The Curious Behavior of Homogeneous Azeotropic Distillation—Implications for Entrainer Selection

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We examine the simplest homogeneous azeotropic distillation sequence of industrial relevance, where an entrainer is added to a binary azeotrope to recover both azeotropic constituents as pure products. Despite its apparent simplicity, such distillation columns can exhibit an unusual behavior not observed in zeotropic distillation:

- *For some mixtures, separation as a function of reflux goes through a maximum. At infinite reflux, no separation is achieved.*
- *In some cases, achieving the same specifications with a larger number of trays requires a larger reflux.*
- *Sometimes the only feasible separation yields the intermediate component as a pure distillate, while the bottom product contains the light and heavy components.*
- *Sometimes the only feasible separation yields the intermediate component as a pure bottom product while the distillate contains the light and heavy components.*

While these unusual features can be regarded as curiosities, they are essential for proper entrainer selection and design. For a minimum boiling azeotrope, the existing and conflicting entrainer selection rules state that one should use a component that introduces no distillation boundary between the azeotropic constituents (Doherty and Caldarola, 1985), and either a low or high boiling component that introduces no additional azeotrope or a component which introduces new minimum boiling azeotropes (Stichlmair et al., 1989). By taking advantage of the curious aforementioned features, as well as our experience involving more than 400 mixtures, we have been able to analyze the assumptions behind these criteria, show when those assumptions break down, and therefore understand the limitations of the criteria.

Introduction

Separating azeotropic mixtures into pure components is a task encountered commonly in the chemical industry. If pressure-swing distillation cannot be used (because the azeotrope composition does not vary much with pressure or because the required pressure leads to product degradation), there are four basic methods to separate a binary azeotrope through distillation:

- Homogeneous azeotropic distillation
- Heterogeneous azeotropic distillation
- Reactive distillation
- "Salted" distillation

These four techniques all involve the addition of a third component, but the action of this entrainer depends on the considered type of distillation. It may alter the relative volatility of the two azeotropic constituents without inducing liquid–liquid phase separation (homogeneous azeotropic distillation), alter the relative volatility and induce a liquid–liquid phase separation (heterogeneous azeotropic distillation), react reversely with one of the azeotropic constituent (reactive distillation), or dissociate ionically and change the azeotrope composition ("salted" distillation). Heterogeneous azeotropic distillation is often preferred industrially because the decantation involved in the condenser makes the scheme attractive economically, but suffers from a major drawback: operating such columns can be very tricky, because upsets can induce

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phase separation inside the column, leading to a severe loss of efficiency (Kovack and Seider, 1987). Because homogeneous azeotropic distillation columns are much easier to operate (Jacobsen et al., 1990) and because they can outperform heterogeneous azeotropic distillation columns that separate the same mixture (Knapp and Doherty, 1990), homogeneous azeotropic distillation is an economically attractive way of separating binary azeotropes.

Given a binary azeotrope to be separated into two pure components, the design of a homogeneous azeotropic distillation sequence performing this separation is usually carried out in two steps: first potential entrainers are screened, and then a separation sequence is synthesized for each selected entrainer. The first step is critical, since an economically optimal design made with an average entrainer can be much more costly than an average design using the best entrainer. Screening potential entrainers should be done with the help of "necessary conditions." If a chemical does not satisfy a given "necessary condition," it *cannot* make the described separation feasible and should therefore be discarded. A "sufficient condition" has the advantage that separation is always feasible with entrainers that satisfy it, but there is always the possibility of missing some entrainers that might be interesting. Over the years, several entrainer selection rules have been developed. However, before analyzing the existing entrainer selection criteria, a good understanding of homogeneous azeotropic distillation is required because homogeneous azeotropic distillation columns can behave in a very unusual manner. Among their strange features, we have found that:

- Increasing reflux in a given column does not always increase separation. In fact, in many cases, there is no separation at all at infinite reflux.
- Meeting the same specifications with a larger number of trays sometimes requires higher internal flows.
- Sometimes, separation is feasible, but neither the direct nor the indirect sequence is possible. Indeed, there are cases where we can recover the intermediate boiler as a pure distillate product, but not the light boiler. There are also cases where we can recover the intermediate boiler as a pure bottom product, but not the heavy boiler.

This article demonstrates the unusual features of homogeneous azeotropic distillation columns and presents the existing entrainer selection criteria, their assumptions, and limitations.

Unusual Behavior of Azeotropic Columns

Background

The term "homogeneous azeotropic distillation" covers the general notion of azeotropic forming mixtures where no reaction or liquid-liquid phase separation takes place. Therefore, this term includes the case where a solvent enhances separation (extractive distillation), as well as the case where the added component introduces a new azeotrope which is removed as either the distillate or the bottoms (classical definition of azeotropic distillation). But it also includes distillation-based separation schemes that are neither extractive nor azeotropic distillation in the conventional sense.

Homogeneous azeotropic distillation units perform the separation of a binary azeotrope into two pure components through the addition of an entrainer that alters the relative volatility of the two azeotrope constituents without inducing liquid–liquid phase separation. Usually, this separation requires two distillation columns (Figure 1).

The first column (called the azeotropic column or the extractive column in the special case of extractive distillation) yields one azeotropic constituent as a pure product, while the other product contains the entrainer and the other azeotropic component. The azeotropic column achieves "no separation at all" when the composition of one of the two products is identical with that of one of the two feeds (this implies that the column just performs a partial mixing of the two feeds). When the entrainer feed and the azeotropic feed are located on different trays, there is an additional section between the two feeds (middle section), which in the case of extractive distillation is called extractive section. The second column (called entrainer recovery column) separates the second azeotropic constituent from the entrainer. The entrainer is usually recycled to the azeotropic column.

Figure 1 depicts the situation typically encountered in industry. Because maximum boiling azeotropes are far less common than minimum boiling azeotropes, homogeneous azeotropic distillation sequences usually separate minimum boiling azeotropes. The entrainer is usually a heavy boiler, fed close to the top of the extractive column. The light boiler is recovered as a pure distillate in the extractive column, while the intermediate boiler is recovered as a pure distillate of the entrainer recovery column. Note that although this is the most commonly used separation sequence, this is not the only possibility (Doherty and Caldarola, 1985; Stichlmair et al., 1989).

Because of the large number of possible separation sequences, we use here a broad definition of separability. Given a binary azeotrope A-B and a candidate entrainer E, we say that separation is feasible and that E acts as entrainer for the A-B azeotrope if there exists at least one separation sequence (with an arbitrary number of columns and recycles) which yields both A and B as pure products. Note that A and B can be recovered as top or bottom products. Also, note that the recycles do not have to contain only pure E; in some cases, an azeotrope of E and either A or B, or even a ternary azeotrope is recycled.

For the examples in this article, we assume that the thermodynamic properties of the ternary mixture azeotropic component #1-azeotropic component #2-entrainer are perfectly described by the Wilson equation (liquid phase), the Antoine equation, and the ideal gas equation (vapor phase). Note that

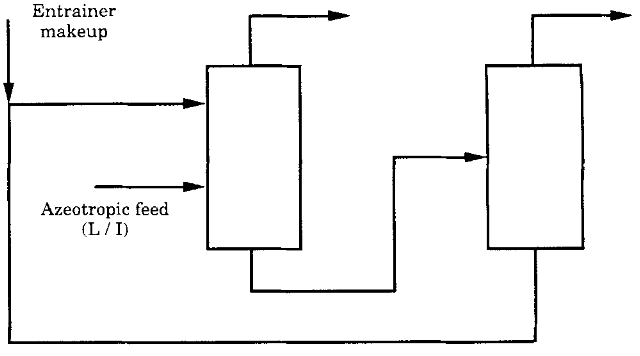


Figure 1. Typical homogeneous azeotropic distillation sequence.

the fundamental conclusions presented here are independent of the specific VLE model employed. We discuss the consequences of these assumptions in the last section.

We examine here the qualitative properties of homogeneous azeotropic distillation columns with two different simulation programs.

The first program is a Caltech-developed dynamic simulation program called Chemsim (Andersen et al., 1989a). This program assumes constant molar overflow and a tray efficiency of 1. We obtain the steady-state column profile by integrating up to a very large time horizon. The thermodynamic routines and data (Wilson coefficients and Antoine coefficients) were provided by Professor Doherty of the University of Massachusetts, Amherst. The second program is Aspen (from Aspen/JSD). We used the RADFRAC routine, in both evaluation and design modes. We included here enthalpy calculations (the constant molar overflow assumption is dropped), but trays were still considered as ideal. We used the Antoine equation coefficients provided by Aspen; we specified the same Wilson equation coefficients as in Chemsim.

When they both converge, these two programs yield results that are qualitatively similar; their quantitative differences come from the difference in the thermodynamic data used as input and from the adoption or not of the constant molar overflow assumption. Although we always obtained convergence with Chemsim, we had in many cases severe convergence problems with Aspen; providing a good initial guess becomes then essential. Upon request, we provide a PC diskette containing the Aspen input files corresponding to the results shown in this article.

Unless stated otherwise, we use the following conventions to refer to a given mixture:

- L (I, H, respectively) corresponds to the component that has the lowest (intermediate, highest, respectively) boiling point; we also denote the entrainer by E.
- Components are listed in the following order: lighter azeotropic constituent–heavier azeotropic constituent–entrainer.
- In the comparison triangle, the upper left (lower right, lower left, respectively) corner corresponds to the lighter azeotropic constituent (heavier azeotropic constituent, entrainer, respectively).

In all simulations presented here, the column operates under atmospheric pressure, there is no pressure drop in the column and the condenser is total. The tray counting starts from the reboiler (number 0) and ends at the top. Finally, in all composition profile figures the *liquid* mole fractions are depicted.

A widely used concept for the description of azeotropic distillation is that of the simple distillation residue curve (hereafter called residue curve). The simple distillation process involves charging a still with a liquid of composition x and gradual heating. The vapor formed is in equilibrium with the liquid left in the still; the vapor is continuously removed from the still.

A residue curve is defined as the locus of the liquid composition remaining at any given time in the still of a simple distillation process. Residue curves are governed by the set of differential equations (Doherty and Perkins, 1978):

$$\frac{dx_i}{d\xi} = y_i - x_i, \quad i = 1, \ldots, C-1$$

where i is the component index, C is the number of pure components in the mixture, y_i (x_i) are the mole fractions of component i in the vapor (liquid) phase, and ξ is the dimensionless warped time.

At infinite reflux, the differential equations which describe packed columns, become identical to the residue curve equations. Thus, residue curves coincide exactly with composition profiles of packed columns operated at total reflux, and they give a very good approximation of composition profiles of tray columns at infinite reflux.

The residue curve map of an ideal mixture is shown in Figure 2a. For such a mixture, the composition of the liquid left in the still approaches pure component H (the heaviest component) for all initial feed compositions. An example of a nonideal mixture is depicted in Figure 2b. A distillation region is a subset of the composition simplex, in which all residue curves originate from a locally lowest-boiling pure component or azeotrope and travel toward a locally highest-boiling one. The curves that separate different distillation regions are called residue curve boundaries (see Figure 2b).

Infinite reflux does not imply maximum separation

The first unusual feature of homogeneous azeotropic distillation columns is the fact that in some cases increasing reflux decreases separation. This never happens in the zeotropic case. When distilling a zeotropic mixture, increasing reflux improves the operating lines, thereby increasing separation. Separation

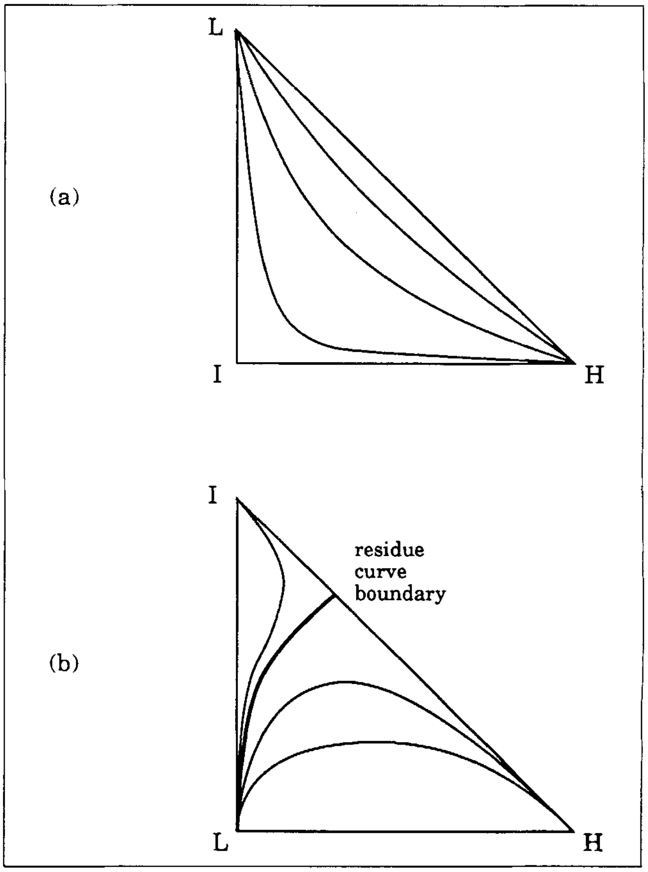


Figure 2. Residue curve maps of an ideal (a) and a nonideal (b) mixture.

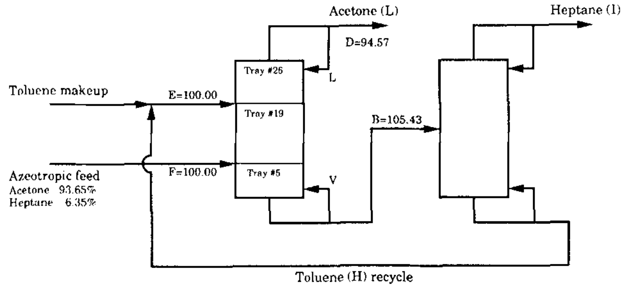


Figure 3a. Acetone-heptane-toluene separation sequence.

