HOMOGENEOUS AZEOTROPIC DISTILLATION:
ENTRAINER SELECTION

Dissertation by

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Homogeneous Azeotropic Distillation:

Entrainer Selection

Lionel Laroche

Abstract

We examine the simplest homogeneous azeotropic distillation sequence of industrial relevance, where we add an entrainer to a binary azeotrope in order 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.
- In some cases the only feasible separation yields the intermediate component as a pure distillate while the bottom product contains the light and heavy components.
- In some cases 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. When designing a homogeneous azeotropic sequence which separates a binary azeotrope into two pure products, we must first

choose the entrainer. Currently available entrainer selection criteria are inadequate: They contradict one another and often lead to incorrect conclusions. Indeed, for a minimum boiling azeotrope, the existing entrainer selection rules state that one should use a high boiling component that introduces no additional azeotrope (Benedict & Rubin 1945), an intermediate boiling component that introduces no additional azeotrope (Hoffman 1964), a component which introduces no distillation boundary between the azeotropic constituents (Doherty & Caldarola 1985), and either a low boiling component that introduces no additional azeotrope or a component that introduces new minimum boiling azeotropes (Stichlmair, Fair & Bravo 1989). By taking advantage of the curious aforementioned features, we have been able to understand when these criteria are correct, or incorrect.

In the case of homogeneous azeotropic distillation, separability at finite reflux and at infinite reflux are not equivalent and must be examined separately. By analyzing in detail the profiles of columns operated at infinite reflux, we have:

- shown that a binary azeotrope can be separated with only one distillation column. We present a necessary and sufficient condition that identifies such situations;
- found a necessary and sufficient condition for separability in a two-column sequence. When separation is feasible, this condition indicates the flowsheet of the corresponding separation sequence;
- shown that separation is very often feasible in a three-column separation if the two azeotropic constituents are located in adjacent distillation regions.

Then, we examine two situations where separation is feasible at finite reflux but not at infinite reflux.

Finally, we present practical solutions (in the case of entrainers that add no azeotropes) to two problems of industrial relevance: Given a binary azeotrope that

we want to separate into pure components, and a set of candidate entrainers, how do we determine which one is the best? Also, for each of these entrainers, what is the flowsheet of the feasible separation sequence(s)? We obtain these solutions by analyzing in detail the mechanisms by which heavy, intermediate and light entrainers make separation feasible, using the new notions of equivolatility curves, of isovolatility curves and of local volatility order. We show that the second question finds an easy solution from the volatility order diagram.

This analysis shows that a good entrainer is a component that "breaks" the azeotrope easily (*i.e*,. even when its concentration is small) and yields high relative volatilities between the two azeotropic consituents. Because these attributes can be easily identified in an entrainer from the equivolatility curve diagram of the ternary mixture azeotropic component #1 - azeotropic component #2 - entrainer, we can easily compare entrainers by examining the corresponding equivolatility curve diagrams. We also demonstrate the validity and limits of this method with numerous examples.

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Chapter 1

Introduction

Separating azeotropic mixtures into pure components is a task commonly encountered 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 reversibly with one of the azeotropic constituents (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 phase separation inside the column, leading to a severe loss of efficiency, (Kovack & 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 & Doherty 1990), homogeneous azeotropic distillation is an economically attractive way of separating binary azeotropes.

Given a binary azeotrope that we want to separate into two pure components, the design of an homogeneous azeotropic distillation sequence[1] performing this separation is usually carried out in two steps: We first screen potential entrainers, then synthesize a separation sequence 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 is usually 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. Over the years, several necessary conditions have been developed and by their very nature potential entrainers should meet all of them. However, some of the "necessary conditions" proposed by various researchers (Benedict & Rubin 1945, Hoffman 1964, Doherty & Caldarola 1985, Stichlmair, Fair & Bravo 1989) have been found to contradict one another: Entrainers that satisfy one necessary condition automatically fail another one, and thus separation should never be feasible. This paradox comes from the poor understanding of homogeneous azeotropic distillation. The "necessary" conditions fail because it has not been recognized that homogeneous azeotropic distillation columns can behave in a very unusual

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[1] A separation sequence usually contains two columns. The first column, called extractive column, breaks the azeotrope and yields the first azeotropic constituent as a pure product. The second column, called entrainer recovery column, separates the second azeotropic constituent from the entrainer, which is recycled to the extractive column (see figure 1.1).

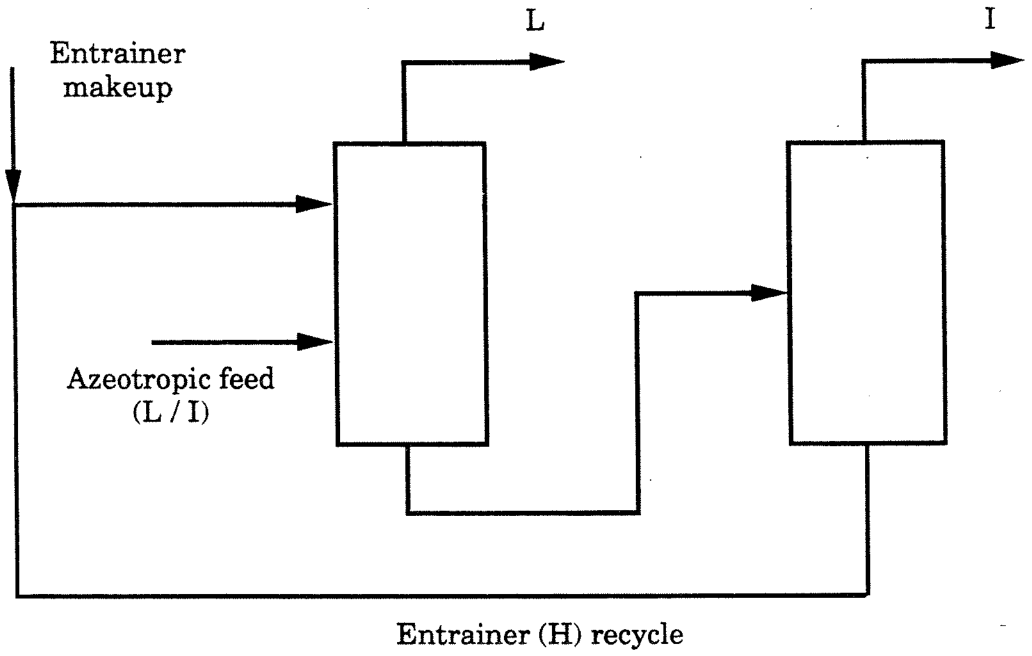


Fig. 1.1: Typical homogeneous azeotropic distillation sequence

manner. Amongst 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 are possible. Indeed, there are cases where we can recover the intermediate boiler but not the light boiler, as a pure distillate product. There are also cases where we can recover the intermediate boiler, but not the heavy boiler,

as a pure bottom product.

Chapter 2 demonstrates the unusual features of homogeneous azeotropic distillation columns, then shows how overlooking the specificity of these columns leads to erroneous entrainer screening criteria. We show that the existing entrainer selection criteria contradict one another: In particular, no component can simultaneously satisfy the "necessary" conditions stated by Doherty & Caldarola and by Stichlmair *et al.* We show that none of these criteria can be used reliably in practice: By examining 15 separable mixtures of azeotropes and entrainers and comparing with the predictions of these criteria, we demonstrate that the criteria reject a significant fraction of suitable entrainers. We also prove that these criteria are wrong because they do not take into account the unusual behavior of homogeneous azeotropic distillation. More precisely, they fail to recognize that separations that are infeasible at infinite reflux may be feasible at finite reflux: Total reflux does not imply maximum separation in the case of homogeneous azeotropic distillation.

Taking these unusual features into account leads us to examine separability at infinite reflux and at finite reflux separately (*cf.* chapter 3). Because the infinite reflux situation represents the limit of high reflux, separability at infinite reflux implies separability at finite reflux, but the converse is not true. At total reflux, composition profiles of packed columns are described by residue curves whereas distillation lines represent the composition profiles of staged columns. By correctly interpreting the information contained in ternary residue curve diagrams (or distillation line diagrams), we obtain the following results:

- A binary azeotrope can be separated into two pure products with only one column. We present a necessary and sufficient condition for separability in one column.

- We develop a necessary and sufficient condition for separability in a two-column separation sequence.
- We show that separation is always feasible in a three-column sequence if the two azeotropic components are located in adjacent distillation regions and if the boundary between these two regions displays no inflexion point and is oriented towards the azeotrope.

These necessary and sufficient conditions have one important additional benefit: They indicate the flowsheet of each feasible separation sequence(s).

In the last section of chapter 3, we examine several practical aspects of separability. We look at the differences between separability at finite reflux and at infinite reflux: Separations that are feasible at infinite reflux are feasible at finite reflux, but the converse is not true. We analyze cases where separation is feasible at finite reflux but not at infinite reflux. Finally, we show that homogeneous azeotropic distillation may be particularly sensitive to vapor-liquid equilibrium data uncertainty.

In practice, the separability criteria presented in chapter 3 have two important advantages: They predict separability reliably and indicate the flowsheet of each feasible separation sequence, including some unusual ones. However, this condition, like the aforementioned conditions (Benedict & Rubin 1945, Hoffman 1964, Doherty & Caldarola 1985, Stichlmair, Fair & Bravo 1989), only answers the following question: Does the considered candidate entrainer enable the separation of a given azeotrope? This entrainer *selection* criterion is actually a *screening* criterion: Given a set of candidate entrainers, it determines which components make separation feasible and which do not; it does not rank those that lead to separability. The obvious way to find the best entrainer is to design, optimize and cost the feasible separation sequence(s) corresponding to each entrainer: The best entrainer yields the lowest cost. However, this is a very time-consuming method. Shortcut comparison methods, both experimental and predictive, exist for heavy entrainers that add no azeotrope.

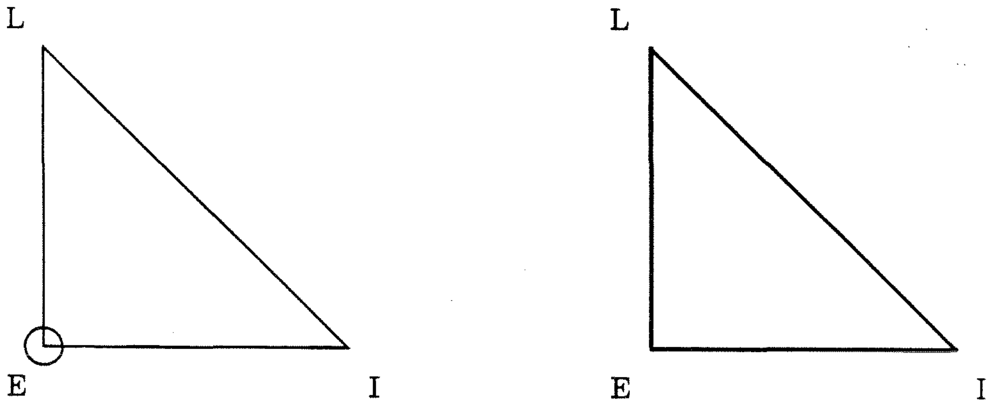
The predictive methods compare entrainers based on an estimated infinite dilution relative volatility (Tassios 1972b, Van Winkle 1976). The experimental methods (Tassios 1970, Tassios 1972a, Kojima & Ochi 1974, Lee & Pahl 1985, Yeh 1986) usually consist in measuring the relative volatility of the two azeotropic constituents at some point or along some segment of the composition space. Figure 1.2 shows which point or which segment these various methods use as their comparison basis:

- Tassios (1970, 1972a) ranks entrainers based on infinite dilution relative volatility, using estimates obtained by gas-liquid chromatography.
- Kojima & Ochi (1974) compare the relative volatility of the two azeotropic consituents along the two edges entrainer - azeotropic component #1 and entrainer - azeotropic component #2. This relative volatility is calculated from binary and ternary bubble-point data (temperature - liquid composition).
- Lee & Pahl (1985) compare the relative volatility of the two azeotropic constituents along the segment shown in figure 1.2, using an Othmer-type equilibrium still to measure vapor-liquid equilibrium data.
- Yeh (1986) draws the pseudo-binary McCabe-Thiele diagram of the two azeotropic consituents at some unspecified entrainer concentration, using an Othmer-type equilibrium still to obtain vapor-liquid equilibrium data.

Both predictive and experimental methods suffer from the same limitations:

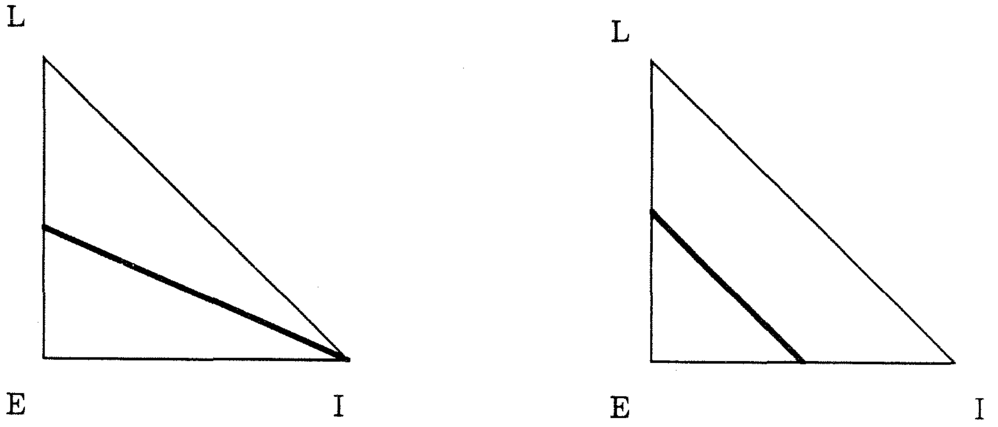
- They only apply to heavy entrainers that add no azeotropes, thereby missing a large number of entrainers.
- These shortcut methods are local in nature: They rank entrainers based on the two azeotropic components' relative volatility in a very restricted area (a point or a segment). This is insufficient to compare entrainers: When we design (or operate) a homogeneous azeotropic distillation column, we vary the entrainer

Fig. 1.2: Comparison points or segments



Tassios

Kojima & Ochi



Lee & Pahl

Yeh

feed and reflux flow rates for a given azeotropic feed flow rate, and the resulting composition profiles span a large region inside the composition space. Over the covered area, the entrainer classification may differ from the classification obtained at that one point or on that one segment. For instance, many shortcut methods rank entrainers by comparing the experimental or calculated relative volatility of the two azeotropic constituents at infinite dilution, *i.e.* when the concentrations of the azeotropic contituents are essentially zero. But finite dilution is the prevailing condition in actual columns. Unfortunately, we cannot deduce the finite dilution entrainer classification from its infinite dilution counterpart: While the relative volatility of the two azeotropic components increases linearly with entrainer concentration for some entrainers (Murti & Van Winkle 1957, Prabhu & Van Winkle 1963), it increases at varying rates (Stephenson & Van Winkle 1962) or even exhibits a maximum (Qozati & Van Winkle 1960, Hess *et al.* 1962) for other entrainers.

- Obtaining high relative volatilities between the two azeotropic components is only one of the requirements a good entrainer must satisfy. As we show in this article, we must also take into account the amount of entrainer needed to achieve high relative volatilities in order to avoid too-high feed ratios.

In chapter 4, we analyze in detail what makes a good entrainer and we present a way of comparing entrainers semi-quantitatively, using as the only information the thermodynamic description of the ternary mixture. This method applies to all entrainers that add no azeotropes (such entrainers almost always lead to separability). This method can be extremely useful at the stage of conceptual design, when only an approximate separation flowsheet is required.

Chapter 2

The Unusual Behavior of Homogeneous Azeotropic Distillation - Implications for Entrainer Selection

2.1 The unusual behavior of extractive columns

2.1.1 Background

We focus here on homogeneous azeotropic distillation units. These 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:

- The first column (called extractive or homogeneous azeotropic distillation column), yields one azeotropic constituent as a pure product, while the other product contains the entrainer and the other azeotropic component. When the entrainer feed and the azeotropic feed are located on different trays, the section between the two feeds 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 extractive column.

Figure 1.1 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 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 & 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 paper, 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 the fundamental conclusions presented in this paper are independent of the specific VLE model employed. We discuss the consequences of this assumption in the last section of this article.

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.* 1989). 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 kindly provided to us 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 heat effects, 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 heat effects. Although we always obtained convergence with Chemsin, we had in many cases severe convergence problems with Aspen; providing a good initial guess then becomes essential. Upon request, we will provide a PC diskette containing the Aspen input files corresponding to the results shown in this paper.

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

- L (I, H respectively) corresponds to the component that has the lowest (intermediate, highest resp.) 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 composition triangle, the upper left (lower right, lower left respectively) corner corresponds to the lighter azeotropic constituent (heavier azeotropic constituent, entrainer resp.).

The notions of residue curves, residue curve boundaries and distillation regions are extensively used throughout this work. A detailed analysis of the properties of residue curve diagrams can be found in the series of articles published by Doherty & Perkins (1978a, 1978b, 1979) and by Van Dongen & Doherty (1984). Very briefly, a residue curve is obtained in the following manner: We consider a still that contains a multicomponent mixture, and we evaporate its content slowly (so that the vapor remains in constant equilibrium with the liquid that remains in the still). By recording the liquid composition as a function of time and plotting it in the composition space, we obtain a residue curve.

A residue curve diagram is obtained by plotting several residue curves that corresponds to different initial still compositions. In the case of an ideal ternary mixture, residue curves all start at the light component corner and all end at the heavy component corner. When the mixture forms azeotropes, we often obtain a more complicated residue curve diagram; this diagram may contain distillation boundaries and distinct distillation regions. We define a distillation region as a subset of the composition space where all residue curves start at the same point and all end at the same point. Thus, in the ideal case, there is only one distillation region: The whole composition space. Finally, we define a residue curve boundary as the curve which separates two distinct distillation regions.

2.1.2 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 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 & Seader 1981). As shown by Andersen, Laroche and Morari (1989), homogeneous azeotropic distillation columns can be much more complex than regular distillation columns.

One important conclusion is the fact that, for a given column and a given feed ratio (ratio of the entrainer feed flow rate to the azeotropic feed flow rate), separation does not increase monotonically with reflux. 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 2.1 to figure 2.8 illustrate these two opposing effects in the case of the acetone (L) - heptane (I) azeotrope, using toluene (H-E) as 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 by the changes in the rectifying and stripping sections composition profiles) 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, we see that the column does not perform any separation.

We reproduced one of these composition profiles with Aspen, and obtained very similar results by increasing reflux by 30% over that used with Chemsim (compare figure 2.3 and figure 2.8). This quantitative difference is explained by the heat effects and is consistent with the results of Knight & Doherty (1986).

This unusual behaviour with changing reflux occurs in most industrial cases; it will occur whenever the entrainer has a higher boiling point than both azeotropes

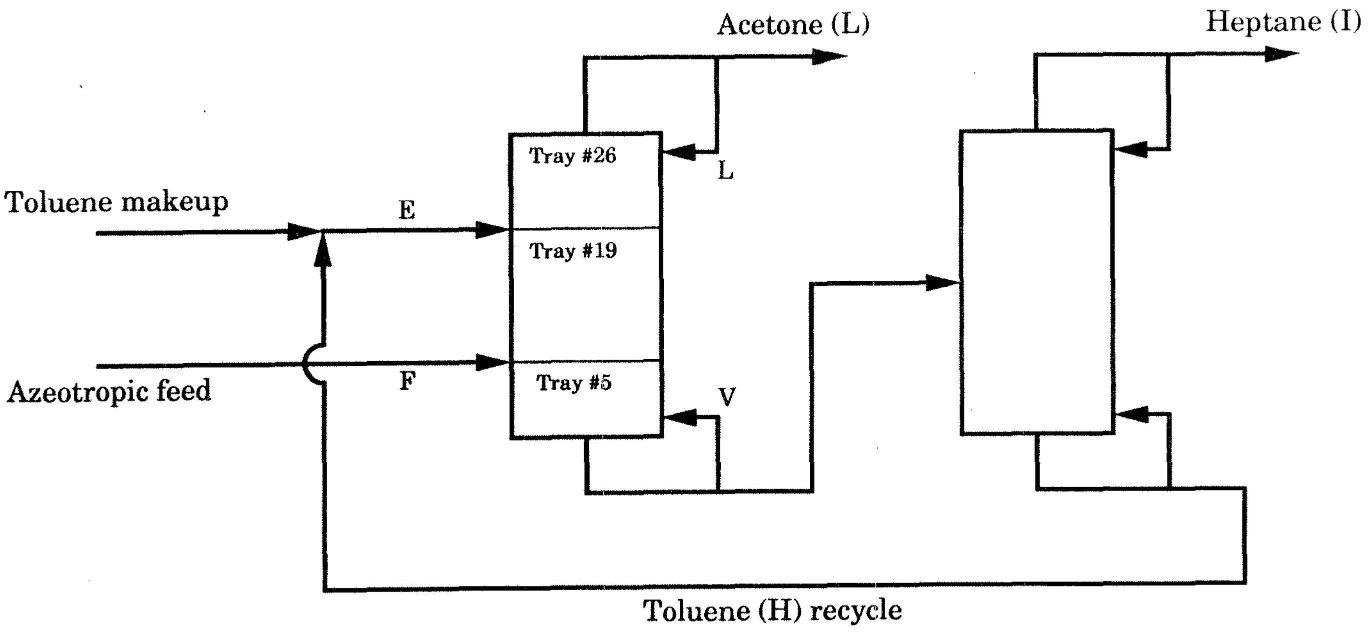
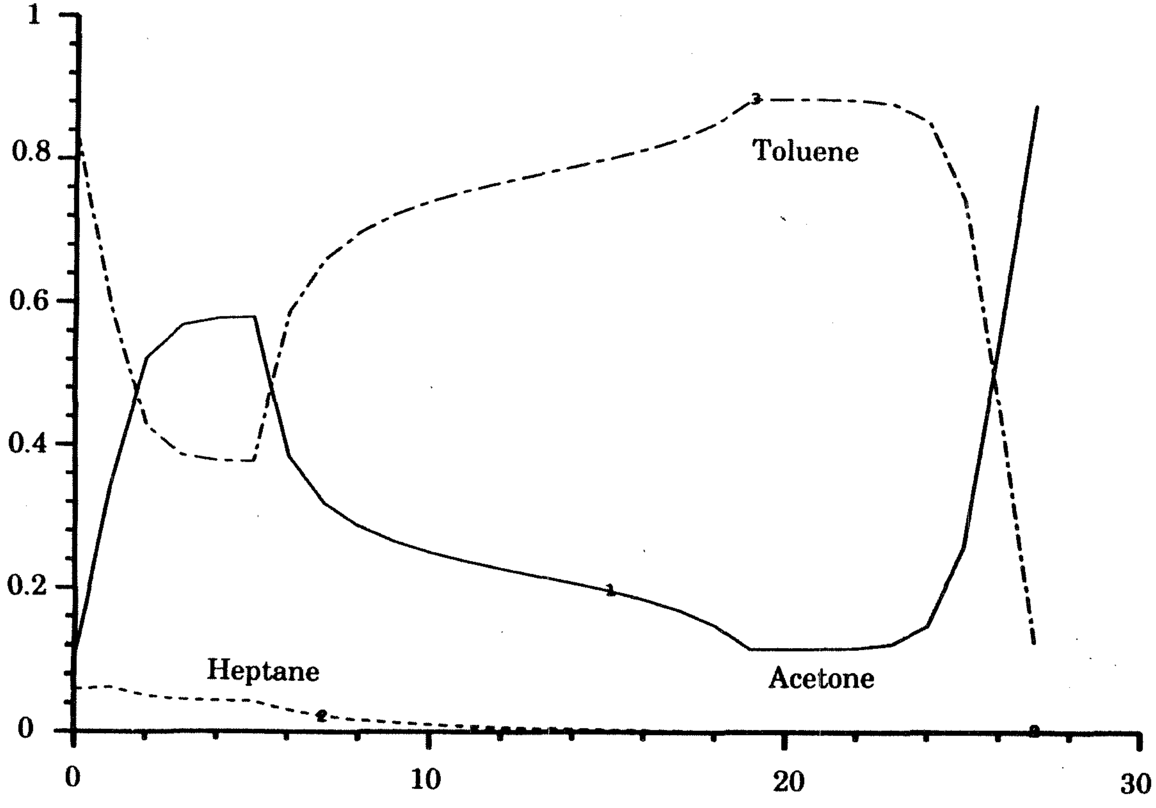


Fig. 2.1: The acetone - heptane - toluene separation sequence

Fig. 2.2: Acetone (1) - heptane (2) - toluene (3) extractive column
composition profile
L/F = 0.8



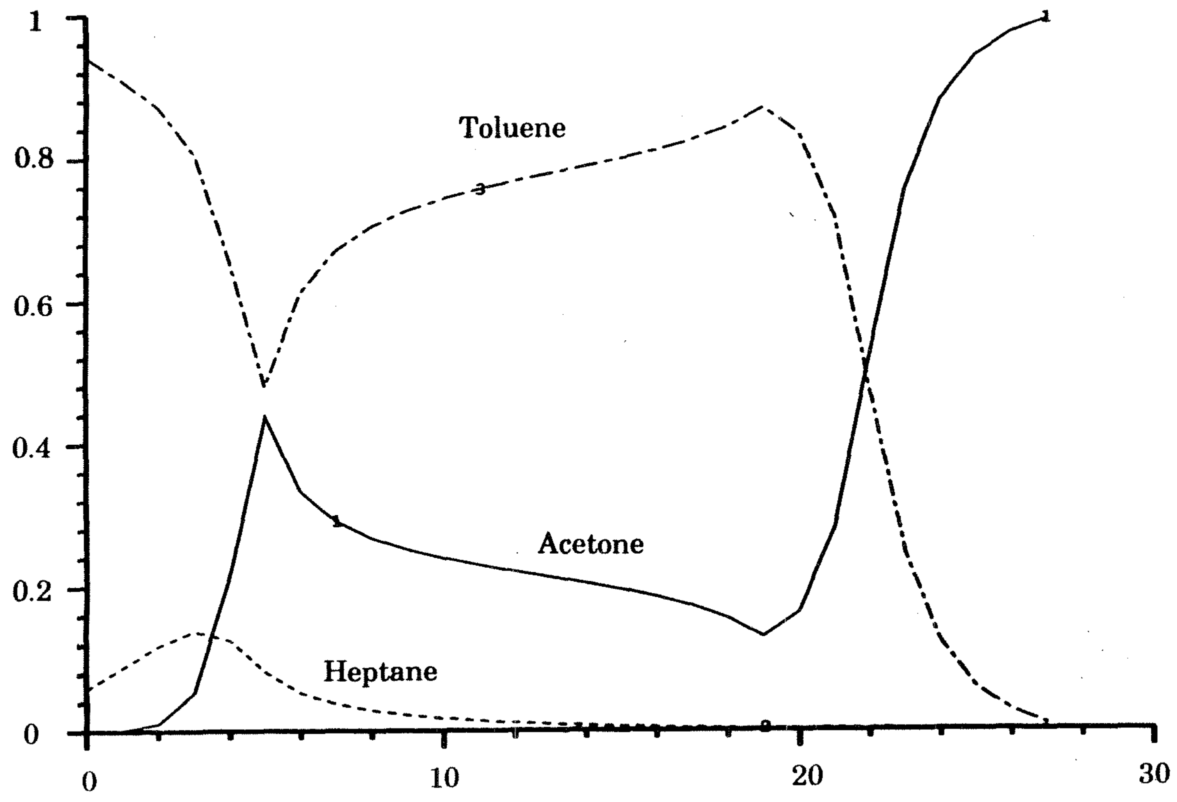


Fig. 2.3: Acetone (1) - heptane (2) - toluene (3) extractive column composition profile
L/F = 1.035

Fig. 2.4: Acetone (1) - heptane (2) - toluene (3) extractive column
composition profile
L/F = 4.0

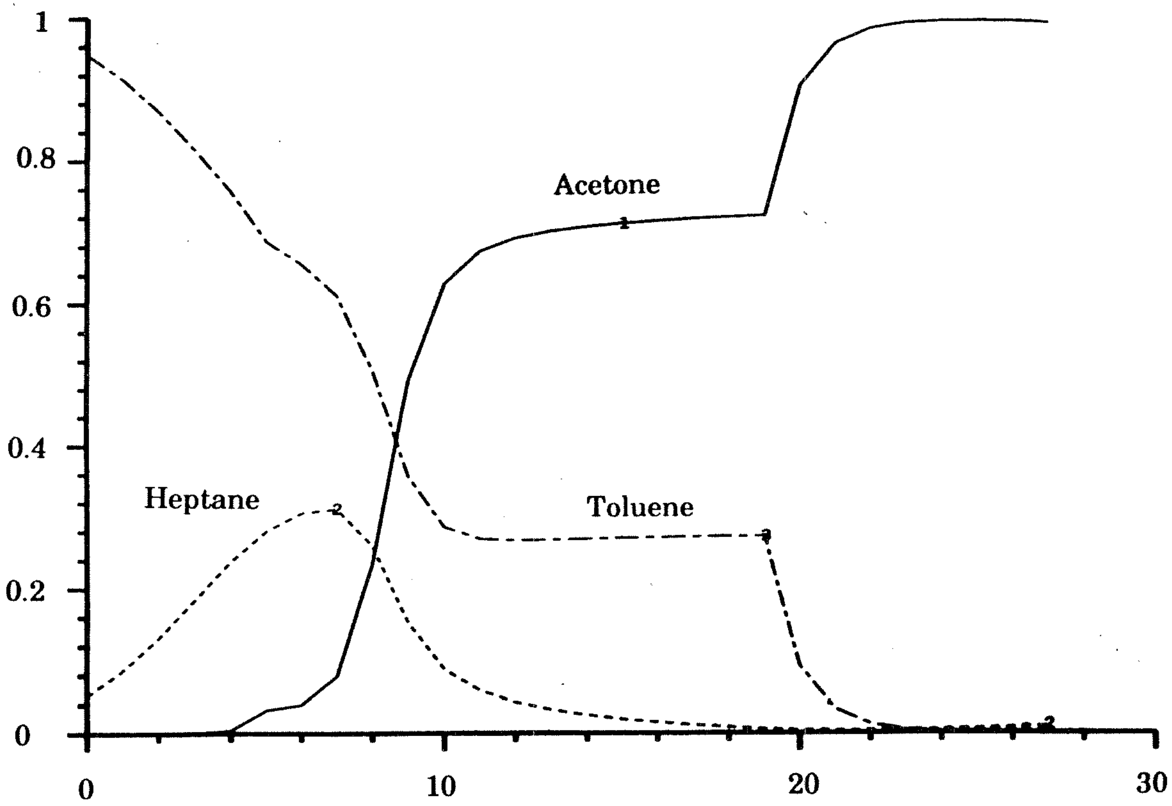


Fig. 2.5: Acetone (1) - heptane (2) - toluene (3) extractive column composition profile
L/F = 5.582

