the assumption of infinite reflux/reboil ratios and infinite number of stages. Under these assumptions, only information coming from the distillation line map and the binodal curve of the mixture is necessary for investigating feasibility. Two feasibility conditions were proposed for this reason. The feasibility results provided the necessary information for the formulation of two simple entrainer selection rules that can be used for “screening” potential entrainers for the process. The entrainer selection task for heteroazeotropic batch distillation with one-phase reflux can then be easily done in a systematic way.

Table 4
Final products for all cases in Tables 1–3

Case	Rectifier column (strategy B)	Rectifier column (strategy A) and multivessel column
a1	L_A, L_E, B	L_A, E, B
a2	L_B, L_E, A	L_B, E, A
a3	Infeasible	
a4	Infeasible	
a5	$L_{A'}$, $L_{E'}$, B	$L_{A'}$, AzEB, B
a6	$L_{B'}$, $L_{E'}$, A	$L_{B'}$, AzEA, A
a7	Infeasible	
a8	Infeasible	
a9	$L_{A'}$, $L_{E'}$, B	$L_{A'}$, AzEB, B
a10	Infeasible	
b1	L_A, L_E, B	L_A, E, B
b2	L_A, L_E, B	L_A, E, B
b3	Infeasible	
b4	Infeasible	
b5	$L_{A'}$, $L_{E'}$, B	$L_{A'}$, AzEB, B
b6	$L_{A'}$, $L_{E'}$, B	$L_{A'}$, AzEB, B
b7	Infeasible	
b8	Infeasible	
b9	Infeasible	
c1	L_A, L_E, B	L_A, E, B
c2	Infeasible	
c3	Infeasible	
c4	$L_{A'}$, $L_{E'}$, B	$L_{A'}$, AzEB, B
c5	Infeasible	
c6	Infeasible	
c7	Infeasible	

Notation

A	light original component
AzAB	binary azeotrope of the two original components A and B
AzEA	binary azeotrope of the entrainer and the original component A
AzEAB	ternary azeotrope of the entrainer and the original components A and B
AzEB	binary azeotrope of the entrainer and the original component B
B	heavy original component
D	final product in the decanter when strategy B is implemented
E	entrainer
F	feed
L_A	entrainer-lean phase
$L_{A'}$	final product of the entrainer-lean phase in the decanter in cases a5, a6, a9, b5, b6 and c4
L_E	entrainer-rich phase
$L_{E'}$	final product of the entrainer-rich phase in the decanter in cases a5, a6, a9, b5, b6 and c4
S_1	still product at the end of the first step when strategy A is implemented

△	saddle point of the distillation line map
●	stable node of the distillation line map
○	unstable node of the distillation line map

Appendix

Additional information about the expected final products in the vessels is given in Table 4.

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