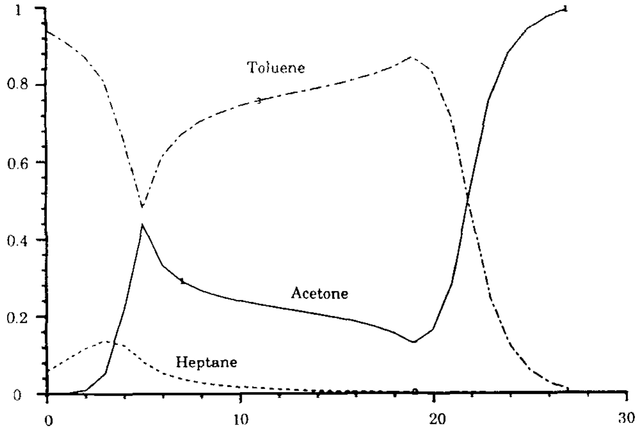


Figure 3b. Acetone (1)-heptane (2)-toluene (3) extractive column composition profile: L/F = 1.035.

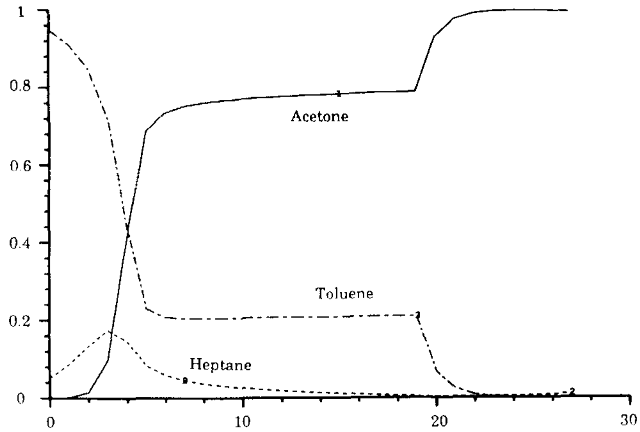


Figure 3c. Acetone (1)-heptane (2)-toluene (3) extractive column composition profile: L/F = 5.582.

is a monotonically increasing function of reflux, and maximum separation in a given column (with a fixed number of trays in each section) is reached at infinite reflux (Henley and Seader, 1981). In the following, we describe the effect of reflux in the less complicated cases of homogeneous azeotropic distillation, namely the cases where no additional azeotrope is introduced by the entrainer. The entrainer can be the heavy, intermediate or light component of the ternary mixture, depending on its boiling temperature.

Heavy Entrainers. This is the case of extractive distillation

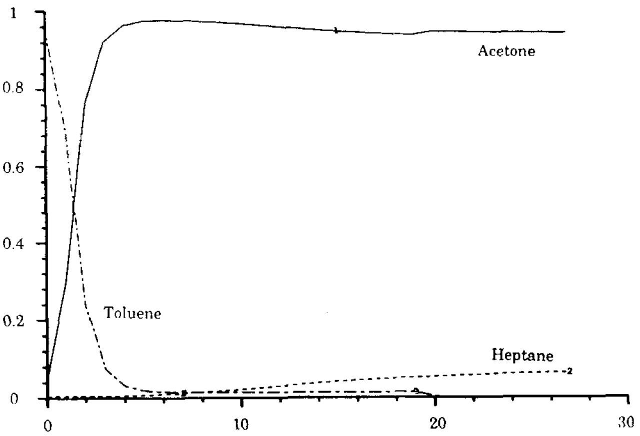


Figure 3d. Acetone (1)-heptane (2)-toluene (3) extractive column composition profile: L/F = 100.0.

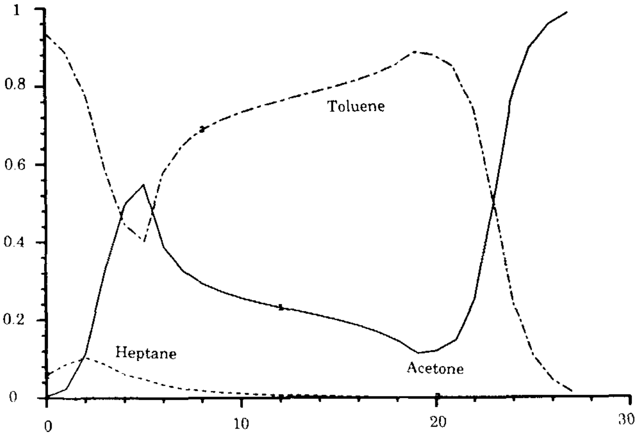


Figure 3e. Acetone (1)-heptane (2)-toluene (3) extractive column composition profile obtained with ASPEN: L/F = 1.355.

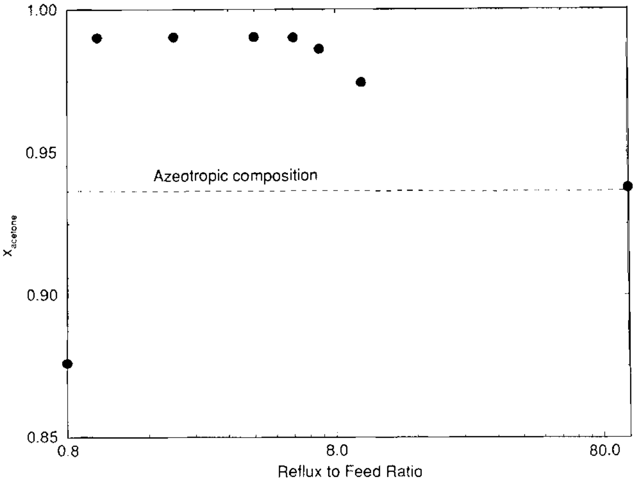


Figure 3f. Acetone composition at distillate vs. reflux to feed ratio.

or the 100 case according to the classification used by Doherty and coworkers. It is known (Van Winkle, 1967) that in this case separation does not increase monotonically with reflux, for a given column and a given feed ratio (ratio of the entrainer feed flow rate to the azeotropic feed flow rate). Indeed, increasing reflux increases separation for low reflux values, while it decreases separation for high reflux values.

This unusual behavior is explained by the fact that the overall effect of a reflux increase is the sum of two competing effects and that the relative magnitude of these effects depends on the operating point. While increasing reflux improves the operating lines in the various sections of the column, thereby increasing separation (positive effect), it also dilutes the entrainer in the extractive section, decreasing the relative volatility of the two azeotropic components, and therefore decreasing separation (negative effect).

Figure 3 shows these two opposing effects in the case of the acetone (L)-heptane (I) azeotrope, using toluene (H-E) as the entrainer. Here, we display the column composition profiles obtained at different reflux flow rates, starting from a small reflux value. The entrainer feed, azeotropic feed, distillate and bottom product flow rates are kept constant. We see that separation first increases for low reflux values, because the operating line improvement (best seen in Figure 3f) overcomes the entrainer dilution. Then, separation reaches a maximum and decreases after that because for high reflux values the entrainer dilution effect takes over the operating line improvement. Indeed, the entrainer concentration in the extractive section goes to zero as reflux goes to infinity. At infinite reflux, the column does not perform any separation.

In Figure 3e we reproduced one of these composition profiles with Aspen, and obtained very similar results by increasing the reflux by 30% over that used with Chemsim (Figure 3b). This quantitative difference is explained by the adoption or

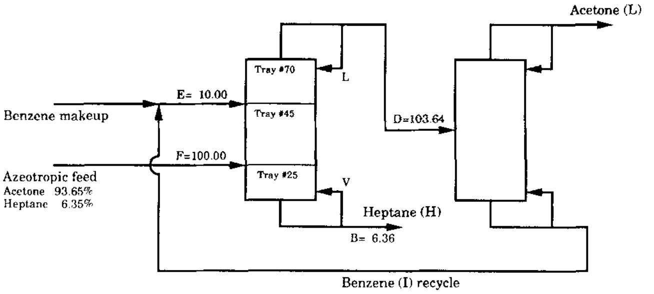


Figure 4a. Acetone-heptane-benzene separation sequence.

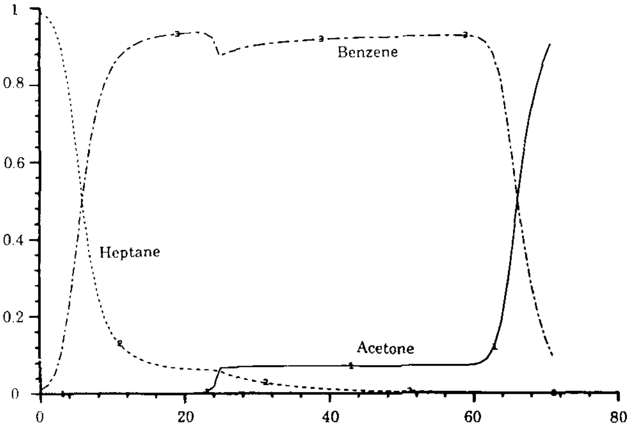


Figure 4b. Acetone-heptane-benzene azeotropic column composition profile: L/F = 5.05.

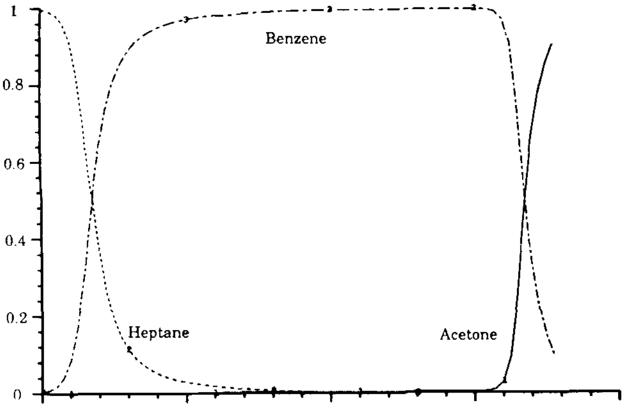


Figure 4c. Acetone-heptane-benzene azeotropic column composition profile: L/F = 100.0.

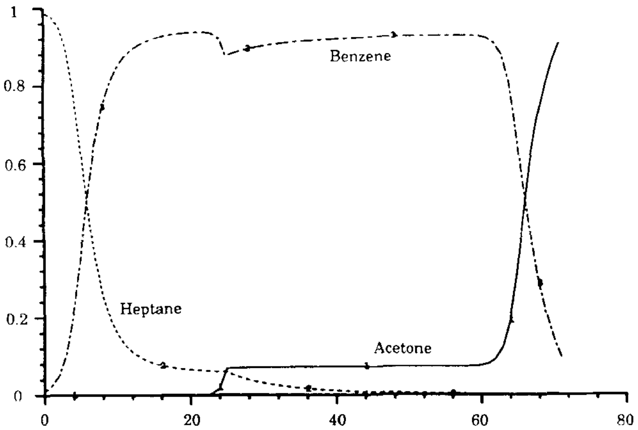


Figure 4d. Acetone-heptane-benzene azeotropic column composition profile obtained with ASPEN: L/F = 5.35.

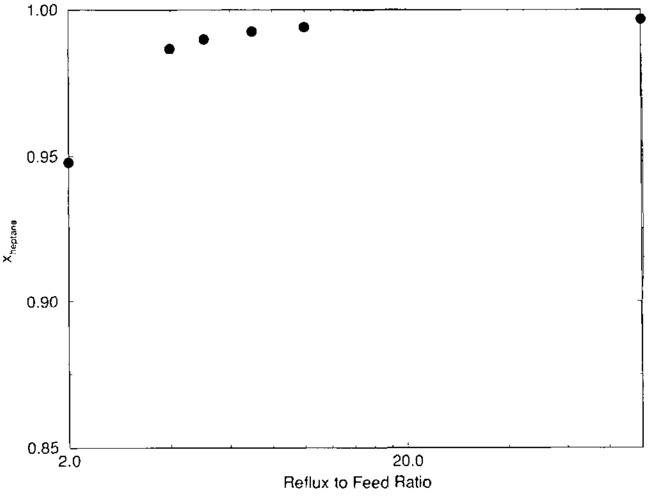


Figure 4e. Heptane composition at bottom vs. reflux to feed ratio.

rejection of the constant molar overflow assumption and is consistent with the results of Knight and Doherty (1986).

Intermediate Entrainers. Contrary to what happens in the heavy entrainer case, increasing reflux does not dilute the intermediate entrainer in the column. Therefore, increasing reflux can only improve the achieved separation. Figure 4 shows the column composition profiles obtained for increasing reflux values in the acetone (L)-heptane (H)-benzene (I-E) case. Benzene, like toluene, can act as an entrainer for the acetone-heptane azeotrope. Again, feed flow rates and product flow rates are kept constant. We see that separation increases monotonically with reflux (Figure 4e) and that infinite reflux does lead to maximum separation. Again, we reproduced one of these composition profiles with Aspen. As in the previous case, we obtained a good agreement between Chemsim and Aspen by increasing the reflux (here by about 10%).

Light Entrainers. In the case of intermediate entrainers that add no azeotropes, separation is a monotonically increasing function of reflux ratio. In the case of heavy entrainers that add no azeotropes (heavy entrainers), separation first increases with the reflux ratio before reaching a maximum and going down to zero for very large reflux ratios. We obtain an even more peculiar situation with light entrainers that add no azeotropes. In this case, separation first increases with reflux ratio, then reaches a maximum, and starts decreasing after that. Contrary to heavy entrainers, however, some separation is still performed with infinite reflux ratio, but not as much as at finite reflux. This unusual behavior of homogeneous azeotropic distillation is depicted by Figure 5 using ethanol (I)-water (H)-methanol (L-E) as example.