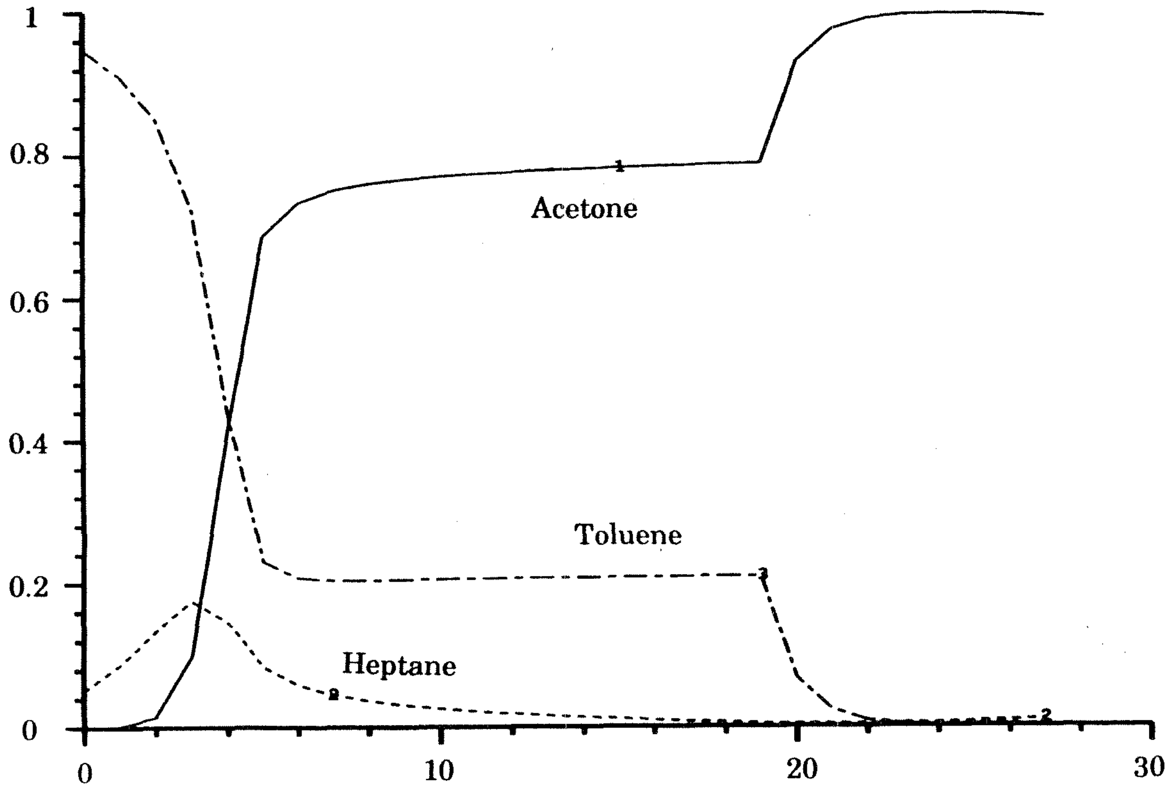


Fig. 2.6: Acetone (1) - heptane (2) - toluene (3) extractive column composition profile
L/F = 10.0

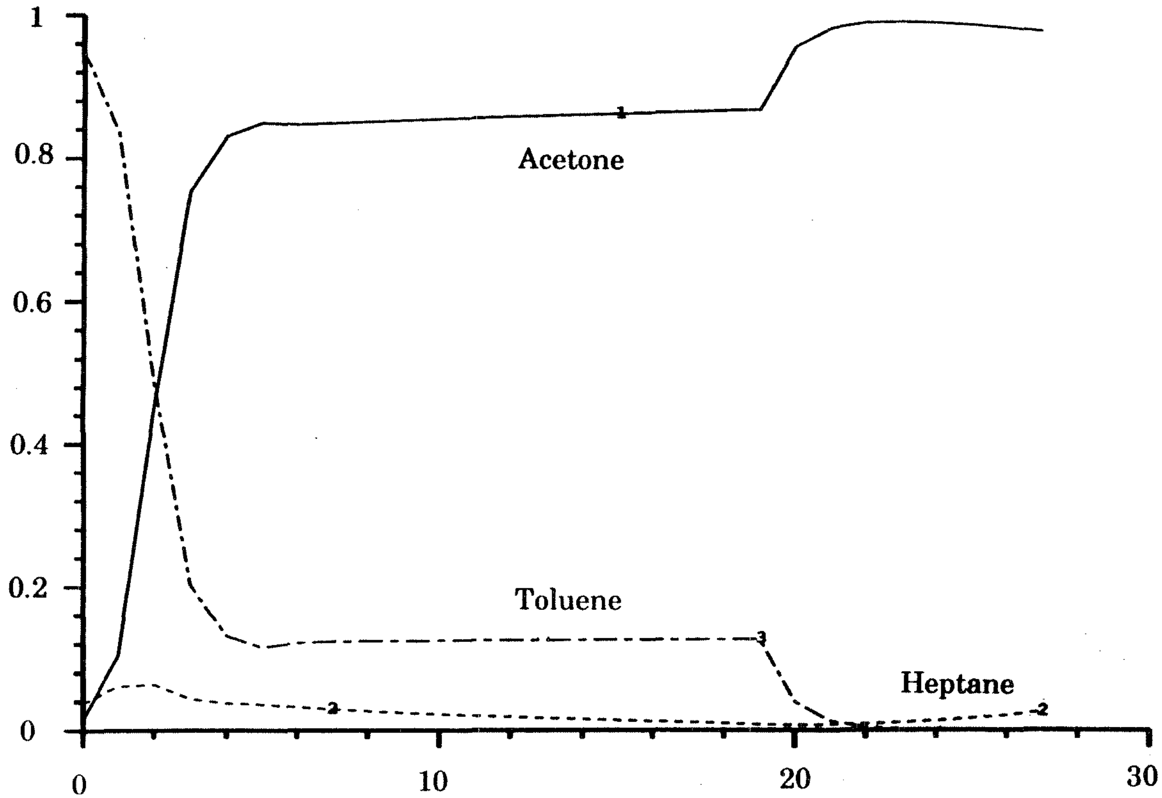


Fig. 2.7: Acetone (1) - heptane (2) - toluene (3) extractive column composition profile
L/F = 100.0

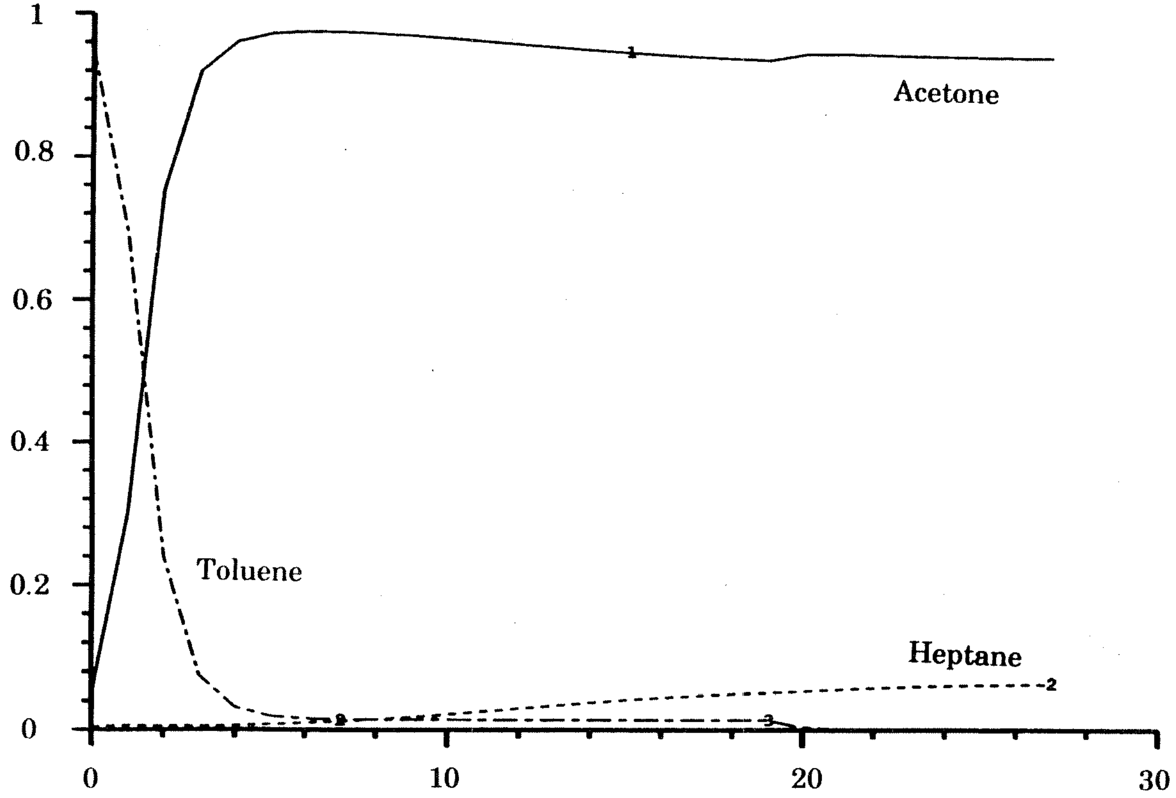
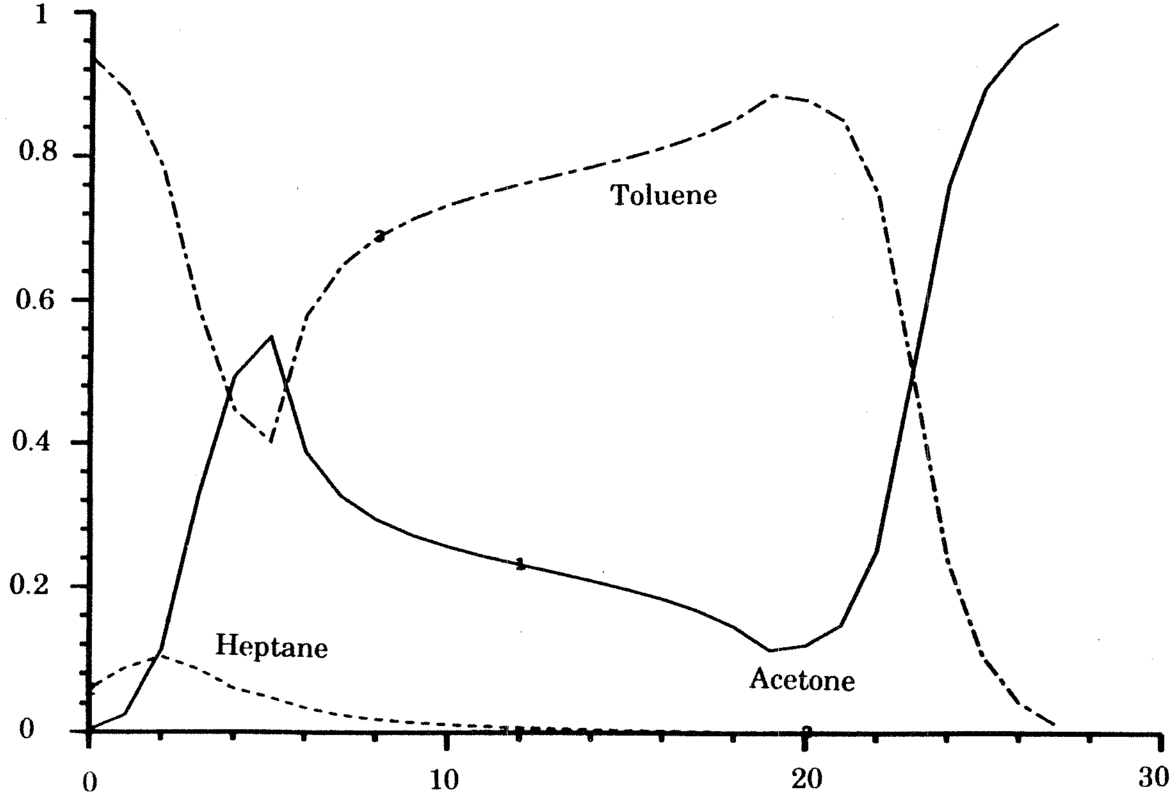


Fig. 2.8: Acetone (1) - heptane (2) - toluene (3) extractive column composition profile obtained with ASPEN
L/F = 1.355



and introduces no new azeotrope (see Andersen *et al.* 1989). Yet there are homogeneous azeotropic distillation examples where infinite reflux does lead to maximum separation. Figure 2.9 to figure 2.14 show the column composition profiles obtained for increasing reflux values in the acetone (L) - heptane (H) - benzene (I-E). Benzene, like toluene, can act as 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. 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, by about 10% in this case (compare figure 2.11 and figure 2.14).

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, separation first increases with 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. However, contrary to heavy entrainers, some separation is still performed with high reflux ratios, but not as much as at finite reflux. This unusual behavior of homogeneous azeotropic distillation is depicted by figure 2.15 to figure 2.21 using ethanol (I) - water (H) - methanol (L-E) as an example.

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

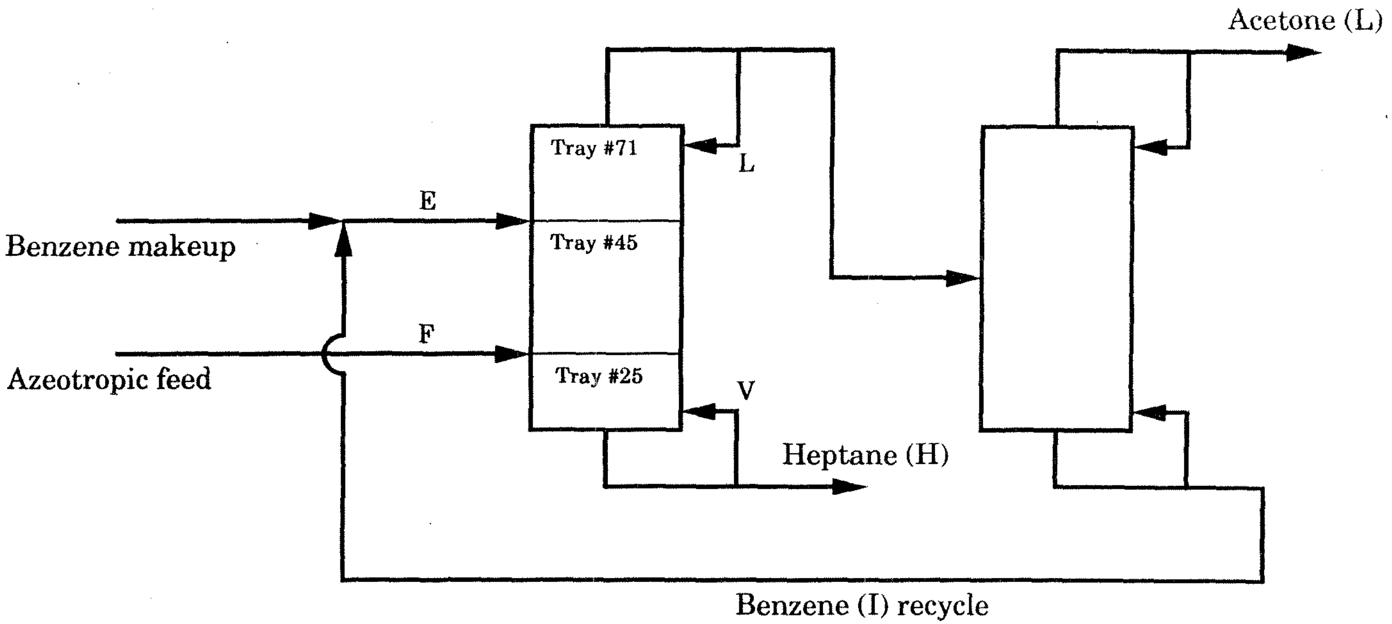


Fig. 2.9: The acetone - heptane - benzene separation sequence

Fig. 2.10: Acetone - heptane - benzene extractive column composition profile
L/F = 2.0

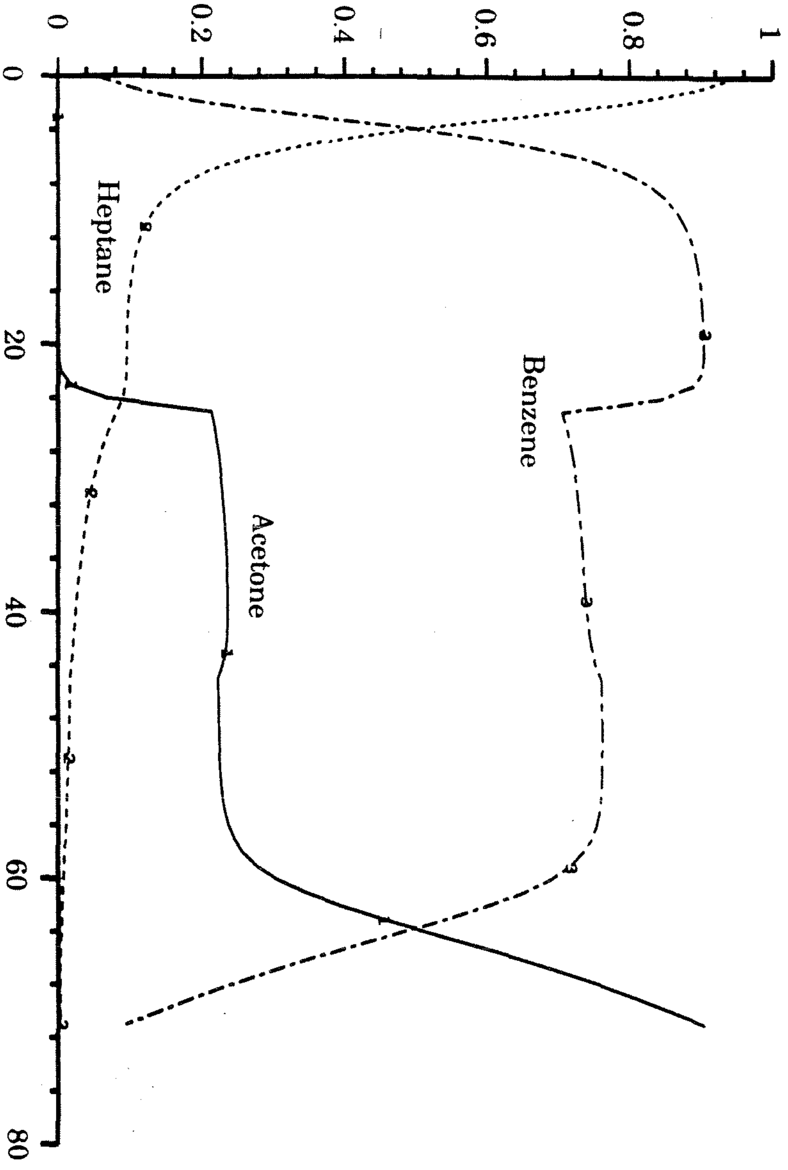


Fig. 2.11: Acetone - heptane - benzene extractive column composition profile
L/F = 5.05

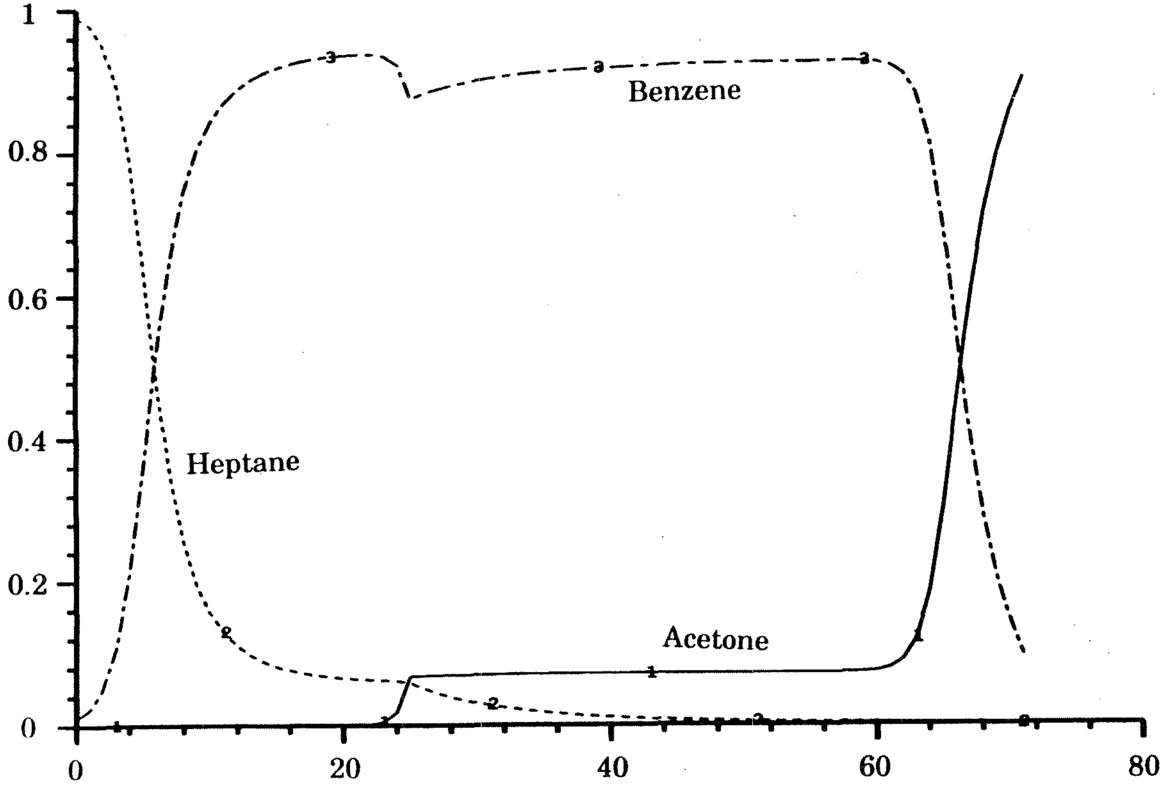


Fig. 2.12: Acetone - heptane - benzene extractive column composition profile
L/F = 10.0

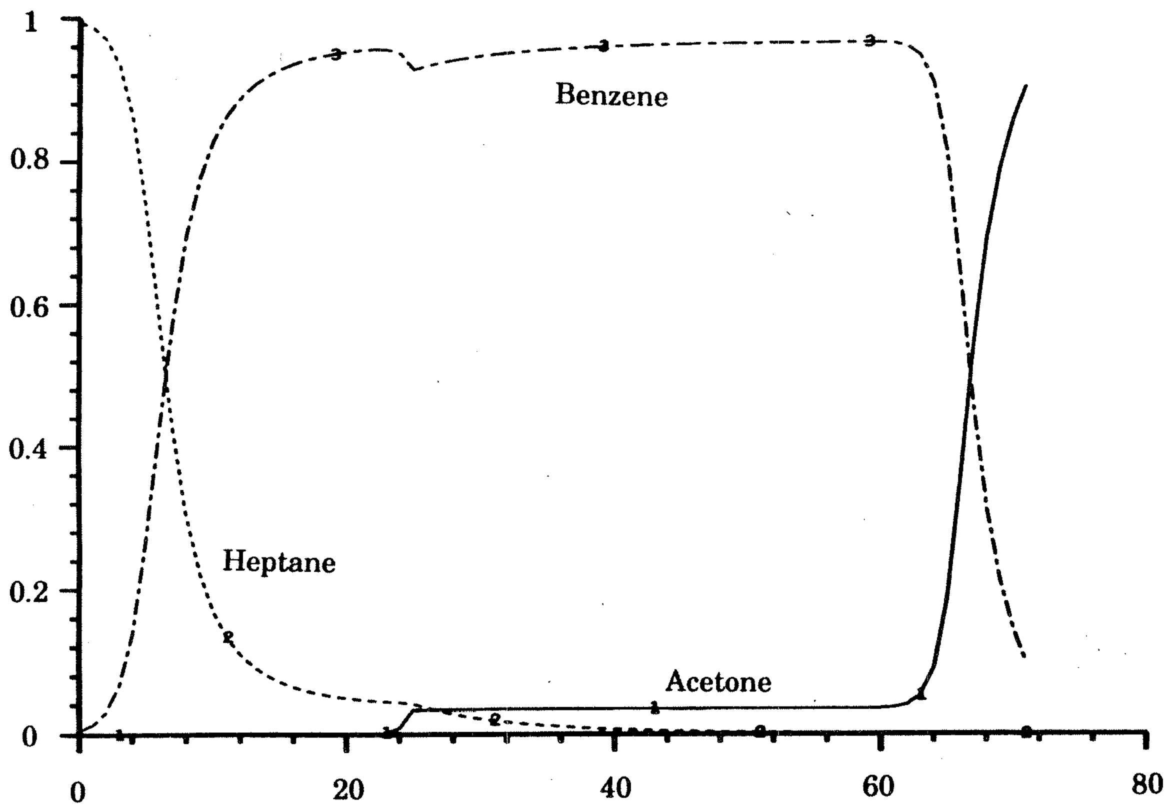


Fig. 2.13: Acetone - heptane - benzene extractive column composition profile
L/F = 100.0

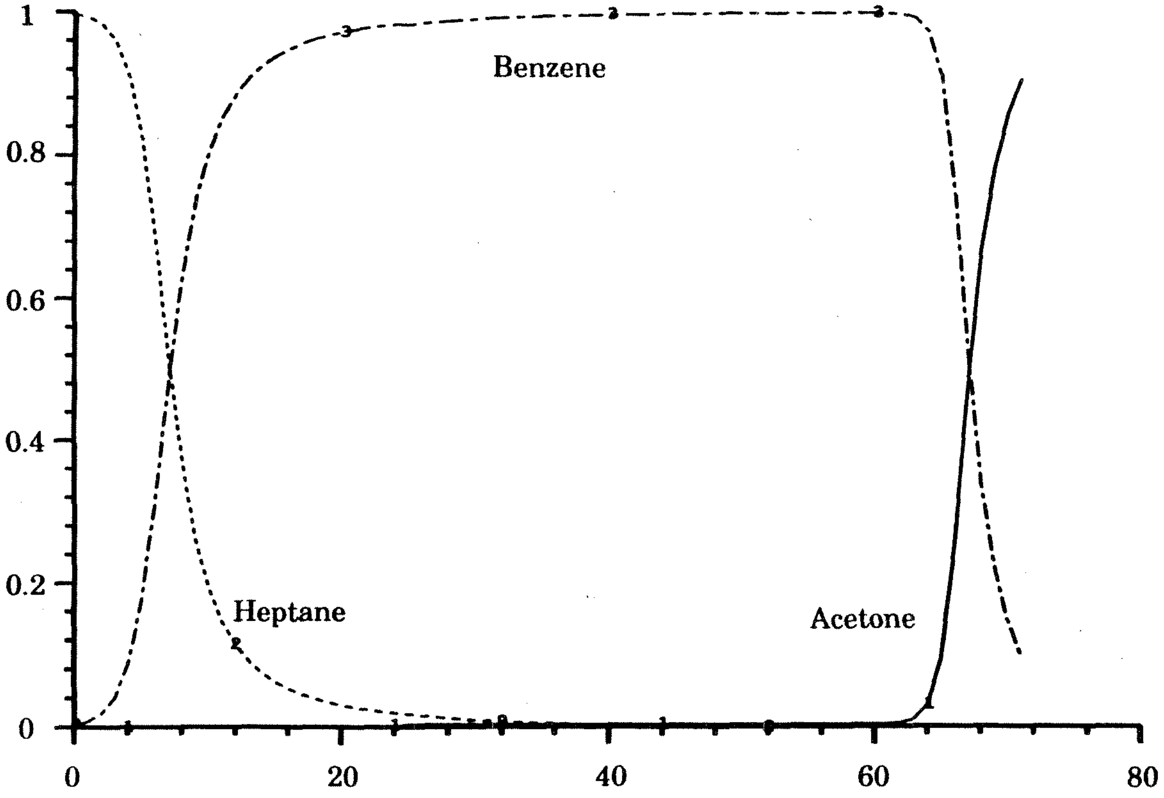
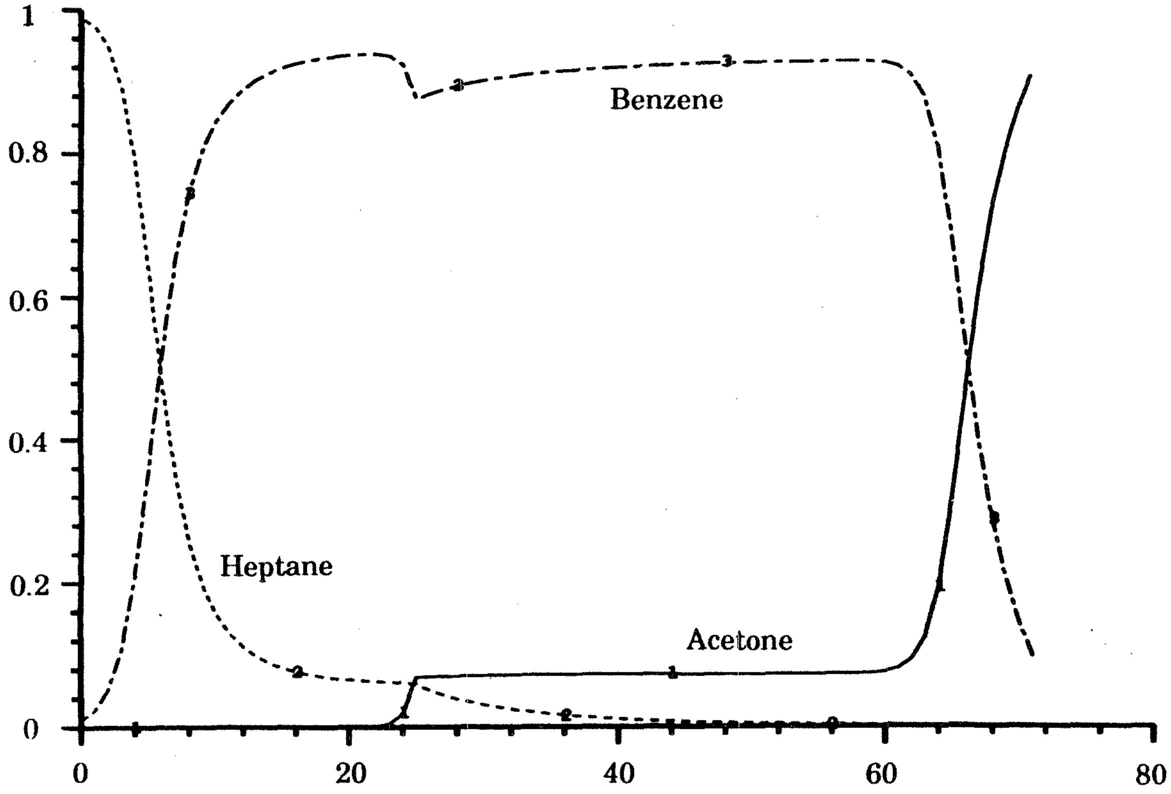


Fig. 2.14: Acetone - heptane - benzene extractive column composition profile obtained with ASPEN
L/F = 5.35



