Analysis and Control of Heteroazeotropic Batch Distillation

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The separation of close-boiling and azeotropic mixtures by heterogeneous azeotropic distillation is addressed in batch columns. Both a common rectifier and a multivessel batch column are considered. Theoretical and graphical analyses of the process are presented for both column configurations and different separation strategies are presented. A simple control scheme is proposed for the practical operation of the columns, the implementation of different separation strategies and the realization of the final results. Dynamic simulations for mixtures classified under Serafimov's topological classes 2.0-2b and 3.1-2 verify the theoretical findings. The results show that heteroazeotropic batch distillation exhibits substantial flexibility. The column profile can be totally restored during the process and lie in regions different from those of the initial feed. The still path can cross distillation boundaries and the still product does not have to be the stable node of the feed region. Such results cannot be obtained by homogeneous azeotropic batch distillation.
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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 industry because of small-scale production of high added-value products and frequent changes of the separation task. Consequently, establishing new and efficient methods for batch distillation of such mixtures is an important issue both for academia and industry.

Separation of azeotropic (or close-boiling) mixtures is impossible (or uneconomical) by common distillation and therefore special techniques have to be applied. If pressure swing distillation is not efficient because of insensitivity of the azeotropic composition to pressure changes then another component, called an *entrainer*, has to be added to facilitate separation and enhance distillation. When a heavy entrainer is added continuously in the top section of the batch column the process is called extractive batch distillation. When an entrainer is added batchwise to the original mixture we simply call it azeotropic batch distillation. If the entrainer is miscible with the components of the original mixture the process is called homogeneous azeotropic (homoazeotropic) batch distillation. The entrainer can form one or more azeotropes with the original components. When the entrainer is immiscible and forms a heterogeneous azeotrope with at least one (and preferably with only one) of the original components, the process is called heterogeneous azeotropic (heteroazeotropic) batch distillation. This study is about heteroazeotropic batch distillation; thus, we study entrainers

added batchwise to the original mixture and leading to the formation of heteroazeotrope(s).

The column configuration used for the separation task is another important issue. The most common batch column is the so-called batch rectifier or regular column, where the feed is charged to the reboiler and the products are taken from the top of the column during a rectification process.[1] Alternatively, an inverted column also called the batch stripper can be used. The feed is charged in the reflux drum at the column top and the products are withdrawn from the bottom during a stripping process.[2] Much attention has been given lately to a special batch configuration called the multivessel column or middle vessel column.[3] The multivessel column can be realized as a combination of a rectifier and a stripper.[4,5] It has both a rectifying and a stripping section and it is possible to obtain simultaneously a light and a heavy fraction from the top and the bottom of the column. An intermediate fraction may also be recovered in the middle vessel. Rectifier and multivessel configurations are studied herein, although batch strippers are not considered.

In contrast to its heterogeneous counterpart, homogeneous azeotropic batch distillation has achieved much attention in the literature.[6-14] Bernot et al.,[6,7] Duessel and Stichlmair,[8] Stichlmair and Fair,[9] and Rodriguez et al.[10] all addressed homoazeotropic distillation in batch rectifiers and strippers, whereas Cheong and Barton[11-13] and Warter and Stichlmair[14] studied the process in multivessel configurations.

Somewhat surprisingly, taking into account its industrial importance, the literature on heteroazeotropic batch distillation is still limited and somewhat controversial. Duessel and Stichlmair[8] showed simulation results for the heteroazeotropic rectification of the mixture pyridine/water using toluene as entrainer. Synthesis methods from homoazeotropic batch distillation were used. The system was revisited by Rodriguez et al.[15,16] who criticized the analysis from Duessel and Stichlmair[8] and pointed out that synthesis methods for homogeneous mixtures cannot be extended to heterogeneous ones without caution. Koehler et al.[17] showed experimental results for the separation of an azeotropic mixture of water and a high-boiling component using a light heterogeneous entrainer, but did not specify the actual components used. They showed that the process behaves differently from homoazeotropic batch distillation and that the still path could cross the distillation boundary. They also proposed different separation strategies and compared them in terms of time requirements. Stichlmair and Fair[9] presented results for the separation of ethanol/water using toluene as a heterogeneous entrainer. The proposed separation scheme was inspired from the corresponding scheme for continuous columns described by Stichlmair and Herguijuela[18] and required one stripper and one rectifier–decanter hybrid. Thus, not all possibilities of the batch process were investigated. The presented results for the last mixture in our work, classified under Serafimov's class 3.1-2, will show that the separation can be performed in a single rectifier–decanter hybrid if we take full advantage of the batch process.

In a series of papers Rodriguez et al.[10,15,16,19] approached the heteroazeotropic batch distillation process both theoretically and experimentally. First, they provided entrainer selection rules and simulation results for heterogeneous mixtures and showed that heterogeneous entrainers offer more possibilities than homogeneous ones for the separation of azeotropic mixtures.[10,15] Later, they verified their simulation results with experiments in a batch rectifier.[19] In their last paper they attempted a more systematic theoretical analysis and developed synthesis methods for the process.[16] Skouras and Skogestad[20] showed simulation results for heteroazeotropic batch distillation in a closed multivessel column and developed feasibility rules for the process. Unfortunately, their feasibility analysis is partially incorrect because synthesis methods from homoazeotropic distillation were used and not all possibilities of the process were investigated. Skouras and Skogestad[21] also provided batch time comparisons for heteroazeotropic batch distillation of ternary mixtures in the closed rectifier and multivessel column and concluded that the multivessel column always performs better than the rectifier for such separations.

The reason for the different results and conclusions on heteroazeotropic batch distillation is that different authors consider different operation modes of the process. If heteroazeotropic distillation is defined as a process where an original mixture is separated in the presence of a heteroazeotropic entrainer and not limited by some additional conditions, there are, generally, two modes to carry out the process.

Mode I

The mixture is separated by distillation to recover all the heteroazeotrope in the decanter (closed operation with no liquid–liquid split), which then, after the distillation, is split into its two immiscible phases: the entrainer-lean phase and the entrainer-rich phase. Thus, Mode I may be viewed as a hybrid process, that is, a combination of two different separation methods (distillation and liquid–liquid split) realized in the sequence. The first step is similar to homoazeotropic distillation and the second step is a liquid–liquid separation. Consequently, Mode I is governed by the rules of homoazeotropic distillation but the postoperational split of the heteroazeotrope gives us the possibility to "break" the azeotrope in contrast to homoazeotropic distillation.

Mode II

The mixture is separated by distillation to obtain some of the heteroazeotrope in the decanter and the liquid–liquid split takes place during distillation with withdrawal or accumulation of the entrainer-lean phase and reflux of all or part of the entrainer-rich phase. In practice, a start-up period is needed for Mode II, where all the mixed phases are refluxed. Mode II may be viewed as a hybrid process, that is, a combination of two different separation methods (distillation and liquid–liquid splitting) carried out simultaneously. The removal (or effective removal by accumulation) of the entrainer-lean phase changes the instant mass balance and the general course of the process compared to Mode I. Thus, Mode II is governed by its own laws and, more important, some limitations on the feasible feed compositions of Mode I that apply to homoazeotropic distillation are not valid for Mode II.

From the above analysis it becomes obvious that Stichlmair and coworkers[8,9] addressed Mode I of the process, whereas Koehler et al.[17] and Rodriguez et al.[10,15,16,19] addressed Mode II. Skouras and Skogestad[20] also considered Mode II and, consequently, the feasibility analysis provided in the report of

their study is partially incorrect because it applies only to the start-up step of the process and the additional possibilities obtained during the main step (Mode II) were not taken into account.

This work addresses Mode II of heteroazeotropic batch distillation and provides analysis of the process in the rectifier and the multivessel column. In addition, practical realization of the final results by implementing simple control schemes is investigated. In a subsequent report,[22] we provide feasibility analysis and entrainer selection rules for the process. This paper is structured as follows. A conceptual analysis of the process, theoretically and graphically, is given first for the rectifier column. Different separation strategies proposed before in the literature are illustrated and discussed. Then a simple control scheme is proposed for the practical operation of the column and the implementation of the different strategies. Detailed simulation results are presented for two common industrial heteroazeotropic separations. The first example is the azeotropic dehydration of 1,4-dioxane by use of benzene as a heteroazeotropic entrainer. The second example is the dehydration of ethanol by use of benzene as an entrainer. The two mixtures are classified under Serafimov's topological classes 2.0-2b and 3.1-2, respectively. The results show the flexibility of the process. The column profile can be totally restored during operation and lies finally in feed regions different from that of the initial feed. The still path can cross distillation boundaries. Such results cannot be obtained by homoazeotropic batch distillation or heteroazeotropic distillation of Mode I. The model used in the simulations is described in detail in the Appendix.

For detailed information on azeotropic phase equilibrium diagrams and Serafimov's classification of ternary azeotropic mixtures, frequently mentioned herein, the reader is advised to refer to the excellent survey from Kiva et al.[23] and the article from Hilmen et al.[24]

Rectifier Column

The objective is to separate an initial binary close-boiling or azeotropic mixture of components A and B, hereafter called the original mixture, into pure components. To facilitate separation, a heterogeneous entrainer (E), partially miscible and forming a heteroazeotrope with only one (preferably) of the original components, is added to the original mixture. Alternatively, the "original" mixture AB can already contain the "entrainer" E and the objective is to separate the ternary mixture ABE into three pure components. In the former case (binary original mixture), it is not usually necessary to recover pure entrainer from the entrainer-rich fraction because it can be recycled to the next batch. In the latter case (ternary original mixture) it is often required to recover pure entrainer. To gain insight into Mode II of heteroazeotropic batch distillation, a short description of the process based on a simple example is useful.