In the case of a light entrainer that adds no new azeotropes, the residue curve diagram looks like the one in Figure 2b. In this case, there is a residue curve boundary running from the azeotrope to the entrainer corner. Since residue curves correspond to infinite reflux column profiles it is apparent that the residue curve boundary limits the feasible product compositions at infinite reflux. Therefore, total reflux does not imply maximum separation in this case. At finite reflux the residue curve boundary can be crossed to a certain extent (Van Dongen, 1983; Levy, 1986) and therefore separation is improved. Once again, the overall effect of a reflux increase is the sum of two competing effects. While increasing reflux improves the operating lines, thereby increasing separation (positive effect), it also decreases the extent of the residue curve boundary crossing, limiting the product compositions and therefore decreasing separation (negative effect). Laroche et al. (1992) have shown that separation is always feasible in this case even at infinite reflux; it just needs a high enough entrainer to azeotropic feed ratio. This explains why some separation is still performed at high reflux ratios.

Contrary to the situation observed in normal distillation, infinite reflux often is not the limiting case for homogeneous azeotropic distillation columns. An immediate consequence of this unusual property is that we cannot screen entrainers using only information on the behavior at infinite reflux of the ternary mixture azeotropic component #1-azeotropic component #2-entrainer. Entrainer selection criteria which reject components automatically if they do not make separation feasible at infinite reflux are incomplete, since these rejected entrainers may actually make separation feasible at finite reflux.

This section has demonstrated that the first golden rule of distillation: "If you want better separation with a given column, increase reflux" does not always apply to homogeneous azeotropic distillation columns. The next section shows that the second golden rule of distillation: "If you want better separation with a given reflux flow rate, increase the number of trays" is not always correct in the case of homogeneous azeotropic distillation columns.

Increasing the number of trays may decrease separation

Another unusual feature of homogeneous azeotropic distillation columns described by Andersen et al. (1989b) is the fact that in some cases, meeting the same specifications with a larger number of trays requires higher internal flows. The fact that increasing the number of trays may decrease separation is illustrated by the acetone (L)-heptane (I) azeotrope using toluene (H-E) as the heavy entrainer. In this case, acetone is recovered as top product of the extractive column. Table 1 shows the simulation results of the concentration of acetone in the distillate as the number of trays increases at a high reflux value. Increasing the number of trays from four to five improves separation, but a further increase results in product purity decrease from 95.92% when using five trays to 93.76% when using 26 trays. In the latter case, there is essentially no separation performed in the column, since the concentration of acetone in the distillate is very close to the azeotropic composition. As far as we know, this behavior does not occur in zeotropic distillation. There, increasing the number of trays in any column section always increases separation (Henley and Seader, 1981). This improvement may be very small; for instance, adding trays to a section that contains a pinch does not increase separation very much. This unusual behavior of homogeneous azeotropic distillation columns is not clearly understood.

Direct or indirect split?

Homogeneous azeotropic distillation also differs from zeotropic distillation by the order in which we can remove the various components. This order is obvious in the case of zeotropic distillation, but can be counterintuitive for homogeneous azeotropic distillation.

Let us consider a ternary mixture containing a light boiler L, an intermediate boiler I, and a heavy boiler H; let us further assume that this mixture is zeotropic, that is, it forms neither binary nor ternary azeotropes. If we want to separate this mixture into three pure components with just two columns, we have the following alternatives:

- In the direct sequence (Figure 6a), L is recovered as a pure distillate product in the first column. The bottom product, which contains both I and H, is separated in the second column into I (distillate) and H (bottom).
- In the indirect sequence (Figure 6b), H is recovered as a pure bottom product in the first column. The distillate, which contains both L and I, is split in the second column into L (distillate) and I (bottom).

In the zeotropic case, the boiling point order dictates in which order we can remove the various components. The only components we can remove as pure products from the first distillation column are the most volatile component (here L) and the least volatile component (here H). There is no way of obtaining I, neither as a pure distillate nor as a pure bottom.

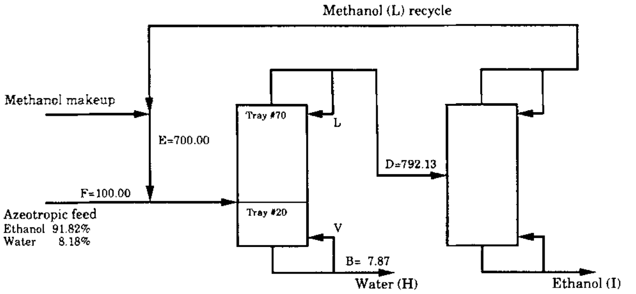


Figure 5a. Ethanol-water-methanol separation sequence.

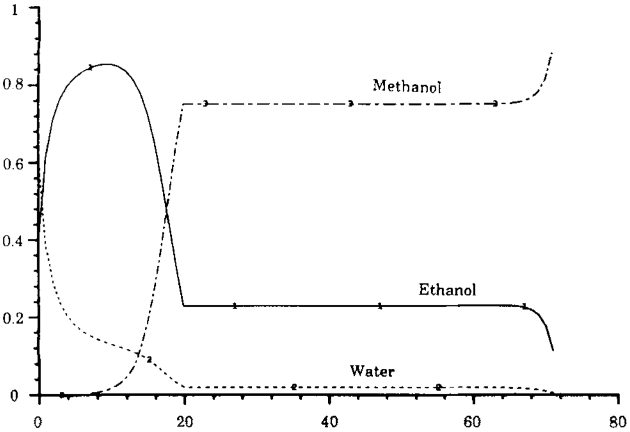


Figure 5b. Ethanol (1)-water (2)-methanol (3) azeotropic column composition profile: L/F = 4.0.

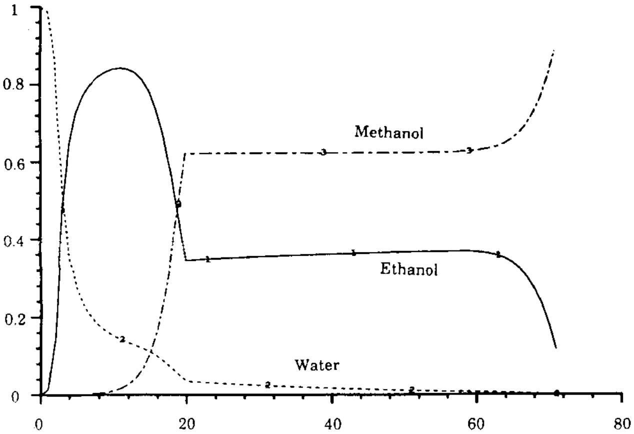


Figure 5c. Ethanol (1)-water (2)-methanol (3) azeotropic column composition profile: L/F = 9.7.

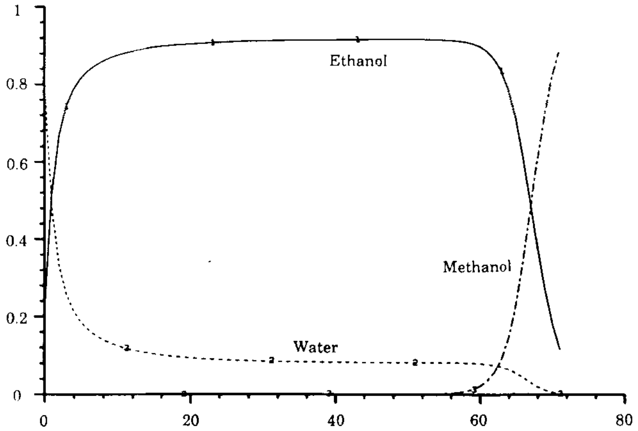


Figure 5d. Ethanol (1)-water (2)-methanol (3) azeotropic column composition profile: L/F = 10,000.0.

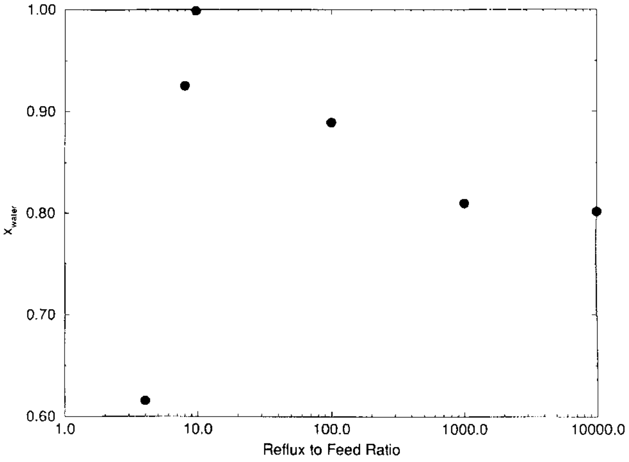


Figure 5e. Water composition at bottom vs. reflux to feed ratio.

Once again, homogeneous azeotropic distillation columns may violate this rule. There are cases where neither the direct split nor the indirect split is possible, but where separation is feasible because we can recover the intermediate component either in the distillate or in the bottom product. This very unusual behavior is illustrated with two different mixtures in Figures 7 and 8 (again, comparable results are obtained with Aspen):

In Figure 7, we use chlorobenzene (H-E) as entrainer for the ethyl ethanoate (L)-ethanol (I) azeotrope. A feasible separation sequence takes ethanol, the intermediate boiler, to the top of the extractive column, leaving ethyl ethanoate and chlorobenzene, the light and heavy boilers, together in the bottom. These two components are then separated in the entrainer recovery column. We were unable to synthesize an extractive column which gives pure ethyl ethanoate. Experimental evidence of this behavior has been recorded first by Buell and Boatright (1947), in the case of cis- and trans-butene-2/1,3-butadiene/furfural and more recently by Berg and Yeh (1985) with several mixtures, including acetone-isopropyl ether-DMSO.

Table 1. Increasing the Number of Trays Decreases Separation in the Acetone-Heptane-Toluene Case

Number of Trays (Middle Section)	Acetone Concentration in the Distillate
4	0.9520
5	0.9592
6	0.9581
8	0.9542
11	0.9491
26	0.9376

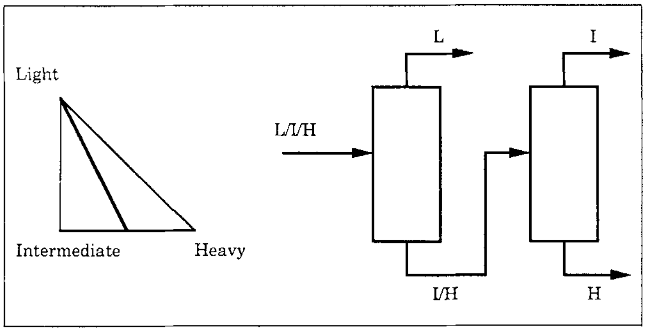


Figure 6a. Direct separation sequence for zeotropic mixtures.

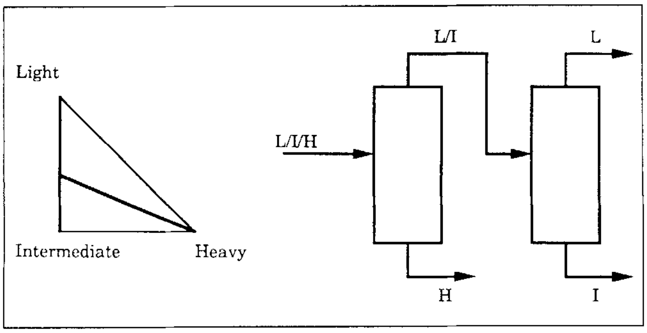
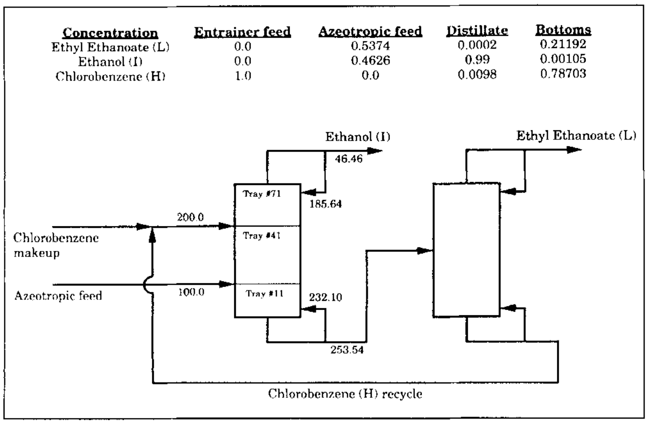


Figure 6b. Indirect separation sequence for zeotropic mixtures.

In Figure 8, we use acetone (L-E) as entrainer for the methyl ethyl ketone (I)-water (H) azeotrope. A feasible separation sequence takes methyl ethyl ketone, the intermediate boiler, to the bottom of the azeotropic column, while the distillate recovers acetone and water, the light and heavy boilers. The entrainer recovery column yields pure water as bottom product and pure acetone as distillate. Acetone is then recycled and acts as entrainer. Again, we were unable to synthesize an azeotropic column which yields water as a pure product. We are not aware of any case reported in the literature where the intermediate component is recovered as the bottom product of the azeotropic column.



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethyl Ethanoate (L)	0.0	0.5374	0.0002	0.21192
Ethanol (I)	0.0	0.4626	0.99	0.00105
Chlorobenzene (H)	1.0	0.0	0.0098	0.78703

Figure 7a. Ethyl ethanoate-ethanol-chlorobenzene separation sequence.