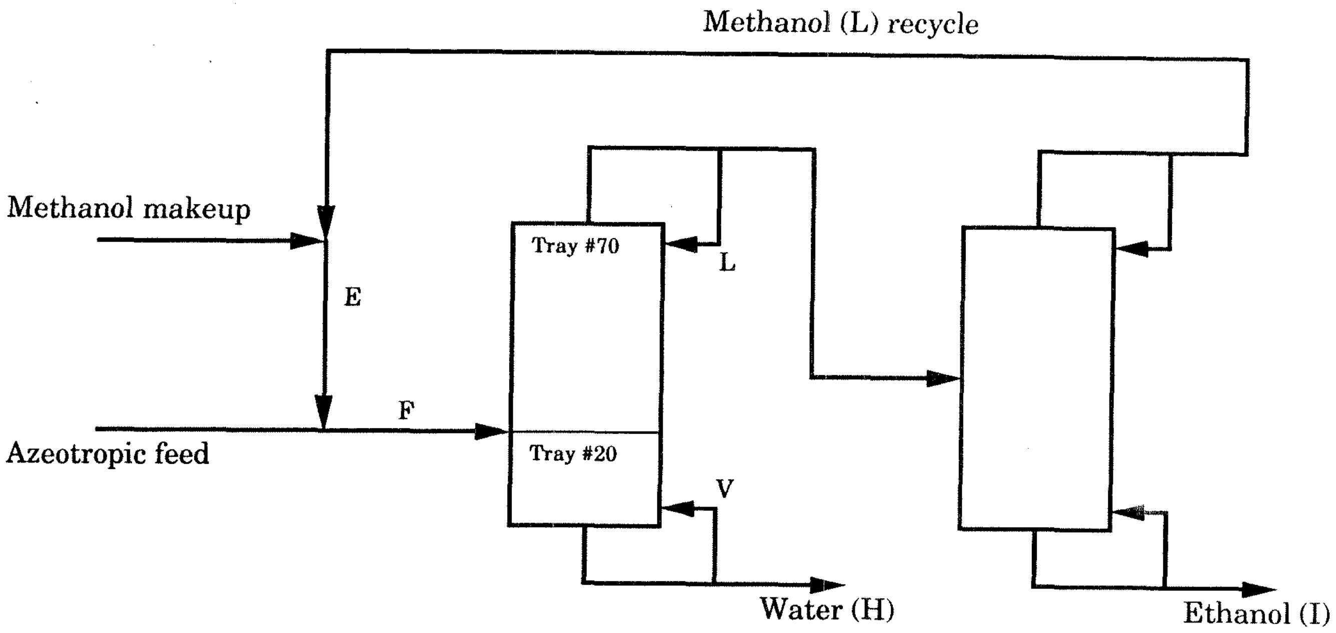


Fig. 2.15: The ethanol - water - methanol separation sequence

Fig. 2.16: Ethanol (1) - water (2) - methanol (3) extractive column composition profile
L/F = 4.0

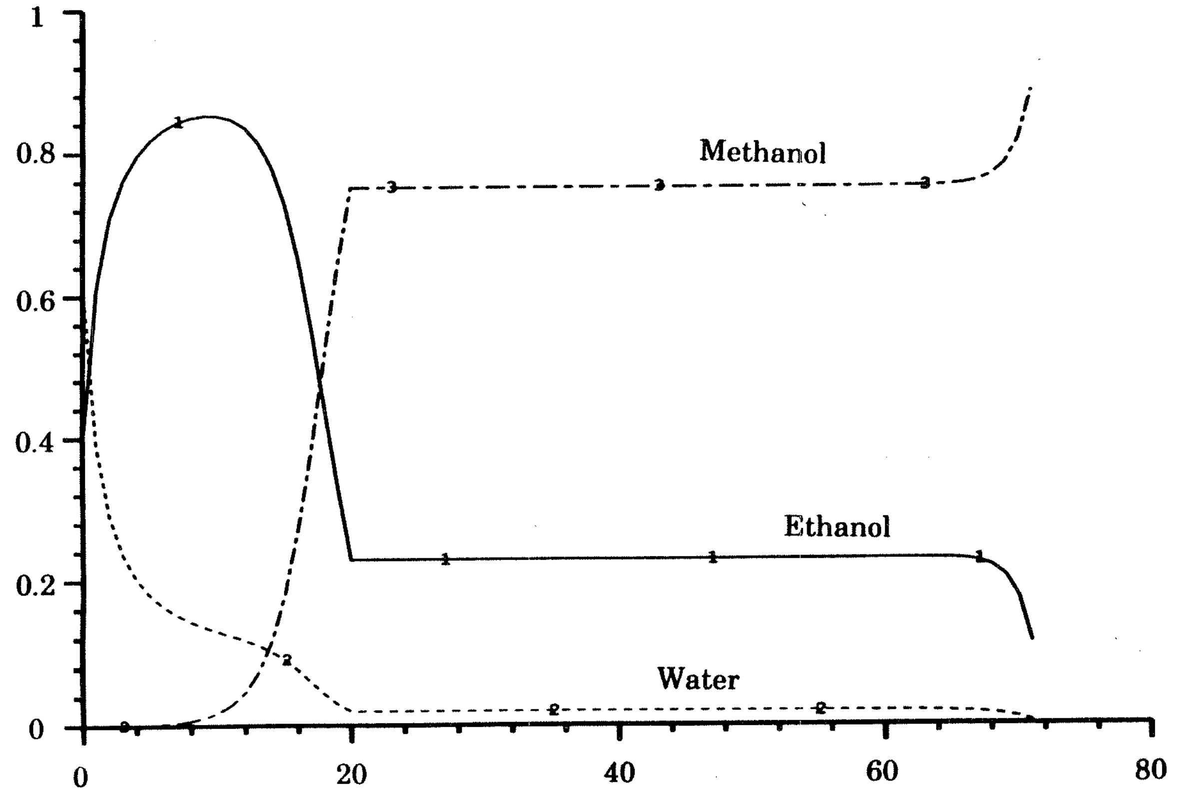


Fig. 2.17: Ethanol (1) - water (2) - methanol (3) extractive column
composition profile
L/F = 8.0

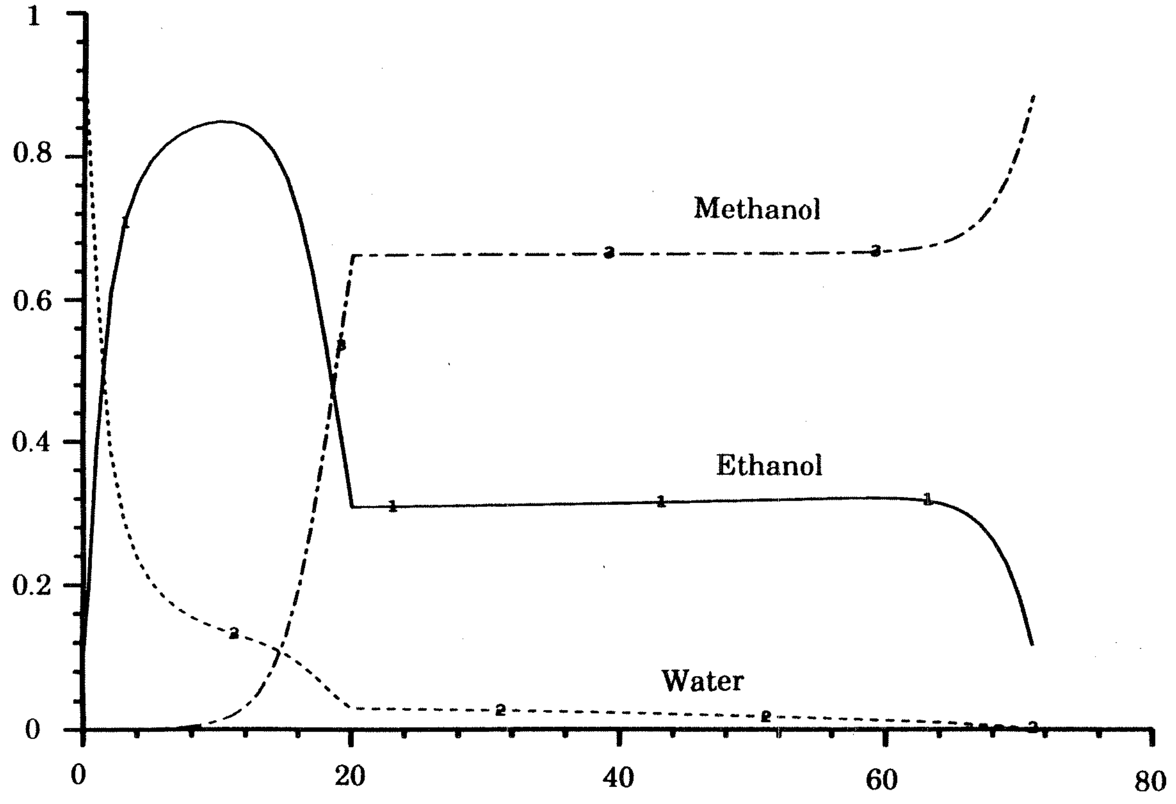


Fig. 2.18: Ethanol (1) - water (2) - methanol (3) extractive column composition profile
L/F = 9.7

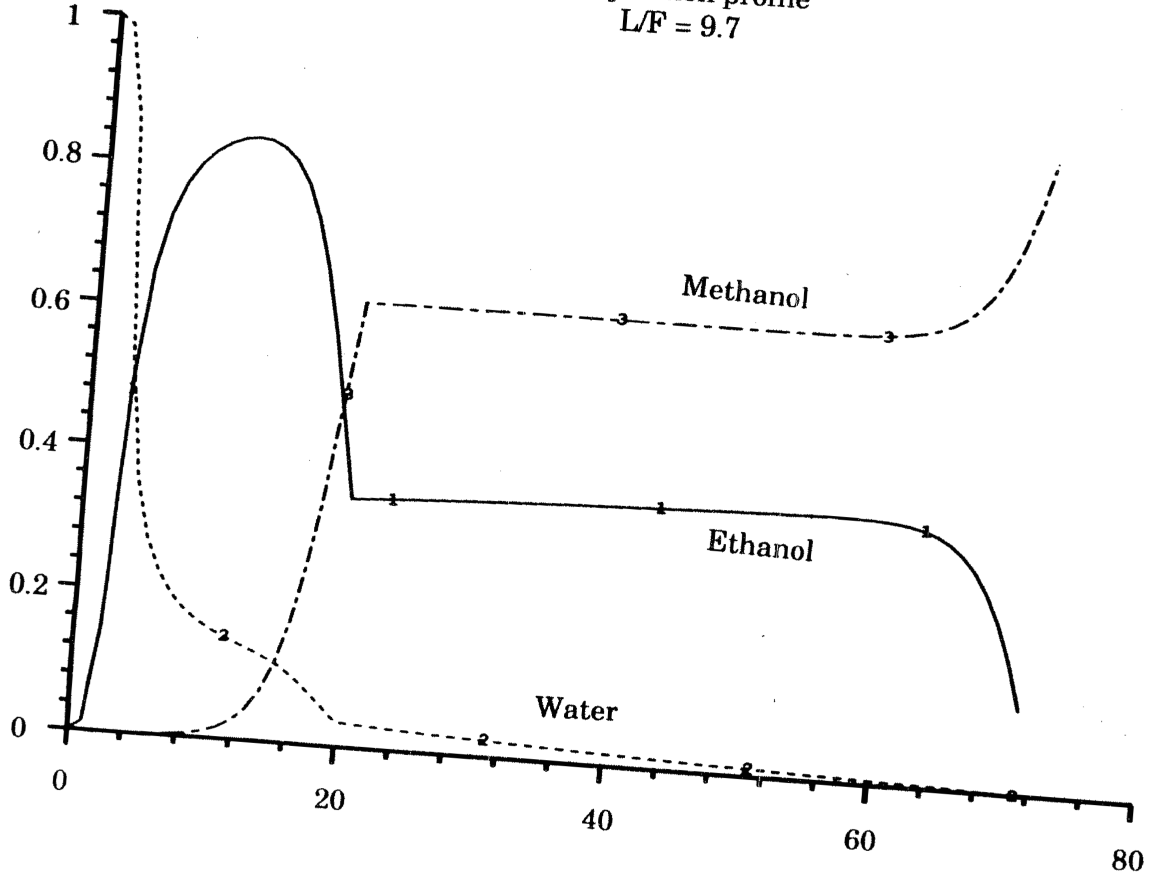


Fig. 2.19: Ethanol (1) - water (2) - methanol (3) extractive column composition profile
L/F = 100.0

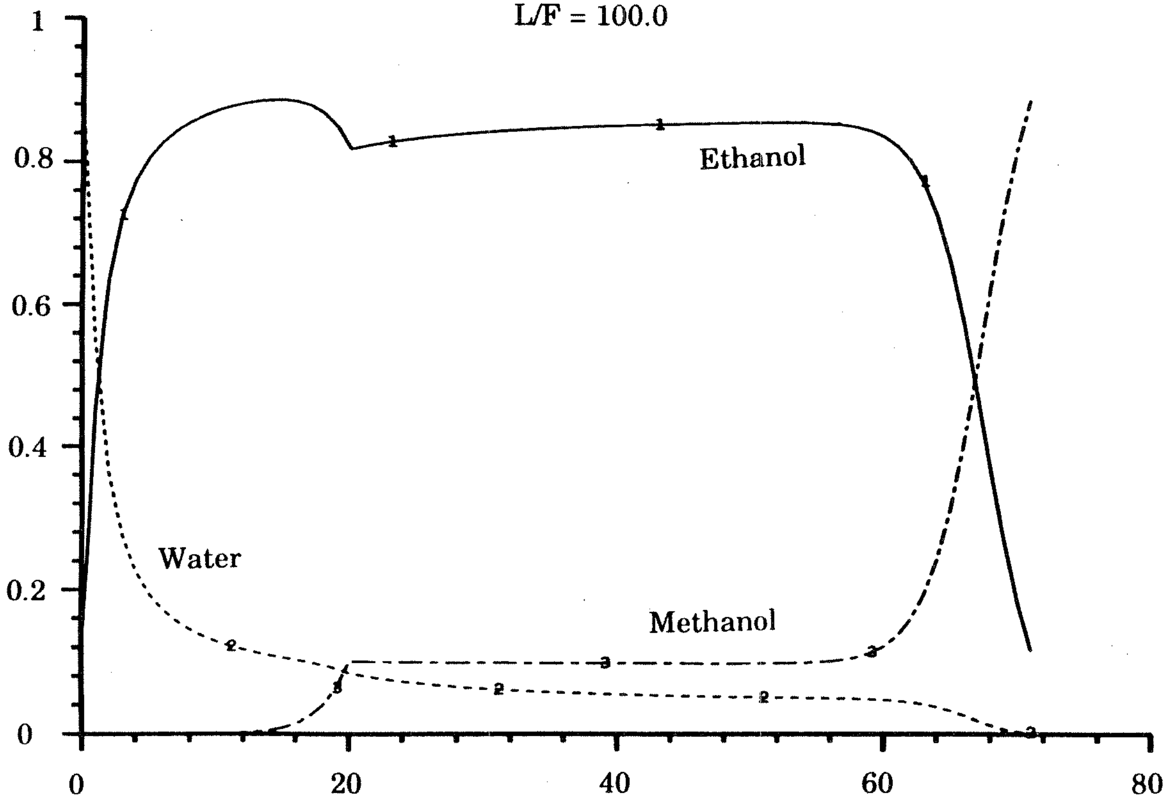


Fig. 2.20: Ethanol (1) - water (2) - methanol (3) extractive column
composition profile
L/F = 1000.0

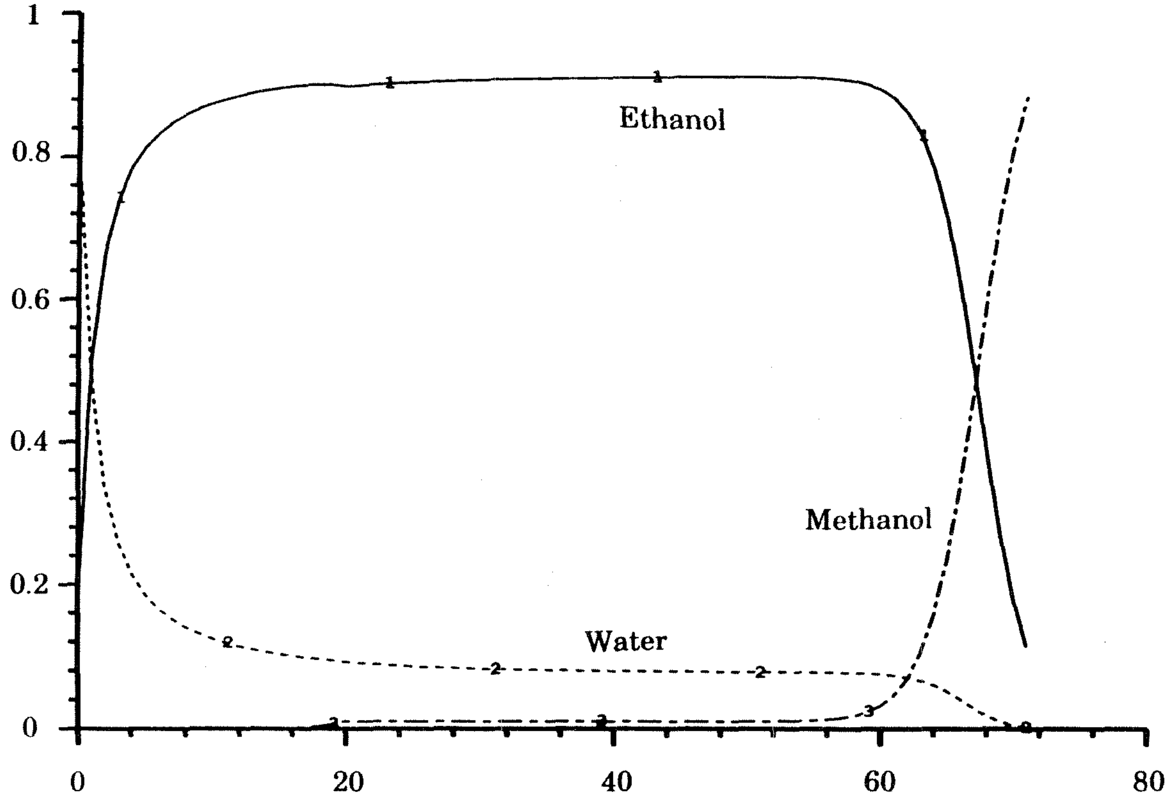
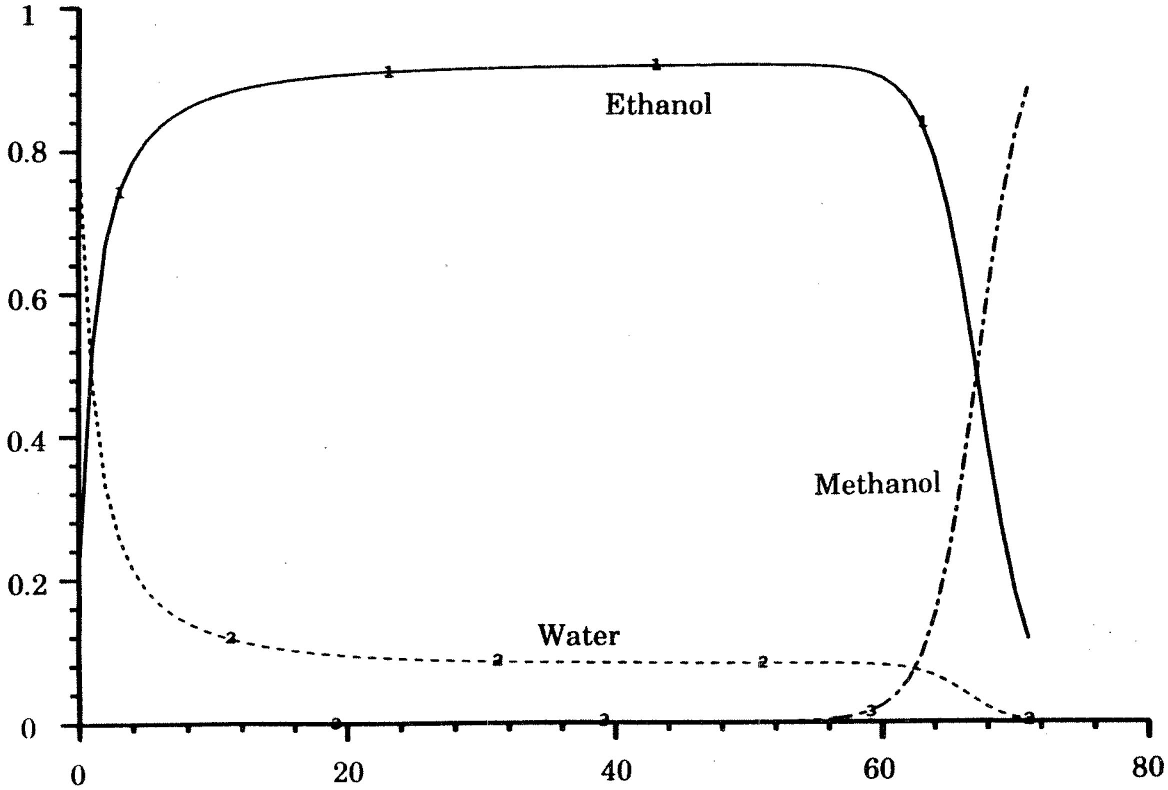


Fig. 2.21: Ethanol (1) - water (2) - methanol (3) extractive column composition profile
L/F = 10000.0



make separation feasible at finite reflux.

This paragraph has demonstrated that the first golden rule of distillation: "If you want better separation with a given column, increase reflux" does not apply to homogeneous azeotropic distillation columns. The next paragraph 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 also incorrect in the case of homogeneous azeotropic distillation columns.

2.1.3 Increasing the number of trays may decrease separation

Another unusual feature of homogeneous azeotropic distillation columns described by Andersen *et al.* (1989) is the fact that, in some cases, meeting the same specifications with a larger number of trays requires higher internal flows. The comparison of Run 1 and Run 2 shows that adding trays in the entrainer section at constant internal flows decreases both top and bottom purities (table 2.1). The comparison of Run 1 and Run 3 shows that meeting given specifications with a larger number of trays in the extractive section actually requires higher internal flows. We also see that Aspen confirms this trend. 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 & 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.

2.1.4 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

Table 2.1
Chemsim (Aspen)

	Run 1	Run 2	Run 3
Boilup	198.11 (230.11)	198.11 (230.11)	199.83
Number of trays (middle section)	14	24	24
Top purity	0.9900 (0.9857)	0.9836 (0.9754)	0.9900
Bottom purity (ratio)	200 (14.28)	10 (4.48)	200

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, *i.e.* it makes 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 2.22), 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 2.23), 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).

Fig. 2.22: Direct Sequence

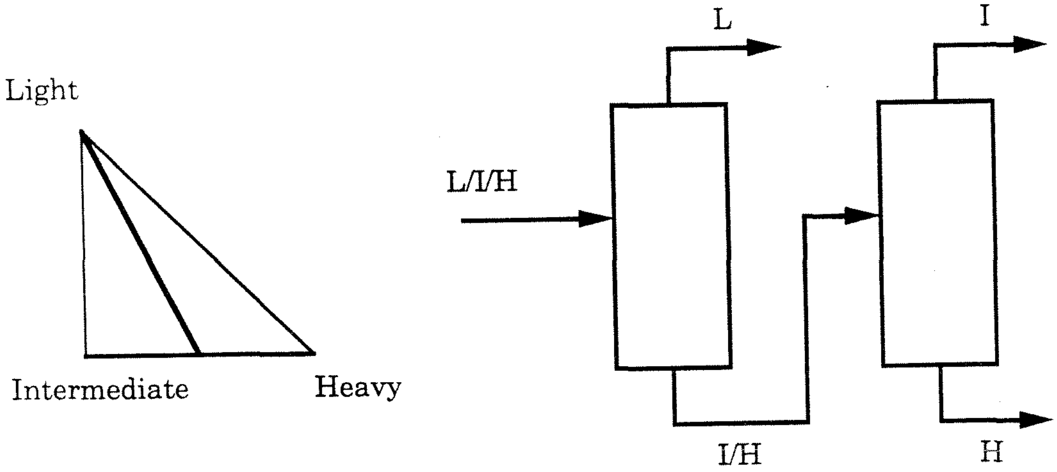
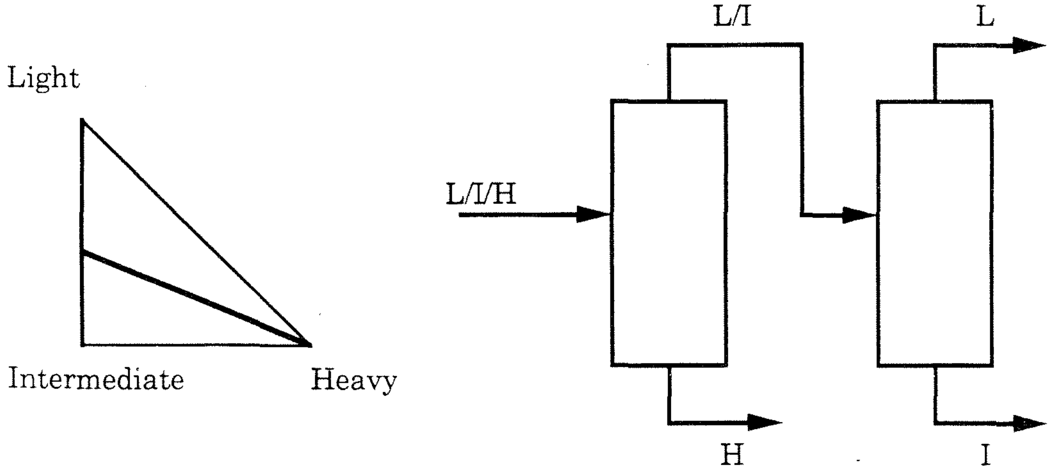


Fig. 2.23: Indirect Sequence



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.

Once again, homogeneous azeotropic distillation columns violate this rule. There are cases where neither the direct split nor the indirect split are 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 (again, comparable results are obtained with Aspen):

- In the first case, 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 (figure 2.24 to figure 2.27). These two components are then separated in the entrainer recovery column. We were unable to synthesize an extractive column that gives pure ethyl ethanoate. Experimental evidence of this behavior has been recorded first by Buell & Boatright (1947), in the case of cis- and trans-butene-2 / 1,3-butadiene / furfural and more recently, by Berg & Yeh (1985) with several mixtures, including acetone - isopropyl ether - DMSO.

- In the second case, 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 extractive column, while the distillate recovers acetone and water, the light and heavy boilers (figure 2.28 to figure 2.31). 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 are unable to synthesize an extractive column that yields

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

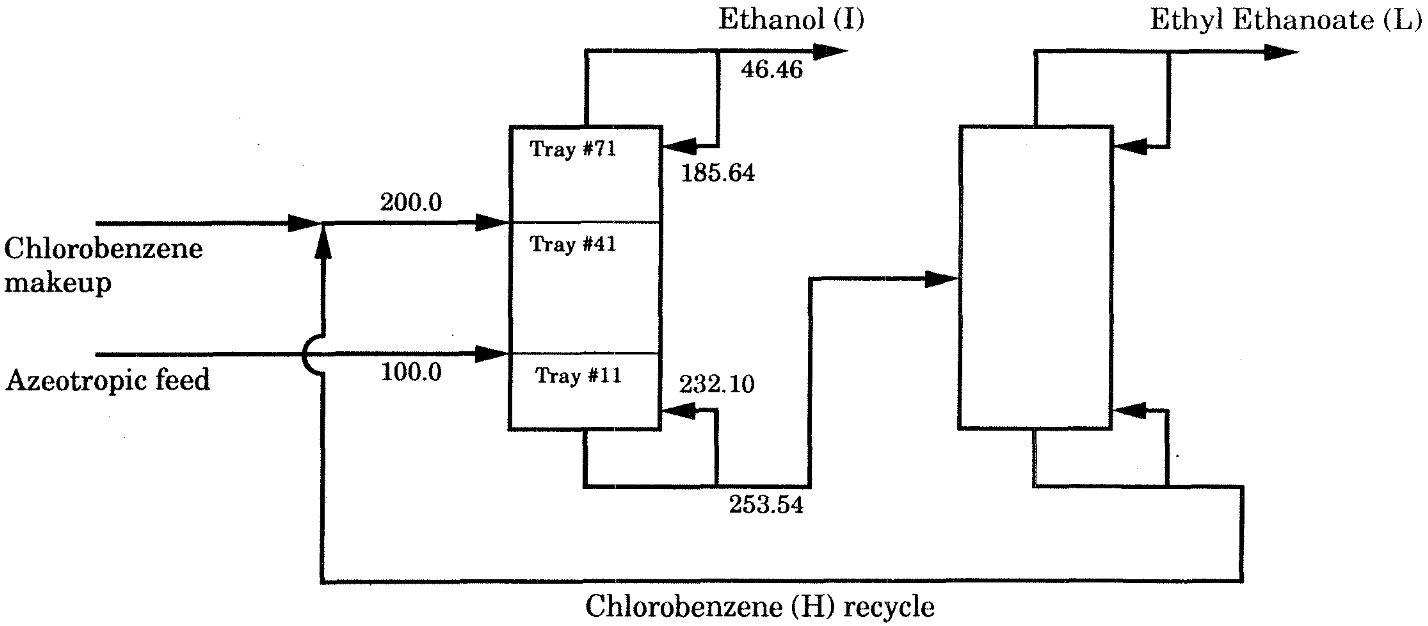


Fig. 2.24: The ethyl ethanoate - ethanol - chlorobenzene separation sequence

Fig. 2.25: Ethyl ethanoate (1) - ethanol (2) - chlorobenzene (3)
extractive column composition profile
L/F= 1.8564