Process description

An original binary close-boiling mixture of components A and B is to be separated in the rectifier column (Figure 1). A heterogeneous light entrainer (E) is added to the original mixture. The entrainer forms a heteroazeotrope with com-
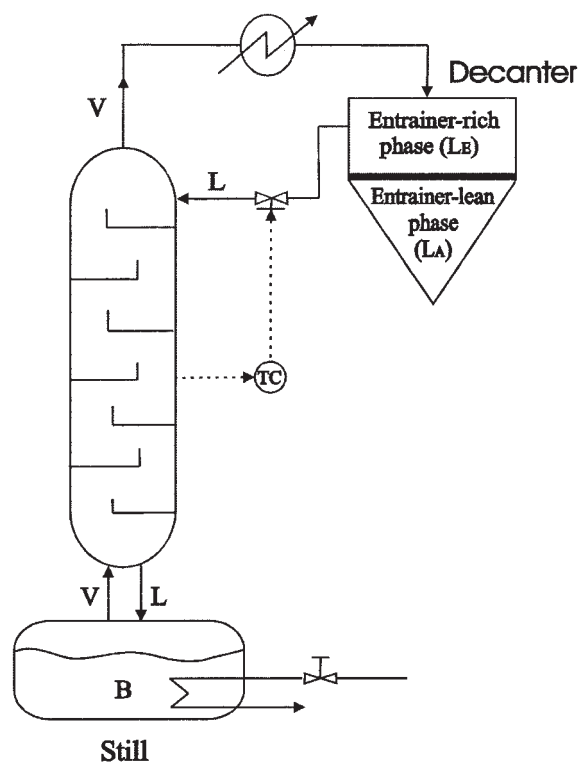

Figure 1. Batch rectifier column with the proposed control scheme.

ponent A, which is an unstable node [un], as shown in Figure 2. The entrainer (E) and the original component A are saddles [s], whereas the original component (B) is the stable node [sn]. Alternatively, the objective could be to separate the ternary heteroazeotropic mixture ABE.

Zeroth Step: Start-Up Period. A mixture F with composition x_F, as shown in Figure 2, is introduced in the still and processed in the rectifier column. An initial start-up period is needed to build up the composition profile in the column and
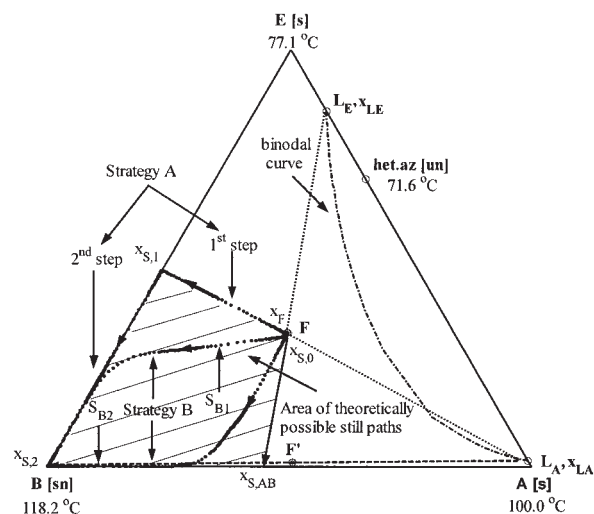

Figure 2. Separation strategies in the rectifier column with the corresponding still paths.

collect some of the heteroazeotrope in the decanter. This period is usually run under total reflux. The main part of the process can now be started and it may be divided in two steps.

First Step: Product Recovery. The heteroazeotrope in the decanter consists of two immiscible liquid phases: the entrainer-rich phase L_E with composition $\mathbf{x}_{LE}$ and the entrainer-lean phase L_A with composition $\mathbf{x}_{LA}$, rich in component A, as shown in Figure 2. The entire entrainer-rich phase L_E, is refluxed in the column, whereas the entrainer-lean phase L_A is withdrawn (open operation) or accumulated (closed operation). During the "product recovery" step, the original component A is removed from the still to the entrainer-lean phase in the decanter. When there is no more of the entrainer-lean phase formed in the decanter, this step is finished.

Second Step: Entrainer Recovery. In the first step the entire entrainer-rich phase is refluxed, so excess entrainer will be accumulated in the still. During the second step, the excess entrainer (E) in the still is recovered in the decanter. We can again withdraw the entrainer fraction (open operation) or let it accumulate (closed operation). When all of the excess entrainer is recovered in the decanter, the "entrainer recovery" step is over and the separation task is completed because component B is left in the still.

It is essential to realize that, in general, both the "product recovery" and the "entrainer recovery" steps are necessary when considering heteroazeotropic batch distillation. However, in practice, it is not necessary to reflux all of the entrainer-rich phase during the first step, even if it is useful for the conceptual description of the process. The process can be run with partial reflux of the entrainer-rich phase. Such operation issues give rise to different separation strategies and result in different paths for the process, as discussed in the following section.

Separation strategies

Koehler et al.[17] showed experimental results for the open rectifier with continuous withdrawal of the entrainer-lean phase and total or partial reflux of the entrainer-rich phase and they called these strategies as A and B, respectively. In our simulations we use closed operation with accumulation of the entrainer-lean phase in the decanter and similar total or partial reflux of the entrainer-rich phase. The results would essentially be the same for both open and closed operations.

Strategy A. This strategy uses total reflux of the entrainer-rich phase. In most cases, this will require that the "product recovery" (first step) and the "entrainer recovery" (second step) are performed independently of each other and sequentially. During the first step a feed F is separated according to the following mass balances, if we neglect the column holdup

$$F = L_A + L_E + S$$

$$F\mathbf{x}_F = L_A\mathbf{x}_{LA} + L_E\mathbf{x}_{LE} + S\mathbf{x}_S$$

and given that the entrainer-rich phase is totally refluxed ($L_E = 0$)

$$F = L_A + S$$

$$F\mathbf{x}_F = L_A\mathbf{x}_{LA} + S\mathbf{x}_S \Rightarrow \mathbf{x}_S = (1 + a)\mathbf{x}_F - a\mathbf{x}_{LA} \quad (1)$$

where $a = L_A/(F - L_A)$. Eq. 1 reveals that the still ($\mathbf{x}_S$) follows a linear path away from the entrainer-lean phase ($\mathbf{x}_{LA}$) accumulated in the decanter, starting from the feed composition $\mathbf{x}_F = \mathbf{x}_{S,0}$ until it reaches the binary edge (EB), at the point $\mathbf{x}_{S,1}$. How fast the still composition moves along this path depends on how fast the entrainer-lean phase (L_A) is accumulated in the decanter. The faster the accumulation rate, the faster the still composition moves along its linear path, illustrated in Figure 2.

Now the second step starts to recover the excess entrainer. At the end of this step pure entrainer is recovered in the decanter, whereas component B is recovered in the still. If we neglect the column holdup, the still content (S_1) at the end of the first step is separated according to the following mass balances

$$S_1 = L_{DE} + S$$

$$S_1\mathbf{x}_{S,1} = L_{DE}\mathbf{x}_E + S\mathbf{x}_s \Rightarrow \mathbf{x}_S = (1 + b)\mathbf{x}_{S,1} - b\mathbf{x}_E \quad (2)$$

where $b = L_{DE}/(S_1 - L_{DE})$. Equation 2 reveals that the still path is moving away from point $\mathbf{x}_{S,1}$ along the binary edge EB, because pure entrainer ($\mathbf{x}_E$) is accumulated in the decanter, arriving at point $\mathbf{x}_{S,2}$, which is the pure component B vertex, as shown in Figure 2. How fast the still is moving along its linear path depends on the accumulation rate of the entrainer in the decanter.

Under special conditions, strategy A can be implemented in one single step (product recovery step) and thus there is no need for the entrainer recovery step. Such cases were described by Rodriguez et al.[16] and are discussed in greater detail later in this paper.

Strategy A is conceptually straightforward but time demanding, as mentioned by Koehler et al.[17] Thus, an alternative strategy B was proposed.

Strategy B. This strategy uses partial reflux of the entrainer-rich phase and requires accumulation of both the entrainer-lean and the entrainer-rich phase in the decanter. The idea is to combine the "product recovery" and the "entrainer recovery" steps to save energy and/or time. The justification is twofold. First, as the "product recovery" step proceeds, the original component A is exhausted from the still and high reflux flows of the entrainer-rich phase are no longer necessary. Second, the total reflux of the entrainer-rich phase keeps the entrainer (E) in the still. It therefore seems reasonable to reduce the reflux of the entrainer-rich phase during the process. When strategy B is implemented and we neglect the column holdup, a feed F is separated according to the following mass balances:

$$F = L_A + L_E + S$$

$$F\mathbf{x}_F = L_A\mathbf{x}_{LA} + L_E\mathbf{x}_{LE} + S\mathbf{x}_S \Rightarrow \mathbf{x}_S$$
$$= (1 + a + b)\mathbf{x}_F - a\mathbf{x}_{LA} - b\mathbf{x}_{LE} \quad (3)$$

Equation 3 implies that the still follows a path away from both the entrainer-lean phase ($\mathbf{x}_{LA}$) and the entrainer-rich phase ($\mathbf{x}_{LE}$), which results in a curved path from the feed point $\mathbf{x}_F = \mathbf{x}_{S,0}$ to the point $\mathbf{x}_{S,2}$, which is the final still composition. The curvature of the still path depends on the accumulation rates of the entrainer-lean and the entrainer-rich phases in the decanter.