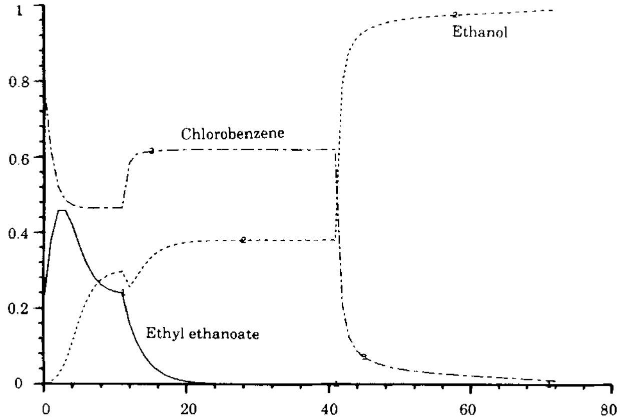


Figure 7b. Ethyl ethanoate (1)-ethanol (2)-chlorobenzene (3) extractive column composition profile: L/F = 1.8564.

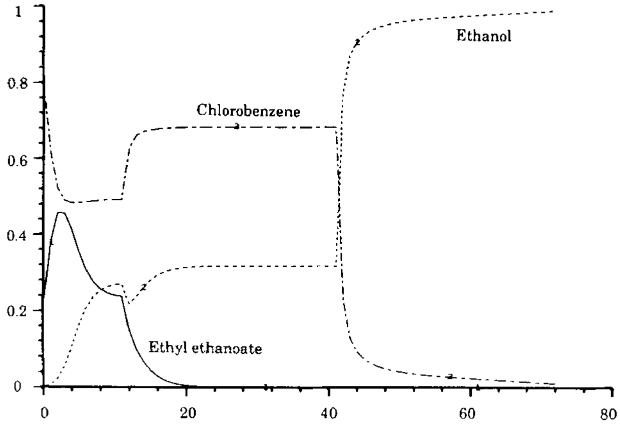


Figure 7c. Ethyl ethanoate (1)-ethanol (2)-chlorobenzene (3) extractive column composition profile obtained with ASPEN: L/F = 1.8564.

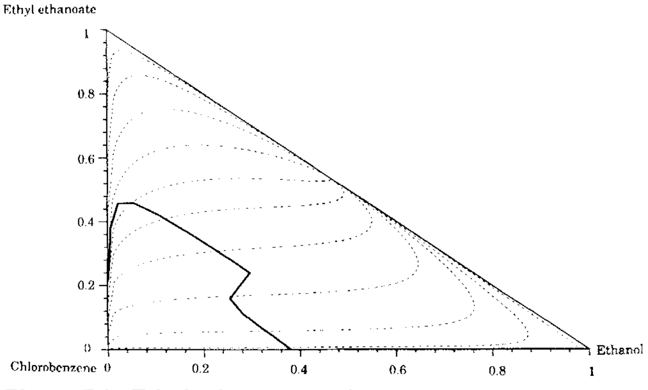
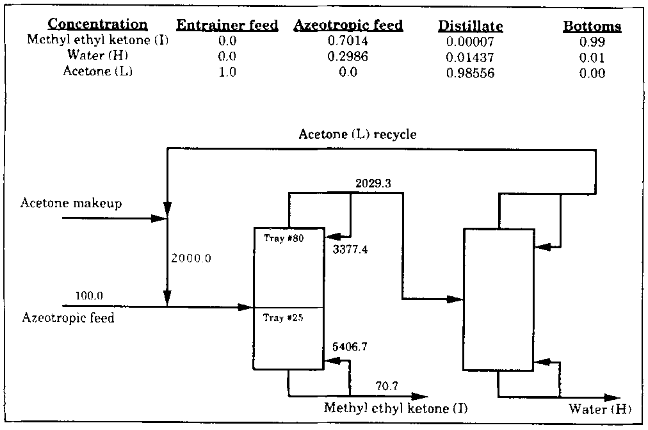


Figure 7d. Ethyl ethanoate-ethanol-chlorobenzene residue curve diagram and extractive column composition profile.

Two separate feeds or one single feed?

In the case of zeotropic distillation, the relative locations of the various feeds (when there are more than one) have no bearing on the separability of a multicomponent mixture. As



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Methyl ethyl ketone (I)	0.0	0.7014	0.00007	0.99
Water (H)	0.0	0.2986	0.01437	0.01
Acetone (L)	1.0	0.0	0.98556	0.00

Figure 8a. Methyl ethyl ketone-water-acetone separation sequence.

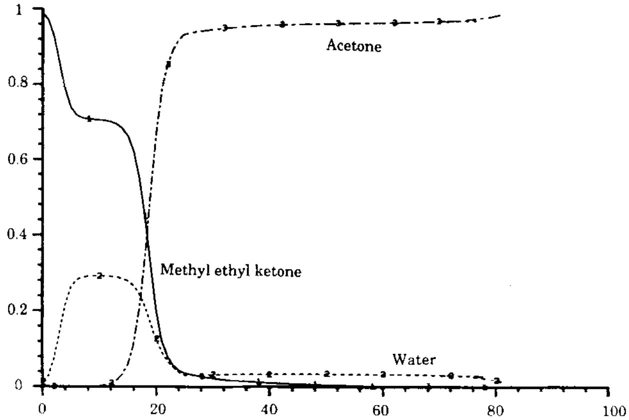


Figure 8c. Methyl ethyl ketone (1)-water (2)-acetone (3) azeotropic column composition profile obtained with ASPEN: L/F = 37.774.

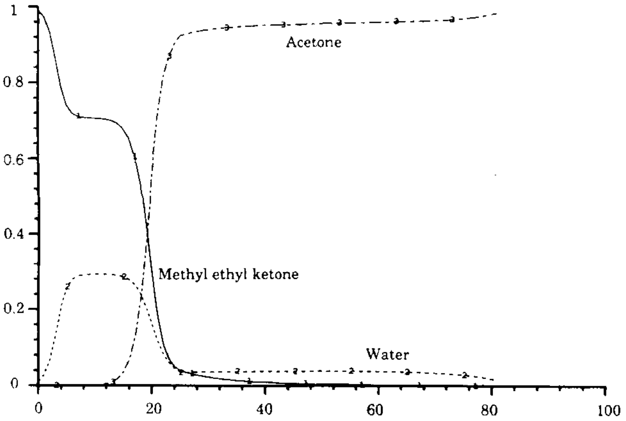


Figure 8b. Methyl ethyl ketone (1)-water (2)-acetone (3) azeotropic column composition profile: L/F = 37.774.

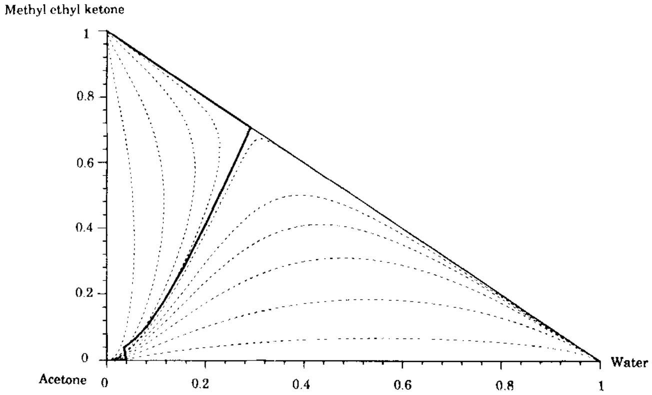


Figure 8d. Methyl ethyl ketone-water-acetone residue curve diagram and azeotropic column composition profile.

seen in the previous paragraph, only the volatility order limits what separation can be performed. This is not always the case for homogeneous azeotropic distillation, where the location of the entrainer feed relative to the azeotropic feed may have a significant impact on separability. In most industrial applications, the entrainer is far less volatile than the two azeotropic constituents. It must, therefore, be fed close to the top of the column and above the azeotropic feed to ensure that the entrainer concentration in the middle, extractive section of the column is large enough to "break" the azeotrope. Separation becomes infeasible if the two feeds are introduced on the same tray because this eliminates the extractive section of the column. Figure 9 illustrates this fact using the ethanol (L)-water (I)-ethylene glycol (H-E) mixture as an example. Because of its low volatility, the ethylene glycol concentration decreases very rapidly above the feed tray, and we do not break the azeotrope.

However, in the cases where extraction does not play any significant role (for example, intermediate and light entrainers which add no new azeotropes), separation is feasible although the entrainer and the azeotrope are fed on the same tray. Figure 10 shows the composition profile of a single-feed acetone (L)-heptane (H)-benzene (I-E) column where heptane is recovered as a pure bottom product. Note that a single-feed column performs almost as well as a double-feed column in this case. In these cases, there are still questions whether it is advantageous or not to use two separate feeds and what are the best feed positions.

Summary

In this section, we have described the surprising behavior of homogeneous azeotropic distillation. Important differences with zeotropic distillation are:

- Increasing reflux in a given column does not always increase separation. Infinite reflux does not necessarily correspond to maximum separation; often separations that are feasible at finite reflux are infeasible at infinite reflux.
- Increasing the number of trays at constant reflux does not always increase separation.
- The order in which components are removed can be counterintuitive, since it is sometimes possible to recover the intermediate boiler first.
- The relative locations of the feeds sometimes limit separability: some separations require that the entrainer feed and the azeotropic feed are separate, some do not.

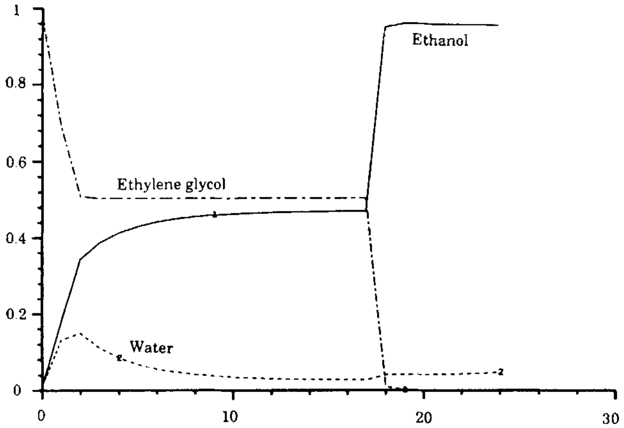


Figure 9a. Ethanol (1)-water (2)-ethylene glycol (3) extractive column composition profile. The combined feed is introduced on tray 17.

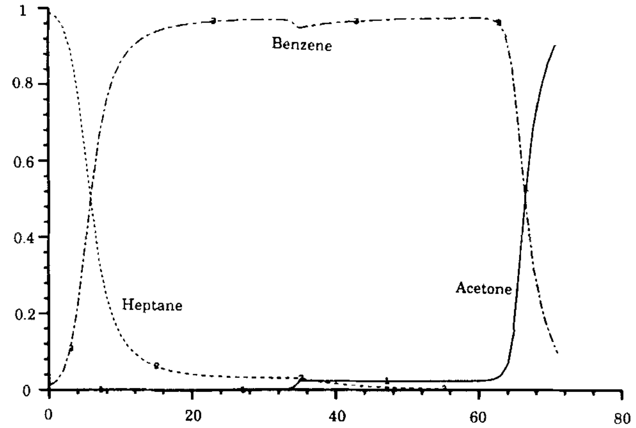


Figure 10a. Acetone (1)-heptane (2)-benzene (3) azeotropic column composition profile. The combined feed is introduced on tray 35.

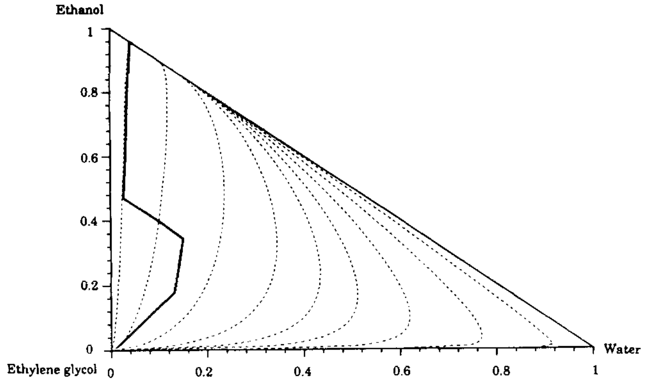


Figure 9b. Ethanol-water-ethylene glycol residue curve diagram and single feed extractive column composition profile.

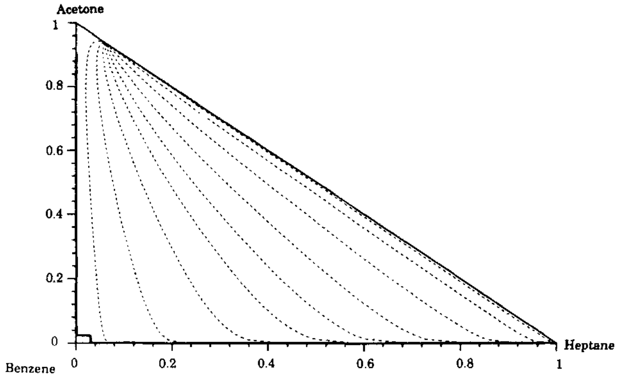


Figure 10b. Acetone-heptane-benzene residue curve diagram and single feed azeotropic column composition profile.

Although these features could be regarded as mere curiosities, they are essential for proper entrainer selection. The next section discusses the existing entrainer selection criteria.

Entrainer Selection Criteria

Existing rules contradict one another

Over the years, several authors (Doherty and Caldarola, 1985; Stichlmair et al., 1989) have tackled the following problem: given a binary azeotrope to be separated into pure components through homogeneous azeotropic distillation and a set of candidate entrainers, find simple conditions that these candidates must satisfy to make separation feasible. A simple necessary condition for separability is quite attractive, since it enables a rapid screening of potential entrainers. Any component that does not satisfy this condition can be immediately discarded. Of course, components that satisfy a necessary condition may not make separation feasible: the selected entrainers must be further examined. On the other hand, a sufficient condition has the advantage that separation is always feasible with entrainers that satisfy the sufficient condition. Of course, there might be components that do not satisfy a sufficient condition, but they still enable the separation of the given azeotrope. Hence, a sufficient condition may exclude a lot of interesting entrainers and therefore it is very useful to know its limitations.