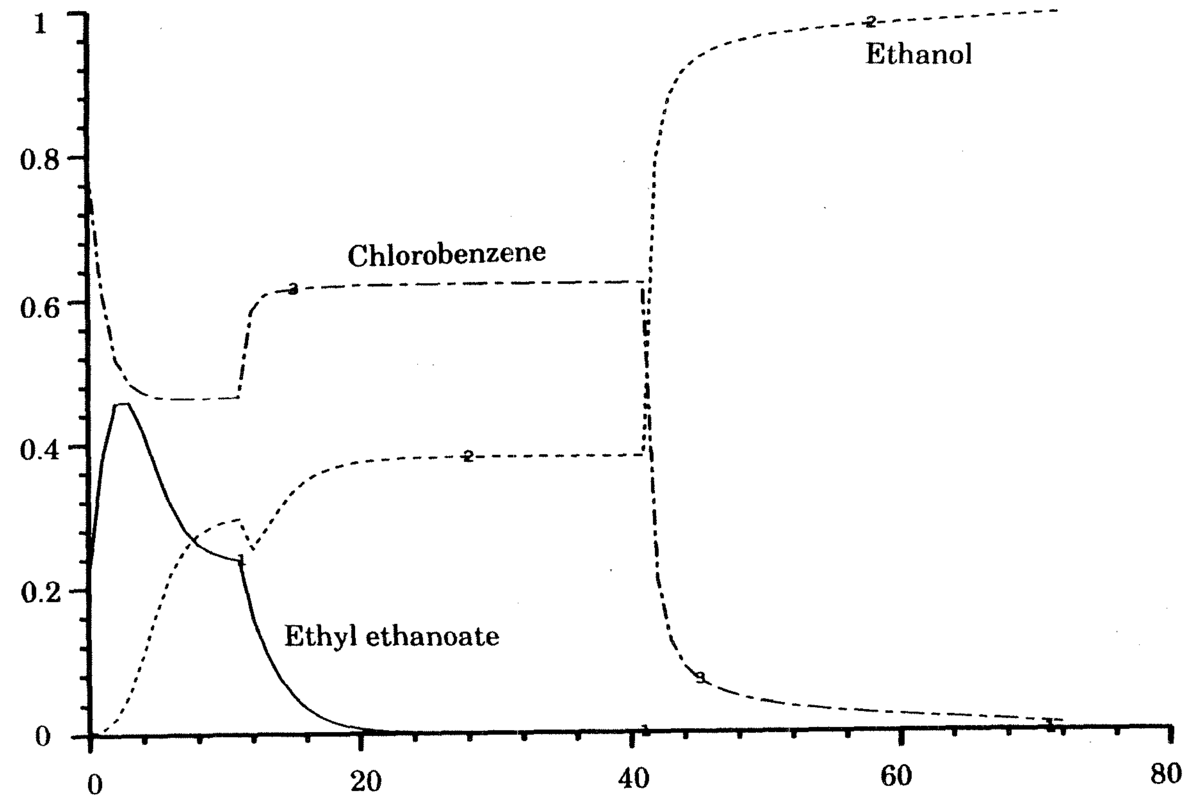


Fig. 2.26: Ethyl ethanoate - ethanol - chlorobenzene residue curve diagram and extractive column composition profile

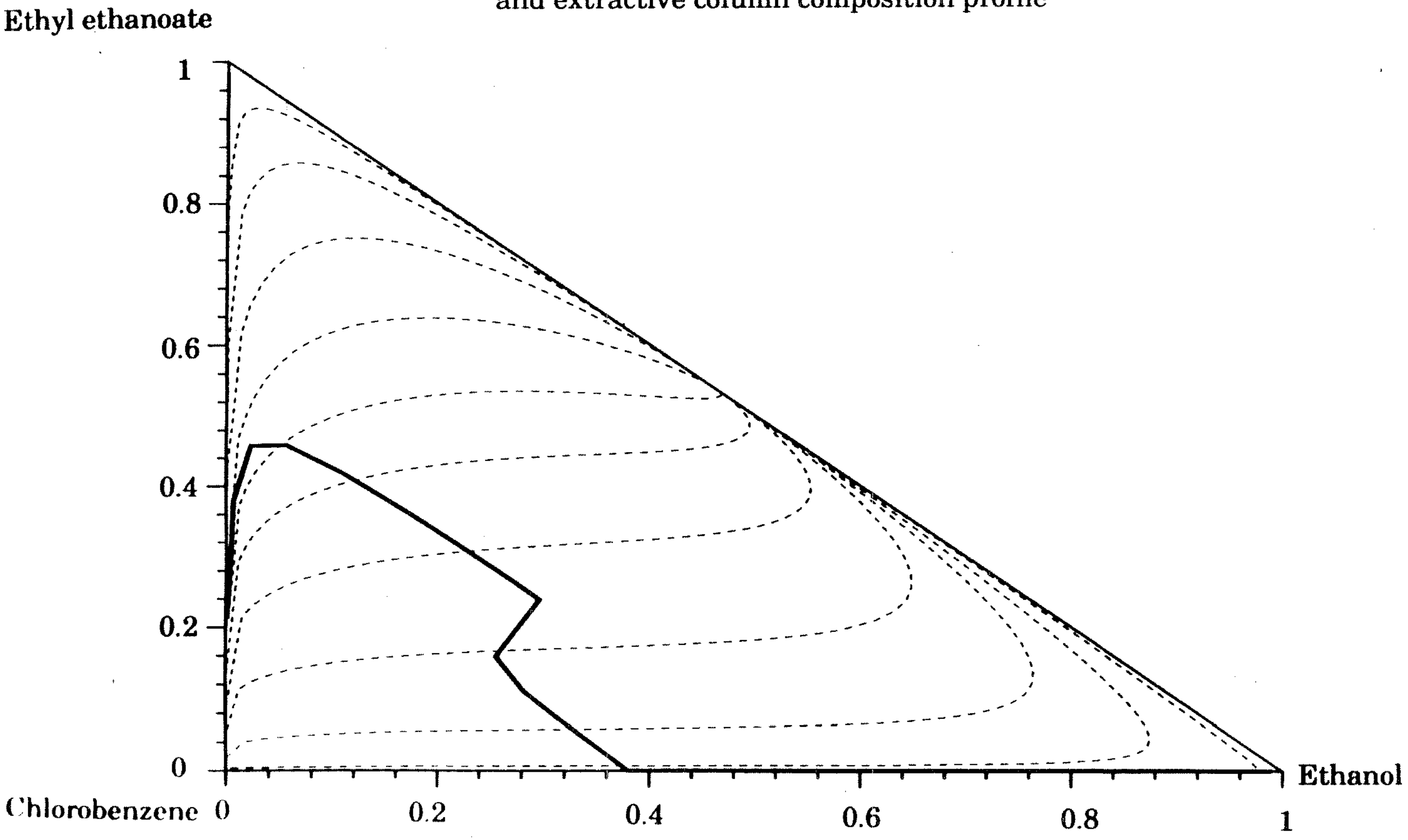
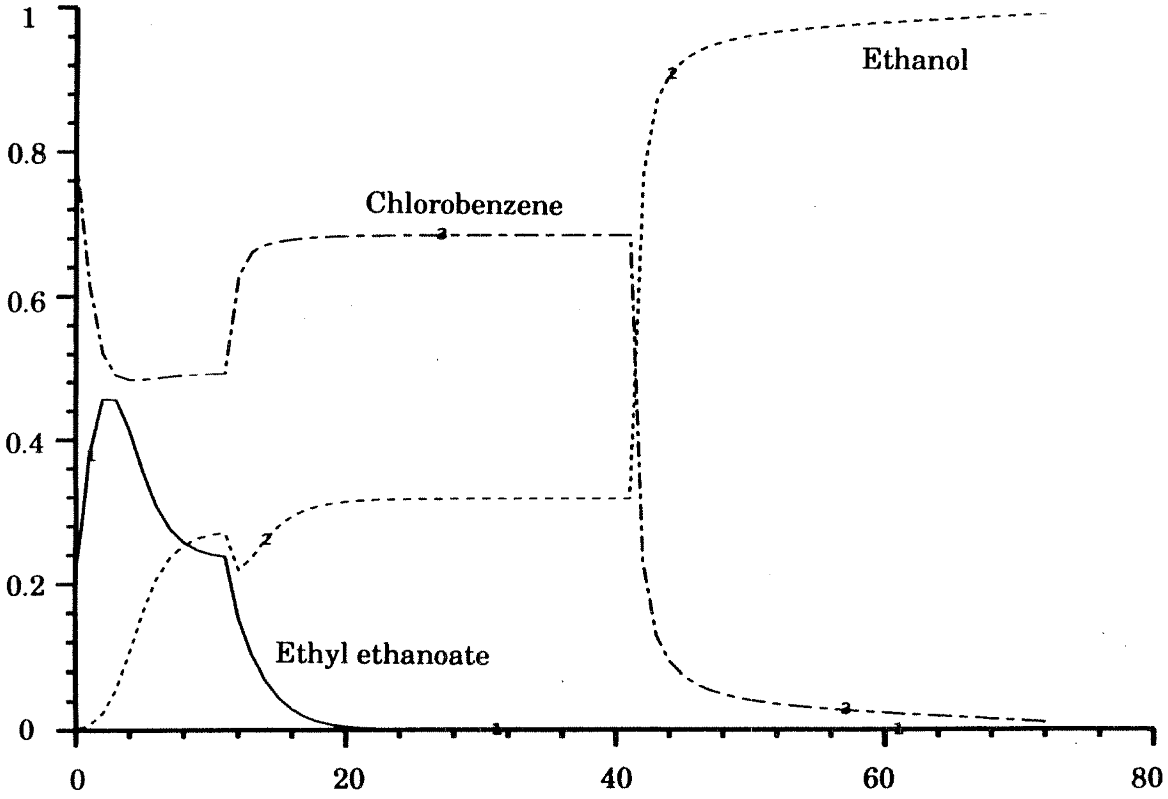


Fig. 2.27: Ethyl ethanoate (1) - ethanol (2) - chlorobenzene (3) extractive column composition profile obtained with ASPEN L/F = 1.8564



water as a pure product.

2.1.5 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 seen in the previous paragraph, only the volatility order limits what separation can be performed. This is not the case for homogeneous azeotropic distillation, where the location of the entrainer feed relative to the azeotropic feed has 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 in order to ensure a concentration large enough to "break" the azeotrope. Separation becomes infeasible if the two feeds are introduced on the same tray. Figure 2.32 and figure 2.32 illustrate 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, there are cases where separation is feasible although the entrainer and the azeotrope are fed on the same tray. Figure 2.34 and figure 2.35 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.

The fact that separability depends on the relative location of the entrainer feed with respect to the azeotropic feed is a distinctive characteristic of homogeneous azeotropic distillation At this point, we do not know how to determine whether we need two separate feeds or if a single feed is sufficient.

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

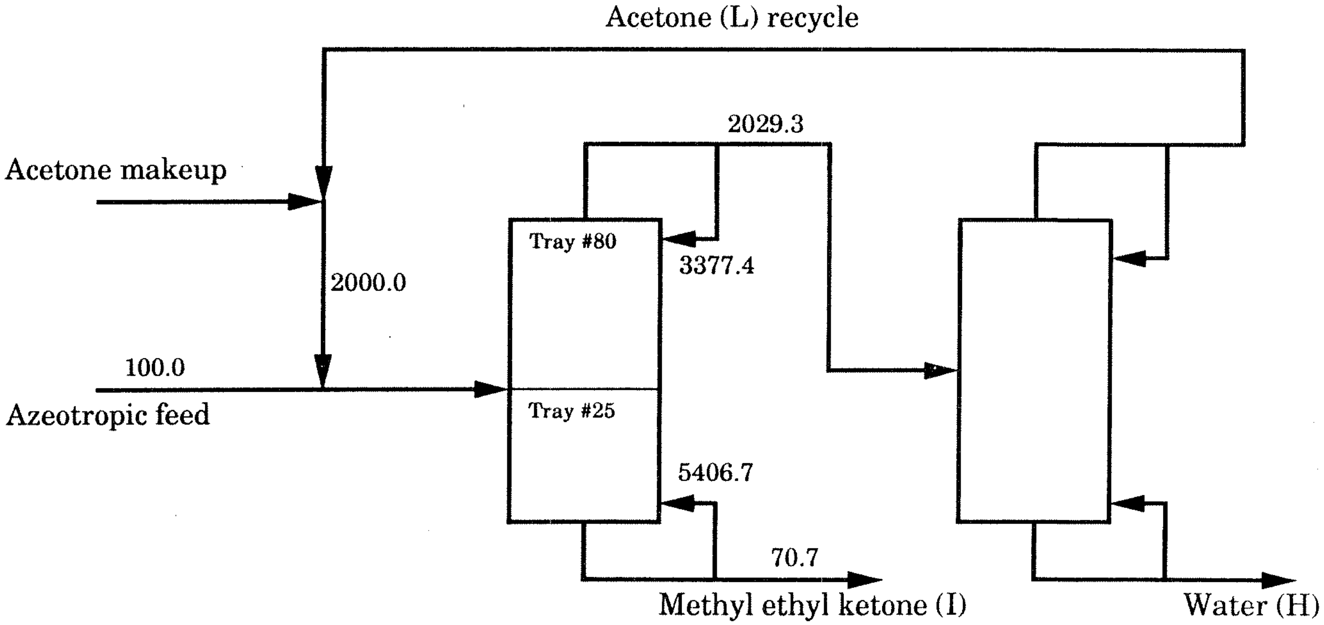


Fig. 2.28: The methyl ethyl ketone - water - acetone separation sequence

Fig. 2.29: Methyl ethyl ketone (1) - water (2) - acetone (3)
extractive column composition profile
L/F = 37.774

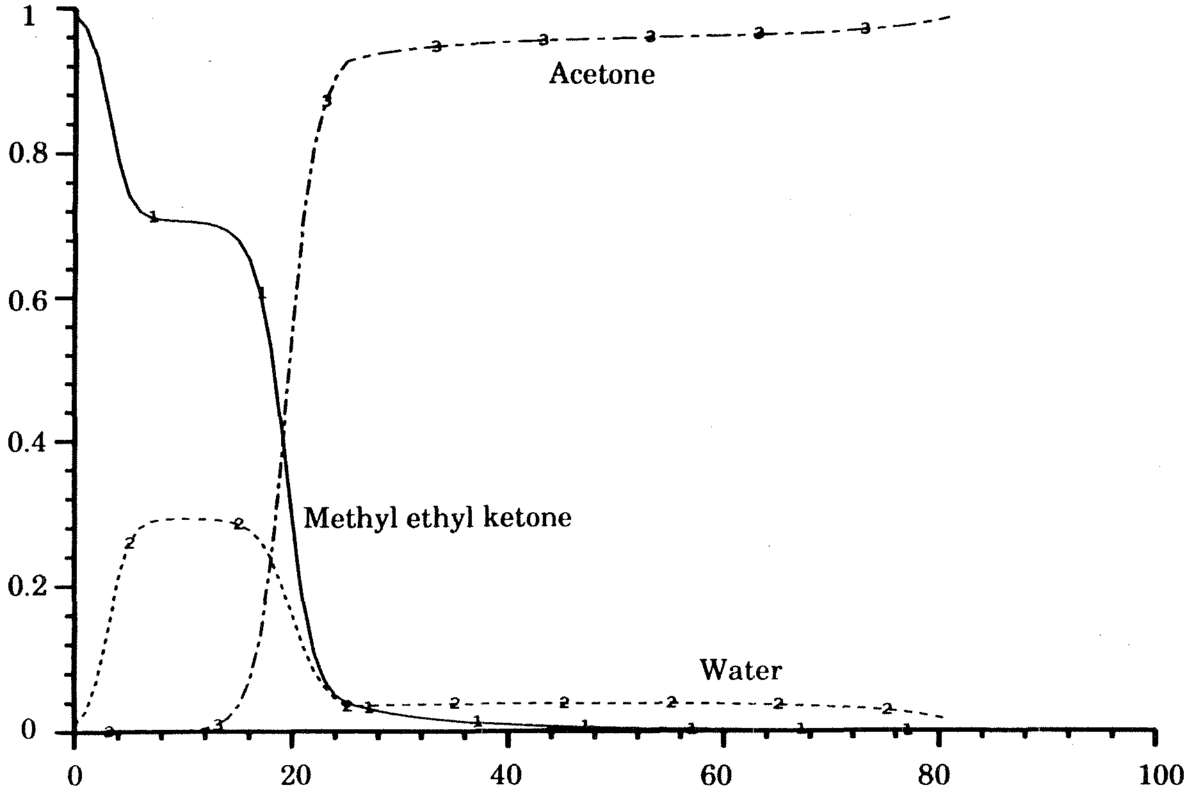


Fig. 2.30: Methyl ethyl ketone - water - acetone residue curve diagram and extractive column composition profile

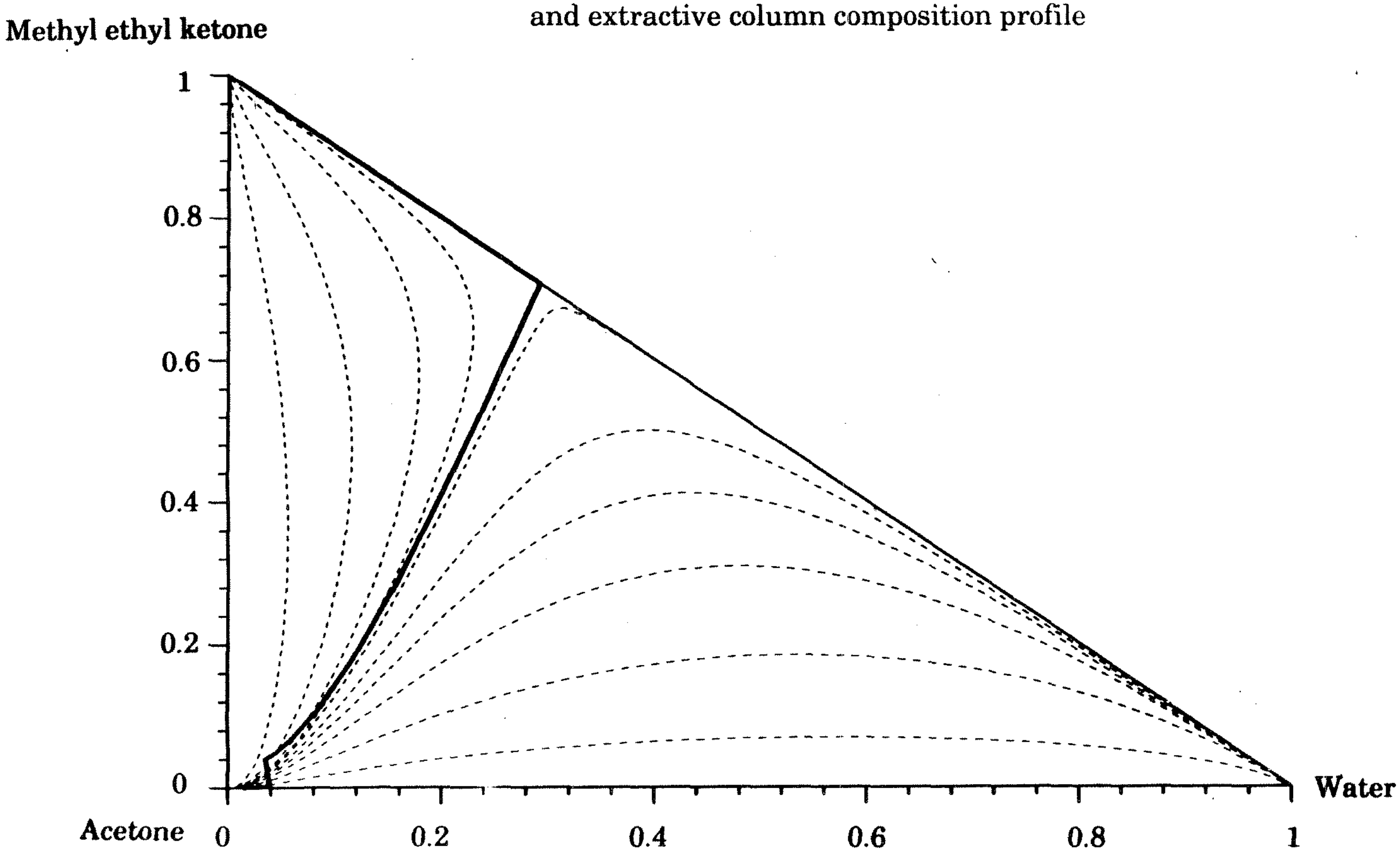


Fig. 2.31: Methyl ethyl ketone (1) - water (2) - acetone (3) extractive column composition profile obtained with ASPEN
L/F = 37.774

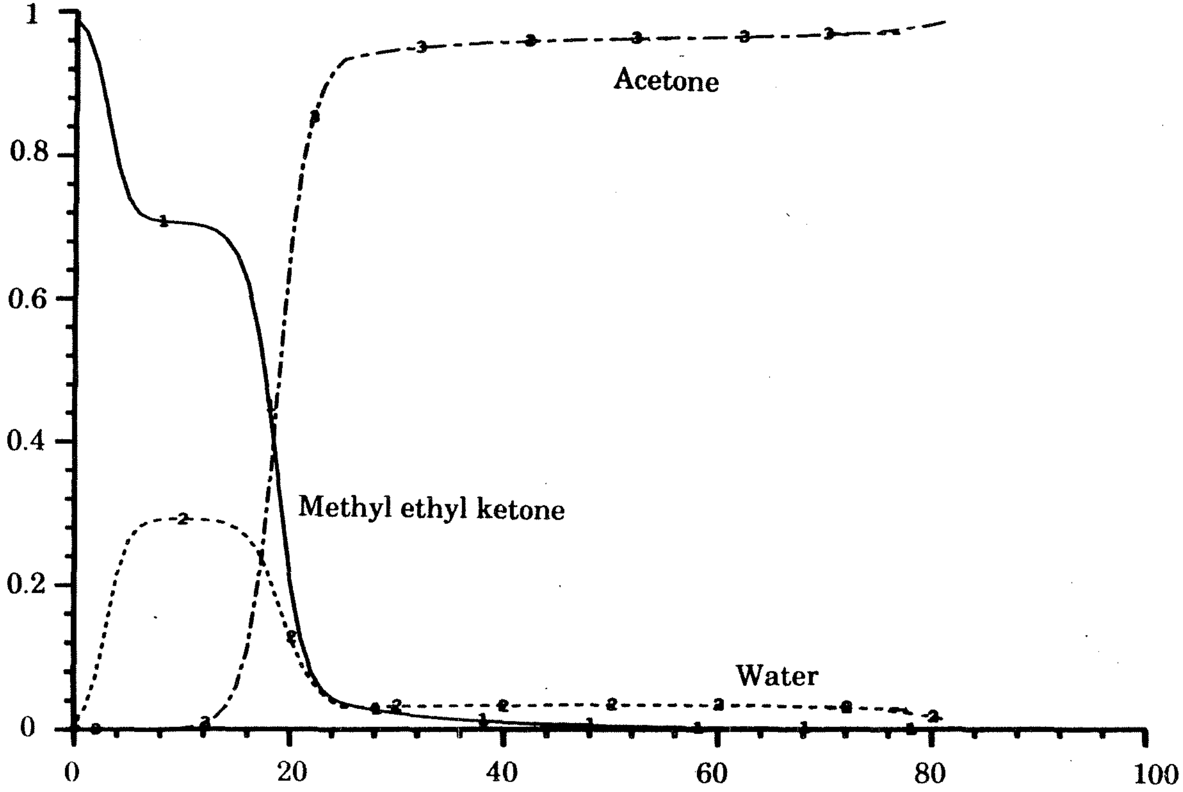


Fig. 2.32: Ethanol (1) - water (2) - ethylene glycol (3)
extractive column composition profile.
The combined feed is introduced on tray 17.

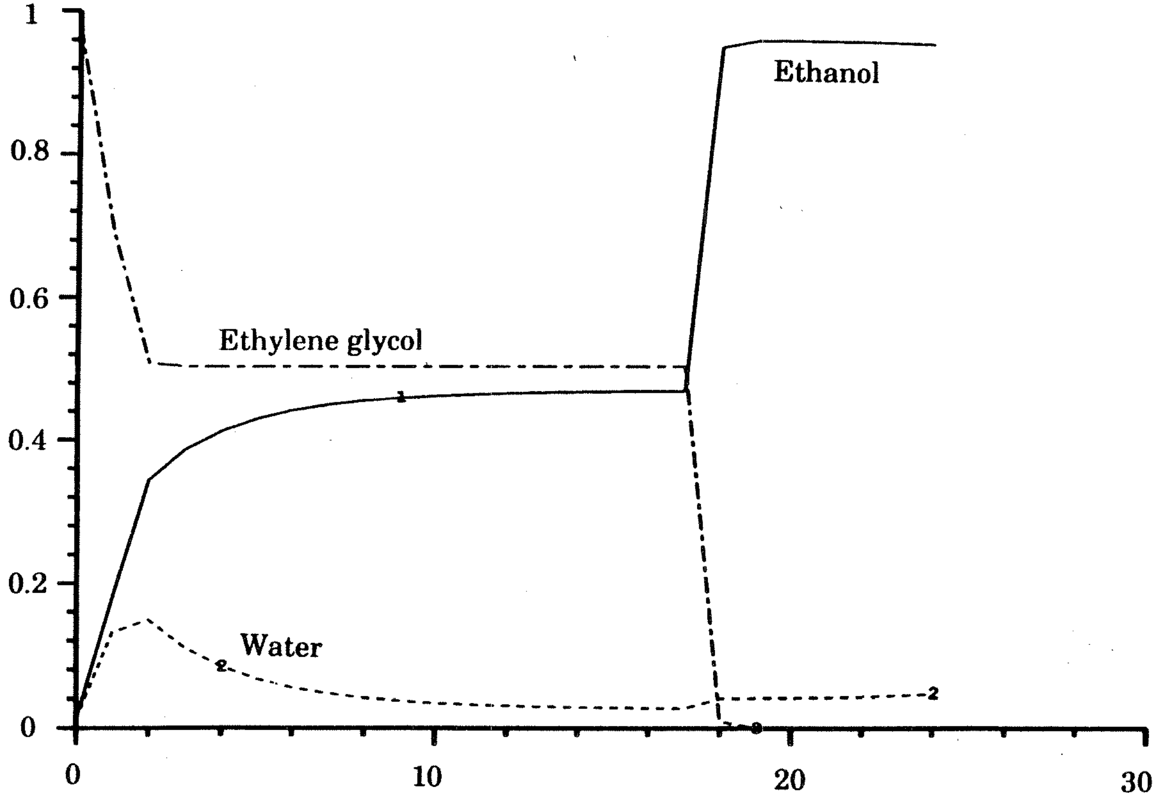


Fig. 2.33: Ethanol - water - ethylene glycol residue curve diagram and single feed extractive column composition profile.

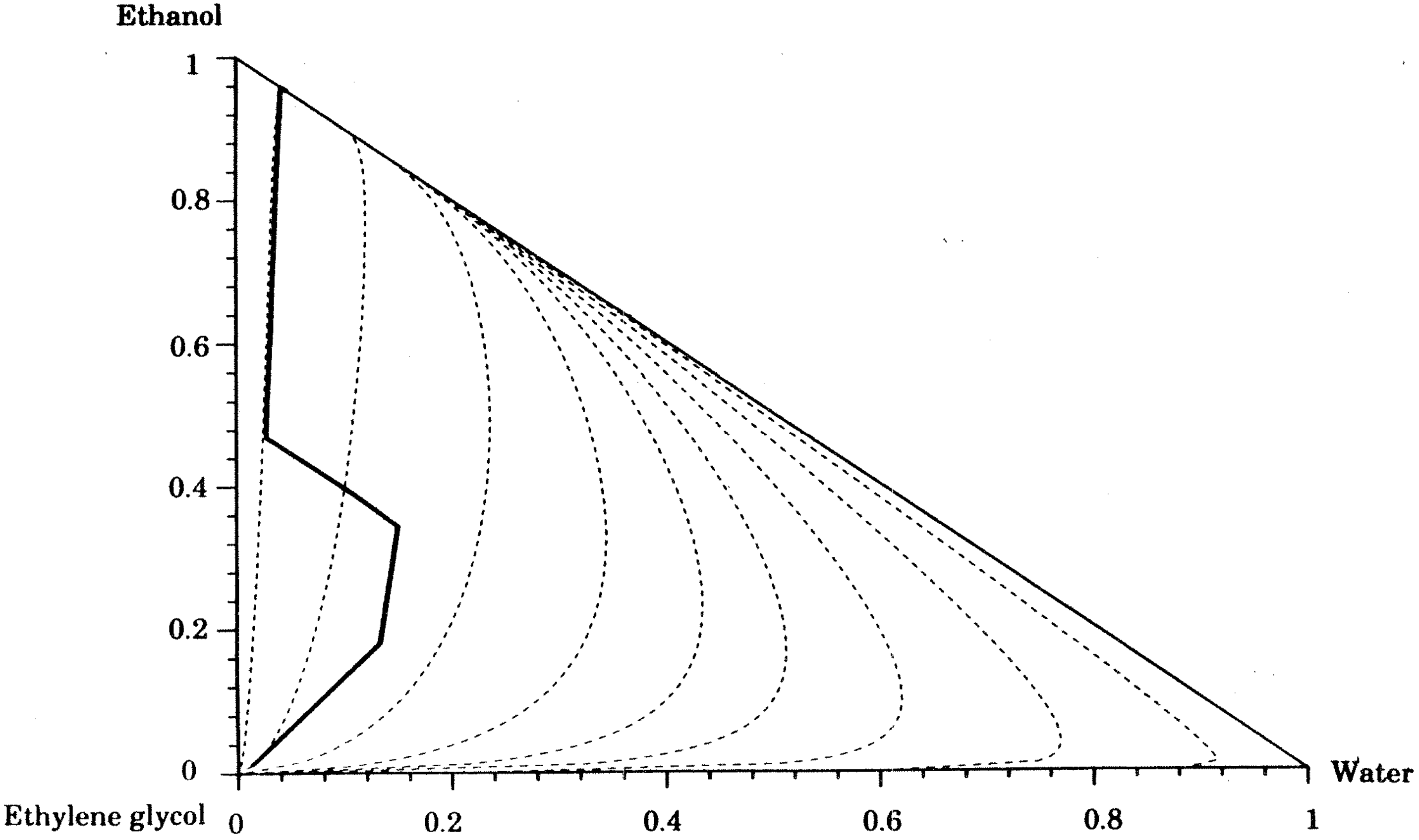


Fig. 2.34: Acetone (1) - heptane (2) - benzene (3) extractive column composition profile. The combined feed is introduced on tray 35.