When component A is recovered faster than the entrainer E, the still path will be like the one called S_{B1} in Figure 2. When the entrainer (E) is accumulated faster than component A, the still path will be like the one called S_{B2}.

The area of possible still paths is limited in one side by the line F–$x_{S,1}$, corresponding to output/accumulation of the entrainer-lean phase only, and on the other side by the line F–$x_{S,AB}$, corresponding to output/accumulation of the entrainer-rich phase only, as illustrated by the shaded area in Figure 2. Even if theoretically possible, however, the still path F–$x_{S,AB}$ is not of practical interest because in such a case the effect of the entrainer is lost and we end up with a still composition on the AB edge.

We should mention here that there is an important potential advantage of strategy A over strategy B. In strategy A we can recover pure entrainer (x_E) during the entrainer recovery step, given that it is possible to have no component A in the still at the end of the product recovery step. In contrast in strategy B we obtain the entrainer (E) in the composition of the liquid–liquid split (x_{LE}), given that both phases are accumulated simultaneously in the decanter.

Connection to previous work

Rodriguez et al.[16] studied the open operation of the rectifier column with withdrawal of the entrainer-lean phase and a flexible reflux policy of one or both of the immiscible phases in the decanter. This reflux policy was then used for steering the still path into the desired final products. The direction of the still path depended on the amount of the two immiscible phases refluxed, which directly affects the accumulation rate of these two phases in the decanter.

This article considers reflux of the entrainer-rich phase only and thus, by following the notation of Rodriguez et al.,[16] all strategies mentioned here correspond to $\varphi = 0$. In greater detail, strategy A corresponds to the case illustrated in Figure 2a of Rodriguez et al.[16] This is the case where the reflux of the entrainer-rich phase equals the amount of this phase contained in the overhead vapor ($\theta = 1$). Such a strategy requires constant holdup of the entrainer-rich phase (L_E) in the decanter. In our approach we keep this holdup constant to zero ($L_E = 0$), whereas in the approach of Rodriguez et al.[16] it is kept constant to its level at the end of the total reflux period. However, both approaches result in straight still paths, such as those illustrated in Figure 2.

Strategy B corresponds to the case illustrated in Figure 2b of Rodriguez et al.,[16] meaning that one refluxes less entrainer than that contained in the overhead vapor ($\theta < 1$). Thus, there is an accumulation of the entrainer-rich phase in the decanter, which in addition to the accumulation/removal of the entrainer-lean phase, results in curved still paths, such as those illustrated in Figure 2.

It is also useful to underline here that Rodriguez et al.[15,16] use, in most cases, a special version of strategy A. The proposed process requires very small amounts of entrainer such that the feed (F′) lies in the straight line (B–L_A) connecting the required still product B and the entrainer-lean phase L_A, as shown in Figure 2. In such a case the process requires only the first "product recovery" step because we can reach the B vertex in the still by removing the entrainer-lean phase L_A during the whole process. Rodriguez et al.[16] called this process "improved heterogeneous azeotropic distillation." However, this version of strategy A requires a careful monitoring of the entrainer added: "Indeed, there is a relationship between the initial amount of entrainer added, . . . the immiscibility region at the defined decanter temperature, the reflux policy . . . and the number of batch tasks needed to obtain the two original components with a high purity."[16] In addition, not all mixtures can be separated in this way, as indicated in Figure 4 of Rodriguez et al.[15] In this example, both the "product recovery" and the "entrainer recovery" steps are necessary because of the higher amount of the added entrainer.

Koehler et al.[17] were the first to present strategies A and B corresponding to total or partial reflux of the entrainer-rich phase, respectively. Their work was experimental and they schematically presented the still paths resulting from each separation strategy. They also compared the two strategies, in terms of time requirements, and they concluded that strategy B is preferable because it requires 25% less process time. However, for a practical implementation of strategy B the following issues have to be addressed. The first issue to decide how fast we should accumulate the entrainer-rich phase in the decanter. There is obviously a trade-off between the time savings achieved with high accumulation rates and the feasibility of the process. Reflux of the entrainer-rich phase is crucial for enhancing separation of the original mixture. However, high reflux flows are undesirable because the return of the entrainer in the column prolongs the separation task and can possibly contaminate the still product. Thus, the reflux of the entrainer-rich phase has to be monitored. The second issue to be addressed is the final holdup of the entrainer-rich phase accumulated in the decanter to obtain an entrainer-free product. This requires knowledge of the amount of entrainer added in the original mixture, the total column holdup, and the liquid–liquid split achieved in the decanter. An underestimation of the entrainer-rich phase holdup leads to a still product contaminated with the entrainer. An overestimation of the holdup reduces the recovery of component B and increases the time requirements.

In the work from Koehler et al.[17] and Rodriguez et al.[16] no systematic effort was done for addressing such issues that are important for the practical operation of the columns and the realization of the final results. In the following we present a simple control scheme that addresses these issues.

Control scheme

Skogestad et al.[5] showed that control strategies based on predetermined holdups in the vessels are not robust because small uncertainties in the feed composition can lead to final results that are different from those desired. Thus, they proposed an indirect level control for adjusting the holdups in the vessels of a multivessel column based on temperature controllers. In our case, such predetermination of the holdups of the two immiscible phases accumulated in the decanter is even more demanding because reliable data for the liquid–liquid splits are required. Therefore, we adopt a similar temperature control scheme that indirectly adjusts the holdup of the entrainer-rich phase in the decanter based on a temperature measurement in the middle of the rectifier column, as shown in Figure 1. This scheme guarantees the feasibility of the process by refluxing an adequate amount of entrainer-rich phase and, at the same time, it ensures an entrainer-free product by accumu-

lating the excess entrainer in the decanter. In this way, the desired final results are obtained with no preliminary calculation of the final holdups in the decanter and no sophisticated reflux policy because only the entrainer-rich phase is refluxed during the process.

The setpoint of the temperature controller is an important parameter because changing it allows us to implement both strategies A and B presented earlier. A low-temperature setpoint increases the reflux flow, thus decreasing the holdup of the entrainer-rich phase in the decanter. A higher setpoint value has the opposite effect, thus increasing the holdup of the entrainer-rich phase in the decanter. In the limiting case, where the setpoint is set to a very low infeasible value, the entrainer-rich phase is totally refluxed and its holdup approaches zero ($L_E \rightarrow 0$). Thus, only the entrainer-lean phase is accumulated in the decanter and strategy A is implemented.

Let us take a closer look at the still paths in Figure 2. The boiling temperature of the heteroazeotrope is 71.6°C, whereas component B, which is the desired still product, has a boiling temperature of 118.2°C. It seems reasonable to set the setpoint as the average of these two temperatures (94.9°C). In this case, the still path S_{B2} is obtained. The resulting accumulation rate of the entrainer-rich phase is high and, consequently, the still path moves faster toward the AB edge (vanishing of the entrainer E) rather than moving toward the BE edge (vanishing of the component A). A lower-temperature setpoint, such as at 80°C, implies a "less-aggressive" control with lower accumulation rates/higher reflux flows. In this alternative case the still follows the S_{B1} path in Figure 2. There, component A vanishes faster than the entrainer and the still moves toward the EB edge.

Strategy A can also be realized with the control scheme. During the first process step (product recovery), a very low setpoint such as 70°C is used. Such a temperature in the middle of the column is infeasible for the given mixture and results in total reflux of the entrainer-rich phase. The holdup of this phase is reduced to zero ($L_E \rightarrow 0$) and the controller allows accumulation of the entrainer-lean phase (L_A) only. Thus, the still path follows the straight line corresponding to the first step (product recovery) of strategy A, shown in Figure 2. Of course if we want to be very accurate we have to say that there is a short transition period where the controller reduces L_E from its value at the end of the total reflux period to zero. During this period, a $\theta > 1$ policy is implemented, according to the notation by Rodriguez et al.[16] However, this period is short and as soon as the holdup of the entrainer-rich phase approaches zero, a $\theta = 1$ policy is implemented throughout the rest of the process. When the product recovery step is finished, the second step (entrainer recovery) of strategy A can then be performed by increasing the setpoint of the controller to the average of the boiling points of components B and the pure entrainer E (such as 97.7°C). This setpoint for the controller allows us to realize the still path from $\mathbf{x}_{S,1}$ to $\mathbf{x}_{S,2}$ shown in Figure 2.

Multivessel Column

Process description

The heteroazeotropic batch distillation separation can alternatively be performed in the multivessel column with a decanter at the top of the column for performing the required liquid–liquid split, as shown in Figure 3. We will describe the
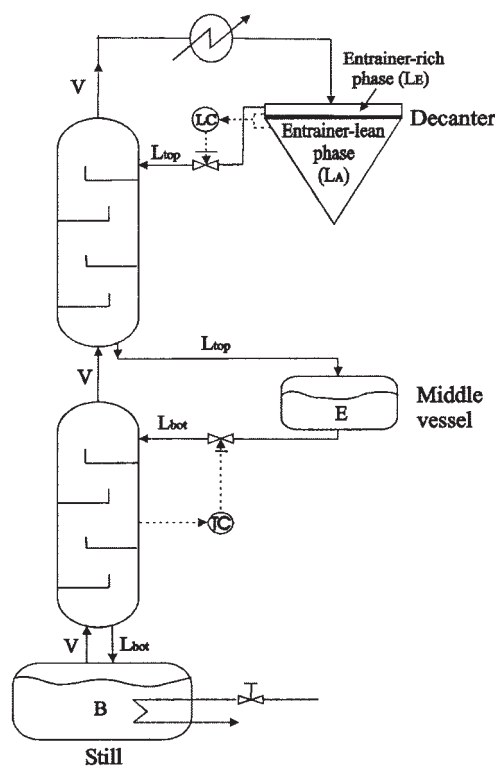

Figure 3. Multivessel batch column with the proposed control scheme.

process briefly because most of the previous analysis for the rectifier column is also valid for the multivessel column.