Most existing rules for entrainer selection in homogeneous azeotropic distillation are incorporated in the ones proposed by Doherty and Caldarola (1985) and by Stichlmair et al. (1989). In the case of a minimum boiling azeotrope, these two rules are as follows:

- *Doherty and Caldarola* (*1985*). According to their criterion, any component "which does not produce an internal distillation boundary between the two components to be separated" can be used as entrainer.
- *Stichlmair et al.* (*1989*). Their criterion has two parts: 1. any component which either has a lower boiling point than both azeotropic components and introduces no new azeotrope ("low boiling substance") or "forms new low boiling binary azeotropes" can be used as entrainer; 2. they consider the process of separating a minimum boiling azeotrope using a high boiling entrainer (extractive distillation) as an absorption process not covered by the first part of their criterion. They accept a high boiler as a possible entrainer for such an "absorption process."

Criterion 1 of Stichlmair et al. and the criterion of Doherty and Caldarola contradict each other. In all cases covered by 1, there is a boundary separating the two azeotropic compo-

Concentration	Entrainer feed	Azeotropic feed	D1	B1	D2	B2
Methyl acetate (L)	0.332	0.676	0.405	0.004	0.332	0.998
Methanol (I)	0.282	0.324	0.251	0.996	0.282	0.002
Hexane (H)	0.386	0.0	0.344	0.0	0.386	0.0

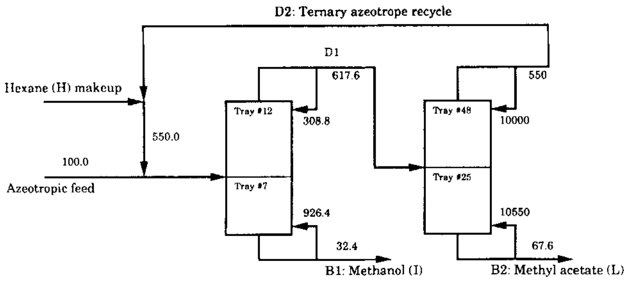


Figure 11a. Hexane-methanol-methyl acetate separation sequence.

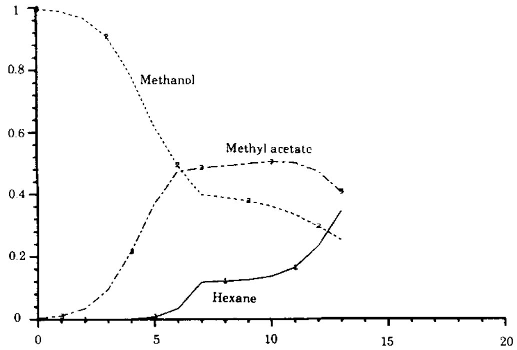


Figure 11b. Hexane (1)-methanol (2)-methyl acetate (3) azeotropic column composition profile.

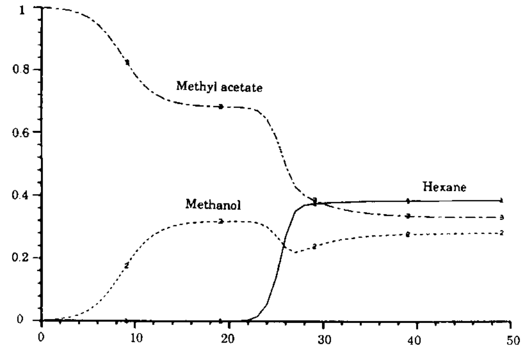


Figure 11c. Hexane (1)-methanol (2)-methyl acetate (3) entrainer recovery column composition profile.

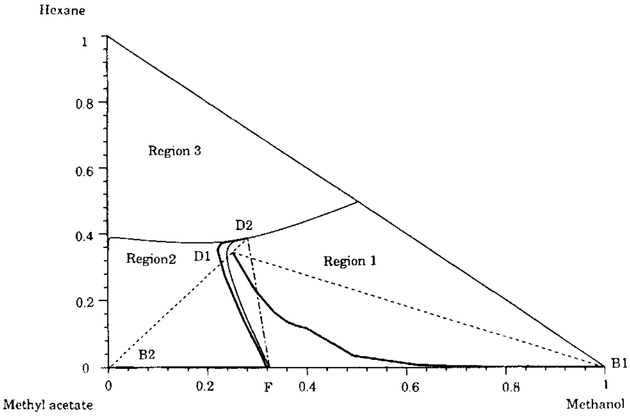


Figure 11d. Composition profiles of the two hexane-methanol-methyl acetate separation sequence columns lie in different distillation regions.

nents. The column sequence uses the curvature of the boundary to achieve separation. On the other hand, although Doherty and Caldarola were aware of this type of separation, they chose to neglect it and hence all these cases do not satisfy their criterion. For instance, light entrainers, which introduce no new azeotropes (020 class according to Doherty and coworkers), are automatically accepted by Stichlmair et al. and systematically rejected by Doherty and Caldarola, because these entrainers introduce a boundary that runs from the entrainer to the azeotrope and puts the two azeotropic constituents in different distillation regions. Contrary to the light entrainer case, there is no boundary in the cases of heavy and intermediate entrainers which introduce no new azeotrope (100 and 001 classes, respectively). The criterion of Doherty and Caldarola includes both these two cases, while the first rule of Stichlmair et al. rejects both of them. The second rule of Stichlmair et al. covers the case of heavy entrainers but still intermediate entrainers are not accepted [the separation of an azeotrope using an intermediate boiler, which adds no new azeotropes, was first noticed by Hoffman (1964)].

These apparent contradictions show that there is a need for further clarification of the existing criteria. In the next two sections, we discuss the derivation, the assumptions and the limitations of those two criteria in more detail.

Doherty and Caldarola (1985)

The criterion of Doherty and Caldarola is based on residue curve boundaries. Their argumentation contains two steps: the first step can be found in Van Dongen and Doherty (1985), and the second step in Doherty and Caldarola (1985). The reader is referred to these articles for details. Their argumentation unfolds as follows:

In the first step, they explain why residue curve boundaries limit the range of feasible separations. The idea is that because distillation column profiles at infinite reflux can be approximated by residue curves and because residue curves cannot cross residue curve boundaries, composition profiles cannot cross residue curve boundaries by much. They write (Van Dongen and Doherty, 1985, p. 462): "From (the residue curve) map, we can immediately determine the simple distillation region boundaries and also the general shape of the expected column profiles at infinite reflux and reboil. These profiles and boundaries would then serve to approximate the profiles and region boundaries for the case of finite reflux and reboil ratio." They conclude that "the topology of the residue curve map [...] constrains the range of possible compositions of the distillate and bottom products."

In the second step, they make "the reasonable working assumption (that) material balance lines joining distillate, feed and bottoms compositions in continuous distillation are forbidden to cross simple distillation region boundaries regardless of the operating conditions in the column." With this as-

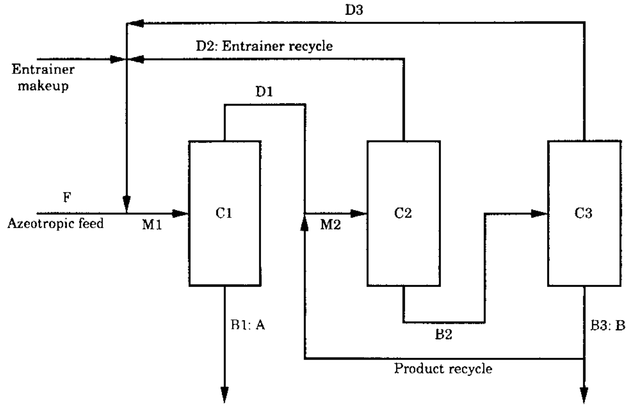


Figure 12a. Stichlmair's corrected separation sequence with product recycle.

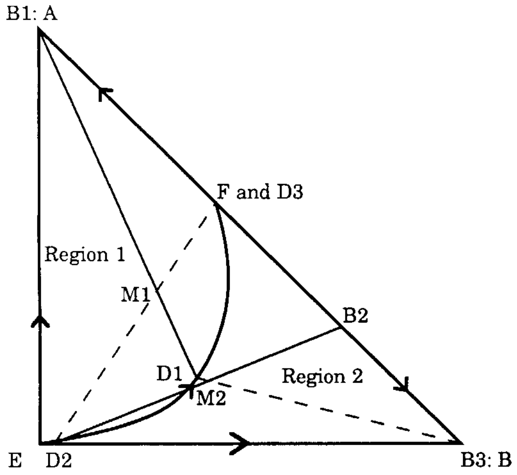


Figure 12b. Stichlmair's corrected separation sequence with product recycle and simplified residue curve diagram.

sumption, they explain why "distillation boundaries within the composition triangle can never be crossed by simple recycle methods," and conclude that "the entrainer selected must be such that the pure components to be separated lie in the same distillation region on a residue curve map."

Actually, Doherty and his coworkers are well aware of the fact that their assumption is not always satisfied. For instance, Figure 11 of Van Dongen and Doherty (1985) and Figure 12 of Levy et al. (1985) display examples of mixtures (hexane-methanol-methyl acetate and acetone-chloroform-benzene, respectively) where distillate and bottom lie in different regions. Levy et al. (1985, p. 470) state that "empirical evidence strongly suggests that the following conjectures are true for continuous azeotropic distillations:

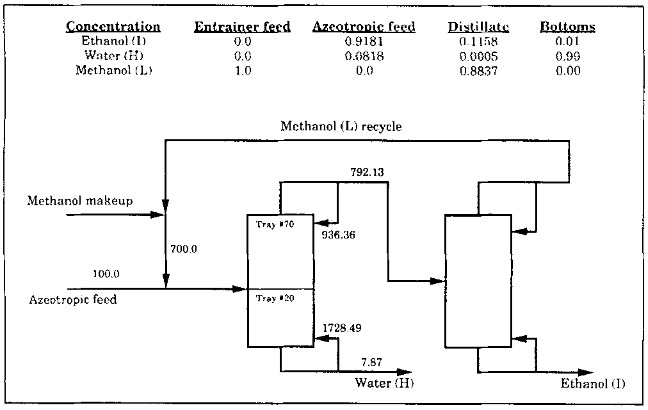
1. If the simple distillation boundary is perfectly linear, then the steady-state composition profile in a continuous distillation column cannot cross the boundary from either side.
2. If the simple distillation boundary is curved, then the steady-state composition profile in a continuous distillation column cannot cross the boundary from the concave side but may cross from the convex side when moving from the product compositions inward."

Doherty and Caldarola (1985, p. 478) state that "for ternary azeotropic mixtures which exhibit simple distillation boundaries, there is reasonable evidence to suggest that continuous distillation profiles and material balance lines do not generally cross their boundaries (see Parts 1 and 2 of this series). There is no definitive study on this very important point, and it is known that sometimes a continuous distillation profile will actually cross a simple distillation boundary in regions of high boundary curvatures."

Doherty and Caldarola, although they knew that simple distillation boundaries can be crossed (Van Dongen, 1983; Levy, 1986), decided to neglect these cases by assuming that crossing such a boundary is an unusual event of little economic significance. We have found that all components that satisfy their criterion always make separation feasible. Hence, their criterion is indeed a sufficient condition for entrainer selection. Therefore, the only questions regarding their rule are those about the assumption of boundary crossing. According to our experience:

Simple distillation boundaries are commonly crossed by composition profiles. Because infinite reflux composition profiles coincide with residue curves (Van Dongen and Doherty, 1985), the distillate and bottom products of a distillation column operated at infinite reflux must lie within the same distillation region. However, we often obtain a different situation at finite reflux, because we can achieve more separation at finite reflux than at infinite reflux. According to our experience, distillate and bottom may often lie in different regions and the assumption that they have to be in the same region is too restrictive in practice. Indeed, the composition profiles of several columns presented in this article cross their corresponding boundaries at their feed trays. Such is the case for the mixtures methyl ethyl ketone (I)-water (H)-acetone (L-E) and ethanol (I)-water (H)-methanol (L-E). In the Appendix, there are examples of simple distillation boundary crossing for the following mixtures: ethanol (I)-water (H)-acetone (L-E), isopropanol (I)-toluene (H)-acetone (L-E), isopropanol (I)-toluene (H)-ethyl ethanoate (L-E) and ethyl ethanoate (I)-ethanol (H)-acetone (L-E).

The feed and composition profile of a column may lie in different distillation regions. Even at infinite reflux, the mass balance line of a distillation column can cross a residue boundary. This phenomenon is made possible by the curvature of residue curve boundaries: the column feed then lies on the concave side of the boundary, while distillate and bottoms lie on the convex side. Figure 11 illustrates this fact in the methyl acetate (L)-methanol (I)-hexane (H-E) case. [Like Van Dongen and Doherty (1985), we use the regular solution equation instead of the Wilson equation for this mixture. We use the same representation convention.] In this case, we can use hexane as entrainer for the methanol-methyl acetate azeotrope. Indeed, a feed of composition D1, which lies in region 1, can be separated in the entrainer recovery column operating at infinite reflux into a distillate D2 and a bottom B2, which both lie in region 2. The entrainer recovery column can perform its task, since we can recover the entrainer and produce almost pure methyl acetate. The azeotropic column also achieves its objective: it separates the mixture of D2 and F into a distillate D1 and a bottom B1, which contains essentially pure methanol. Note that the feed and products of the first column all lie in region 1: the separation performed in this column follows the



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethanol (I)	0.0	0.9181	0.1158	0.01
Water (H)	0.0	0.0818	0.0005	0.99
Methanol (L)	1.0	0.0	0.8837	0.00

Figure 13a. Ethanol-water-methanol separation sequence.