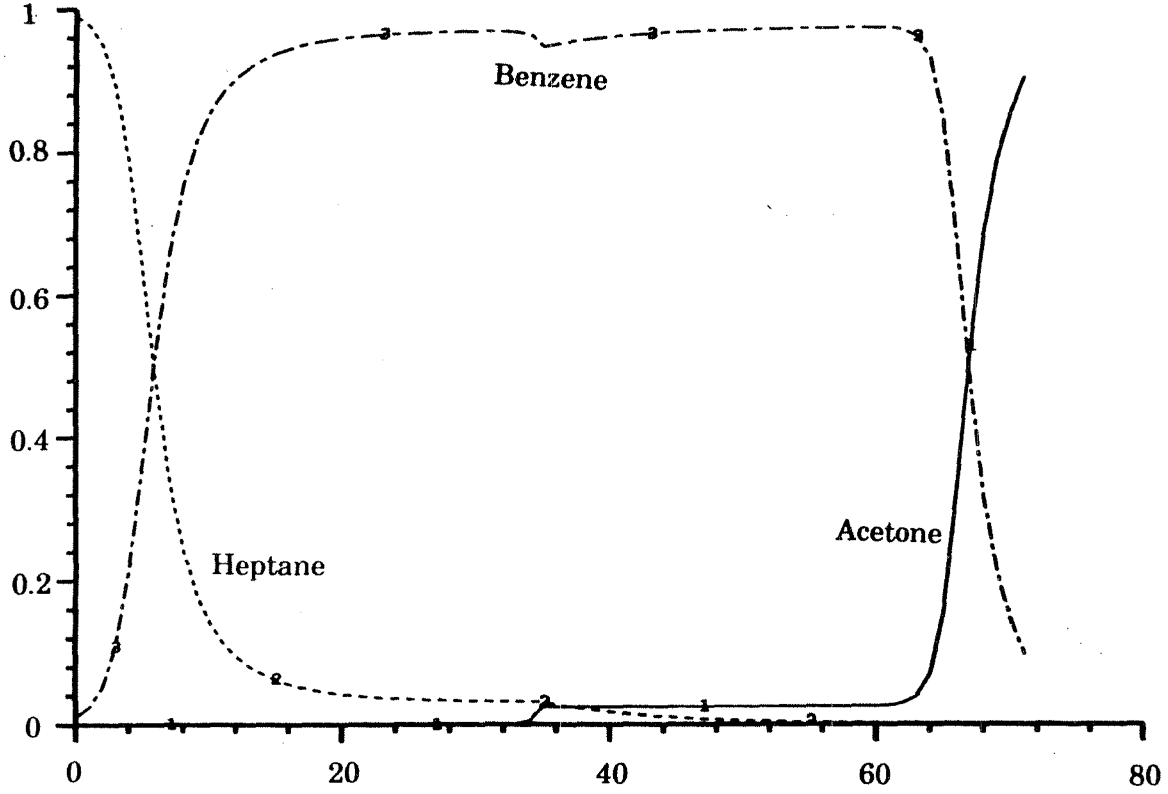
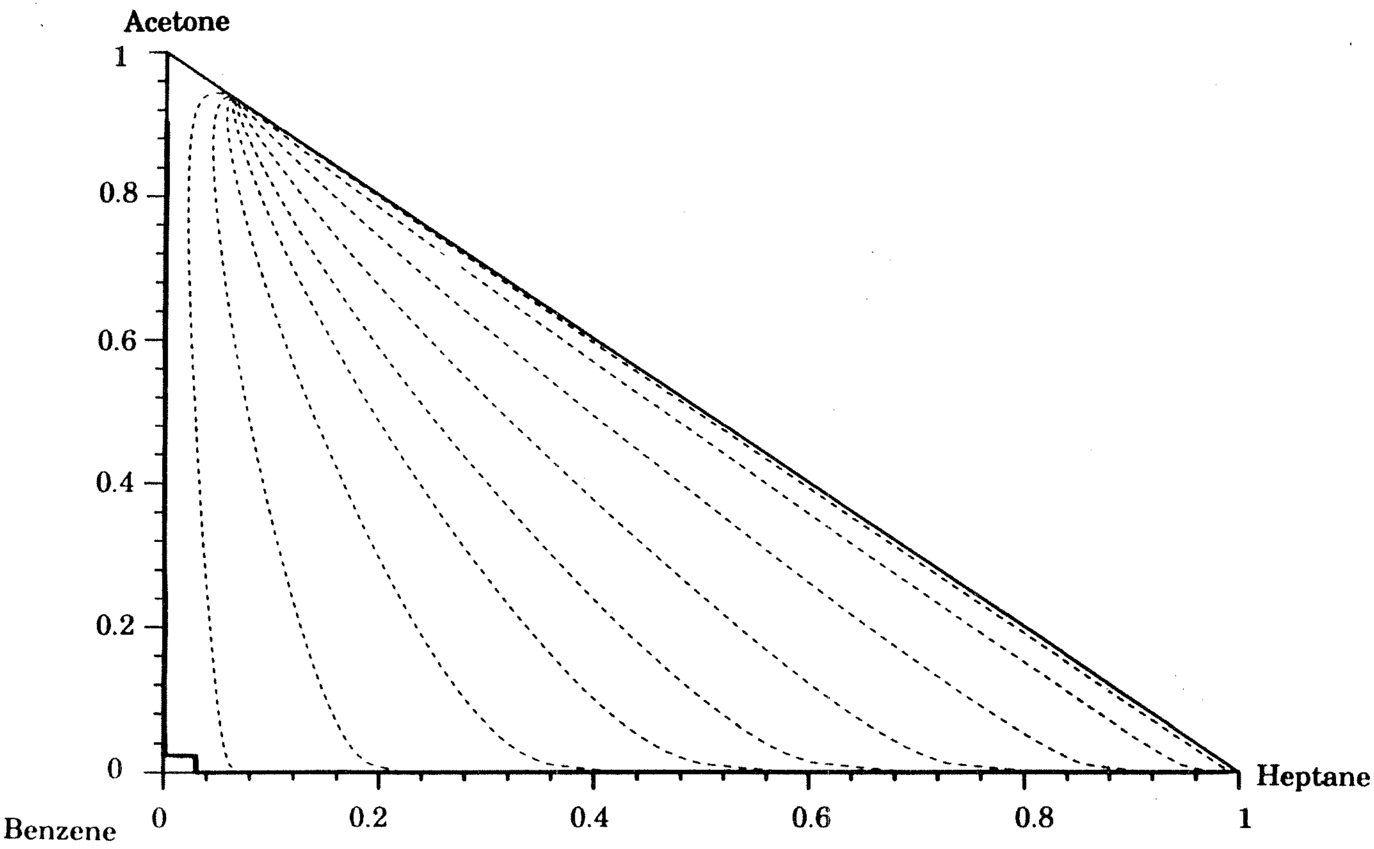


Fig. 2.35: Acetone - heptane - benzene residue curve diagram and single feed extractive column composition profile.



2.1.6 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 counter-intuitive, 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.

Although these features could be regarded as mere curiosities, they are essential for proper entrainer selection. As demonstrated in the next section, the fact that infinite reflux is not the limit case explains why several existing entrainer selection criteria fail: They reject candidate entrainers because they do not make separation feasible at infinite reflux, while these candidates actually make separation feasible at finite reflux.

2.2 Entrainer selection criteria

2.2.1 The existing rules contradict one another

Over the years, several authors (Benedict & Rubin 1945, Hoffman 1964, Doherty & Caldarola 1985, Stichlmair, Fair and Bravo 1989) have tackled the following problem:

Given a binary azeotrope that we want to separate into pure components through homogeneous azeotropic distillation and a set of candidate entrainers, find simple conditions that these candidates must satisfy in order 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.

The conditions that a candidate entrainer must meet in order to ensure separability depend on the chosen reference. For instance, in the case of a minimum boiling azeotrope, we should use as entrainer:

- According to Benedict & Rubin (1945), a component that has a higher boiling point than both azeotropic components and that introduces no additional azeotrope. Scheibel (1948), Berg (1969), Tassios (1972) and Yeh (1986) also use this condition.

- According to Hoffman (1964), a component that has a boiling point located between the two azeotropic component boiling points and that introduces no additional azeotrope.

- According to Doherty & Caldarola (1985), a component "which does not produce an internal distillation boundary between the two components to be separated".

- According to Stichlmair, Fair and Bravo (1989), a component that 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".

These conditions obviously contradict one another. The criterion of Benedict & Rubin and Hoffman's criterion are mutually exclusive, since one requires a high boiler while the other requires an intermediate boiler. The criterion of Doherty & Caldarola includes these two rules as special cases, since the conditions imposed by Benedict & Rubin or Hoffman ensure that there is no distillation boundary. In the classification proposed by Doherty & Caldarola, they correspond to the 100 and 001 cases respectively. The criterion of Stichlmair *et al.* and the criterion of Doherty & Caldarola also contradict each other. For instance, light entrainers that introduce no new azeotropes are automatically accepted by the former and systematically rejected by the latter, because these entrainers introduce a boundary that runs from the entrainer to the azeotrope and puts the two azeotropic constituents in different distillation regions. Also, heavy or intermediate entrainers that introduce no new azeotropes are automatically accepted by Doherty & Caldarola and systematically rejected by Stichlmair *et al.*

Because these criteria are necessary conditions, an entrainer that actually makes separation feasible should satisfy them all. Yet no component can satisfy simultaneously these conflicting conditions, so we can only conclude that at least one of these criteria is wrong. The next section shows that all four are actually incorrect.

2.2.2 These criteria exclude many feasible separations

Since at least one entrainer selection criterion is wrong, the next obvious question is: Which criteria should we trust? Which should we reject? We examine here this question from a practical point of view. We first look at existing industrial separations, which are obviously feasible, and see which of the four conditions are satisfied. We consider the following applications of homogeneous azeotropic distillation:

- The separation of the ethanol (L) - water (I) azeotrope using ethylene glycol (H-E) as entrainer. This well known separation has been extensively studied by Black & Distler (1972), Black (1980), Knight & Doherty (1989) and Knapp & Doherty (1990). Ethylene glycol is a high boiler which introduces no new azeotrope and there is no distillation boundary in the ternary diagram ethanol - water - ethylene glycol (see figure 2.36).

- The separation of the acetone (L) - methanol (I) azeotrope using water (H-E) as entrainer (Knapp & Doherty 1990). At normal operating pressure (atmospheric), water is a high boiler that introduces no new azeotrope and there is no distillation boundary in the ternary diagram acetone - methanol - water (see figure 2.37).
- 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 that 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.*).
- The separation of the ethanol (I) - water (H) azeotrope using methanol (L-E) as entrainer. Although no industrial column actually performs this separation, Hunek *et al.* (1989) have "checked its reliability with pilot-plant experiments". At normal operating pressure (atmospheric), methanol is a low-boiler that introduces no new azeotrope in the system. In the ternary diagram ethanol - water - methanol, a distillation boundary runs from the pure methanol point to the ethanol - water azeotrope (see figure 2.38).

By comparing these examples with the aforementioned entrainer screening rules, we see that:

- The criterion of Benedict & Rubin would reject the last two separations, because sulfuric acid is a high boiler (the azeotrope is maximum boiling) and methanol

Fig. 2.36: Ethanol - water - ethylene glycol residue curve diagram

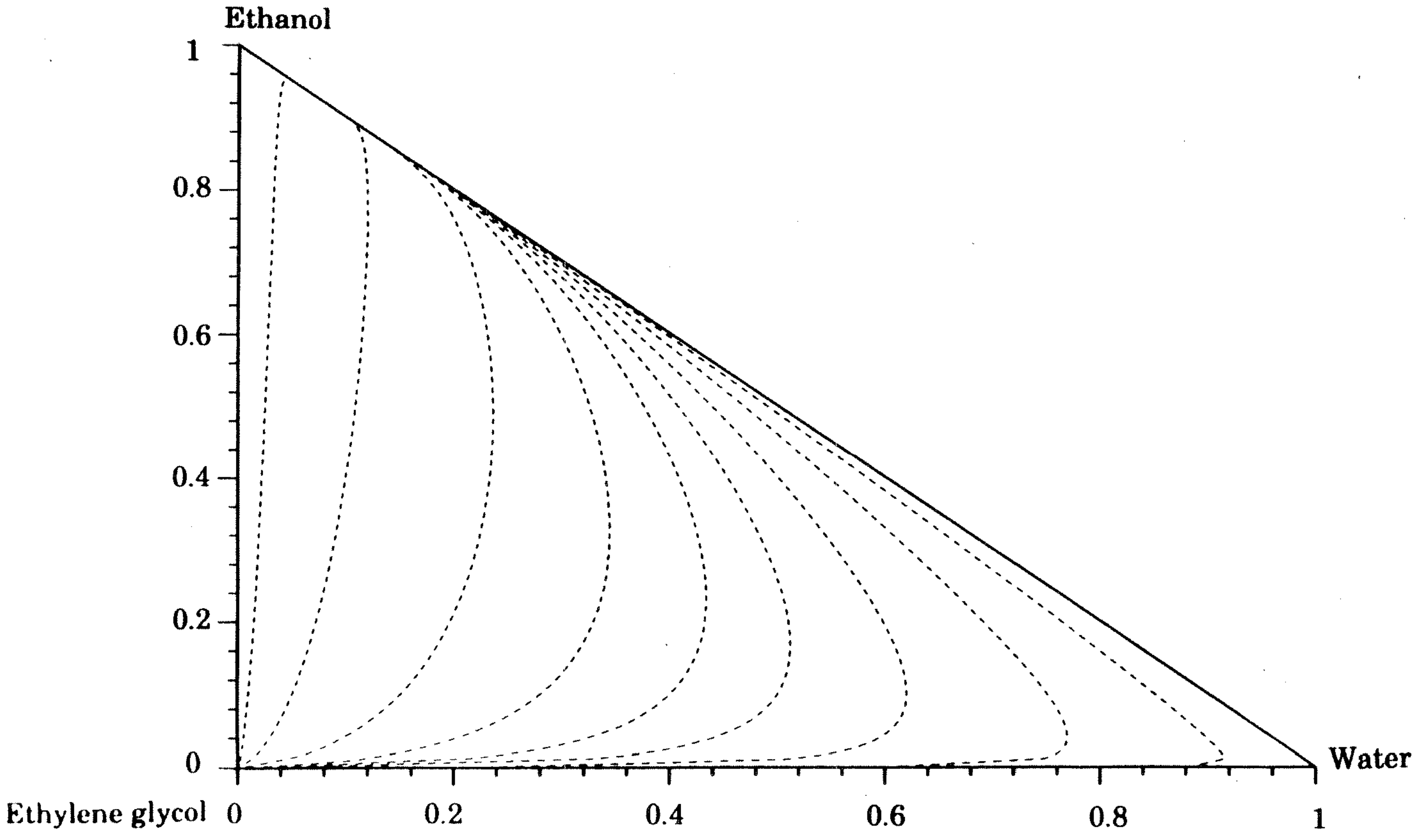


Fig. 2.37: Acetone - methanol - water residue curve diagram

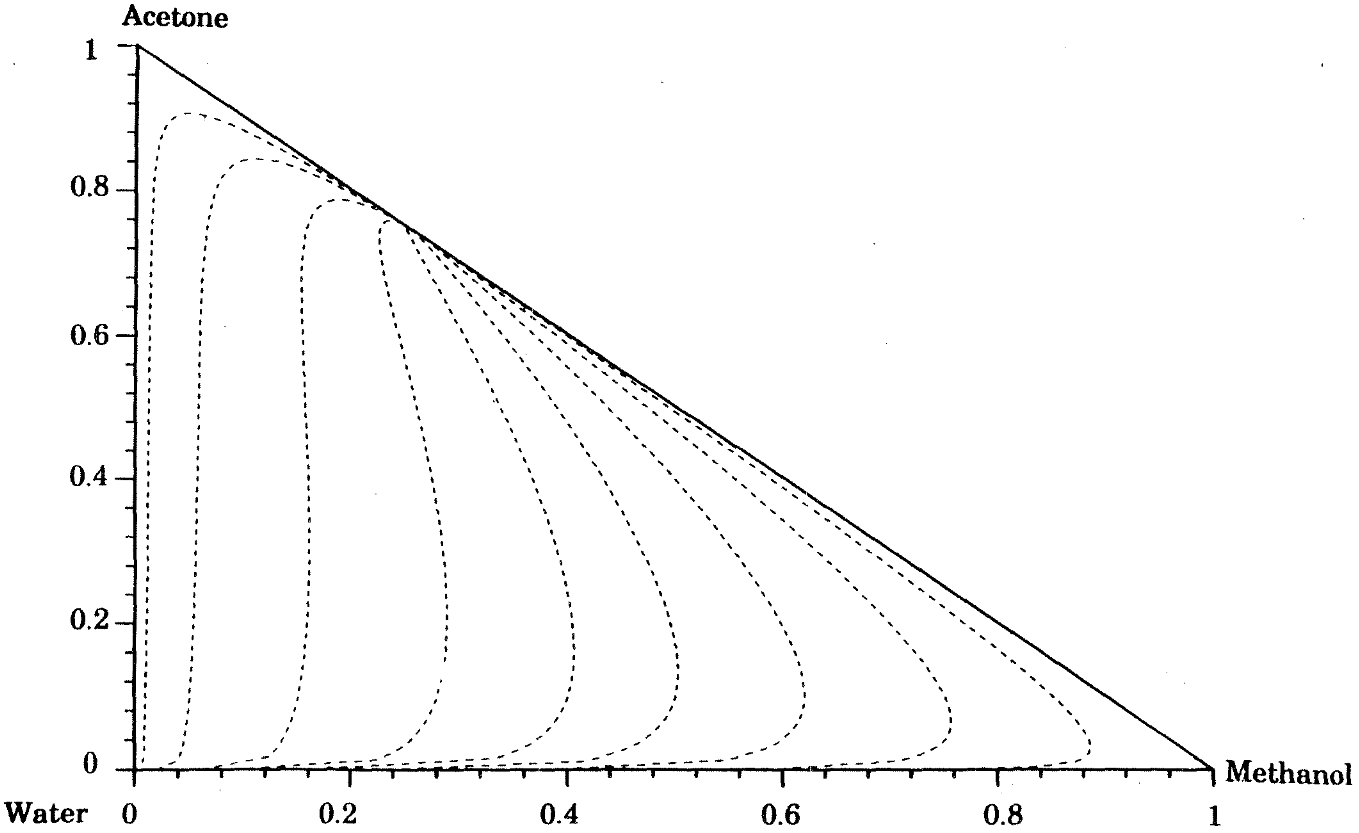
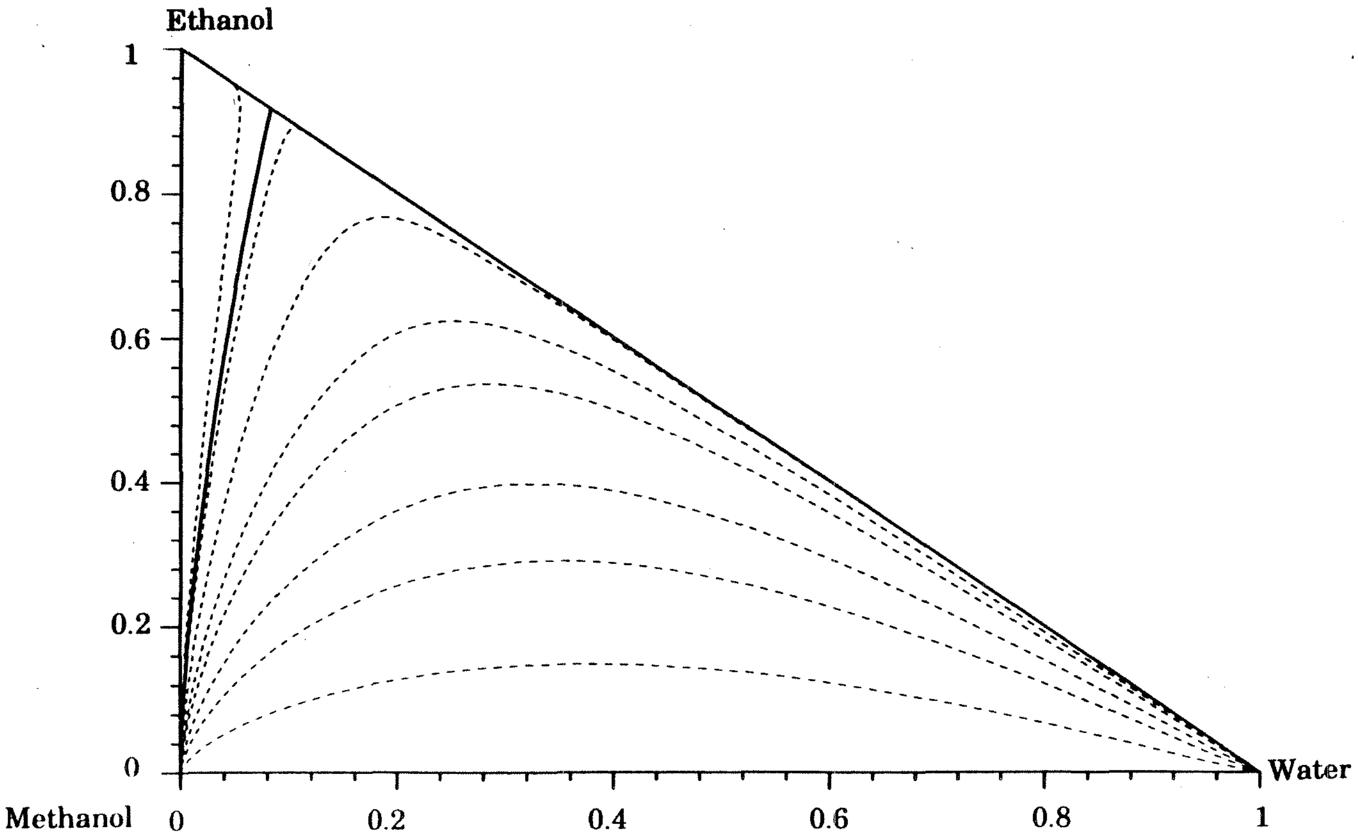


Fig. 2.38: Ethanol - water - methanol residue curve diagram



is a low boiler.

- Hoffman's rule would reject all four separations, because none of the considered entrainers is intermediate boiling.
- The criterion of Doherty & Caldarola would reject the last two separations because, in both cases, the two desired components lie on opposite sides of a distillation boundary.
- The criterion of Stichlmair *et al.* would reject the first two separations because, in both cases, the entrainer is a high boiler that does not introduce additional azeotropes.

The obvious conclusion from these four examples is that all four entrainer selection criteria are erroneous. In order to examine how often they fail, we consider five minimum boiling azeotropes. For each of these azeotropes, we have identified entrainers that make separation feasible:

- Ethyl ethanoate - ethanol: Chlorobenzene, acetone
- Ethanol - water: Methanol, ethylene glycol, acetone
- Acetone - heptane: Benzene, toluene
- Acetone - methanol: Water, chlorobenzene, ethanol, isopropanol
- Isopropanol - toluene: Methanol, ethanol, acetone, ethyl ethanoate

Appendix 1 shows the feasible separation sequence and the residue curve diagram that correspond to each of these 15 cases. We see that:

- The criterion of Benedict & Rubin is correct in 7 cases.
- Hoffman's rule is correct in 1 case.

- The criterion of Doherty & Caldarola is correct in 8 cases.
- The criterion of Stichlmair *et al.* is correct in 7 cases.

This study shows that none of these criteria can be used in practice, since all of them reject incorrectly a large fraction of entrainers.

We have now established that all four existing entrainer selection criteria are incorrect. In the next paragraph, we use the understanding gained in the previous section of the fundamental characteristics of homogeneous azeotropic distillation to explain the failures of these criteria.

2.2.3 Why do these rules fail?

Benedict & Rubin

This rule is based on industrial experience. In 1945, most entrainers were high boilers that did not add azeotropes in the system. By using the rule of Benedict & Rubin, we can utilize the experience gained in industry with such entrainers. But the chemical industry at large does not take full advantage of the possibilities offered by homogeneous azeotropic distillation (this fact has already been underlined by Doherty & Caldarola (1985)).

Hoffman

This rule is based on a graphical representation of the infinite reflux situation. At infinite reflux, separations such as ethanol (L) - water (I) - ethylene glycol (H-E) and acetone (L) - methanol (I) - water (H-E), which are two of the most common applications of homogeneous azeotropic distillation) are impossible. Hoffman's graphical procedure correctly predicts this fact. However, because infinite reflux is not the limiting case, this does not imply that separation is infeasible for finite reflux values.

Doherty & Caldarola

The criterion of Doherty & Caldarola is based on residue curve boundaries. Their argumentation contains two steps: The first step can be found in Van Dongen & Doherty (1985), the second step in Doherty & Caldarola (1985). The reader is referred to these papers 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. Implicitly, they assume that composition profiles at finite reflux are very similar to composition profiles at infinite reflux. They write (Van Dongen & 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 assumption they explain why "distillation boundaries within the composition triangle can never be crossed by simple recycle methods."

As we saw in the first section, profiles at finite reflux and at infinite reflux can differ significantly in the case of homogeneous azeotropic distillation. Therefore, the implicit assumption that composition profiles at finite reflux are similar to composition profiles at infinite reflux is incorrect. Composition profiles in the extractive section often go across residue curves. For instance, in the case of ethanol (L) - water (I) - ethylene glycol (H-E), the comparison of figures 10 and 13 of Levy & Doherty (1986) shows that the extractive section composition profile is perpendicular to the residue curves it intersects.

Because infinite reflux composition profiles coincide with residue curves (Van Dongen & 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. For instance, figure 11 of Van Dongen & Doherty (1985) and figure 12 of Levy, Van Dongen and Doherty (1985) display examples of mixtures where distillate and bottom lie in different regions. According to our experience, the assumption that distillate and bottom have to be in the same region is too restrictive. Indeed, the composition profiles of several columns presented in this article cross their corresponding boundaries[1]; the distillate and bottom then lie in different distillation regions.

While distillate and bottom must lie in the same distillation region at infinite reflux, the feed can belong to a different region. Even at infinite reflux, the mass balance line of a distillate 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 2.39 to figure 2.42 illustrate this fact in the methyl acetate (L) - methanol (I) - hexane (H-E) case[2]: We can use hexane as entrainer for the methanol - methyl

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[1] Such is the case for the following mixtures: Methyl ethyl ketone (I) - water (H) - acetone (L-E), ethanol (I) - water (H) - methanol (L-E), ethanol (I) - water (H) - acetone (L-E), sec butanol (I) - water (H) - ethanol (L-E), isopropanol (I) - toluene (H) - acetone (L-E), isopropanol (I) - toluene (H) - ethyl ethanoate (L-E), ethyl ethanoate (I) - ethanol (H) - acetone (L-E).

acetate azeotrope. Indeed, a feed of composition D1, which lies in region 1, can be separated in a 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 extractive 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 the products of the first column all lie in region 1: The separation performed in this column follows the rule of Doherty & Caldarola. As a conclusion, their argumentation breaks down because of an incorrect analysis of homogeneous azeotropic distillation columns composition profiles: Feed, distillate and bottoms can lie in different distillation regions.

As a final note, we reworked the example presented in figures 6 and 7 of Doherty & Caldarola. In their example, the separation of the ethanol - water azeotrope is attempted using an unknown entrainer that forms a binary minimum boiling azeotrope with water and that is lighter than ethanol (no other azeotrope). Because we have no data for such an entrainer, we used the sec butanol (H) - water (I) - ethanol (L-E) example. By comparing figure 7 of Doherty & Caldarola with figure 2.43, we see that the residue curve diagrams are identical. Ethanol plays the role of the unknown entrainer, sec butanol replaces ethanol, and water has the same role in both cases. Doherty & Caldarola could not obtain the desired separation, mostly because they tried to recover the heavy component, namely water, first. As figure 2.44, figure 2.45 and figure 2.46 show, separation is feasible in a two-column sequence if we recover the intermediate component, *i.e.* sec butanol, first as a bottom product. The second column separates water from the ethanol - water azeotrope. This azeotrope is recycled and acts as entrainer. We attempted to reproduce this result with Aspen, but

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[2] Like Van Dongen & Doherty (1985), we use the regular solution equation instead of the Wilson equation for this mixture. We use the same representation convention.