The process begins with a start-up period to build up the composition profile in the column, as in the rectifier case. During this initial period the column is run under total reflux and some of the heteroazeotrope is accumulated in the decanter.

When the total reflux period is over the main part of the process can start and the two steps (product recovery and entrainer recovery step) mentioned before for the rectifier column have to be performed. However, the multivessel column has an additional vessel (middle vessel) and an additional section (stripping section) and it is possible for a third component (entrainer) to be recovered in the middle vessel. Thus, the product recovery and the entrainer recovery steps can be performed simultaneously in the rectifying and stripping section of the multivessel column, respectively. We describe qualitatively how the process evolves.

The entrainer-rich phase L_E accumulated in the decanter during the start-up period is totally refluxed and only the entrainer-lean (product) phase L_A is accumulated in the decanter. This resembles the first "product recovery" step, in the rectifier column. The entrainer refluxed back in the column has to be recovered during the second "entrainer recovery" step. In the multivessel column this can be performed simultaneously with the first step because the middle vessel can be used for accommodating the entrainer. Consequently, as a rough approximation, we can say that the rectifying section performs the "product recovery" step with the entrainer-lean (product) phase accumulated in the decanter, whereas the stripping sec-

tion performs the "entrainer recovery" step with the pure entrainer accumulated in the middle vessel.

The separation in the multivessel column is an implementation of strategy A, described before for the rectifier column, and thus it is possible to recover the entrainer in pure form in compositions higher than those obtained by the liquid–liquid split. This is important if the original mixture is ternary and we want to recover all three components.

Control scheme

The control scheme used for implementing the aforementioned separation strategy is shown in Figure 3. The entrainer-rich phase in the decanter is totally refluxed and it is only the entrainer-lean phase that accumulates in the decanter. A level controller is used to accommodate the total reflux of the entrainer-rich phase in the decanter. At the same time, the stripping section performs the separation between the entrainer and the original component miscible with the entrainer. As in the rectifier case, a temperature controller is used for indirect level control in the middle vessel. The setpoint is set to the average of the boiling points of the entrainer (E) to be recovered in the middle vessel and the original component B to be recovered in the still.

Results

The separation in both the rectifier and the multivessel column using the proposed control schemes will be illustrated by dynamic simulation for two azeotropic mixtures. The details for the simulations are given in the Appendix. The main characteristics and the flexibility of the process will be illustrated and the results are far from being trivial.

Serafimov's topological class 2.0-2b

The mixture benzene/water/1,4-dioxane is an example of Serafimov's topological class 2.0-2b. Organic synthesis of 1,4-dioxane leads to a mixture of water/dioxane, which has to be further dehydrated and purified before it can reach the market. However, the original mixture exhibits a minimum homoazeotrope. Adding a heterogeneous entrainer, such as benzene, enhances separation. Benzene forms a binary heteroazeotrope with water, which boils at a temperature lower than that of the homoazeotrope, thus replacing the initial homoazeotrope and becoming the unstable node [un] of the ternary system. The homoazeotrope then becomes a saddle [s], the two original components become stable nodes [sn], and the entrainer becomes a saddle [s]. Figure 4 shows the structure of the distillation-lines map of the mixture. There is one distillation boundary (unstable separatrix), running from the heteroazeotrope [un] to the homoazeotrope [s], thus dividing the composition space in two feed regions. Moreover, the left feed region is divided in two batch regions by a straight batch distillation boundary, running from the dioxane vertex [sn] to the heteroazeotrope [un]. This leads to three distillation regions, I, II and III, which lead to different product sequences under batch distillation. Regions II and III require the addition of small amounts of entrainer. We study the case where the feed is placed in region III because it better illustrates the flexibility of Mode II of heteroazeotropic batch distillation.

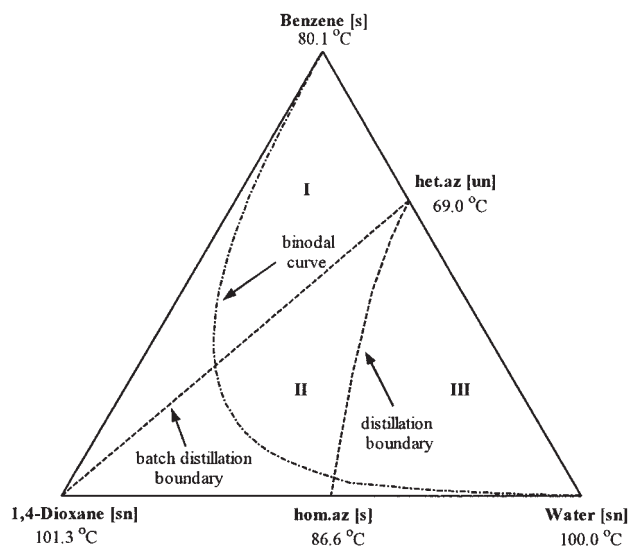*Separation in the Rectifier Column.* An initial feed F with

Figure 4. Distillation line map for the benzene/water/ 1,4-dioxane mixture.

composition $\mathbf{x}_F$ = [0.2, 0.6, 0.2] located in region III is distributed 10% to the decanter and 90% to the still of the rectifier column, as shown in Table A2 in the Appendix. The separation is illustrated in Figure 5. During the start-up period the column is run under total reflux for 1 h and the composition profile is established. The heteroazeotrope boils overhead and is accumulated in the decanter ($\mathbf{x}_{D,0}$). The still follows a path away from the feed (F) toward the water–dioxane edge and the still composition ends at point ($\mathbf{x}_{S,0}$) at the end of this start-up period. The column profile is limited by the boundary because of the total reflux condition and lies inside region III. When the main period begins, the controller is set on and the column is refluxed with the entrainer-rich phase ($\mathbf{x}_{LE}$). The controller automatically adjusts the amount of the entrainer-rich (organic) phase refluxed and the amount accumulated in the decanter together with the entrainer-lean (aqueous) phase. The composition of the vapor boiling overhead (heteroazeotrope) is dif-
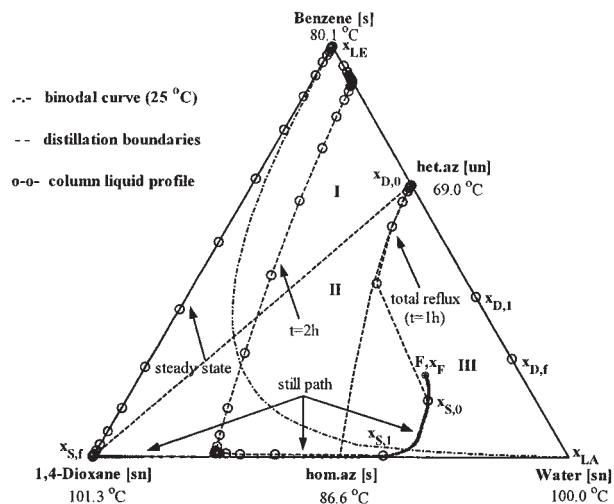

Figure 5. Separation of benzene/water/1,4-dioxane in the rectifier column.

ferent from that of the reflux stream (x_{LE}). This decoupling of the top vapor composition and the reflux composition, which is a unique characteristic of Mode II of heteroazeotropic distillation, gives the flexibility of the process and differentiates it from homoazeotropic batch distillation and Mode I of heteroazeotropic distillation where the top vapor and the reflux stream have the same composition.

Rodriguez et al.[16] note that: "Heteroazeotropic batch distillation [they refer to Mode II] feasibility means that during the whole process, there exists at least one liquid profile connecting each punctual composition x_S on the still path with the liquid composition leaving the first tray . . . when the distillation begins [what we call main period in this work], the feasibility condition has to be achieved through the liquid reflux policy at the top of the column." This means that the final column composition profile should connect the still composition ($x_{S,f}$) with the composition of the entrainer-rich phase (x_{LE}) refluxed in the column. As we see in Figure 5, the reflux (x_{LE}) is located in region I. Thus, the column profile will deviate from the one obtained during the start-up period and will eventually be located entirely in region I. The implication for the still path is straightforward. In batch distillation the still composition belongs to the column profile itself and, consequently, when we start refluxing the entrainer-rich (organic) phase, the still path will start moving from region III toward the dioxane vertex, which is the common stable node of regions I and II, thus crossing the distillation boundary (Figure 5).

We should make clear at this point that crossing an unstable separatrix by batch rectification is predicted and allowed theoretically. Only stable separatrices act as barriers for the still path in batch rectification. However, this crossing of the unstable separatrix is far from being trivial and is a unique characteristic of Mode II of heteroazeotropic distillation. Crossing the same boundary in homoazeotropic distillation or Mode I of heteroazeotropic distillation would not be possible. In this case the column profile has to lie in the same region as the initial feed F because the decoupling of the top vapor composition and the reflux composition (x_{LE}) is not possible. As a result, the initial feed F has to be placed in a feed region where the desired still product lies or, in other words, the feed has to be in a region where the desired still product (1,4-dioxane) is a stable node. However, in heteroazeotropic batch distillation of Mode II we can recover pure dioxane in the still even if the feed is placed in region III where the stable node is water and not dioxane. As we mentioned earlier in the introductory section, Mode II is a more flexible process and some limitations on the feasibility of heteroazeotropic distillation under Mode I or homoazeotropic distillation are not valid for Mode II. A more detailed discussion on the feasibility issues for Modes I and II is given in a subsequent paper.[22]

The column profile at an intermediate time $t = 2$ h is also shown in Figure 5. The column profile has deviated from that obtained under total reflux ($t = 1$ h) and it is now inside all three regions, I, II, and III. However, the still composition ($x_{S,1}$) is still in region III. At the end of the process, the column profile lies entirely in region I, following the dioxane–benzene edge, and the still composition ($x_{S,f}$) is at the pure dioxane vertex.