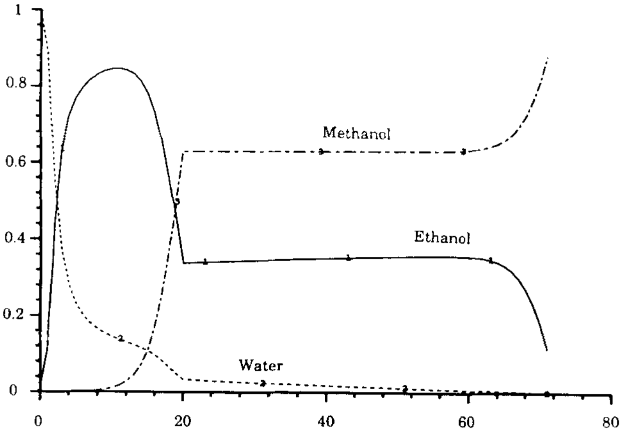


Figure 13b. Ethanol (1)-water (2)-methanol (3) azeotropic column composition profile.

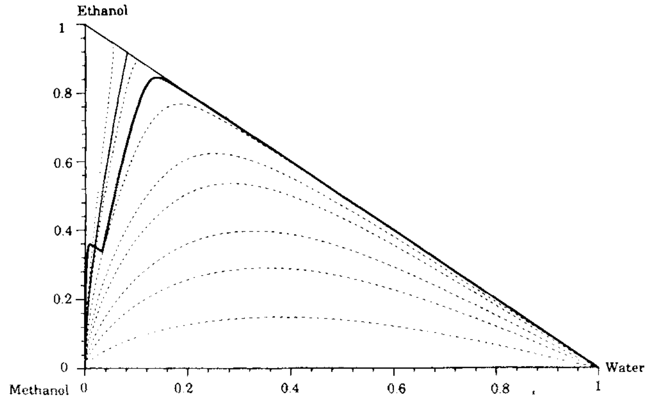


Figure 13c. Ethanol-water-methanol residue curve diagram and azeotropic column composition profile.

rule of Doherty and Caldarola. Also note that Van Dongen (1983) first presented a sequence performing the same separation. The difference between his sequence and ours is that his first column profile crosses the simple distillation boundary, hence the distillate D1 lies in region 2 and the phenomenon described above does not occur.

Distillation boundaries can be crossed by recycle, as communicated to us by Stichlmair (1990). Indeed, in the corrected separation flowsheet of Stichlmair et al. (1989) shown in Figure 12, the distillation boundary that runs from the entrainer to the binary azeotrope is crossed by mixing a small amount of product B to D1: D1 lies in region 1, while the resulting stream M2, which is fed to the second column, lies in region 2. This technique of crossing distillation boundaries is actually quite general: it applies to all situations where the two components to be separated form only one azeotrope and where this azeotrope is a binary saddle in the azeotropic component #1-azeotropic component #2-entrainer residue curve diagram. More details about this three-column separation sequence can be found in Laroche et al. (1992).

Due to the above three facts, the criterion of Doherty and Caldarola rejects many candidate entrainers that actually make separation feasible. For instance, it rejects industrial separations such as the separation of the nitric acid (L)-water (I) maximum boiling azeotrope using sulfuric acid (H-E) as entrainer (Stichlmair et al., 1989). Sulfuric acid is a high boiler which introduces no new azeotrope. In the ternary diagram nitric acid-water-sulfuric acid a distillation boundary runs from the nitric acid-water azeotrope to the pure sulfuric acid point, separating the water and nitric acid corners (cf. Figure 7 of Stichlmair et al.). Another similar separation, which the criterion of Doherty and Caldarola rejects, is that of the hydrochloric acid-water azeotrope using sulfuric acid as entrainer.

It also rejects all light boilers which introduce no new azeotrope (light entrainers). In this situation, the two azeotropic components always lie on opposite sides of a residue curve boundary that runs from the entrainer corner to the binary azeotrope. If this boundary were a straight line in the *mathematical* sense, it could not be crossed, but physical systems always show some curvature, and this is enough to make separation feasible. In practice, we have found that separation is almost always feasible in the case of light entrainers. Separation is feasible even when the boundary looks almost straight, as the ethanol (I)-water (H)-methanol (L-E) system demonstrates (Figure 13). Our experience, based on a study of 416 binary azeotrope-entrainer systems, indicates that:

- Light entrainers are common, almost as common as heavy entrainers: we have found 20 mixtures of the 020 type (minimum boiling binary azeotrope with a light component which does not introduce additional azeotropes) compared with 31 examples of the 100 type (minimum boiling binary azeotrope with a heavy component that does not introduce additional azeotropes).
- Light entrainers often represent the only viable alternative: for many binary azeotropes, we could not find any component that satisfies the criterion of Doherty and Caldarola, while we found light entrainers. For instance, acetone (L-E) can be used as entrainer for the following azeotropes: methyl ethyl ketone (I)-water (H), ethanol (I)-toluene (H), isopropanol (I)-toluene (H), methyl ethyl ketone (I)-isopropanol (H) and ethyl ethanoate (I)-isopropanol (H). Other components were also found to make the separation feasible, but they all introduce a distillation boundary between the two components of interest; they would therefore also be rejected by the criterion of Doherty and Caldarola.
- Light entrainers can perform as well or better than en-

trainers which satisfy the criterion of Doherty and Caldarola. For example: acetone is a much better entrainer (requiring both lower feed ratios and lower reflux ratios) than toluene for the ethyl ethanoate-methyl ethyl ketone azeotrope (in this case acetone is a light entrainer, while toluene is a heavy entrainer); acetone is a much better entrainer than normal butanol for the ethanol-methyl ethyl ketone azeotrope and is comparable to sec-butanol (acetone requires 30% lower feed ratios but 30% higher reflux ratios than sec-butanol). Here acetone is a light entrainer, while normal butanol and sec-butanol are both heavy entrainers.

It should be noted though that there is no published report of an industrial column performing the separation of an azeotrope using a light entrainer. The only experimental evidence of such a separation is the one presented by Hunek et al. (1989). They proposed the use of methanol (L-E) as entrainer for the separation of the ethanol (I)-water (H) azeotrope, and they have "checked its reliability with pilot-plant experiments." At normal operating pressure (atmospheric), methanol is a low boiler which introduces no new azeotrope in the system. In the ternary diagram ethanol-water-methanol, a distillation boundary runs from pure methanol to the ethanol-water azeotrope (see Figure 14).

For more details on the comparative advantages and disadvantages of light and heavy entrainers, the reader is referred to Laroche et al. (1991). However, the importance of light entrainers and therefore whether it is justified or not to neglect them can be concluded only after a thorough economical analysis.

Stichlmair et al. (1989)

Criterion 1 is based directly on the idea that if the considered component does not make separation feasible at infinite reflux, then it can be discarded. Their argumentation unfolds in the following manner:

- They first define the "distillation lines" for a given ternary mixture. "The distillation lines for a ternary mixture can be seen as representing possible concentration profiles in a column when operation is at the total (or high) reflux condition." Note that the procedure they use to determine infinite reflux column profiles can be found in Hoffman (1964). Distillation lines are very similar to residue curves. Orientation aside, the only difference is that distillation lines represent infinite reflux profiles of tray columns, while residue curves represent infinite reflux profiles of packed columns.
- When distilling a zeotropic multicomponent mixture, only the most volatile and least volatile components can be recovered as pure products of a column. They generalize this property to azeotropic mixtures in the following manner: "Only those constituents that are located at the end points of distillation lines can be obtained in pure form."
- Therefore, a candidate entrainer makes separation feasible only if the two azeotropic constituents are end points of distillation lines in the ternary diagram azeotropic components-entrainer. Implicitly they assume that if separation is not feasible at infinite reflux, then it is not feasible at finite reflux.

The first rule of Stichlmair et al. missed the following points:

- *Saddle components can be recovered in pure form*, even at infinite reflux. The generalization made in the second step is incorrect: a component can be obtained as a pure product even if distillation lines neither start from it nor end at it. This point is illustrated by Figure 15 in the acetone (L)-heptane (H)-benzene (I-E) case: although acetone (L) is a saddle, it can be recovered as pure distillate of a column operating at high reflux.
- *Separations which are infeasible at infinite reflux may be feasible at finite reflux*, as we have shown in the first section. Indeed, toluene (H-E) does not make the separation of the acetone (L)-heptane (I) azeotrope feasible at infinite reflux, but it does make this separation feasible at finite reflux (see Figure 3).

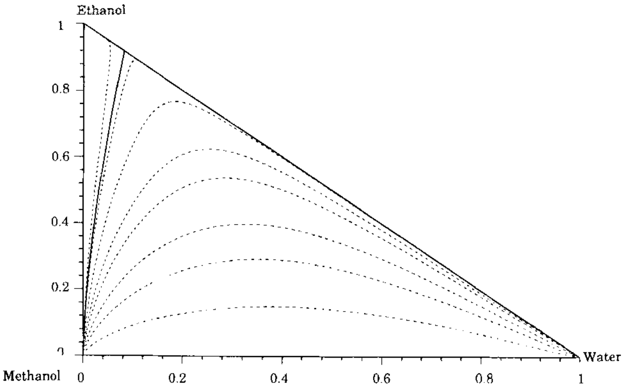


Figure 14. Ethanol-water-methanol residue curve diagram.

As a conclusion, their argumentation breaks down because they generalized from the zeotropic case to the homogeneous azeotropic case and because separations which are infeasible at infinite reflux may be feasible at finite reflux.

As mentioned earlier, Stichlmair et al. realized that their first rule rejects industrial extractive distillations such as the separation of the ethanol (L)-water (I) azeotrope using ethylene glycol (H-E) as the entrainer. They, however, explain this exception to their rule by saying that the extractive section of the homogeneous azeotropic distillation column actually performs an *absorption*, rather than a *distillation*. Their second rule takes care of this omission by including heavy entrainers in the selection criterion.

Through private communications, Stichlmair (1990) provided us with two corrected versions (Figures 12 and 16) of the three-column separation sequence flowsheet shown on Figure 4 of Stichlmair et al. (1989). These two flowsheets differ by the presence of a small product recycle. Although this recycle is not necessary to make separation feasible, its presence makes the crossing of the distillation boundary possible. Indeed, the feed of the second column is located in region 2 of Figure 12, while it is located in region 1 of Figure 16. Although it introduces some economic inefficiency, this recycle might be advantageous from an operational point of view. Note that the desired separation can often be performed in a two-column separation sequence, as illustrated in Figure 13 with the ethanol (I)-water (I)-methanol (L-E) example.

From a practical point of view, the criterion of Stichlmair et al. has two deficiencies:

- This criterion rejects some classes of candidate entrainers which make separation feasible, for example, the intermediate

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.9365	0.99	0.0003
Heptane (H)	0.0	0.0635	0.00	0.0602
Benzene (I)	1.0	0.0	0.01	0.9395

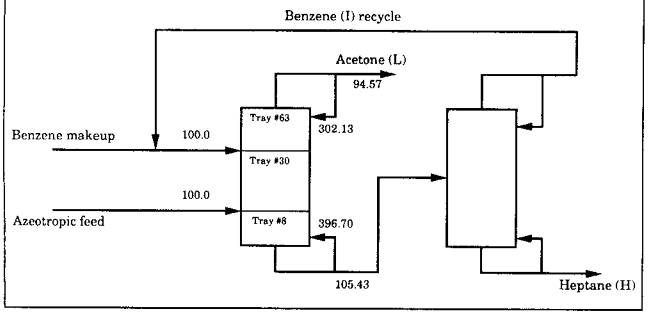


Figure 15a. Acetone-heptane-benzene separation sequence.

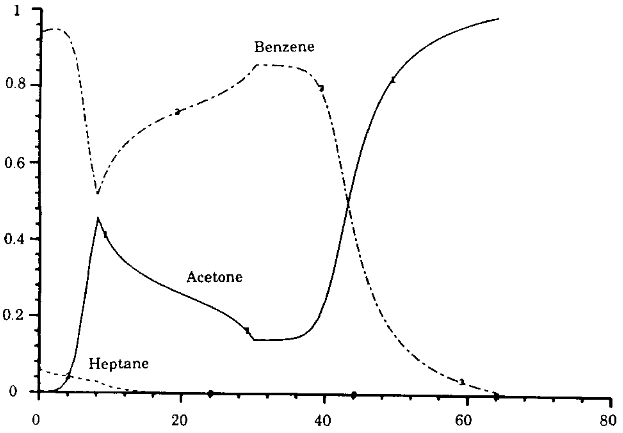


Figure 15b. Acetone (1)-heptane (2)-benzene (3) azeotropic column composition profile.

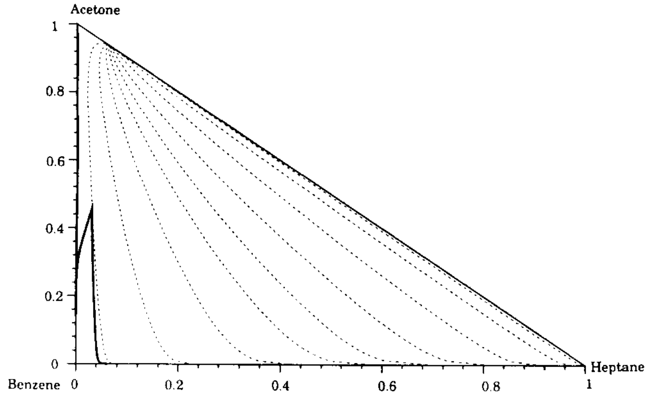


Figure 15c. Acetone-heptane-benzene residue curve diagram and azeotropic column composition profile.

components that do not introduce additional azeotropes. It should be noted though that these rejected classes of entrainers are very rare in practice. Therefore, although their criterion is not exactly a necessary condition, in practice it can be considered as such.