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

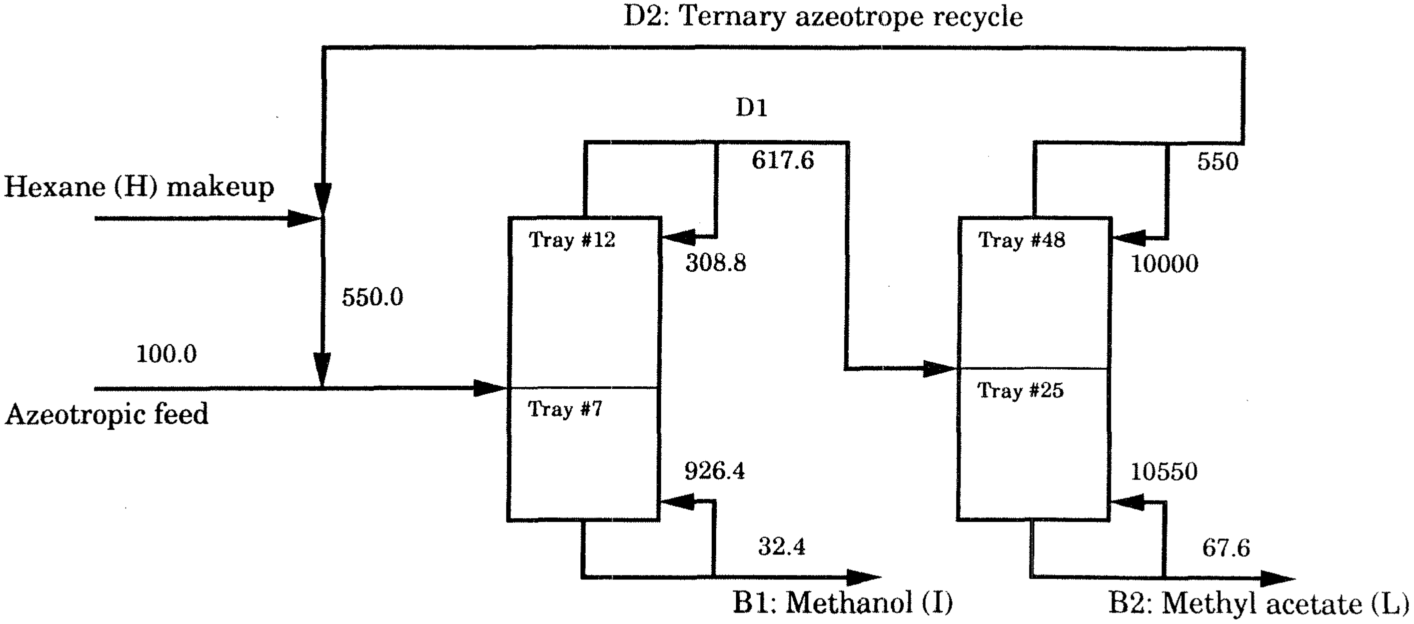


Fig. 2.39: The hexane - methanol - methyl acetate separation sequence

Fig. 2.40: Hexane (1) - methanol (2) - methyl acetate (3)
extractive column composition profile

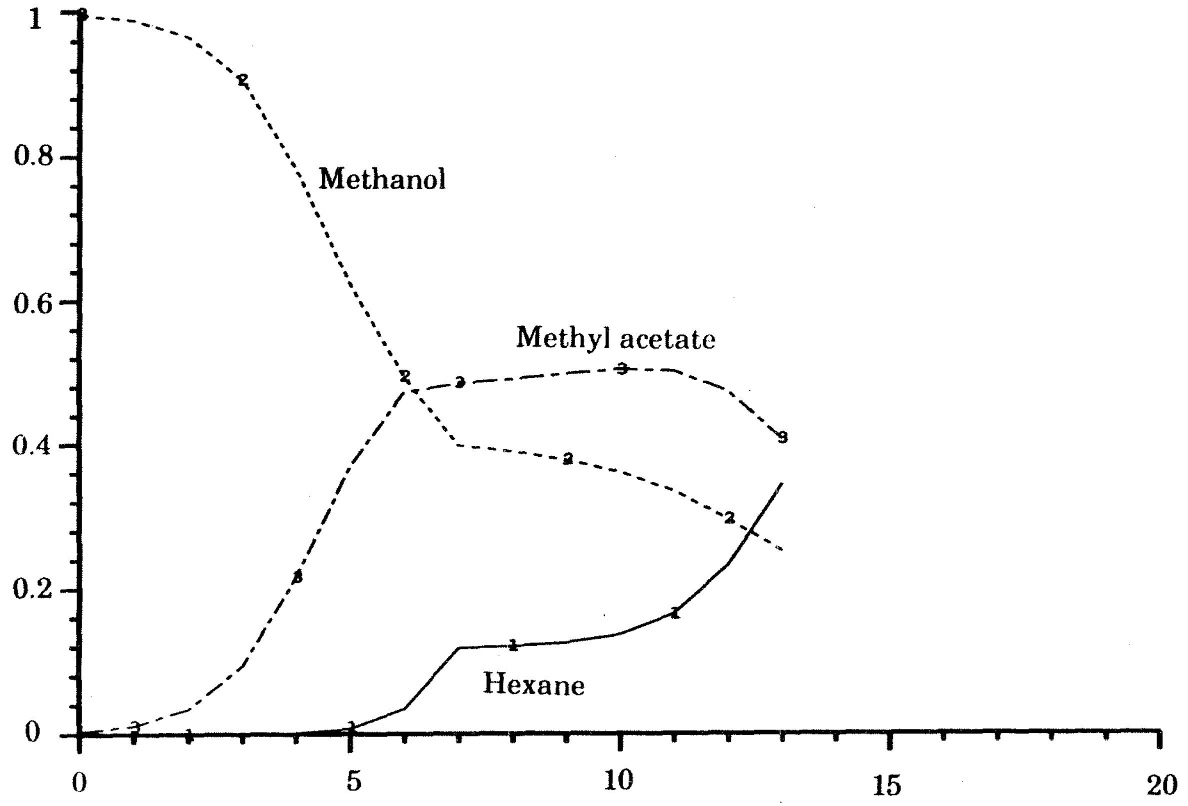


Fig. 2.41: Hexane (1) - methanol (2) - methyl acetate (3) entrainer recovery column composition profile

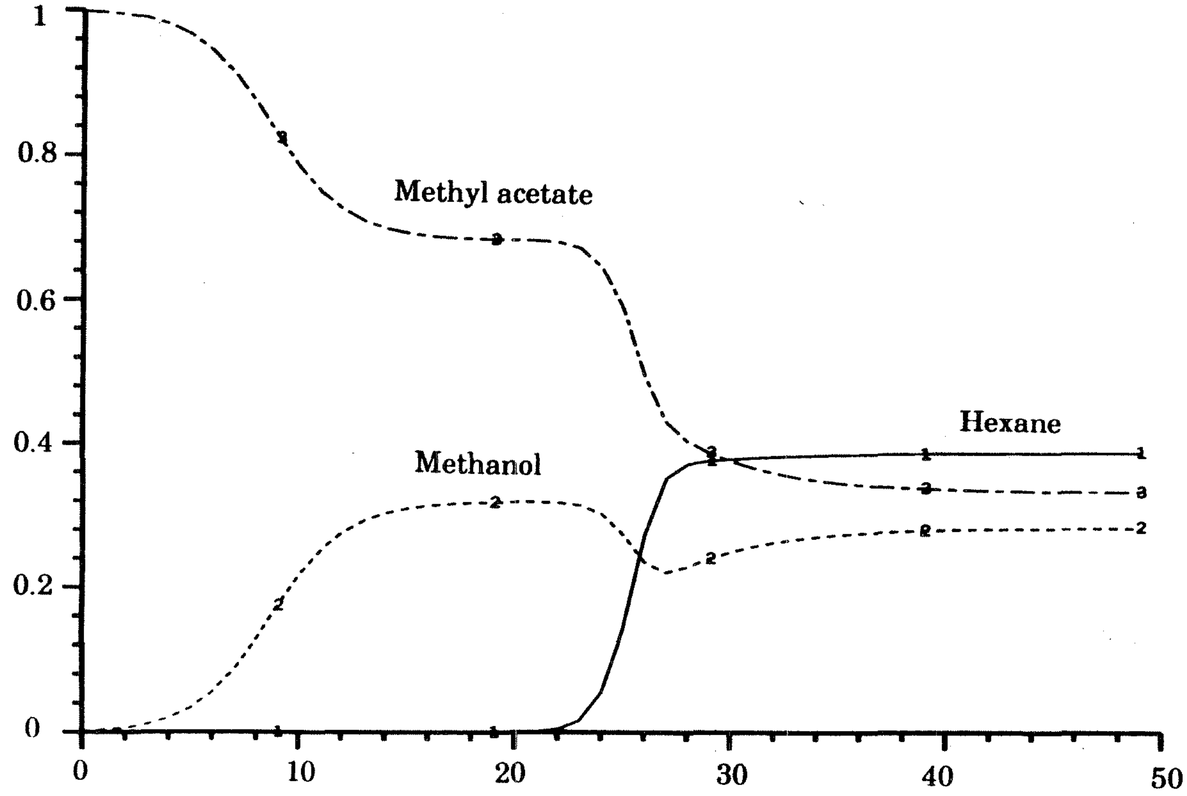
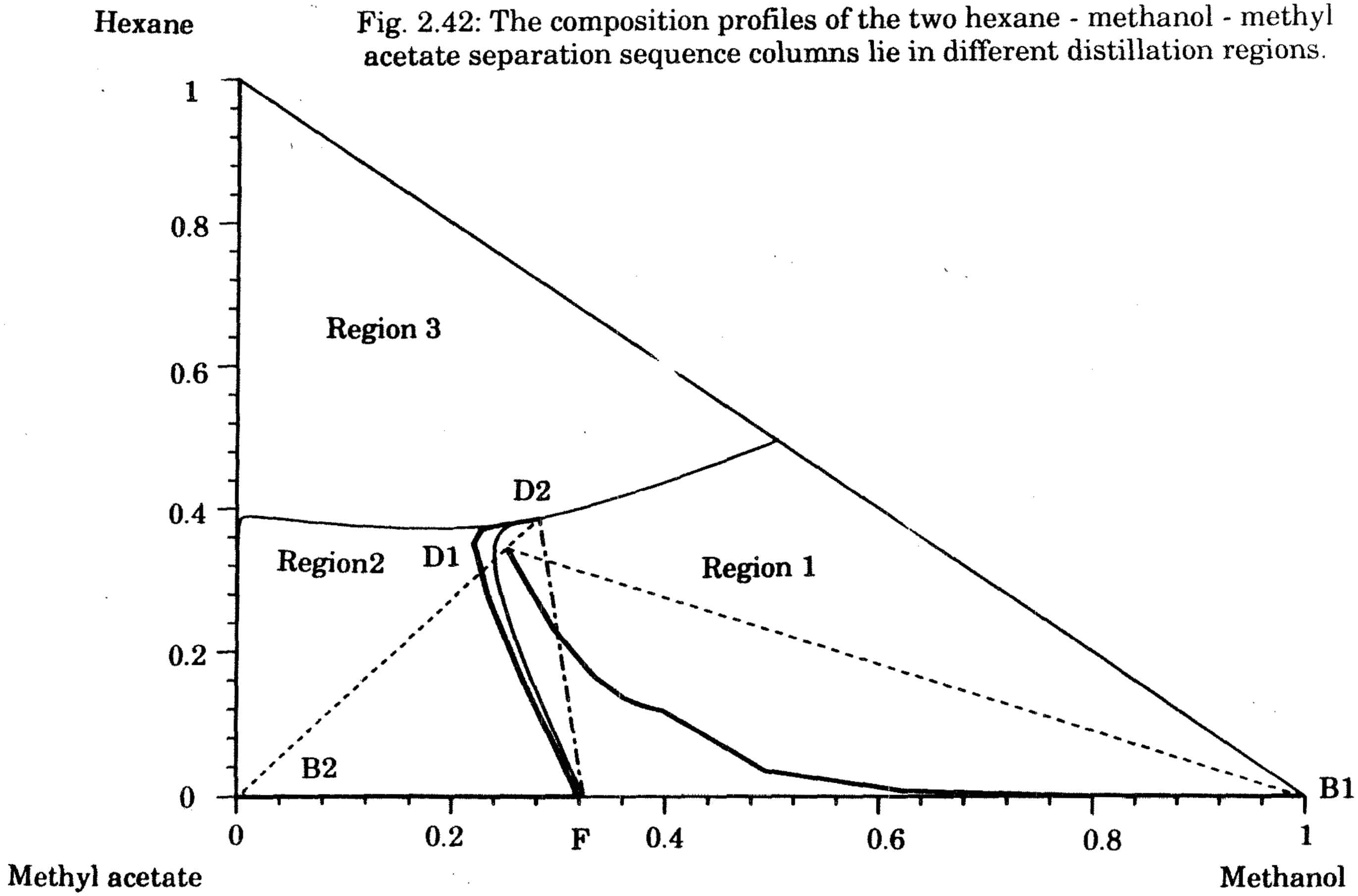


Fig. 2.42: The composition profiles of the two hexane - methanol - methyl acetate separation sequence columns lie in different distillation regions.



could not make it converge.

The criterion of Doherty & Caldarola rejects many candidate entrainers that actually make separation feasible. For instance, it rejects all light boilers that introduce no new azeotrope. 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. Separation may be easy even when the boundary looks almost straight, as the ethanol (I) - water (H) - methanol (L-E) system demonstrates (figure 2.47, figure 2.48 and figure 2.49).

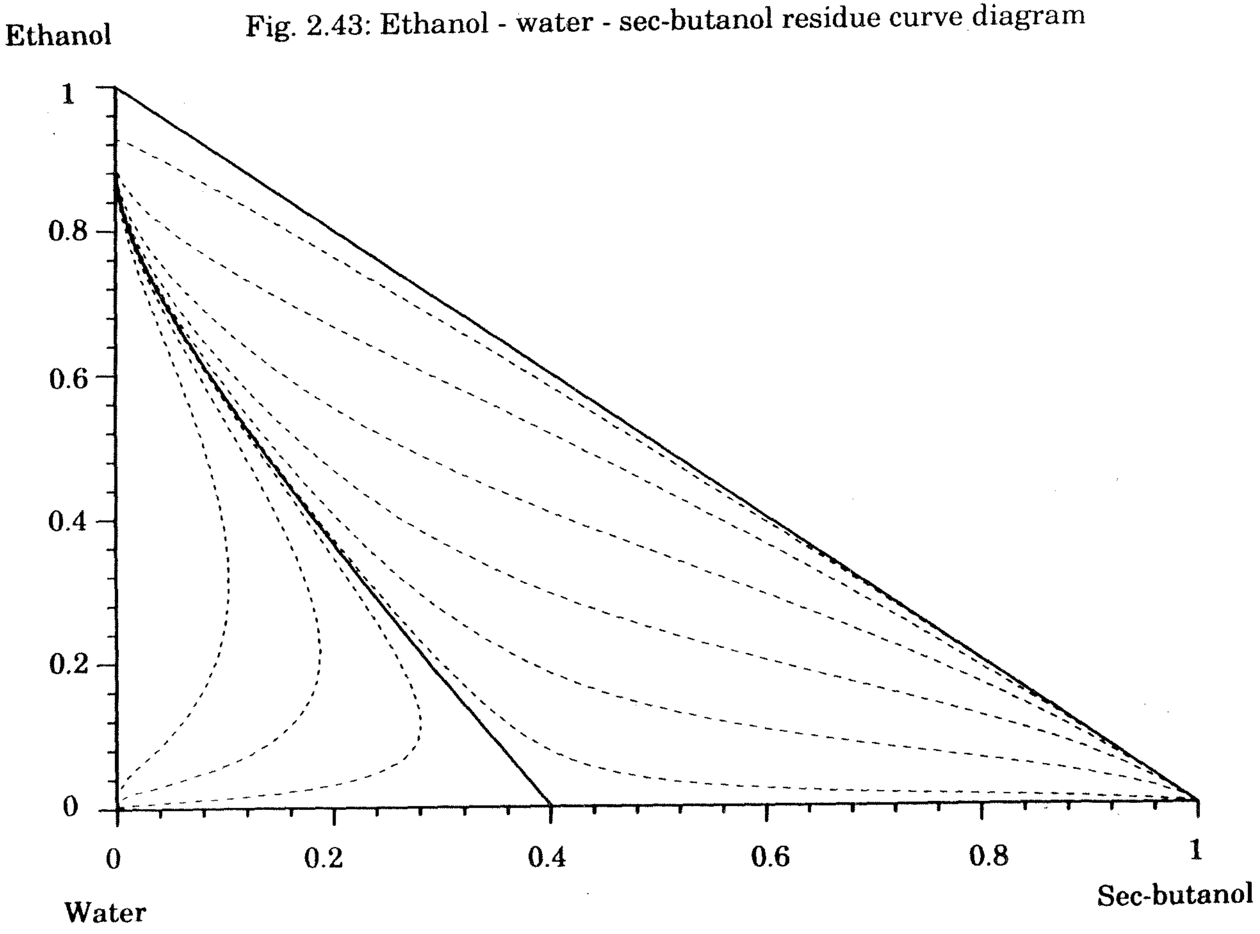
Stichlmair, Fair and Bravo

Their criterion is directly based 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

Fig. 2.43: Ethanol - water - sec-butanol residue curve diagram



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Sec-butanol (I)	0.0	0.4008	0.00024	0.99
Water (H)	0.0818	0.5992	0.13335	0.01
Ethanol (L)	0.9182	0.0	0.86641	0.00

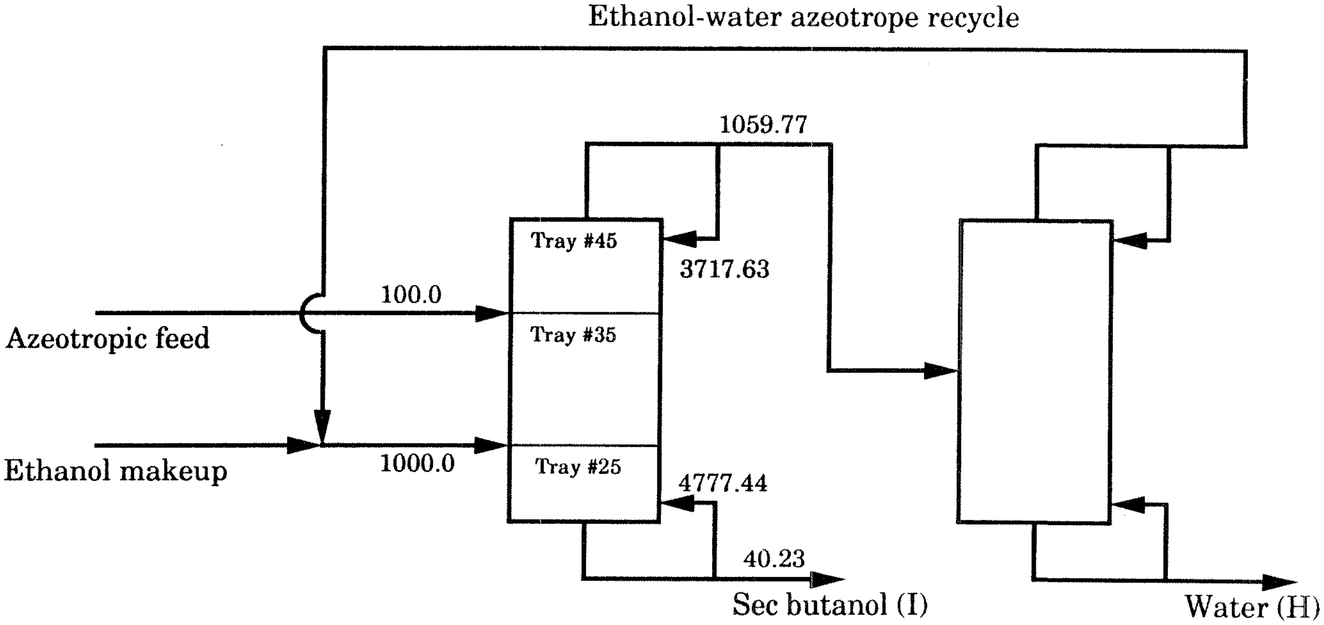


Fig. 2.44: The sec-butanol - water - ethanol separation sequence

Fig. 2.45: Sec-butanol (3) - water (2) - ethanol (1)
extractive column composition profile

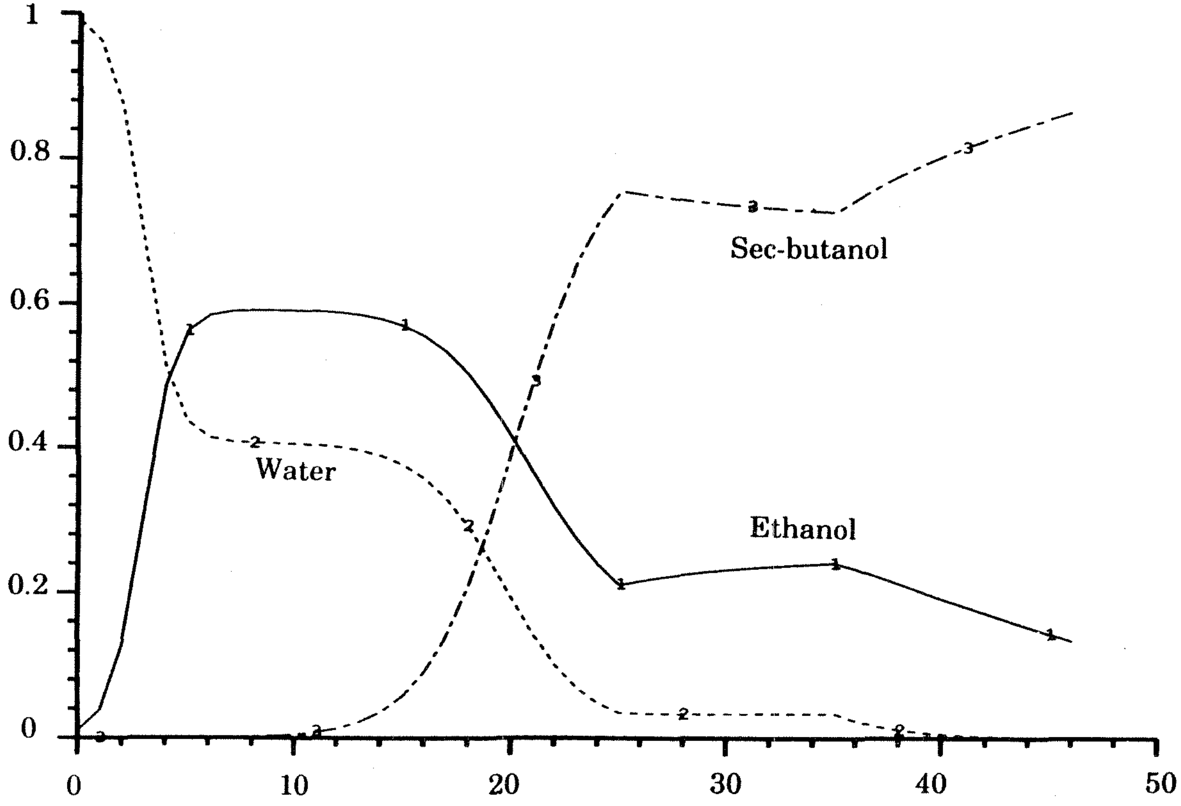
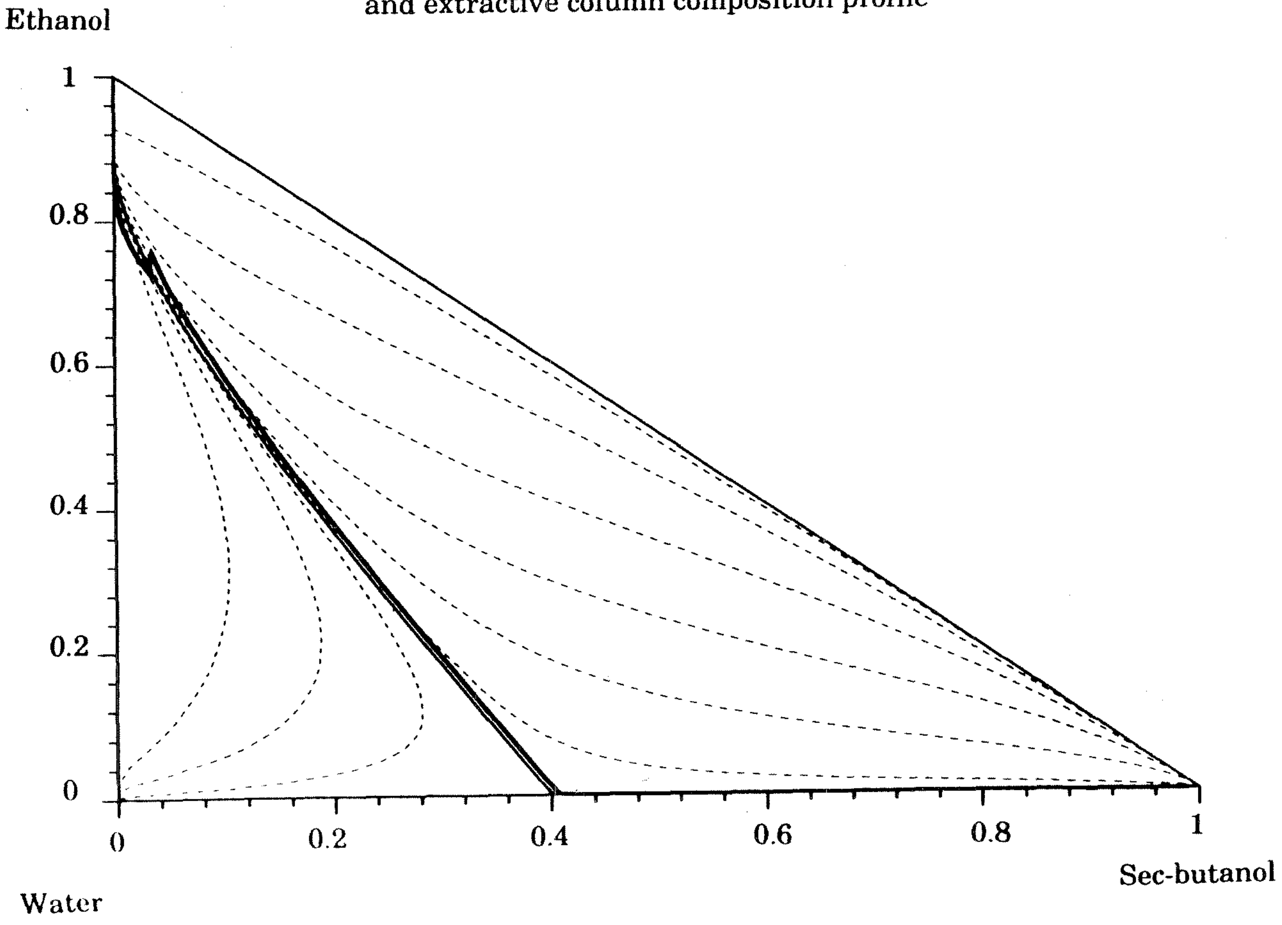


Fig. 2.46: Sec-butanol - water - ethanol residue curve diagram
and extractive column composition profile



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

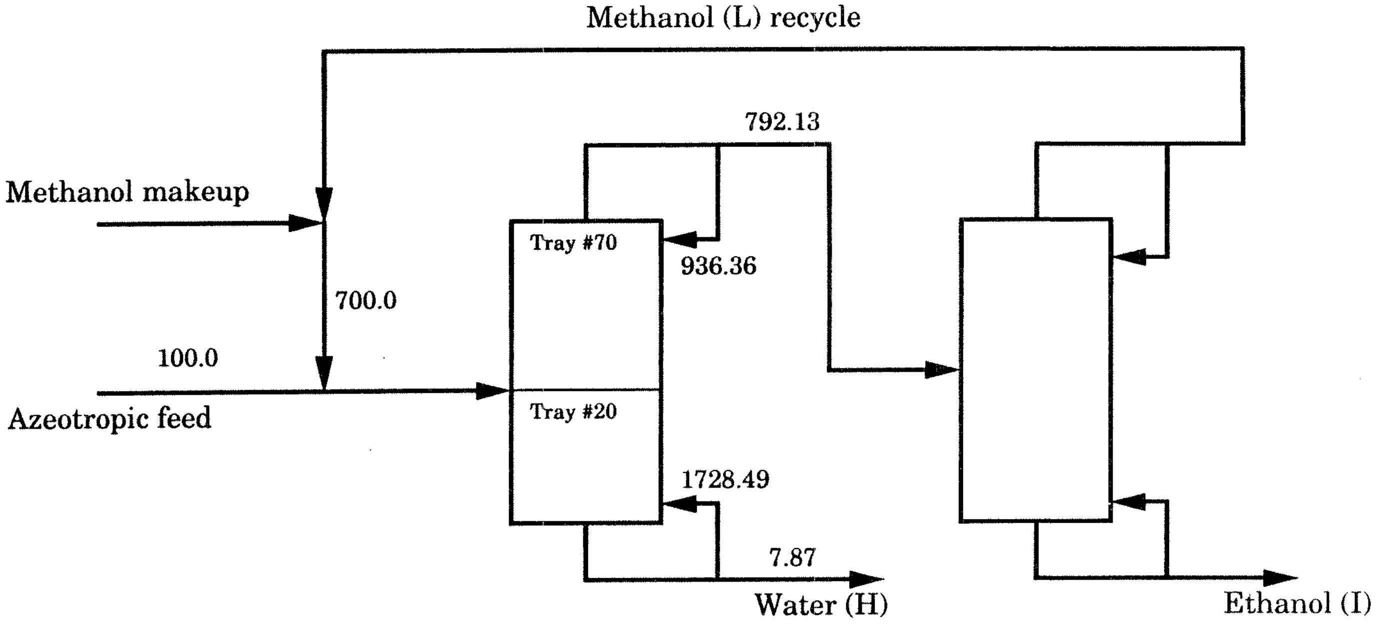


Fig. 2.47: The ethanol - water - methanol separation sequence

Fig. 2.48: Ethanol (1) - water (2) - methanol (3) extractive column composition profile

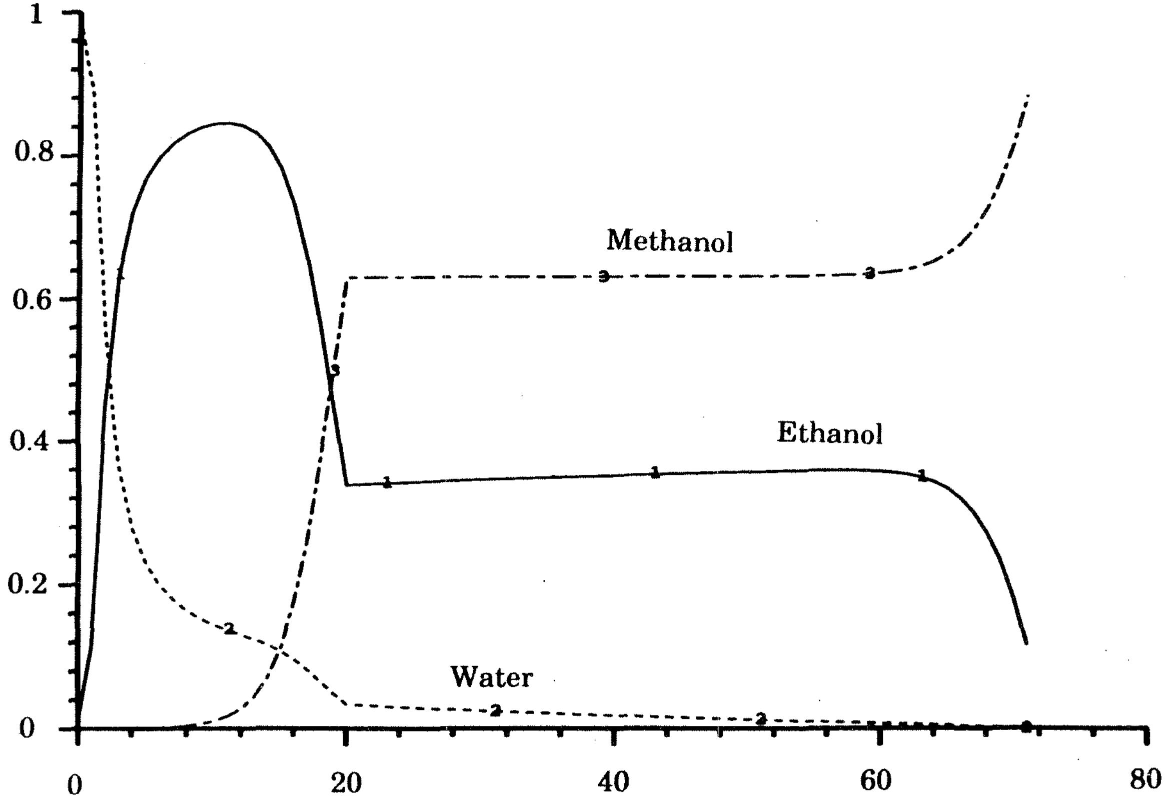
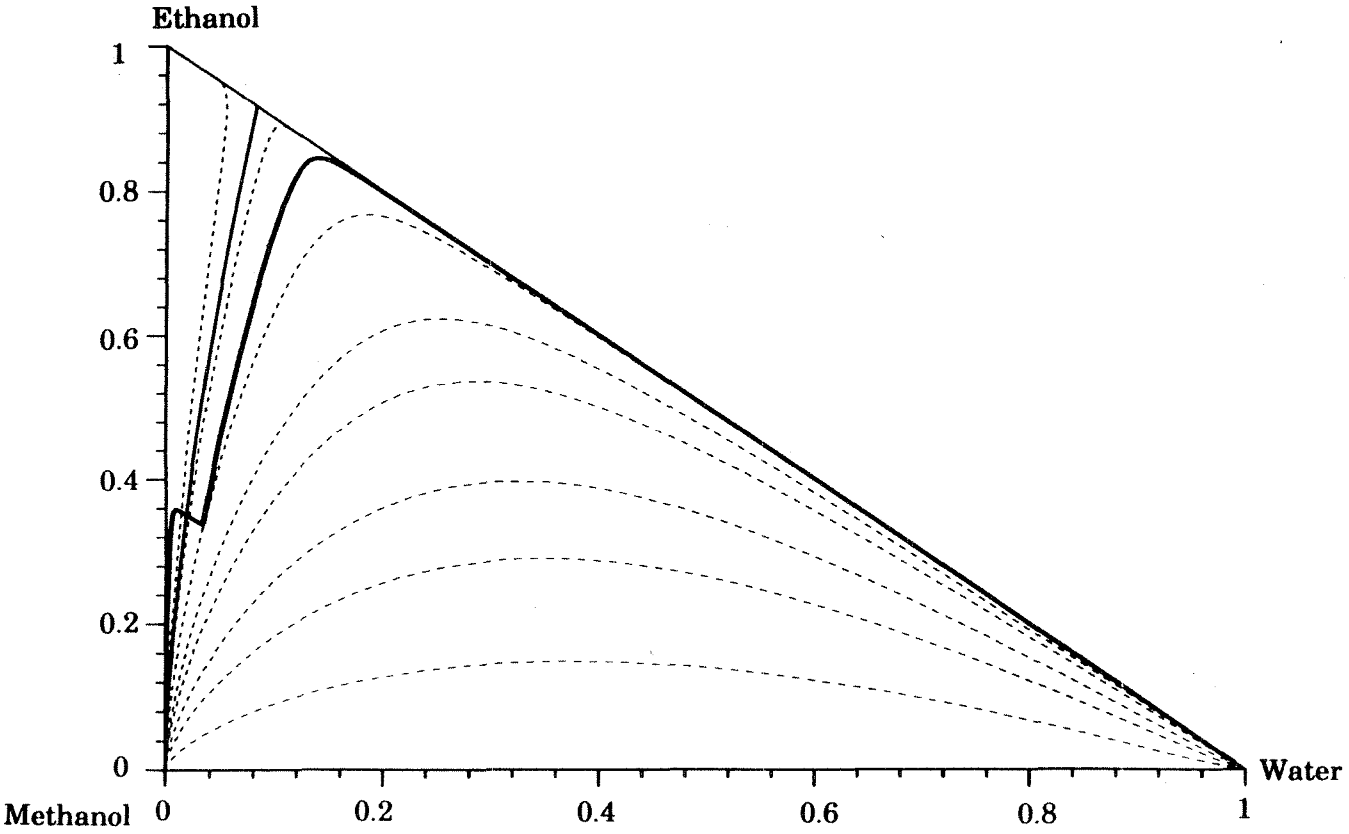


Fig. 2.49: Ethanol - water - methanol residue curve diagram and extractive column composition profile



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 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.