Table 1 shows the final compositions and recoveries for all components. Water is recovered with the aqueous phase (x_{water} = 0.998), whereas the entrainer (benzene) is recovered with the

Table 1. Final Results for the Separation of the Mixture Benzene/Water/1,4-Dioxane

	Rectifier Column Decanter		
	Aqueous Phase	Organic Phase	Still
Holdup (kmol)	3.065	0.965	0.970
$x_{benzene}$	0.002	0.998	0.000
x_{water}	0.998	0.002	0.000
$x_{dioxane}$	0.000	0.000	1.000
Recovery (%)	99.9	94.4	95.1

	Multivessel Column		
	Decanter (Aqueous Phase)	Middle Vessel	Still
Holdup (kmol)	3.125	0.878	0.987
$x_{benzene}$	0.002	0.999	0.000
x_{water}	0.998	0.000	0.000
$x_{dioxane}$	0.000	0.000	1.000
Recovery (%)	100	86.0	96.8

organic phase ($x_{benzene}$ = 0.998), which can be recycled to the next batch. The still product is anhydrous and benzene-free dioxane ($x_{dioxane}$ = 1). The entrainer loss is 5.6%, the water is almost completely recovered, and finally 95% of the dioxane is recovered.

Separation in the Multivessel Column. The same feed F with composition x_F = [0.2, 0.6, 0.2] is processed in the multivessel column and the separation is illustrated in Figure 6. First, the column is run under total reflux for 1 h and the composition profile is built up (start-up period). The water–benzene heteroazeotrope boils overhead and is accumulated in the decanter ($x_{D,0}$) because it is the unstable node [un] in region III. An intermediate fraction ($x_{M,0}$) is recovered in the middle vessel and the still path ($x_{S,0}$) is moving toward the stable node [sn] of the feed region, which is the water vertex. The column profile stays inside region III because of the total reflux condition and the boundary running from the binary heteroazeotrope to the binary homoazeotrope acts like a barrier for the process. When we start refluxing the organic phase (x_{LE}) the boundary is no longer a barrier for the process and the composition profile in the column can be restored. The reflux (x_{LE})
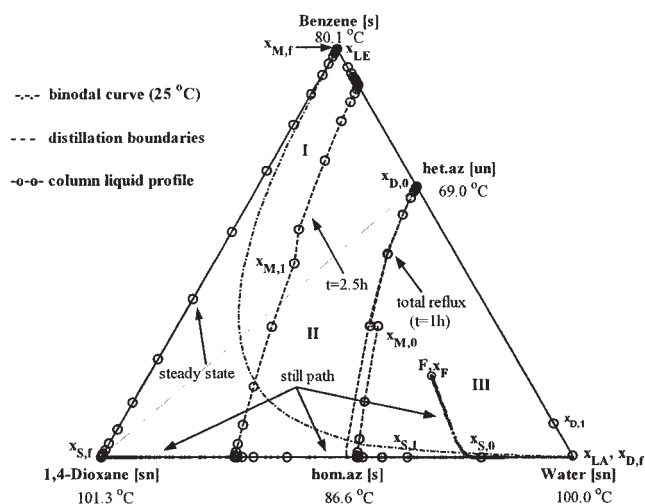

Figure 6. Separation of benzene/water/1,4-dioxane in the multivessel column.

is placed in region I and the column profile is forced to move toward the same region, and thus it moves toward region I. At an intermediate time ($t = 2.5$ h) the column profile lies in all three regions. The still composition ($\mathbf{x}_{S,1}$) is in region III, the stripping section of the column is in region II, the middle vessel ($\mathbf{x}_{M,1}$) lies in region I, and the same is true for the rectifying section of the column. As the process reaches its end, the still path is moving toward the dioxane vertex, which is the desirable still product. At the end, the amount of the organic phase in the decanter is equal to the setpoint of the level controller (0.001 kmol) and practically zero. Thus, the total composition in the decanter ($\mathbf{x}_{D,f}$) is almost equal to the composition of the aqueous phase (x_{LA}), as shown in Figure 6. Pure benzene is recovered in the middle vessel ($\mathbf{x}_{M,f}$) and pure dioxane in the still ($\mathbf{x}_{S,f}$). The final column profile follows the dioxane–benzene edge in region I and lies entirely in region I. The still path is crossing the distillation boundary (unstable separatrix) and ends up in the dioxane vertex ($\mathbf{x}_{S,f}$), even if the initial feed was placed in region III, where the stable node was water.

The results for the multivessel column in Table 1 show that the entrainer is recovered in a composition ($\mathbf{x}_{benzene} = 0.999$) higher that that determined by the liquid–liquid equilibrium at the decanter's temperature ($\mathbf{x}_{benzene} = 0.998$), which was the case for the rectifier column. The difference is that when strategy B is implemented in the rectifier column, the entrainer is recovered with the entrainer-rich phase ($\mathbf{x}_{LE}$) in the decanter. In the multivessel column the stripping section is used for separating the entrainer (benzene) from the original component miscible with the entrainer (dioxane) and it is possible to recover pure entrainer in case we have enough stages in the column section. The difference in the compositions is not significant for this mixture because the liquid–liquid split in the heteroazeotrope (see the binodal curve) is very sharp. However, in other cases, such as in the mixture shown in Figure 2, the liquid–liquid split gives an entrainer-rich phase (L_E), which still contains a lot of water. In this case the additional purification of the entrainer-rich phase possible in the multivessel column is significant.

In practice, the choice between performing the separation in the rectifier or in the multivessel column depends on the objectives of the separation task. If the task is to separate a binary azeotropic mixture by the addition of a heterogeneous entrainer then the need for a pure entrainer fraction is not crucial and the rectifier column is preferred, unless further studies suggest reduced time or energy requirements for the multivessel column. If the objective is to separate a ternary heteroazeotropic mixture into pure components then we must use either strategy A in the rectifier column or the multivessel column. Further studies can indicate which column configuration requires less time or energy requirements for such separations.

Serafimov's topological class 3.1-2

The second mixture studied is the "classical" example in heteroazeotropic distillation, that is, the dehydration of ethanol by using benzene as a heterogeneous entrainer. The mixture represents Serafimov's class 3.1-2. The task is to obtain anhydrous ethanol, which is usually used for pharmaceutical reasons. Equally important is to obtain entrainer-free ethanol. The addition of a heteroazeotropic entrainer, such as benzene, in the
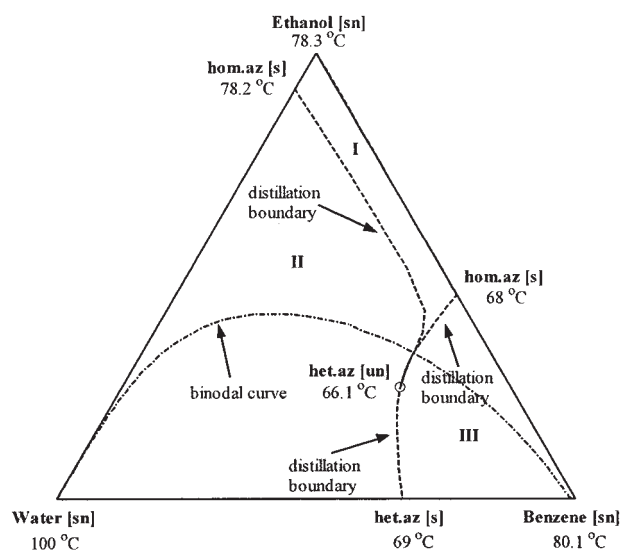

Figure 7. Distillation lines map for the mixture ethanol/benzene/water.

original ethanol/water mixture complicates the structure of the distillation-lines map, as seen in Figure 7. The system exhibits two binary homoazeotropes, between water–ethanol and ethanol–benzene, one binary heteroazeotrope, between benzene–water, and a ternary heteroazeotrope. The ternary heteroazeotrope is the only unstable node [un]. The three binary azeotropes are saddles [s] and the three pure components vertices are stable nodes [sn]. Three distillation boundaries (unstable separatrixes), running from the ternary heteroazeotrope to each one of the binary azeotropes, divide the composition space in three regions, I, II, and III, as shown in Figure 7. Moreover, each of these regions is split in two batch regions by a straight line connecting the pure components [sn] with the ternary heteroazeotrope [un] (not shown in Figure 7). Regions I and II are of practical interest because they require the addition of small amounts of entrainer (benzene). We study the
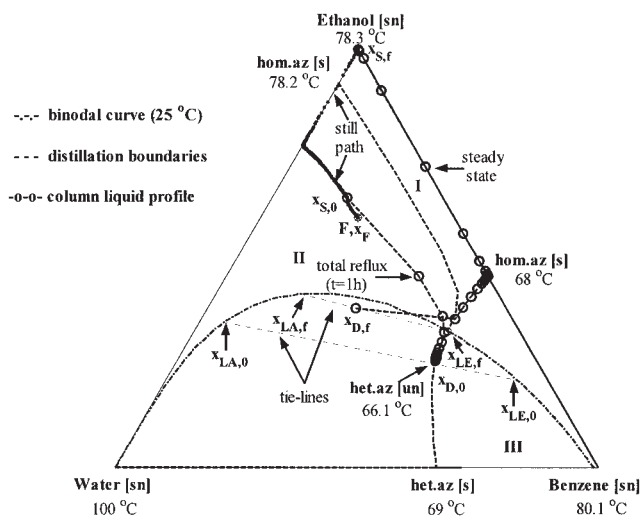

Figure 8. Separation of ethanol/benzene/water in the rectifier column.