- In its present form, this criterion accepts many candidate entrainers that do not appear to make separation feasible. Indeed, the separation sequence flowsheets presented in Figures 12 and 16 both use the fact that the azeotrope to be separated is a saddle. The composition profile of the second column must connect the entrainer recycle point and a mixture B2 that does not contain any entrainer. This separation is possible when the azeotrope is a saddle: the composition profile moves along the distillation boundary and along the A-B edge. The second column, however, cannot perform the same separation when the A-B azeotrope is a node, and we have not found any sequence enabling us to separate the A-B azeotrope in that case. As a result, their criterion is not a sufficient condition either.

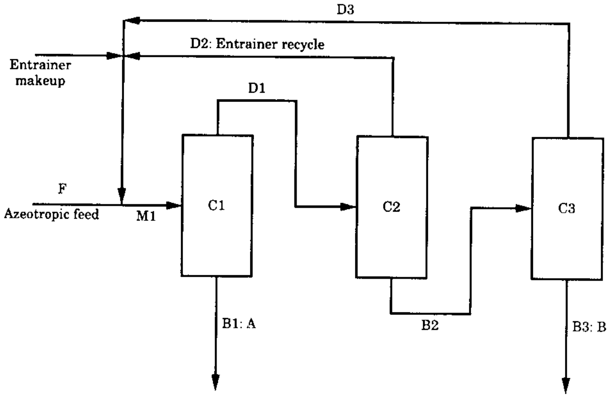


Figure 16a. Stichlmair's corrected separation sequence without product recycle.

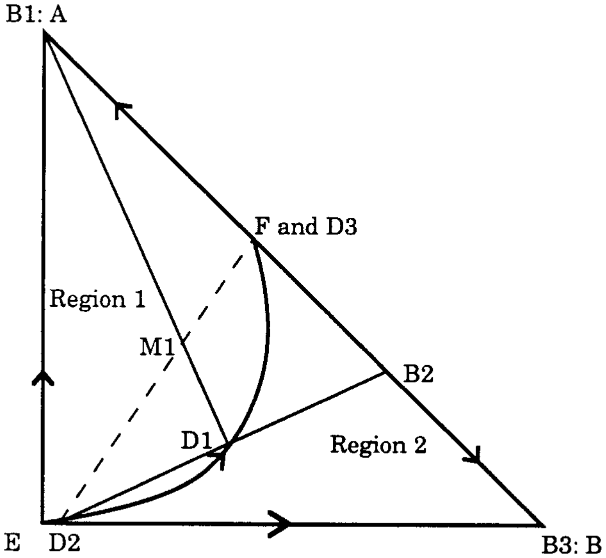


Figure 16b. Stichlmair's corrected separation sequence without product recycle and simplified residue curve diagram.

Entrainer selection in practice

We present here some practical considerations regarding entrainer selection based on the results of an extensive survey of 416 distinct binary minimum boiling azeotrope-entrainer systems. We have plotted the residue curve diagram of each of these mixtures, and then applied the various entrainer selection rules.

In 32 cases out of 416, the two azeotropic constituents are located in the same distillation region:

- In 31 of these 32 cases, the entrainer is a heavy component that does not introduce additional azeotropes.
- In 1 of these 32 cases, the entrainer is an intermediate component that does not introduce any additional azeotrope.

In the remaining 384 out of 416, the two azeotropic constituents are separated by a distillation boundary:

- In 20 of these 384 cases, the entrainer is a light component that does not introduce additional azeotropes.
- In 362 of these 384 cases, the binary azeotropes introduced by the entrainer are all minimum boiling. The considered binary azeotrope is a saddle in 165 cases and a node in the 197 remaining cases.
- In 2 of these 384 cases, at least one of the binary azeotropes introduced by the entrainer is maximum boiling. The considered binary azeotrope is a node in one of the cases and saddle in the other.

This survey indicates that the two azeotropic constituents very often end up in different distillation regions. This results from the fact that minimum boiling azeotropes are far more common than maximum boiling azeotropes. The examination of Figure 10 of Doherty and Caldarola, which displays all the residue curve diagrams such that the two azeotropic components lie in the same distillation region, reveals that the two azeotropic components lie in distinct distillation regions whenever the binary azeotropes introduced by the entrainer are all minimum boiling. Actually, all but 4 of the 35 residue curve diagram classes specified by Doherty and Caldarola require that the entrainer introduces at least one maximum boiling azeotrope. Therefore, we expect such classes to be rather uncommon. At this point, we only know of one example, the butanol (L)-butyl acetate (H)-acetic acid (I-E) mixture (Foucher et al., 1990), which belongs to the 401 class.

According to our experience:

- Heavy components that do not introduce additional azeotropes almost always make separation feasible. These entrainers are commonly used in industry.
- Intermediate components that do not introduce additional azeotropes always make separation feasible. Moreover, a candidate entrainer makes the separation of a given binary azeotrope feasible if the residue curve diagram of the azeotropic component #1-azeotropic component #2-entrainer mixture belongs to the 401 or 410 class (as defined by Doherty and Caldarola, 1985) because these diagrams are very similar to those of intermediate entrainers.
- A candidate entrainer makes the separation of a given binary azeotrope feasible if this azeotrope is a saddle in the residue curve diagram of the azeotropic component #1-azeotropic component #2-entrainer mixture. This observation comes directly from the fact that in this case we can always perform the desired separation using the three-column separation sequences shown in Figures 12 and 16. Light entrainers belong to this category.

It should be noted, however, that many other types of entrainers may lead to separation. However, we tentatively reject them at this point, because we do not know how to perform the desired separation, that is, synthesize the distillation train, with other types of entrainers. For instance, because the three-column separation sequence cannot separate binary azeotropic nodes and because we have not found any other way of separating such azeotropes, we reject candidate entrainers that make the desired azeotrope a node in the residue curve diagram of the azeotropic components-entrainer mixture. There is no point in examining a candidate entrainer for which we cannot find a sequence of distillation columns performing the desired separation.

We, therefore, find that the desired separation can be performed in 217 cases (31 heavy entrainer cases, 1 intermediate entrainer case, 20 light entrainer cases, and 165 saddle cases). Based on this information, we obtain the following results:

- The sufficient criterion of Doherty and Caldarola considers separable the 32 cases where the two azeotropic components lie in the same distillation region (heavy and intermediate entrainers) and rejects the rest. This criterion rejects the 185 cases of light entrainers and saddle azeotropes.
- The criterion of Stichlmair et al. considers separable the 382 cases where the entrainer is either a light component which does not introduce new azeotropes or introduces only minimum boiling azeotropes and the 31 heavy entrainer cases. This criterion misses only the intermediate entrainer, but incorrectly accepts 197 entrainers that do not make separation feasible using the three-column separation sequence (the node azeotrope cases).

Because at least half of the considered entrainers make the desired separation feasible, this survey highlights the need for an efficient entrainer screening procedure. Indeed, designing and optimizing the separation sequence corresponding to each candidate entrainer that makes separation feasible would be very time-consuming. Therefore, we need a procedure that singles out the most promising candidates for further study. In Laroche et al. (1991), we present such a procedure for the case where the entrainer does not introduce additional azeotropes.

Sensitivity to thermodynamic data uncertainty

The qualitative results presented in this article do not depend on the specifics of the thermodynamic relationships used. However, the quantitative results shown here depend heavily on these specifics: the position and curvature of distillation boundaries may change significantly when we change the thermodynamic representation of the mixture. For instance, using the Van Laar equation to describe liquid activity coefficients, instead of the Wilson equation, often increases residue curve boundary curvatures. We have found that many separations used as examples here are easier (they require less entrainer, less reflux and/or less trays) with the Van Laar equation than with the Wilson equation. For instance, ethylene glycol (H-E) appears to be a much better entrainer for the ethanol (L)-water (I) azeotrope if the Van Laar equation is used [as Knapp and Doherty (1990) have done in the flowsheet which is to be patented] rather than the Wilson equation. In some cases [such as ethyl ethanoate (I)-ethanol (H)-methanol (L-E)], separation is feasible if we use the Van Laar equation but is impossible with the Wilson equation. (Although, in principle, the separation is feasible even with the Wilson equation, we were unable to simulate it because it requires enormous reflux, entrainer to feed ratio and/or trays.)

Homogeneous azeotropic distillation is usually sensitive to

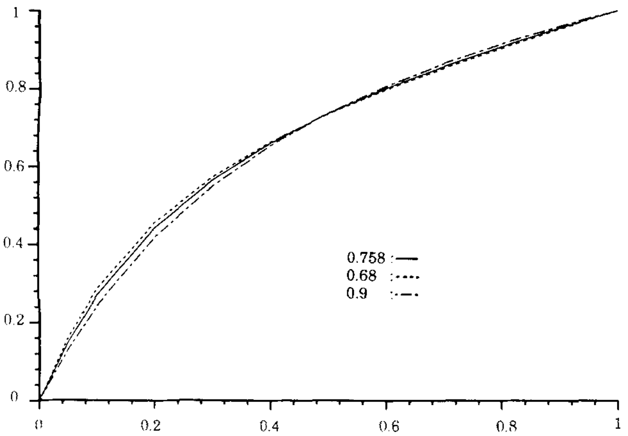


Figure 17. Binary x-y diagram of ethyl ethanoate and toluene for varying Wilson parameters.

thermodynamic data inaccuracy, much more so than zeotropic distillation. Indeed, small deviations in the binary interaction parameters used in activity coefficient calculations can lead to dramatically different results. In practice, this makes homogeneous azeotropic distillation column design very difficult: because these parameters are usually obtained by fitting vapor-liquid equilibrium data over the whole composition range, the error margins obtained for these parameters are fairly large and designs may be uncertain.

This point is illustrated by Figures 17 and 18 with the ethyl ethanoate (L)-methyl ethyl ketone (I)-toluene (H-E) mixture. We varied slightly the binary interaction parameter of toluene and ethyl ethanoate a_{T-EE} around its nominal value, 0.758, keeping all other parameters constant. Figure 17 shows that varying a_{T-EE} from 0.758 to 0.68 or to 0.90 hardly changes the vapor-liquid equilibrium of ethyl ethanoate and toluene; therefore, identifying accurately the value of this parameter within the range 0.68-0.90 would be difficult experimentally. Yet, the behavior of the ethyl ethanoate-methyl ethyl ketone-toluene mixture depends heavily on the precise value of this parameter.

At the nominal value, toluene acts as entrainer for the ethyl ethanoate-methyl ethyl ketone azeotrope, enabling the recovery of ethyl ethanoate as pure top product of the extractive column. When we decrease a_{T-EE} below its nominal value, separation becomes increasingly easy, since it requires a lower minimum reflux ratio for the same feed ratio (Figure 18). When we increase a_{T-EE} above its nominal value, separation becomes more and more difficult, and is impossible for the given feed ratio value when a_{T-EE} is between 0.77 and 0.89. For values above 0.89, separation becomes again increasingly easy with increasing values of a_{T-EE}, but the flowsheet must be modified: we now recover methyl ethyl ketone in the distillate instead of ethyl ethanoate. Therefore, a small error in the evaluation of the binary interaction parameter of ethyl ethanoate and toluene can lead to very different separation sequences.

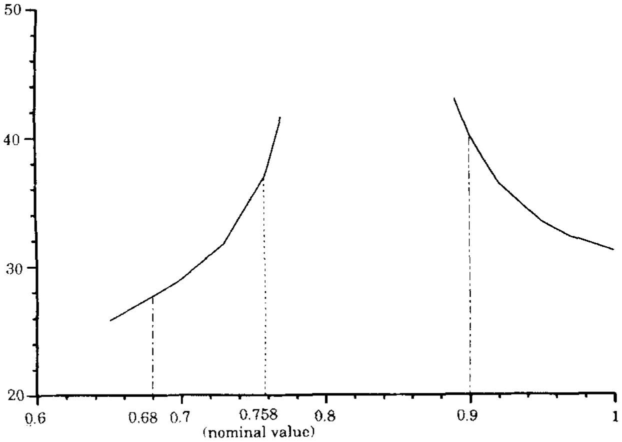


Figure 18. Minimum reflux ratio for varying ethyl ethanoate-toluene Wilson parameters. The feed ratio is equal to 50.

Conclusion

We have shown that homogeneous azeotropic distillation can behave in a very unusual manner. Among its surprising features, we find that:

- One should sometimes decrease reflux to increase purity. In many, but not all cases, increasing reflux above a certain point decreases separation; in many cases, no separation is performed at infinite reflux.
- One should sometimes decrease the number of trays to increase purity. Meeting the same specifications with a larger number of trays may require higher internal flows.
- One can sometimes recover other components than the least volatile or the most volatile as pure products. There are cases where neither the direct nor the indirect sequence is possible, but where separation is still feasible, because we can recover the intermediate boiling component as a pure distillate or pure bottom product.