This argumentation is flawed because the generalization made in the second step is incorrect. A component can be obtained in pure form even if distillation lines neither start from it nor end at it. Figure 2.36 illustrates this point in the ethanol (L) - water (I) - ethylene glycol (H-E) case. Ethanol is not a node of the distillation line diagram, but a saddle. Although ethanol cannot be recovered at infinite reflux, it can be recovered at finite reflux. Note that saddle components can sometimes be recovered at infinite reflux. This point is demonstrated by figure 2.50, figure 2.51 and figure 2.52 in the acetone (L) - heptane (H) - benzene (I-E) case. Although acetone is again a saddle, it can be recovered as pure distillate of a column operating at infinite reflux. As a conclusion, their argumentation breaks down because they incorrectly generalized from the zeotropic case to the homogeneous azeotropic case and because separations that are infeasible at infinite reflux may be feasible at finite reflux.

Another important mistake in their paper is the fact that the material balance of their three-column separation sequence cannot be closed, as communicated to us by Doherty (1989). Using arguments similar to Doherty & Caldarola (1985, p. 479), we see that closing the material balance around the first column requires that D3, B1 and A (pure component a corner) are aligned (see figure 4 of Stichlmair *et al.*). This is clearly not the case. However, separation is feasible in the situation they describe, because the distillation boundary can be crossed (note that this distillation boundary is essentially the same as in Doherty & Caldarola). A two-column separation sequence, rather than the incorrect three-column sequence, can perform the described

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

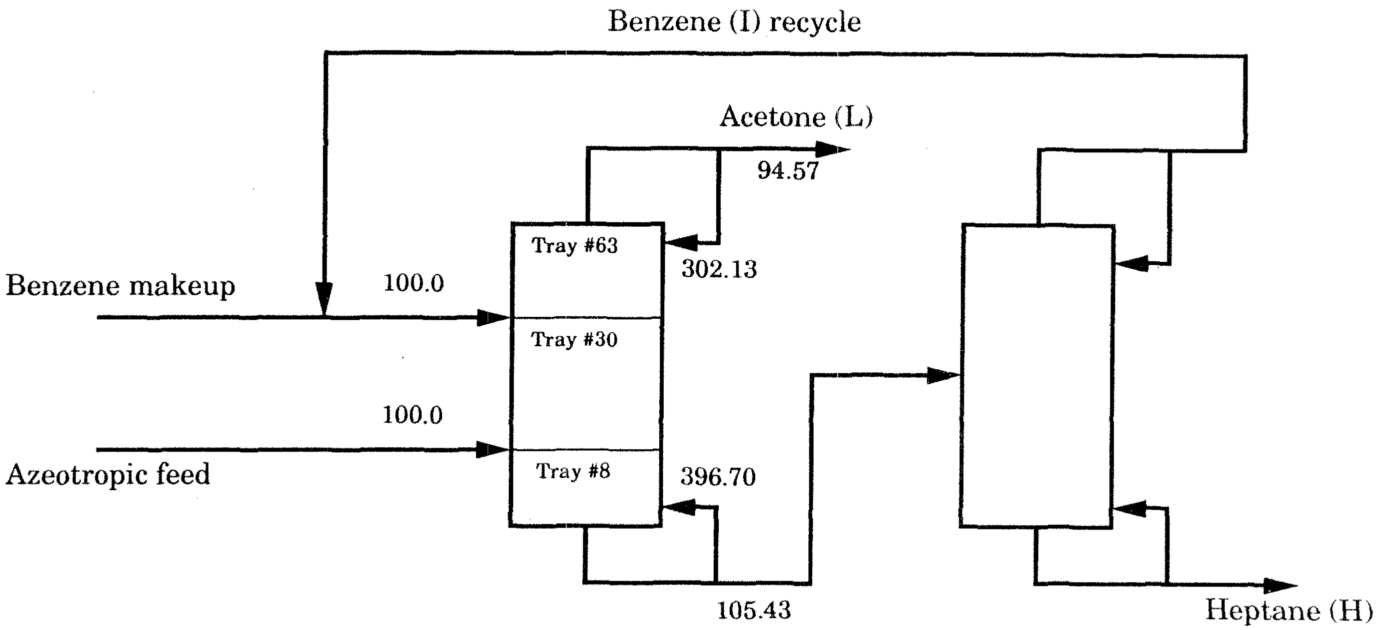


Fig. 2.50: The acetone - heptane - benzene separation sequence

Fig. 2.51: Acetone (1) - heptane (2) - benzene (3) extractive column composition profile

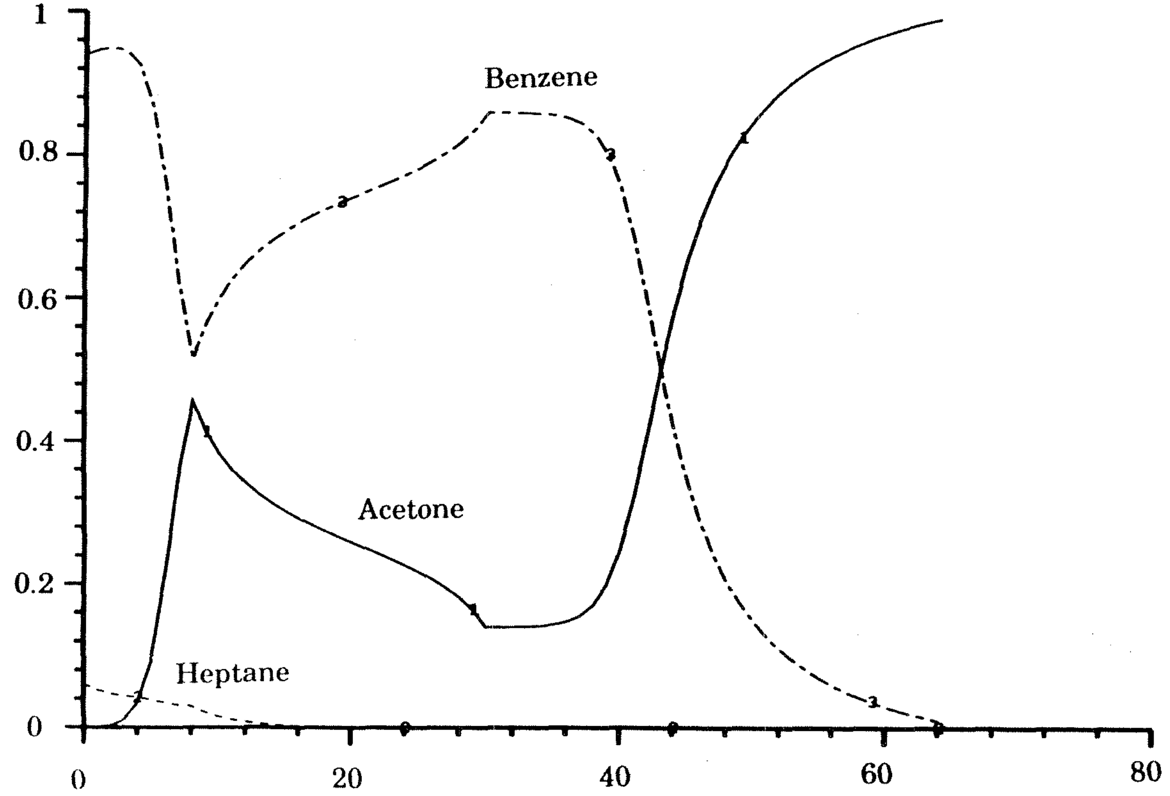
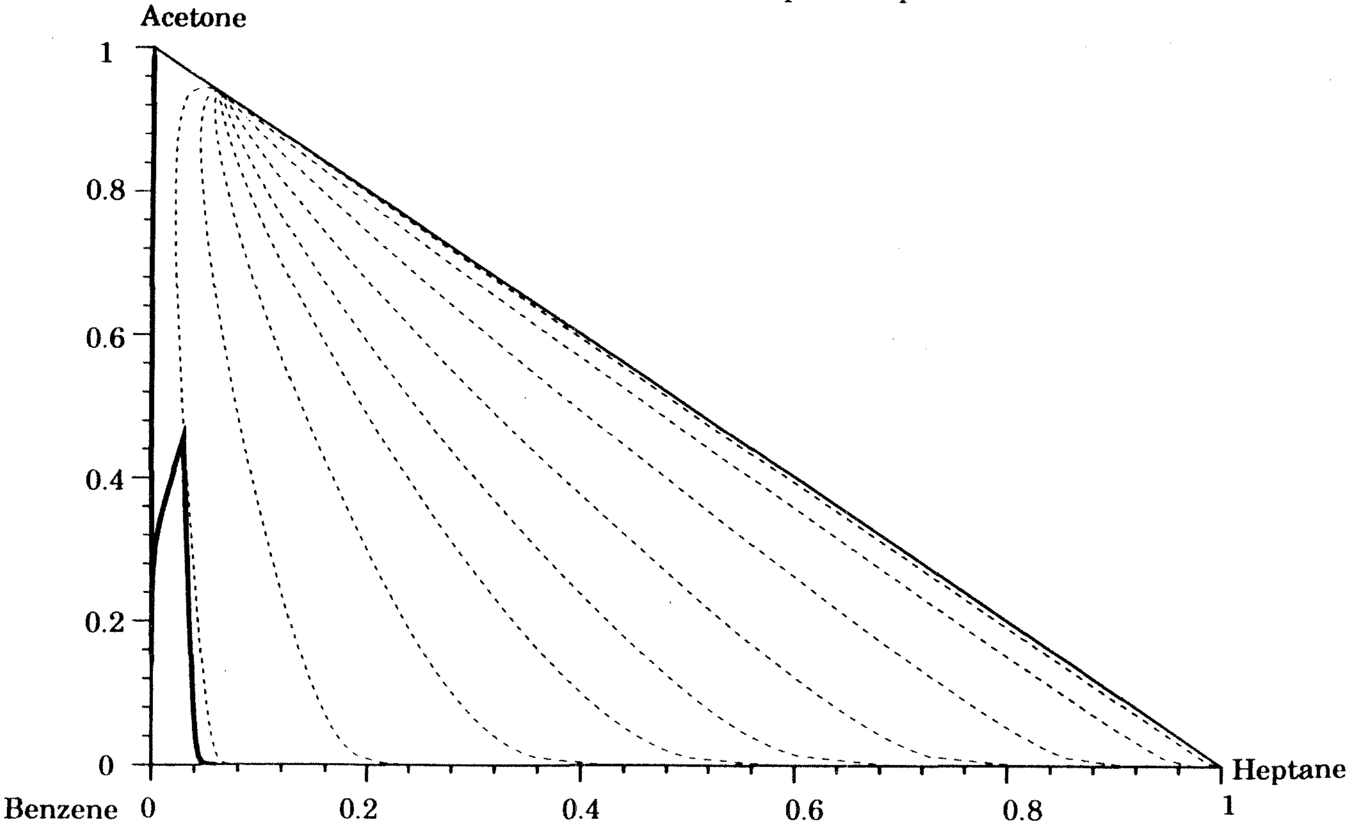


Fig. 2.52: Acetone - heptane - benzene residue curve diagram and extractive column composition profile



separation, as illustrated in figure 2.47 with the ethanol (I) - water (I) - methanol (L-E) example.

2.2.4 Remarks on the thermodynamics

The qualitative results presented in this article do not depend on the specifics of the thermodynamic relationships used. For instance, the feed and products of a column can be on different sides of a distillation boundary, regardless of the mixture of thermodynamics. 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 instead of the Wilson equation to describe liquid activity coefficients 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 & Doherty (1990) have done in the flowsheet that 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.

Homogeneous azeotropic distillation is usually sensitive to 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 figure 2.53 and figure 2.54 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 2.53 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 2.54). 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.

Fig. 2.53: Binary x-y diagram of ethyl ethanoate and toluene for varying Wilson parameters

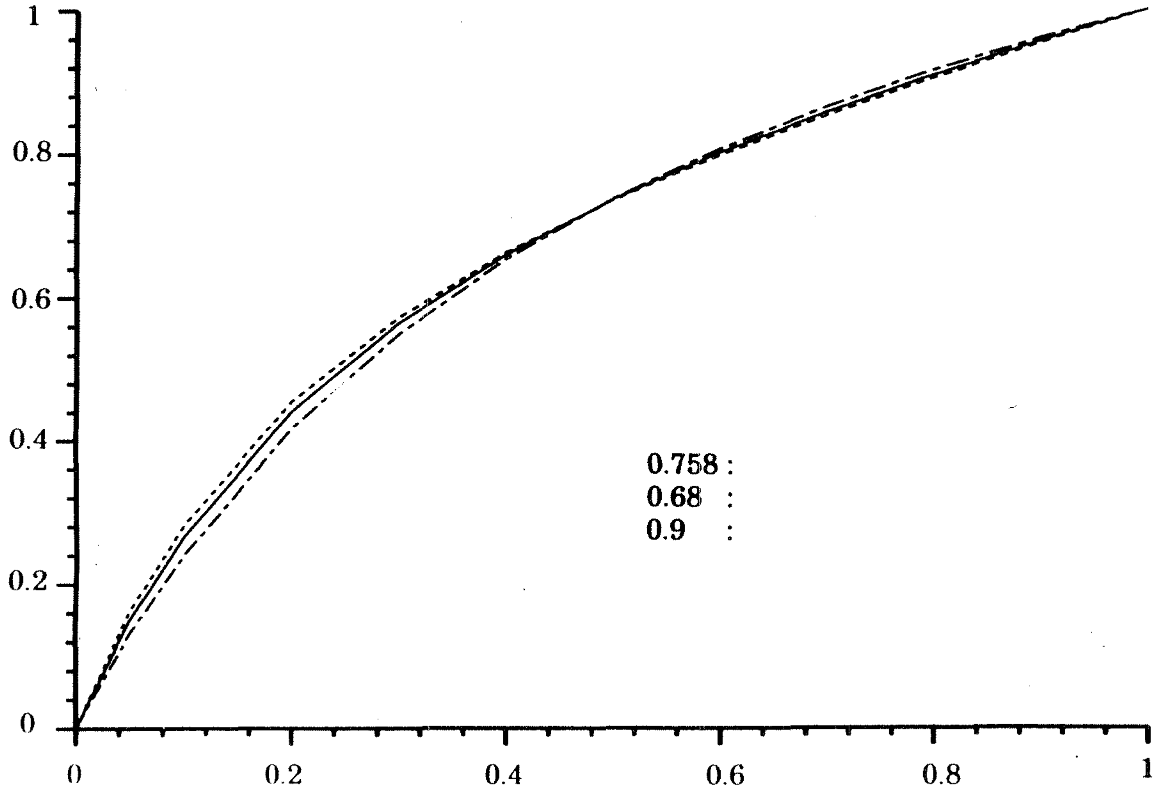
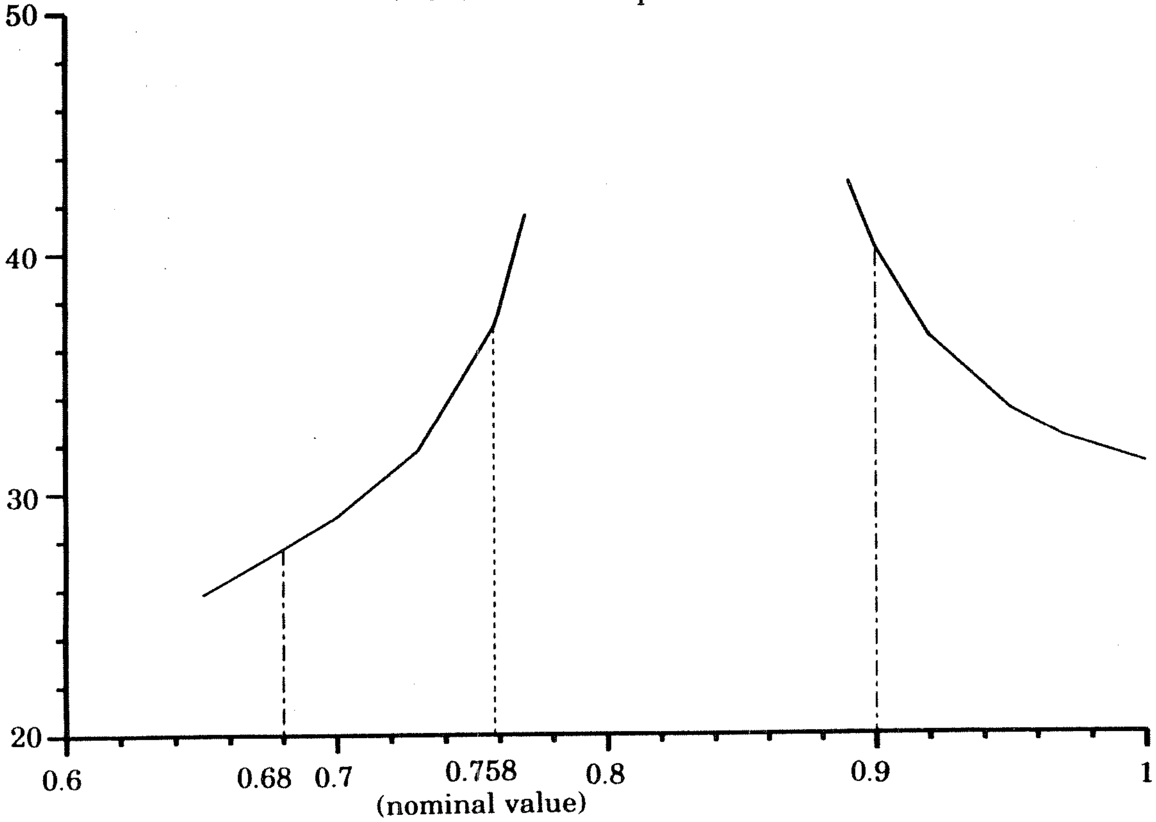


Fig. 2.54: Minimum reflux ratio for varying ethyl ethanoate-toluene Wilson parameters. The feed ratio is equal to 50.



Chapter 3

Separability and Flowsheet Synthesis

3.1 Separability at infinite reflux

In the case of zeotropic distillation, infinite reflux implies maximum separation. By examining the infinite reflux situation, we can derive useful information such as the minimum number of trays required for a desired separation. The situation is different in the case of homogeneous azeotropic distillation: Infinite reflux does not always imply maximum separation. We cannot determine the minimum number of trays by examining the infinite reflux case, because we can often obtain better separation at finite reflux. In particular, separations that are infeasible at infinite reflux may be feasible at finite reflux.

This does not take away all interest from the infinite reflux case. Several reasons remain for investigating this case. Firstly, because the infinite reflux situation can be approached only in the limit, separations that are feasible at infinite reflux are feasible at high reflux, so separability at infinite reflux implies separability at finite reflux. Secondly, the infinite reflux situation has the advantage of simplicity: The distillation column composition profiles can be easily deduced from the thermodynamic data (Hoffman 1964, Van Dongen & Doherty 1985, Stichlmair *et al.* 1989) and infinite reflux composition profiles depend neither on the number of feeds nor on their locations.

3.1.1 Composition profile representation

We focus here on composition profiles of columns operated at infinite reflux. We limit ourselves to columns separating ternary mixtures. Such profiles have been studied extensively by Hoffman (1964), Van Dongen & Doherty (1985) and Stichlmair, Fair & Bravo (1989). Chapters 5 and 6 of Hoffman's book describe a graphical method for obtaining these profiles, and its applications. The method is based on the fact that, at total reflux, no product comes out of the column. Therefore, the composition of the liquid that flows from a given tray to the tray below is equal to the composition of the vapor that rises from the tray below to the considered tray. As shown by Hoffman, infinite reflux composition profiles are described by a succession of tie lines. Stichlmair *et al.* simplify this representation by removing the individual points; they call the resulting curve a "distillation line."

Van Dongen & Doherty (1985) discard the plate-to-plate difference equation approach and describe column sections by differential equations. They show that composition profiles obtained with these differential equations do not differ significantly from composition profiles obtained with the usual difference equations. As we show in appendix 2, the similarity between composition profiles obtained with difference equations and with differential equations comes from the fact that differential equations represent the composition profiles of *packed* columns, while difference equations represent the composition profiles of *staged* columns.

At infinite reflux, the differential equations that 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. Because they are continuous (distillation lines are actually a set of discrete points), better understood (*cf.* the series of articles published by Doherty & Perkins (1978a, 1978b, 1979) and Van Dongen & Doherty (1984)) and easier to compute, we use hereafter residue curves to describe infinite reflux composition profiles. The results presented in this section apply only to packed columns *per se*; however, since there is very little difference between tray and packed columns, they should also cover the tray column case.

3.1.2 Possible separations within one column

Residue curves represent the composition profiles of packed columns at infinite reflux. Therefore, two points D and B located in the composition triangle may represent respectively the distillate and bottom of a packed column operated at total reflux only if there exists a residue curve connecting D and B. Conversely, if such a residue curve exists, it represents the profile of a packed column that gives D as distillate and B as bottom product. So we obtain the following theorem:

Theorem 3.1 *Two points D and B located in the composition triangle represent the distillate and the bottom product respectively of a packed column operated at infinite reflux if and only if there exists a residue curve going from D to B.*

At infinite reflux, the number of feeds and their locations have no influence on the composition profile; only the overall feed composition is important. Because the material balance must be closed, we obtain the following theorem:

Theorem 3.2 *A feed F can be separated in a packed column operated at infinite reflux into a distillate D and a bottom B if and only if:*

- *D, F and B are aligned and F is located between D and B.*
- *A residue curve goes from D to B.*

A given feed can be separated in a large number of ways, as long as they satisfy the two conditions stated in theorem 3.2. The distillate and bottom compositions depend on the column height and the distillate-to-bottom ratio. We can have multiple solutions even for fixed D, B and h, because multiple steady states actually occur. Figure 3.1 and figure 3.4 illustrate this point: A column separating a mixture of acetone (L) - heptane (H) - benzene (L-E) yields in the first case 99% acetone at the top and 95% heptane at the bottom (figure 3.2 and figure 3.3) while it performs very little separation in the other case (figure 3.5 and figure 3.6). Note that distillate flow rate, bottom flow rate, number of trays (and reflux: we cannot truly achieve infinite reflux with Chemsim) are identical in both cases.

Because residue curves are constrained by residue curve boundaries, composition profiles of packed columns operated at infinite reflux must be entirely contained within one distillation region. This implies that distillate and bottom must lie in the same distillation region. However, it does not imply that the feed must lie in the same distillation region as the composition profile. Indeed, the curvature of residue curve boundaries, which are never straight lines in the mathematical sense, makes it possible for the feed to lie in one distillation region while the distillate and bottom lie in another region. Figure 2.39, figure 2.40 and figure 2.41 illustrate this fact in the methyl acetate (L) - methanol (I) - hexane (H-E)[1] case: The feed of the second column lies in region 1 while its profile lies in region 2. This fact, which was overlooked by Doherty & Caldarola (1985), explains why their criterion fails for infinite reflux separability.

Theorem 3.2 helps us solve the following question: Given a feed F, can we recover a product P, not necessarily an essentially pure component, from it? We can determine the answer to this question through the following procedure:

1. We first locate F and P in the ternary diagram.
2. Because the material balance must be closed, the possible compositions of the product obtained at the other end of the column must lie on the segment FQ.

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[1] Like Van Dongen & Doherty, we use the regular solution equation instead of the Wilson equation for this mixture.

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.90	0.99	0.0
Heptane (H)	0.0	0.10	0.0043	0.9513
Benzene (I)	1.0	0.0	0.0057	0.0487

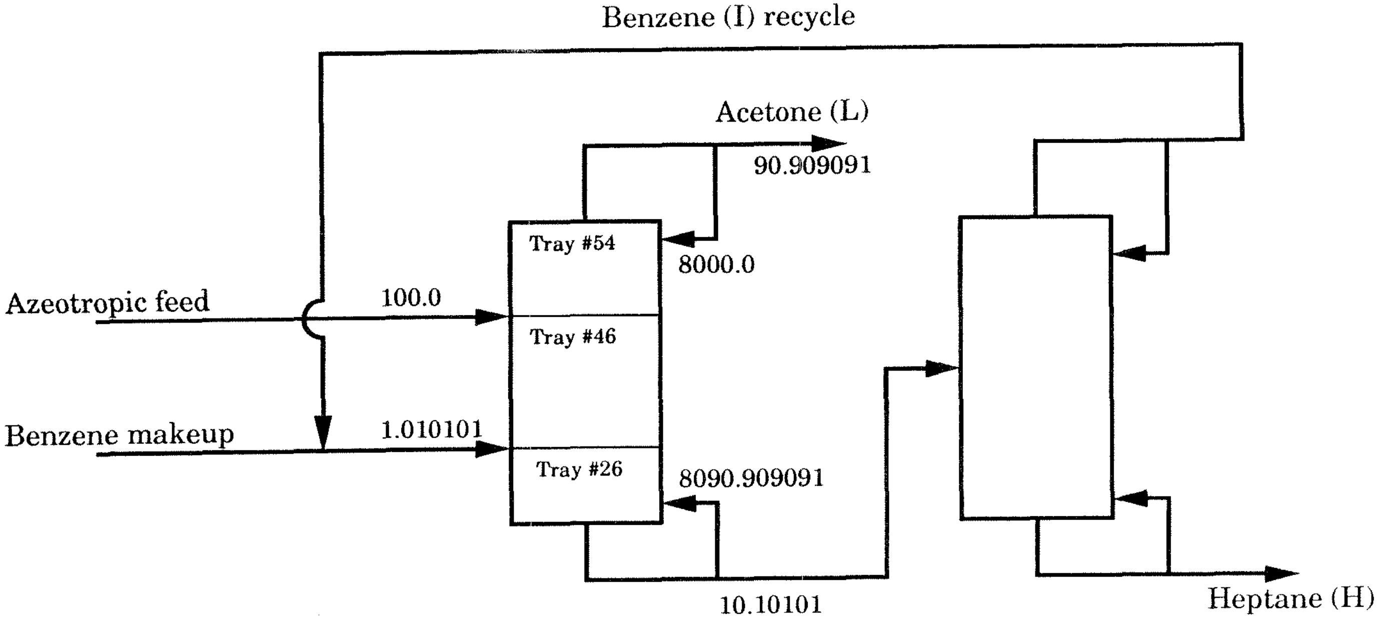


Fig. 3.1: The acetone - heptane - benzene separation sequence.
First steady-state.

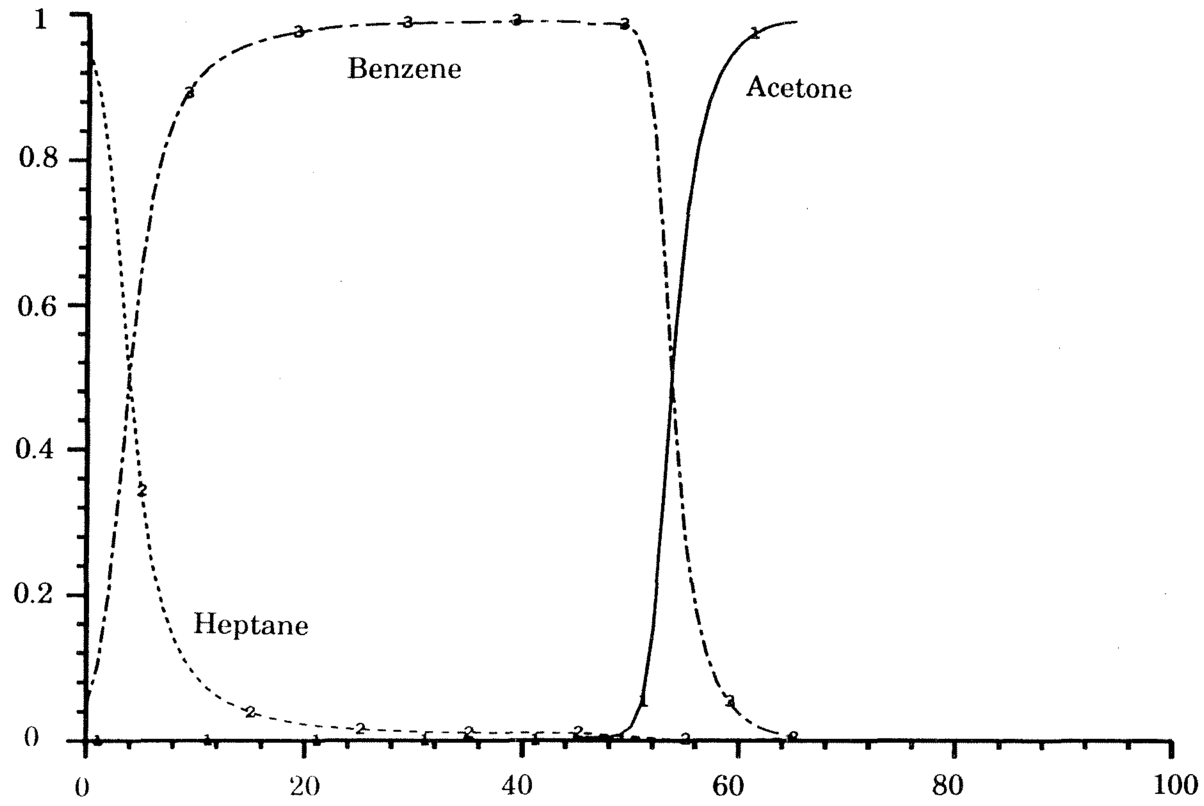
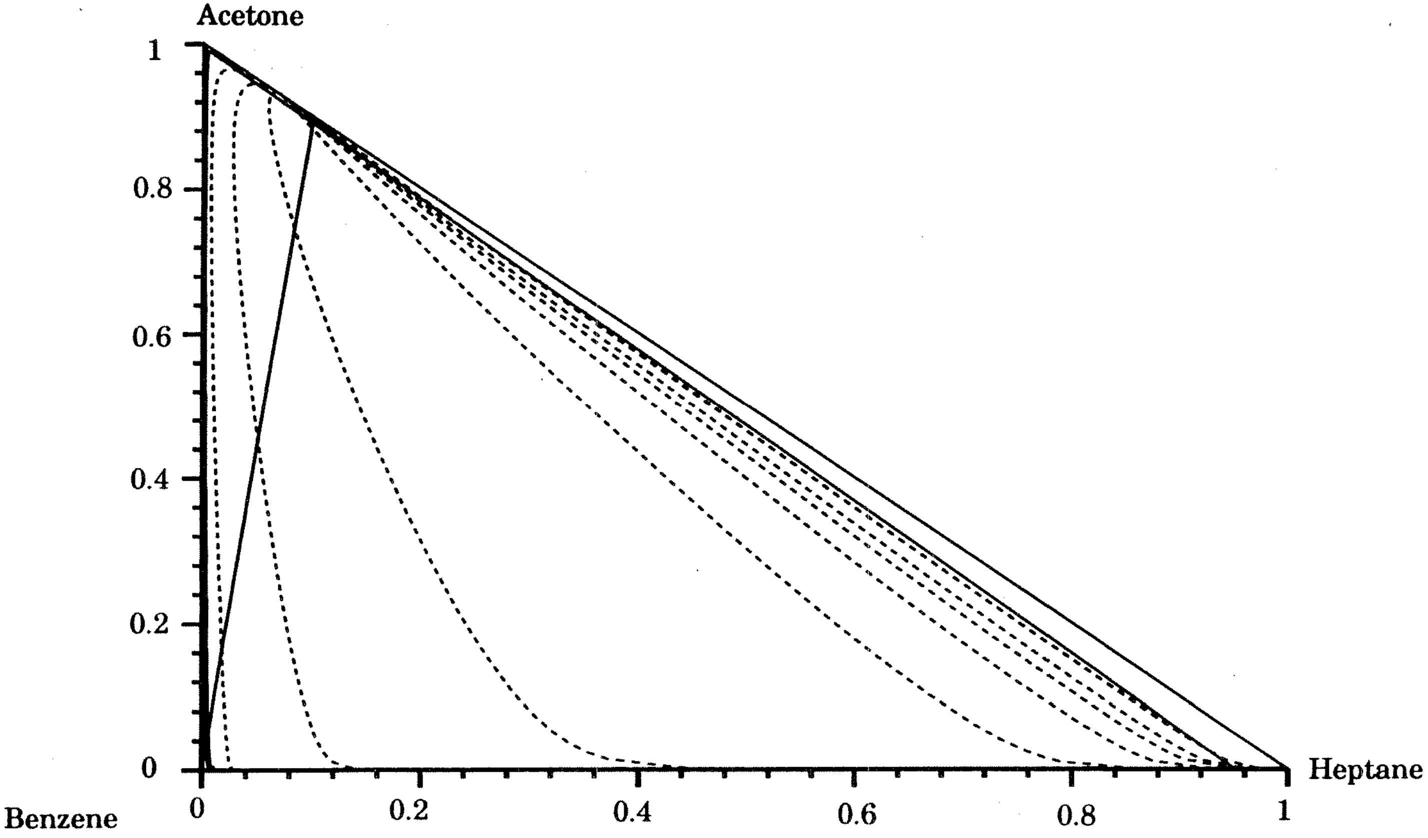


Fig. 3.2: Acetone (1) - heptane (2) - benzene (3)
extractive column composition profile.
First steady-state.