Table 2. Final Results for the Separation of the Mixture Ethanol/Benzene/Water

	Rectifier Column Decanter		
	Aqueous Phase	Organic Phase	Still
Holdup (kmol)	2.042	1.217	1.741
$x_{ethanol}$	0.415	0.327	1.000
$x_{benzene}$	0.175	0.525	0.000
x_{water}	0.410	0.148	0.000
Recovery (%)	84.7	63.9	58.0

	Multivessel Column		
	Decanter (Aqueous Phase)	Middle Vessel	Still
Holdup (kmol)	2.485	1.000	1.505
$x_{ethanol}$	0.415	0.459	1.000
$x_{benzene}$	0.176	0.541	0.000
x_{water}	0.409	0.000	0.000
Recovery (%)	100	54.1	50.2

case where the initial feed F is located in region II because this allows us to illustrate the flexibility of the process.

Separation in the Rectifier Column. A feed F with composition $x_F = [0.6, 0.2, 0.2]$ in region II is processed in the rectifier column. Figure 8 illustrates the process. The column is initially run under total reflux for 1 h to establish the column profile. The ternary heteroazeotrope is boiling overhead and accumulates in the decanter ($x_{D,0}$), whereas the still is moving away from the feed F and arrives at point $x_{S,0}$. The column profile is restricted by the distillation boundary separating region II and I because of the total reflux condition. Now the main period of the process can start. The temperature controller is activated with a setpoint as the average of the boiling points of the heteroazeotrope (66.1°C) and pure ethanol (78.2°C) to be recovered in the still. The aqueous phase is accumulated in the decanter, whereas the temperature controller indirectly adjusts the organic phase holdup in the decanter.

An important aspect distinguishes this mixture from the one studied previously. In Figure 8 we see that when we start refluxing the organic phase, the reflux ($x_{LE,0}$) belongs to region III, which is not the region where the final still product (ethanol) should lie (region I). This was not the case is the previous mixture (see Figure 5) where the reflux (x_{LE}) belonged in the region where the final column profile should lie. At first it seems impossible to obtain a final column profile in region I by refluxing the column with the fraction $x_{LE,0}$ that belongs in region III. However, the process is feasible because the composition (x_{LE}) of the organic phase refluxed is constantly changing during the process, given that it is impossible to keep the ternary heteroazeotrope boiling overhead over time. As the process proceeds the total composition in the decanter moves from the ternary heteroazeotrope ($x_{D,0}$) to the final point $x_{D,f}$. Consequently, the liquid–liquid split in the decanter (see the tie-lines in Figure 8) forces the reflux (x_{LE}) to move along the binodal curve from point $x_{LE,0}$ until it finally reaches the point $x_{LE,f}$, which is the final reflux composition. This is the point where the binodal curve meets the boundary separating regions I and III (Figure 8). At the end, the column profile is entirely in region I, following partly the ethanol–benzene edge and partly the boundary separating regions I and III. The still path is moving from region II ($x_{S,0}$) to region I ($x_{S,f}$), thus allowing recovery of pure and benzene-free ethanol.

The final results for the process are given in Table 2. Pure ethanol ($x_{ethanol} = 1$) is recovered in the still, although the recovery is low ($r_{ethanol} = 58\%$) because 42% of the initial ethanol is lost in the two phases accumulated in the decanter arising from the ternary heteroazeotrope. The recovery of water in the aqueous phase is much higher ($r_{water} = 84.7\%$) but still not total, and the composition is low ($x_{water} = 0.410$), again because of the existence of the ternary heteroazeotrope. Obviously, further purification of the aqueous phase is needed to recover the water and the ethanol from this fraction. The recovery of the entrainer (benzene) in the organic phase is not satisfying either ($r_{benzene} = 64\%$) because 36% of the added entrainer is lost in the aqueous phase in equilibrium with the organic phase. The entrainer composition is also low ($x_{benzene} = 0.525$) but this fraction can be recycled in the next batch.

Separation in the Multivessel Column. The same feed F with composition $x_F = [0.6, 0.2, 0.2]$ in region II is processed in the multivessel column and the process is illustrated in Figure 9. During the initial total reflux period, the composition profile is established. The ternary heteroazeotrope is accumulated in the decanter ($x_{D,0}$) because it is the unstable node [un] in feed region II. An intermediate fraction is recovered in the middle vessel ($x_{M,0}$) and the still ($x_{S,0}$) moves initially toward the water–ethanol edge and eventually toward water, which is the stable node [sn] of the feed region. The column profile is restricted by the unstable separatrix between the binary water–ethanol azeotrope and the ternary heteroazeotrope because of the total reflux condition. After 1 h the total reflux period is terminated. The controllers are set on and we start refluxing the entire organic (benzene-rich) phase ($x_{LE,0}$), whereas the aqueous phase ($x_{LA,0}$) is accumulated in the decanter. The column profile deviates from that obtained during the initial total reflux period and at the end it lies entirely in region I. It is partly following the ethanol–benzene edge up to the ethanol–benzene homoazeotrope, which is the middle vessel product ($x_{M,f}$) and partly following the boundary separating regions I and III, as illustrated in Figure 9. The still composition ($x_{S,f}$) is at the ethanol vertex, which means that the still path crossed the boundary (unstable separatrix) separating regions I and II. As
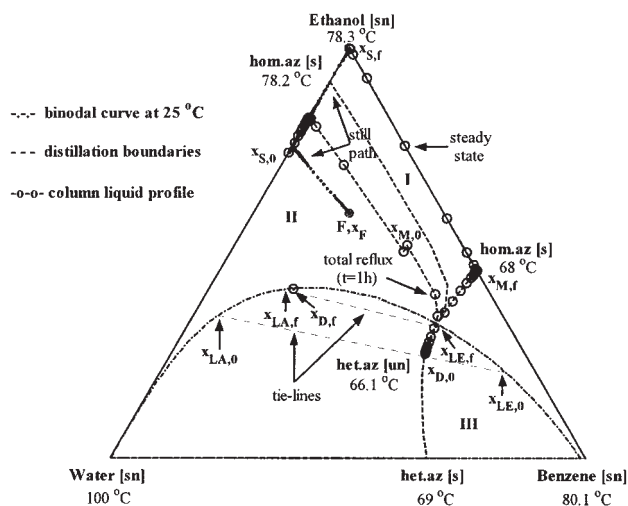

Figure 9. Separation of ethanol/benzene/water in the multivessel column.

in the rectifier case, the reflux path moves along the binodal curve and arrives in the meeting point of the binodal and the boundary between regions I and III ($\mathbf{x}_{LE,f}$).

The final results for the process are given in Table 2. The aqueous phase ($\mathbf{x}_{LA,f}$) is recovered in the decanter; the ethanol–benzene homoazeotrope is recovered in the middle vessel and can be recycled to the next batch cycle; and, finally, anhydrous and benzene-free ethanol is recovered in the still. A very small amount of organic phase (0.01 kmol), equal to the setpoint of the level controller, still exists in the decanter at the end and therefore the total decanter composition ($\mathbf{x}_{D,f}$) is very close but not equal to that of the aqueous phase ($\mathbf{x}_{LA,f}$). The recovery of ethanol is also low in the multivessel column ($r_{ethanol} = 50.2\%$); 34.5% of the initial ethanol is lost in the aqueous phase collected in the decanter; and the rest, 15.3%, in the homoazeotrope in the middle vessel. On the other side, the multivessel column provides total recovery of water, whereas in the rectifier column some of the water is lost in the organic phase in equilibrium with the aqueous phase in the decanter.

As a final note we mention that an important difference exists between the first example (class 2.0-2b) and this example (class 3.1-2). In the latter, the mixture ethanol (B)/benzene (E)/water (A), the entrainer (E) forms a homoazeotrope with the original component B to be recovered in the still. This was not the case in the first example, the mixture benzene (E)/water (A)/1,4-dioxane (B), where the entrainer (E) did not form an azeotrope with the original component B. Thus, the advantage mentioned before for the multivessel column—that is, the further purification of the entrainer-rich phase—is no longer possible in this case. The stripping section of the column performs an azeotropic separation in the ethanol/benzene edge and it is this homoazeotrope that is recovered in the middle vessel instead of the pure entrainer. Thus, the multivessel column is not recommended for heteroazeotropic mixtures of class 3.1-2.

Conclusions

Heteroazeotropic batch distillation was addressed in the rectifier and the multivessel column. Different separation strategies, resulting in different still paths, were analyzed and graphically illustrated. Simple control schemes were proposed for implementing different separation strategies and ensuring the desired final results in the columns with no preliminary calculations and minimum operator's intervention.

Dynamic simulations for two different topological classes of heteroazeotropic mixtures—Serafimov's classes 2.0-2b and 3.1-2—illustrated the flexibility of the process. The still path is able to cross distillation boundaries and the product recovered in the still is no longer necessary to be the stable node of the feed region. The column profile can be completely restored in batch columns and the final column profile can lie in regions different from those of the initial feed.