This unusual behavior has important consequences on the entrainer selection procedure. In particular, since separations which are infeasible at infinite reflux may be feasible at finite reflux, infinite reflux is not the limiting case. A critical review of two existing entrainer screening criteria reveals that they contradict each other. The discussion of their derivation, assumptions and limitations can be summarized in the following:

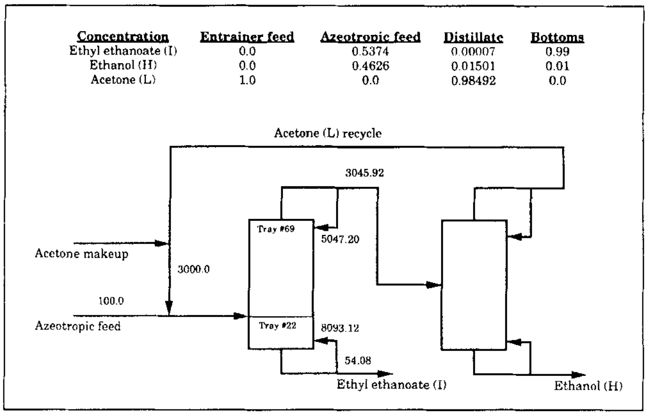
- Doherty and Caldarola developed a sufficient condition based on the assumptions that the feed and composition profile of a distillation column must lie in the same distillation region, regardless of operating conditions and that distillation boundaries cannot be crossed by recycle. We found, however, that these assumptions may often be too restrictive. As a consequence, this criterion rejects many candidate entrainers, among them the class of light entrainers and a couple of industrial separations.
- The first rule of Stichlmair et al. eliminates components that do not make separation feasible at infinite reflux; however, with these components separation may be feasible at finite reflux. It also assumes that saddle components cannot be recovered in pure form. The second rule covers this omission partially by including heavy entrainers, but it still does not include the rare case of intermediate entrainers. More important, their criterion accepts many candidate entrainers that do not appear to make separation feasible (the cases where the azeotropic constituents are separated by a boundary and the binary azeotrope is a node).

Although the qualitative results presented here do not depend on the specifics of the thermodynamics used, the quantitative results shown here depend heavily on these specifics. Homogeneous azeotropic distillation can be very sensitive to thermodynamic data uncertainty. In particular, small variations of the liquid activity coefficient parameters can lead to very different flowsheets.

This article clearly demonstrates that the problem of entrainer selection for homogeneous azeotropic distillation requires more efforts and further studies. This is the subject of related articles (Laroche et al., 1992; Laroche et al., 1991).

Acknowledgment

We gratefully acknowledge the financial support of Rhône-Poulenc,



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethyl ethanoate (I)	0.0	0.5374	0.00007	0.99
Ethanol (H)	0.0	0.4626	0.01501	0.01
Acetone (L)	1.0	0.0	0.98492	0.0

Figure A1a. The ethyl ethanoate-ethanol-acetone separation sequence

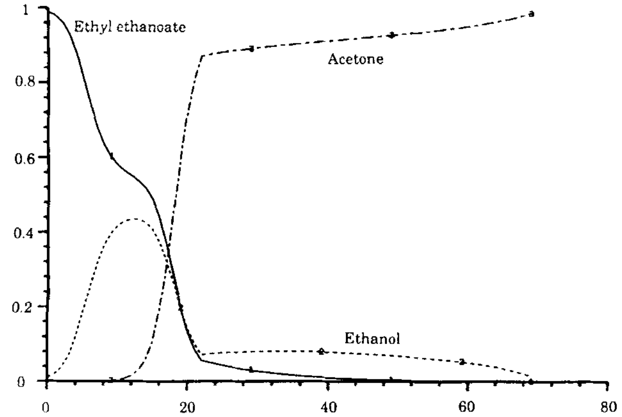


Figure A1b. Ethyl ethanoate (1)-ethanol (2)-acetone (3) azeotropic column composition profile

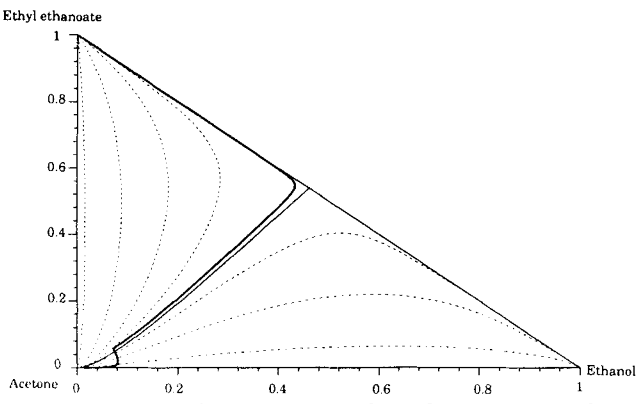
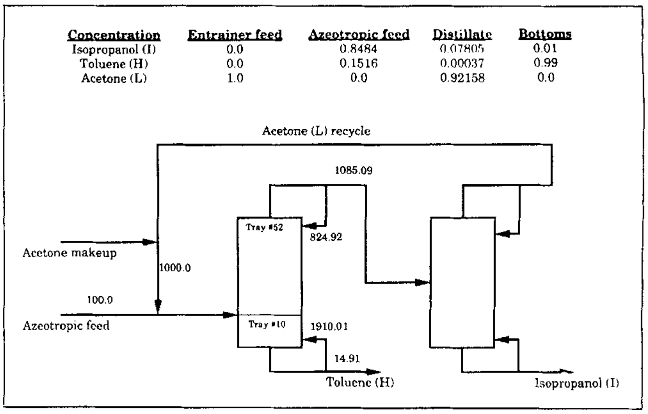


Figure A1c. Ethyl ethanoate-ethanol-acetone residue curve diagram and azeotropic column composition profile



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Isopropanol (I)	0.0	0.8484	0.07805	0.01
Toluene (H)	0.0	0.1516	0.00037	0.99
Acetone (L)	1.0	0.0	0.92158	0.0

Figure A2a. The isopropanol-toluene-acetone separation sequence

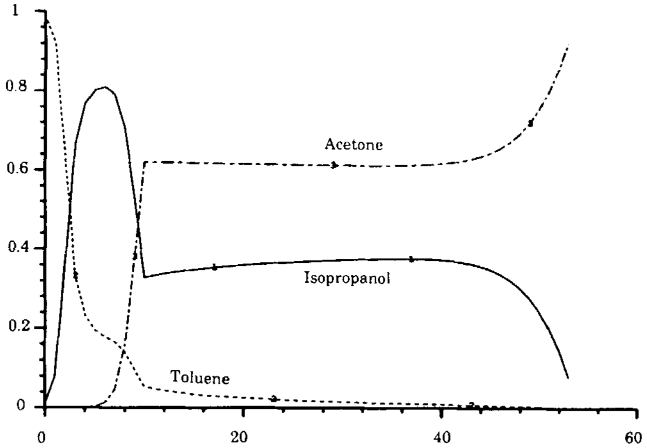


Figure A2b. Isopropanol (1)-toluene (2)-acetone (3) azeotropic column composition profile

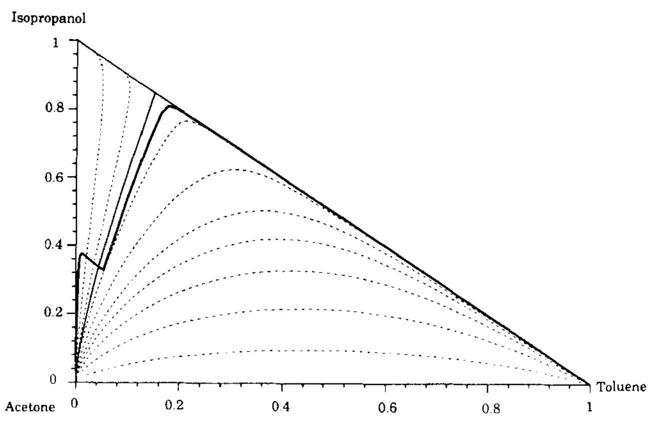


Figure A2c. Isopropanol-toluene-acetone residue curve diagram and azeotropic column composition profile

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethanol (I)	0.0	0.9182	5.5d-6	0.99
Water (H)	0.0	0.0818	0.00073	0.01
Acetone (L)	1.0	0.0	0.99927	0.0

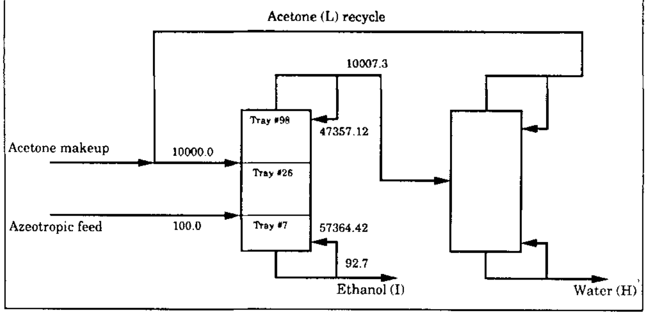


Figure A3a. The ethanol-water-acetone separation sequence

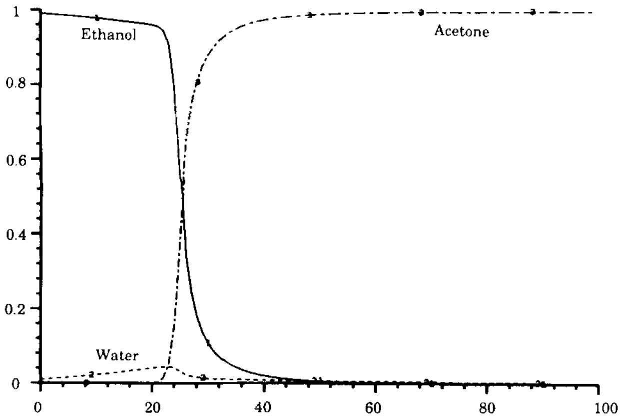


Figure A3b. Ethanol (1)-water (2)-acetone (3) azeotropic column composition profile

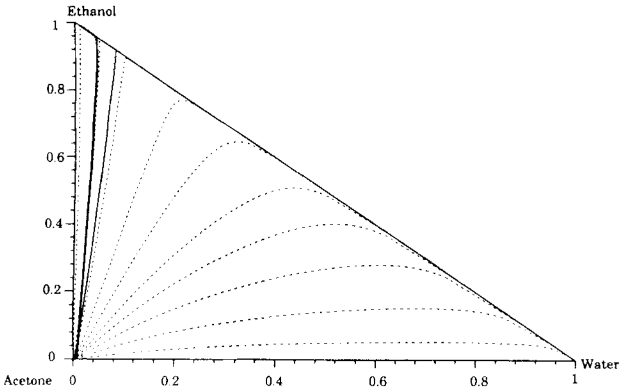


Figure A3c. Ethanol-water-acetone residue curve diagram and azeotropic column composition profile

of the Donors of the Petroleum Research Fund administered by the American Chemical Society, and of the I. S. Latsis Foundation. We thank Prof. Doherty and Jeffrey Knapp (University of Massachusetts, Amherst) for providing us thermodynamic data and subroutines, and Dr. Anthony Skjellum for helping us develop our simulation program. We also thank Prof. Stichlmair (Universität-GH Essen) for several enlightened discussions. Finally, we acknowledge use of the Harwell sparse matrix solver (Hopper, 1981) and of Aspen (from Aspen/JSD).

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Isopropanol (I)	0.2675	0.8484	0.32460	0.01
Toluene (H)	0.0	0.1516	0.00029	0.99
Ethyl ethanoate (L)	0.7325	0.0	0.67511	0.0

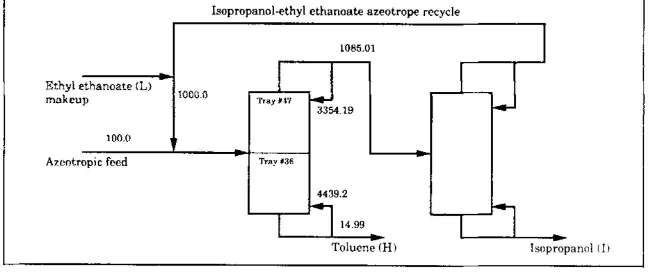


Figure A4a. The isopropanol-toluene-ethyl ethanoate separation sequence

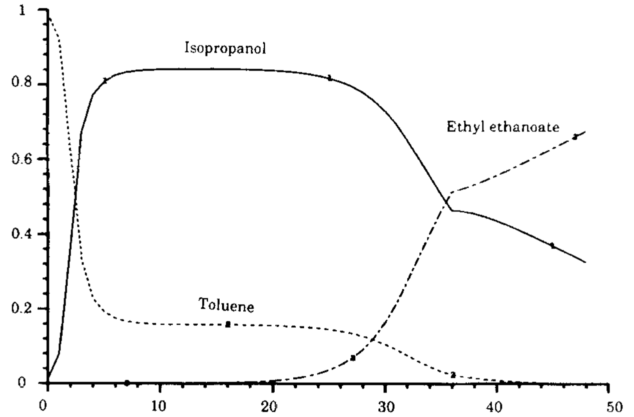


Figure A4b. Isopropanol (1)-toluene (2)-ethyl ethanoate (3) azeotropic column composition profile

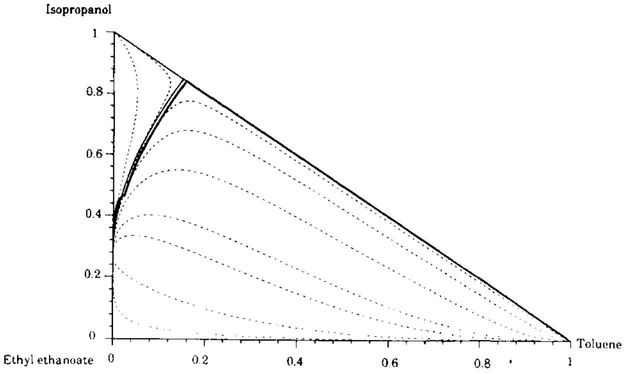


Figure A4c. Isopropanol-toluene-ethyl ethanoate residue curve diagram and azeotropic column composition profile

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Appendix

The Appendix contains flowsheets and composition profiles of the azeotropic columns for the following mixtures:

- Ethyl ethanoate–ethanol–acetone
- Isopropanol–toluene–acetone
- Ethanol–water–acetone
- Isopropanol–toluene–ethyl ethanoate

These separation sequences are designed to show separability and were not optimized in any sense (see Figures A1 to A4). Some of these separations require very high entrainer and/or reflux flow rates, and are therefore impractical, but this is beyond the scope of this article.

Manuscript received Jan. 8, 1991, and revision received June 1, 1992.