Notation

F = feed, kmol
F′ = feed for "improved heterogeneous azeotropic distillation" proposed by Rodriguez et al.,[16] kmol
I, II, III = feed regions
L_A = holdup of the entrainer-lean phase in the decanter, kmol h^{-1}
L_{DE} = holdup of the entrainer in the decanter during the "entrainer recovery" step at Strategy A, kmol

L_E = holdup of the entrainer-rich phase in the decanter, kmol
S = holdup in the still, kmol
S_{B1} = still path when the entrainer-lean phase is accumulated faster than the entrainer-rich phase
S_{B2} = still path when the entrainer-rich phase is accumulated faster than the entrainer-lean phase
$\mathbf{x}_{D,0}$ = total decanter composition at the end of the total reflux period
$\mathbf{x}_{D,1}$ = total decanter composition at an intermediate time $t = t_1$
$\mathbf{x}_{D,f}$ = final total decanter composition
$\mathbf{x}_E$ = entrainer composition in the decanter during the "entrainer recovery" step at Strategy A
$\mathbf{x}_F$ = feed composition
$\mathbf{x}_{M,0}$ = middle vessel composition under total reflux
$\mathbf{x}_{M,1}$ = middle vessel composition at an intermediate time $t = t_1$
$\mathbf{x}_{M,f}$ = final middle vessel composition
$\mathbf{x}_{LA}$ = entrainer-lean phase composition
$\mathbf{x}_{LA,0}$ = entrainer-rich (organic) phase composition at the end of the total reflux period
$\mathbf{x}_{LA,1}$ = entrainer-rich (organic) phase composition at an intermediate time $t = t_1$
$\mathbf{x}_{LA,f}$ = final entrainer-rich (organic) phase composition
$\mathbf{x}_{LE}$ = entrainer-rich (organic) phase composition
$\mathbf{x}_{LE,0}$ = entrainer-rich (organic) phase composition at the end of the total reflux period
$\mathbf{x}_{LE,1}$ = entrainer-rich (organic) phase composition at an intermediate time $t = t_1$
$\mathbf{x}_{LE,f}$ = final entrainer-rich (organic) phase composition
$\mathbf{x}_S$ = still composition
$\mathbf{x}_{S,0}$ = still composition under total reflux
$\mathbf{x}_{S,1}$ = still composition in an intermediate time $t = t_1$
$\mathbf{x}_{S,AB}$ = still composition under total reflux of the entrainer-lean phase
$\mathbf{x}_{S,f}$ = final still composition
[s] = saddle
[sn] = stable node
[un] = unstable node

Greek letters

φ = reflux fraction of the entrainer-lean phase contained in the overhead vapor. (Notation used by Rodriguez et al.[16])
θ = reflux fraction of the entrainer-rich phase contained in the overhead vapor. (Notation used by Rodriguez et al.[16])

Literature Cited

1. Diwekar UM. *Batch Distillation: Simulation, Optimal Design and Control* (Series in Chemical and Mechanical Engineering). London, UK: Taylor & Francis; 1995.
2. Sorensen E, Skogestad S. Comparison of regular and inverted batch distillation. *Chem Eng Sci.* 1996;51:4949.
3. Robinson CS, Gilliland ER. *Elements of Fractional Distillation*. Vol. 4. New York, NY: McGraw-Hill; 1950.
4. Hasebe S, Abdul Aziz B, Hashimoto I, Watanabe T. Optimal design and operation of complex batch distillation column. Proc of IFAC Workshop on Interactions between Process Design and Process Control. Oxford, UK: Pergamon Press; 1992:177.
5. Skogestad S, Wittgens B, Litto R, Sorensen E. Multivessel batch distillation. *AIChE J.* 1997;43:971.
6. Bernot C, Doherty MF, Malone MF. Patterns of composition change in multicomponent batch distillation. *Chem Eng Sci.* 1990;45:1207.
7. Bernot C, Doherty MF, Malone MF. Feasibility and separation sequencing in multicomponent batch distillation. *Chem Eng Sci.* 1991; 46:1311.
8. Duessel R, Stichlmair J. Separation of azeotropic mixtures by batch distillation using an entrainer. *Comput Chem Eng.* 1995;S19:S113.
9. Stichlmair JG, Fair JR. *Distillation: Principles and Practice*. New York, NY: Wiley–VCH; 1998.
10. Rodriguez-Donis I, Gerbaud V, Joulia X. Entrainer selection rules for the separation of azeotropic and close-boiling-temperature mixtures by homogeneous batch distillation process. *Ind Eng Res.* 2001a;40:2729.
11. Cheong W, Barton PI. Azeotropic distillation in a middle vessel batch column. 1. Model formulation and linear separation boundaries. *Ind Eng Chem. Res.* 1999;38:1504.
12. Cheong W, Barton PI. Azeotropic distillation in a middle vessel batch

column. 2. Nonlinear separation boundaries. *Ind Eng Chem. Res.* 1999;38:1531.

13. Cheong W, Barton PI. Azeotropic distillation in a middle vessel batch column. 3. Model validation. *Ind Eng Chem. Res.* 1999;38:1549.

14. Warter M, Stichlmair JG. Batch distillation of azeotropic mixtures in a column with a middle vessel. Proc of ESCAPE-10, Amsterdam, The Netherlands: Elsevier Science B.V.; 2000:691.

15. Rodriguez-Donis I, Gerbaud V, Joulia X. Heterogeneous entrainer selection for the separation of azeotropic and close boiling temperature mixtures by heterogeneous batch distillation. *Ind Eng Res.* 2001b;40:4935.

16. Rodriguez-Donis I, Gerbaud V, Joulia X. Feasibility of heterogeneous batch distillation processes. *AIChE J.* 2002;48:1168.

17. Koehler J, Haverkamp H, Schadler N. Zur diskontinuierlichen Rektifikation azeotroper Gemische mit Hilfsstoffeinsatz. *Chem-Ing-Tech.* 1995;67:967.

18. Stichlmair JG, Herguijuela J-R. Separation regions and processes of zeotropic and azeotropic ternary distillation. *AIChE J.* 1992;38:1523.

19. Rodriguez-Donis I, Pardillo-Fontdevila E, Gerbaud V, Joulia X. Synthesis, experiments and simulation of heterogeneous batch distillation processes. *Comput Chem Eng.* 2001c;25:799.

20. Skouras S, Skogestad S. Separation of ternary heteroazeotropic mixtures in a closed multivessel batch distillation-decanter hybrid. *Chem Eng Process* (*Special Issue*). 2004a;43:291.

21. Skouras S, Skogestad S. Time requirements for heteroazeotropic distillation in batch columns. *Comput Chem Eng.* 2004b;28:1689.

22. Skouras S, Kiva V, Skogestad S. Heteroazeotropic batch distillation: Feasible separations and entrainer selection rules. *Chem Eng Sci.* 2005 in review.

23. Kiva VN, Hilmen EK, Skogestad S. Azeotropic phase equilibrium diagrams: A survey. *Chem Eng Sci.* 2003;58:1903.

24. Hilmen EK, Kiva VN, Skogestad S. Topology of ternary VLE diagrams: Elementary cells. *AIChE J.* 2002;48:752.

25. Gmehling J, Onken J. *Vapor–Liquid Equilibrium Data Collection.* Frankfurt am Main, Germany: DECHEMA Chemistry Data Series; 1977.

26. DDBST GmbH. *Dortmund Data Bank Software Package* (*Educational Version: Release2002*). Oldenburg, Germany: DDBST GmbH, www.ddbst.de; 2002.

27. Sorensen JM, Arlt W. *Liquid–Liquid Equilibrium Data Collection.* Frankfurt am Main, Germany: DECHEMA Chemistry Data Series; 1980.

28. The MathWorks Inc. *MATLAB 6.5* (*Release 13*), Natick, MA: The MathWorks, www.mathworks.com; 2002.

29. Furlonge HI, Pantelides CC, Sorensen E. Optimal operation of multivessel batch distillation columns. *AIChE J.* 1999;45:781-801.

Appendix

Model description

The model used in our simulations consists of overall and component material balances. The energy balances are simplified by assuming constant molar flows in the column sections, and the temperatures at all stages are obtained by bubble point calculations [vapor–liquid equilibrium (VLE)] at constant atmospheric pressure, $P = 1$ atm. The activity coefficients for the phase equilibria are modeled by the NRTL (Nationally Recognized Testing Laboratory) equation with parameters taken from Gmehling and Onken[25] and DDBST GmbH[26] for the VLE in the column sections and from Sorensen and Arlt[27] for the liquid–liquid equilibrium (LLE) in the decanter. The thermodynamic data for the mixtures studied in this paper are given in Table A1.

We assume staged distillation column sections with a high number of stages. Constant molar liquid holdups at all stages are assumed. The liquid holdup in the columns is small compared to the initial charge (2%). The vapor holdups are neglected. In the multivessel column the vapor flows are equal in both sections of the column. Perfect mixing and equilibrium in all stages and ideal vapor phase are assumed. The resulting mathematical model takes the form of a set of differential and algebraic equations (DAE system) and is solved in Matlab® [28] with the DAE solver ODE15s.

The initial stage compositions and temperatures constitute

Table A1. Thermodynamic Data for the Mixtures Studied*

Class 2.0-2b: benzene (1)/water (2)/1,4-dioxane (3)			
VLE	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$a_{ij} = a_{ji}$
1-2	1522.2402	1821.8322	0.3547
1-3	−293.8487	434.1172	0.3022
2-3	1551.5163	1097.8251	0.5457
Binodal (25°C)	A_{ij} (K)	A_{ji} (K)	$a_{ij} = a_{ji}$
1-2	1411.4	1320.6	0.2
1-3	129.49	11.834	0.2
2-3	525.41	49.551	0.2
Antoine	A	B	C
1	6.87987	1196.760	219.161
2	8.07131	1730.630	233.426
3	7.43155	1554.679	240.337
Class 3.1-2: ethanol (1)/benzene (2)/water (3)			
VLE	A_{ij} (cal/mol)	A_{ji} (cal/mol)	$a_{ij} = a_{ji}$
1-2	775.7625	1118.9759	0.6268
1-3	−109.6339	1332.3134	0.3031
2-3	1522.2402	1821.8322	0.3547
Binodal (25°C)	A_{ij} (K)	A_{ji} (K)	$a_{ij} = a_{ji}$
1-2	87.744	118.04	0.2
1-3	−441.74	376.33	0.2
2-3	986.99	2797.7	0.2
Antoine	A	B	C
1	8.11220	1592.864	226.184
2	6.87987	1196.760	219.161
3	8.07131	1730.630	233.426

*From Gmehling and Onken,[25] DDBST GmbH,[26] and Sorensen and Arlt.[27]

Table A2. Column and Simulation Data

Parameter	Rectifier	Multivessel Column
Stages per section	$N_{\text{total}} = 51$	$N_r = 25$, $N_s = 25$
Initial feed	$M_F = 5.0$ kmol	$M_F = 5.0$ kmol
Initial decanter holdup	$M_{T0} = 0.5$ kmol	$M_{T0} = 0.5$ kmol
Initial middle vessel holdup	No middle vessel	$M_{F0} = 2.0$ kmol
Initial still holdup	$M_{B0} = 4.5$ Kmol	$M_{B0} = 2.5$ kmol
Stages holdup	$M_i = 1/510$ kmol	$M_i = 1/500$ kmol
Vapor flow	$V = 5$ kmol h^{-1}	$V = 5$ kmol h^{-1} (both sections)

that of the feed at its boiling point (hot column simulations). The ratio of the vapor flow relative to the feed is V/F = 1.1 h^{-1}. This is a measure of how many times the feed is reboiled every hour. Detailed simulation, column, and controller data are given in Tables A2 and A3.

In the rectifier column the simulations were performed as follows:

Filling. Concerning the feed F, 10% was placed in the decanter and the remaining 90% in the still.

Start-Up Period. The column is run under total reflux and no control is applied. The heteroazeotrope starts accumulating in the decanter and the composition profile in the column is established. This period in our simulations was terminated after 1 h.

Main Period. The temperature controller is activated and the setpoint is set at the average of the boiling points of the heteroazeotrope and the component to be recovered in the still, thus implementing the T-strategy. The entrainer-rich phase is partially refluxed. The simulation is terminated when the column has reached its end point. This means that the entrainer-rich and entrainer-lean phases are entirely recovered in the decanter and the still product is entrainer-free.

In the multivessel column the dynamic simulations were performed as follows:

Filling. The feed F was distributed in the still (50%), the middle vessel (40%), and the rest in the decanter (10%).

Start-Up Period. The column is run under total reflux and no control is applied. The heteroazeotrope is accumulated in the decanter and the composition profile is established. This period in our simulations was terminated after 1 h.

Main Period. The level controller in the decanter and the temperature controller in the middle vessel are activated. The entire entrainer-rich phase is refluxed back in the column. The process is terminated when the column has reached its end point, which means that no more of the entrainer-rich phase is

formed in the decanter and the final holdup of this phase in the decanter is negligible ($L_E \rightarrow 0$), as shown in Figure 3.

Model equations

Mass Balances. The total and component mass balances for the multivessel column are given by the following equations:

- Top vessel or decanter

$$\frac{dM_T}{dt} = V_1 - L'_T \tag{A1}$$

$$\frac{dM_T x_{T,j}}{dt} = V_1 y_{1,j} - L'_T x_{T,j} \tag{A2}$$

- Rectifying section (stage $i = 1, \ldots, N_1$)

$$0 = L_{i-1} + V_{i+1} - L_i - V_i \tag{A3}$$

$$M_i \frac{dx_{i,j}}{dt} = L_{i-1} x_{i-1,j} + V_{i+1} y_{i+1,j} - L_i x_{i,j} - V_i y_{i,j} \tag{A4}$$

- Middle vessel

$$\frac{dM_M}{dt} = L_{N1} - L'_M \tag{A5}$$

$$\frac{dM_M x_{M,j}}{dt} = L_{N1} x_{N1,j} - L'_M x_{M,j} \tag{A6}$$

- Stripping section (stage $i = 1, \ldots, N_2$)

Table A3. Initial Feed and Controller Data

Example 1: Serafimov's topological class 2.0-2b (benzene/water/1,4-dioxane)		
Rectifier column: One P temperature controller		
T-controller: $K_C = 0.155$ kmol h^{-1} °C^{-1}	$T_{set} = 85.2$°C	
Multivessel column: One PI level controller and one P temperature controller		
L-controller: $K_C = 5$ h^{-1}	$\tau_I = 1$ h	$M_{set} = 0.001$ kmol
T-controller: $K_C = 0.236$ kmol h^{-1} °C^{-1}	$T_{set} = 90.7$°C	
Example 2: Serafimov's topological class 3.1-2 (ethanol/benzene/water)		
Rectifier column: One P temperature controller		
T-controller: $K_C = 0.41$ kmol h^{-1} °C^{-1}	$T_{set} = 72.2$°C	
Multivessel column: One PI level controller and one P temperature controller		
L-controller: $K_C = 5$ h^{-1}	$\tau_I = 1$ h	$M_{set} = 0.01$ kmol
T-controller: $K_C = 0.485$ kmol h^{-1} °C^{-1}	$T_{set} = 73.2$°C	

$$0 = L_{i-1} + V_{i+1} - L_i - V_i \quad \text{(A7)}$$

$$M_i \frac{dx_{i,j}}{dt} = L_{i-1}x_{i-1,j} + V_{i+1}y_{i+1,j} - L_i x_{i,j} - V_i y_{i,j} \quad \text{(A8)}$$

- Bottom vessel

$$\frac{dM_B}{dt} = L_{N2} - V_B \quad \text{(A9)}$$

$$\frac{dM_B x_{B,j}}{dt} = L_{N2}x_{N2,j} - V_B x_{B,j} \quad \text{(A10)}$$

The closed rectifier (two-vessel) column has only the rectifying column section, and the mass balances are described by Eqs. A1, A2, A3, A4, A9, and A10.

Temperature and Level Controllers. The liquid flows out of the top (L_T) and middle vessel (L_M) are given by proportional temperature controllers or by proportional–integral level controllers, which are described by the following equations:

- P-temperature controller

$$L = L_0 + K(T_m - T_{set}) \quad \text{(A11)}$$

- PI-level controller

$$L = K(M_m - M_{set}) + \frac{K}{\tau} \int (M_m - M_{set})dt \quad \text{(A12)}$$

In addition we do not allow the holdup in a vessel to become zero or negative, which obviously has no physical meaning. Zero holdup in a vessel would result in zero liquid flows in the column section below this vessel. To achieve a smooth "turn off," the liquid reflux out of the vessels determined by the controllers is modified by an exponential function, as described in Furlonge et al.[29]:

$$L' = L\left[1 - \exp\left(-\frac{M}{M_{min}}\right)\right] \quad \text{(A13)}$$

Vapor–Liquid Equilibria (VLE) and Liquid–Liquid Equilibria (LLE)

- VLE

If ideal vapor phase is assumed, vapor–liquid equilibrium for component $j = 1, 2, 3$ is described by the equation

$$Py_j = x_j\gamma_j P_j^s \quad \text{(A14)}$$

The vapor pressures (P^s) are given by the Antoine equation:

$$\log_{10}P_j^s = A_j - \frac{B_j}{T + C_j} \quad \text{(A15)}$$

The activity coefficients (γ_j) are given by the NRTL equation, which is described in Table 4 in Gmehling and Onken.[25]

- LLE

Liquid–liquid equilibrium for component $i = 1, 2, 3$ is described by

$$x_j^{\mathrm{I}}\gamma_j^{\mathrm{I}} = x_j^{\mathrm{II}}\gamma_j^{\mathrm{II}} \quad \text{(A16)}$$

The activity coefficients (γ_j) are given by the NRTL equation, which is described in Table 4 in Gmehling and Onken.[25]

The Matlab files used for the simulations are available at the homepage of S. Skogestad (http://www.nt.ntnu.no/users/skoge).

The symbols used in Eqs. A1–A.16 are explained as follows.

Notation

A, B, C = coefficients for Antoine equation
K = controller gain
L = liquid flows, kmol h^{-1}
L' = modified liquid flows, kmol h^{-1}
M = holdup on the stages, kmol
N = number of stages
P = pressure, mmHg
T = temperature, °C
t = time, h
V = vapor flows, kmol h^{-1}
x = liquid compositions
y = vapor compositions

Greek letters

γ = activity coefficient
τ = integration time, h

Subscripts

B = bottom vessel
i = stage index
j = component index
M = middle vessel
m = measured value
min = minimum value
set = setpoint value
T = top (decanter) vessel
0 = nominal values

Superscripts

I, II = liquid phases in equilibrium
s = saturated