Fig. 3.3: Acetone - heptane - benzene residue curve diagram
and extractive column composition profile.
First steady-state.



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.90	0.9317	0.5247
Heptane (H)	0.0	0.10	0.0683	0.3753
Benzene (I)	1.0	0.0	0.0	0.1000

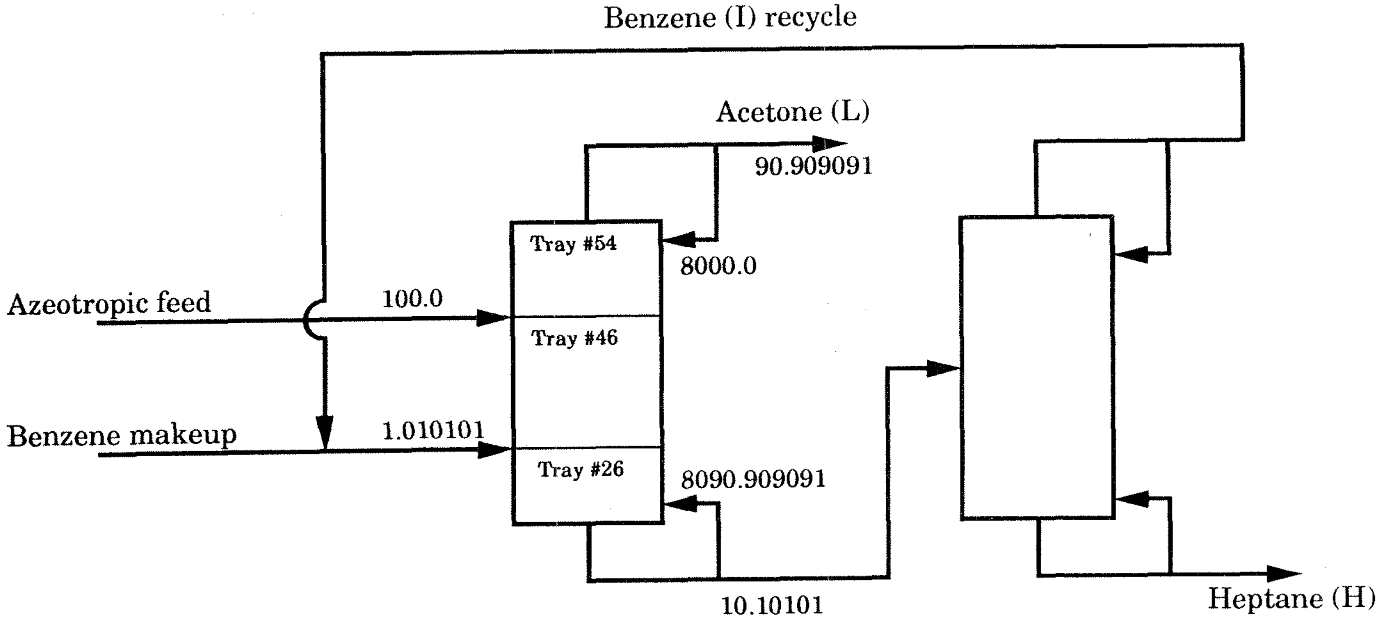


Fig. 3.4: The acetone - heptane - benzene separation sequence.
Second steady-state.

Fig. 3.5: Acetone (1) - heptane (2) - benzene (3)
extractive column composition profile.
Second steady-state.

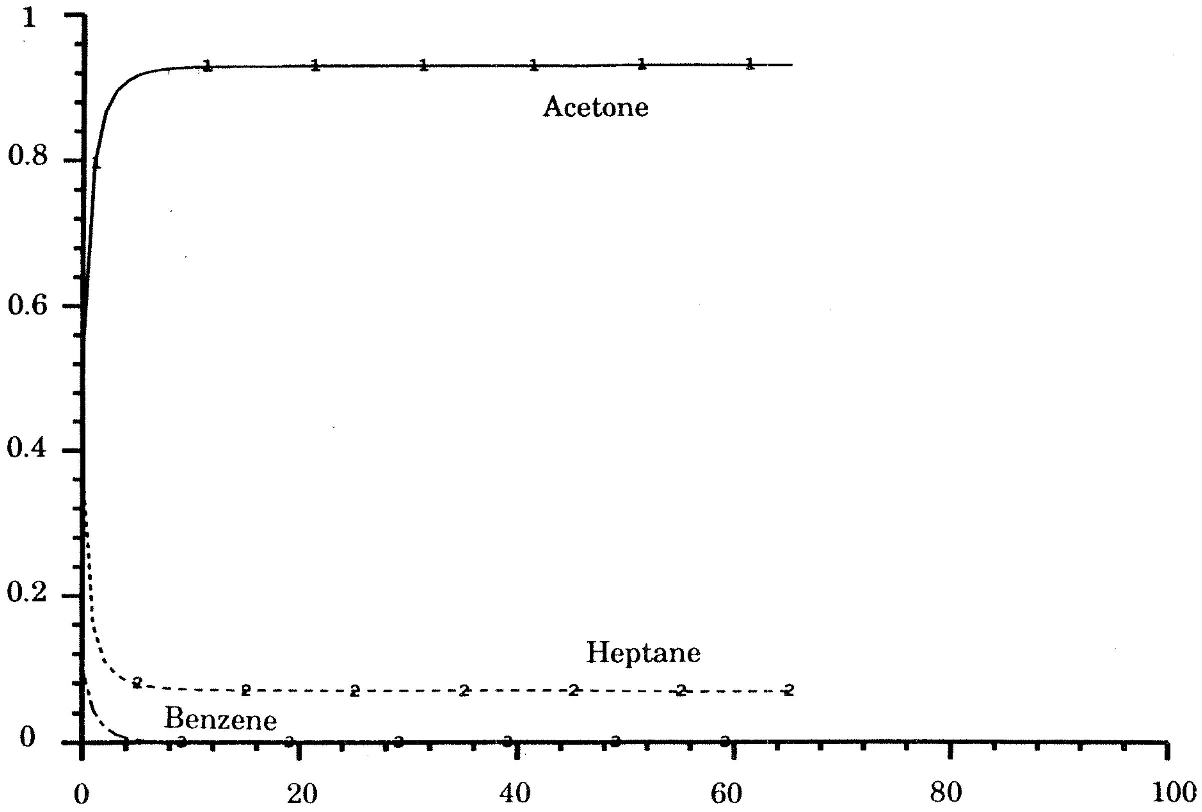


Fig. 3.6: Acetone - heptane - benzene residue curve diagram
and extractive column composition profile.
Second steady-state.

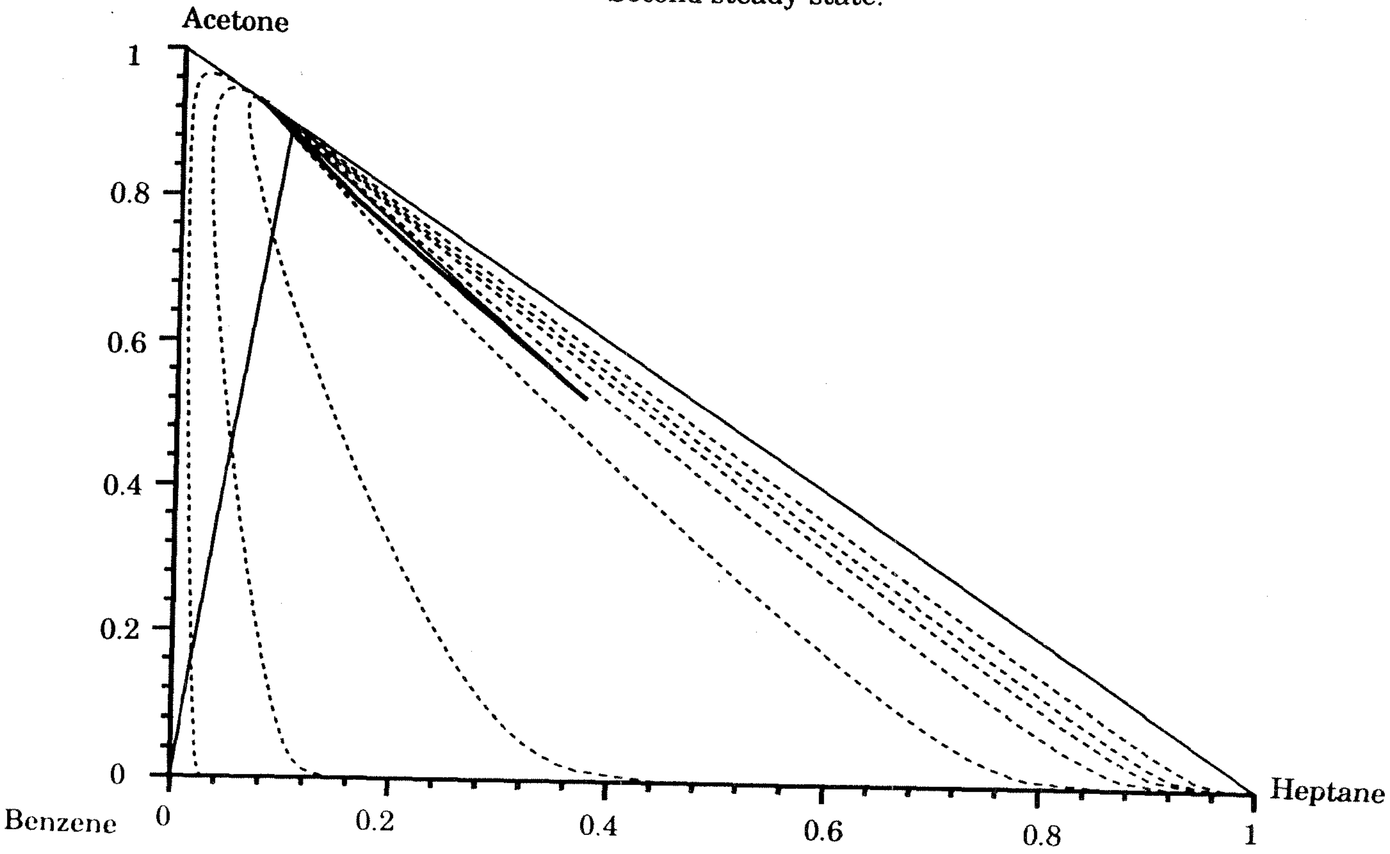
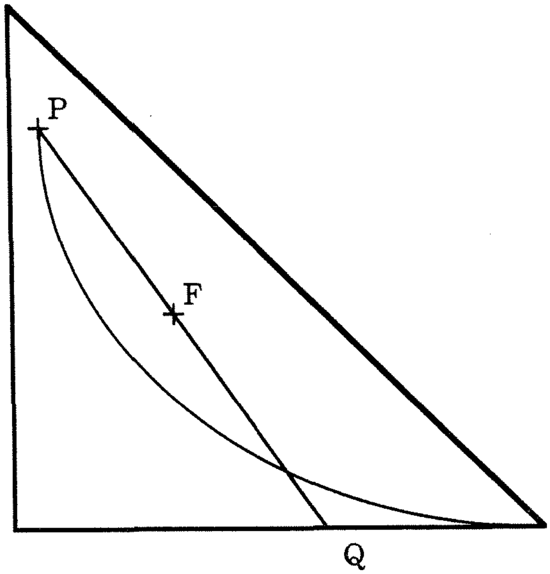


Fig. 3.7: Separation is feasible



3. Then we examine whether the residue curve that contains P intersects FQ or not. If so, separation is feasible (figure 3.7); if not, separation is infeasible (figure 3.8).

A more common and more important question is: Given a feed F, can we recover component A from F with a certain purity (for instance, 99% A)? In this case, the desired product can be anywhere within a region. Specifying a minimum purity on component A requires that the corresponding product must lie inside triangle $\mathcal{T}$ (figure 3.9 and figure 3.10). In this case, separation is feasible if and only if at least one residue curve that goes through $\mathcal{T}$ intersects the triangle FQR (figure 3.9). Figure 3.10 shows a situation where separation is infeasible, because a residue curve boundary stands between FQR and $\mathcal{T}$. In theory, checking whether separation is feasible or not would require the examination of every curve that goes through $\mathcal{T}$. In practice, because residue curves are well-behaved curves except around residue curve boundaries, we need to check only a few curves.

Fig. 3.8: Separation is infeasible

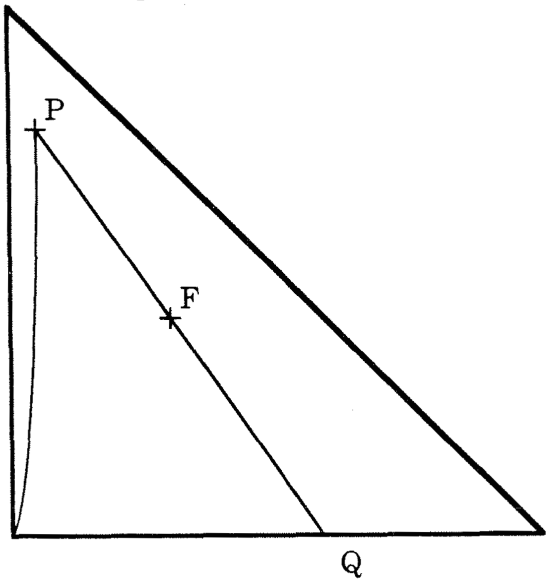
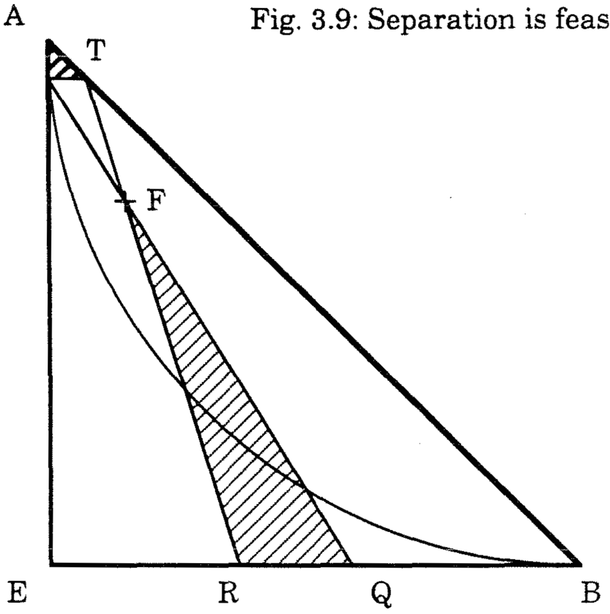


Fig. 3.9: Separation is feasible



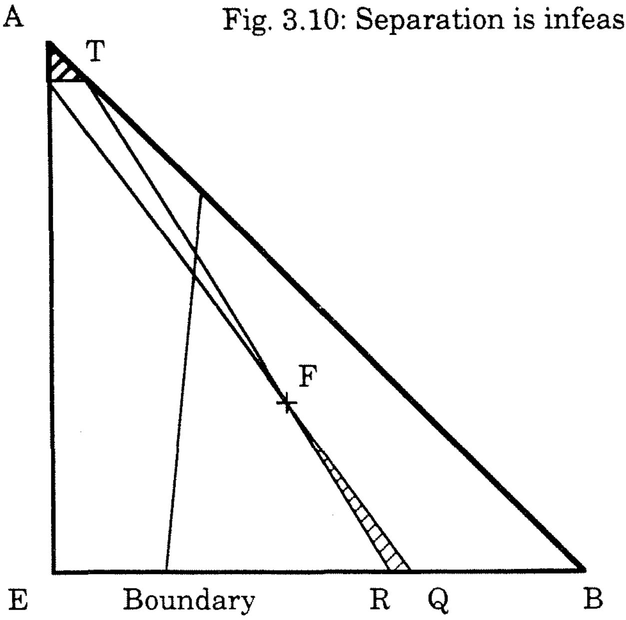


Fig. 3.10: Separation is infeasible

By applying this procedure to the acetone - heptane - benzene case (figure 3.1, figure 3.2 and figure 3.3), we see that acetone can be recovered as distillate of a packed column operated at infinite reflux. Thus components may be recovered as pure products even when they are saddles in the residue curve diagram. This fact, which was overlooked by Stichlmair *et al.*, explains why their criterion does not predict infinite reflux separability correctly.

3.1.3 Separating a binary azeotrope with one column

It is widely accepted that the separation of a binary azeotrope into two essentially pure components requires at least two separating units, such as two distillation columns or a distillation column and a flash drum (if two components can be very easily separated). For example, Douglas (1989) writes that "splitting (an) azeotrope normally requires two columns." Shinskey (1984) also writes that "to separate a binary azeotrope requires two columns."

This generalization is incorrect: Sometimes, we can separate a binary azeotrope into two pure products with only one column.

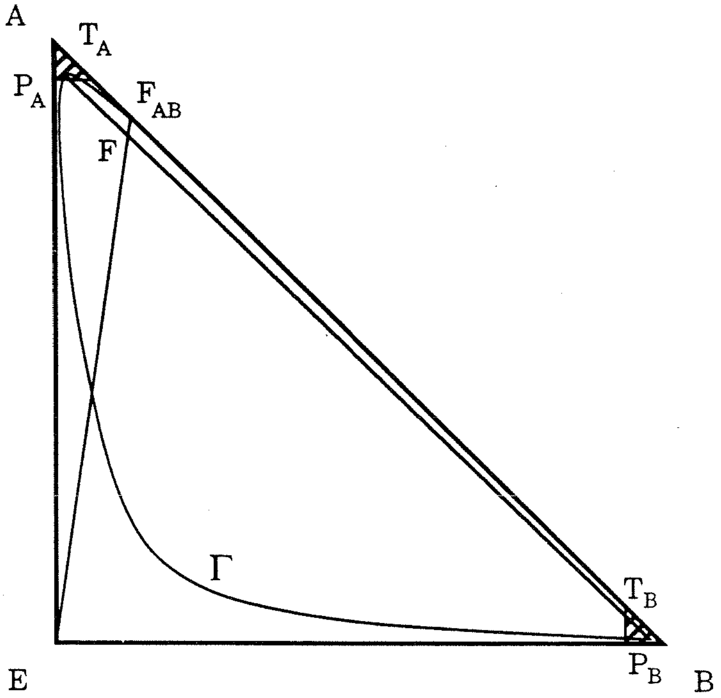
Theorem 3.3 *Given a binary azeotrope A-B which we want to separate into products of given purities, a candidate entrainer E makes this separation feasible with one packed column operated at infinite reflux if and only if one residue curve connects $\mathcal{T}_A$ and $\mathcal{T}_B$.*

Here, $\mathcal{T}_A$ and $\mathcal{T}_B$ denote the areas that correspond to the specifications on A and B respectively.

Necessity is obvious: If separation is feasible with only one column, one of its products satisfies the specifications on A and is therefore located in $\mathcal{T}_A$ while the other product satisfies the specifications on B and lies in $\mathcal{T}_B$. So the column profile, which coincides with a residue curve, connects $\mathcal{T}_A$ and $\mathcal{T}_B$. Reciprocally, let Γ be the residue curve that joins $\mathcal{T}_A$ and $\mathcal{T}_B$ (figure 3.11), and let P_A (P_B respectively) be a point of Γ in $\mathcal{T}_A$ ($\mathcal{T}_B$ resp.). By construction, P_AP_B intersects EF_{AB} (where F_{AB} is the azeotropic feed); let F be the intersection point. By mixing E and F_{AB} in adequate proportions, we obtain the overall feed F. Because P_A, F and P_B are aligned and because P_A and P_B are connected by Γ, we can apply theorem 3.2: There exists a packed column separating F into P_A and P_B.

This surprising result is illustrated by figure 3.12 and figure 3.13 in the acetone - heptane - benzene case. The specifications are 99% acetone and 99% heptane; if we add less than one part of benzene for a hundred parts of azeotrope, we can separate the acetone - heptane azeotrope with only one column. Such a separation scheme has the obvious advantage of eliminating the entrainer recovery column and the entrainer recycle, enabling us to reduce significantly the diameter of the extractive column. Another advantage is the small amount of entrainer required to achieve the separation; the higher the product specifications, the smaller this amount. However, there are some obvious drawbacks: This column must be large, because its profile follows a residue curve that comes close to a saddle (benzene) and shows significant

Fig. 3.11: Separation is feasible with only one column.



curvature. And the higher the product specifications are, the larger the column must be. Also, the fact that the entrainer goes through only one pass can be costly if the entrainer is expensive. Whether this scheme is economically attractive or not depends on the specifics of the problem. Nevertheless, it represents a new separation method that may be of interest in some cases and should therefore be considered.

3.1.4 Separating a binary azeotrope with two columns

Most homogeneous azeotropic distillation sequences use at least two columns to perform the separation. In this section, we examine the following question: Given a binary azeotrope A-B which we want to separate into products of given purities, un-

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.90	0.99	0.0
Heptane (H)	0.0	0.10	0.0005	0.9964
Benzene (I)	1.0	0.0	0.0095	0.0036

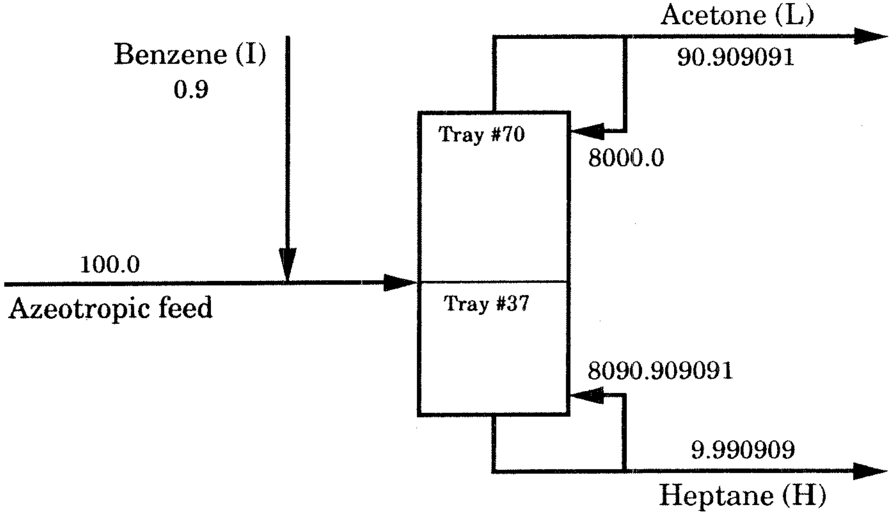
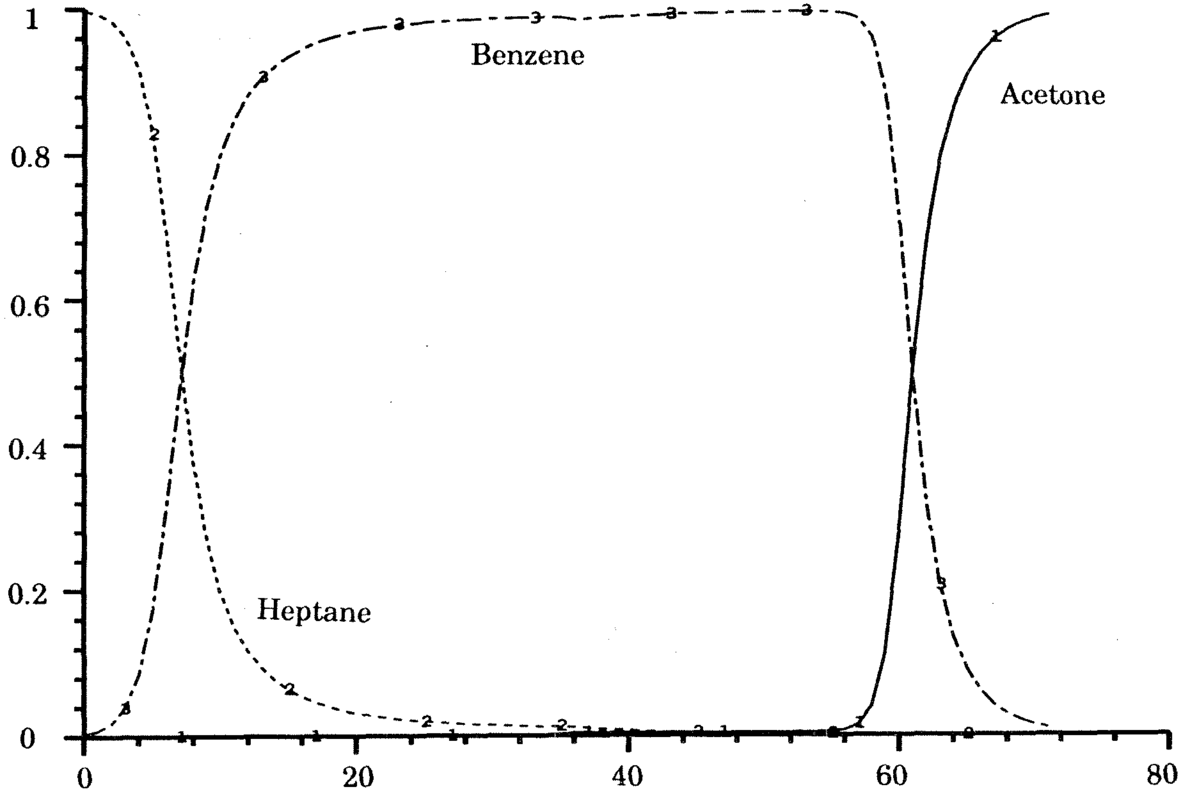


Fig. 3.12: The acetone - heptane - benzene one-column separation sequence

Fig. 3.13: Acetone (1) - heptane (2) - benzene (3)
distillation column composition profile



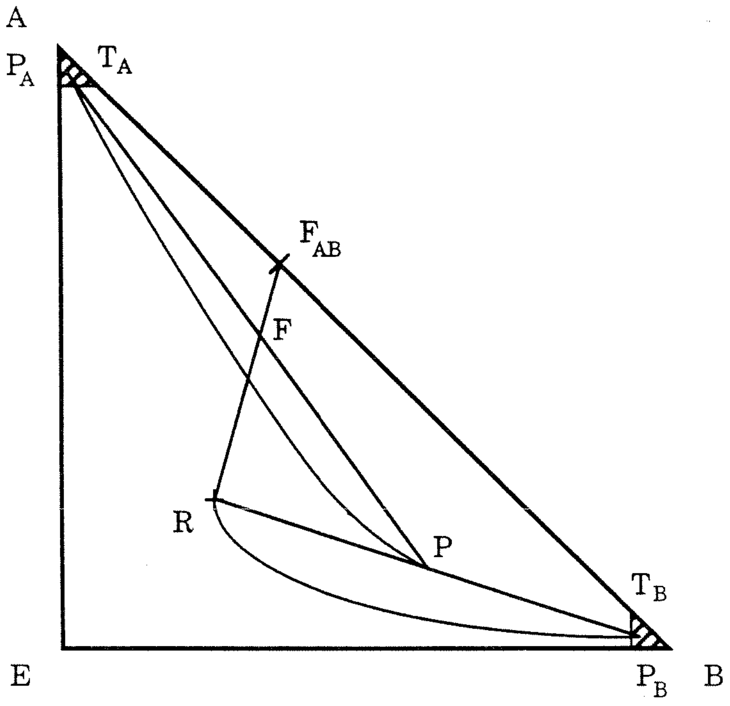
der which conditions does a candidate entrainer E make this separation feasible in a two-column separation sequence?

The specifications on each product translate into two regions $\mathcal{T}_A$ and $\mathcal{T}_B$. To be successful, a separation sequence must yield two products which are located inside $\mathcal{T}_A$ and $\mathcal{T}_B$ (see figure 3.14). Now, let R be the recycle composition, and let us assume that we want to recover A first. Then the separation sequence must operate in the following manner: The first column separates the combined feed F (which is the sum of the recycle R and of the azeotropic feed F_{AB}) into a product P_A located in $\mathcal{T}_A$ and a product P. P is then fed to the second column, which separates it into R and a product P_B located in $\mathcal{T}_B$. Again, we assume that both columns are at total reflux. If this separation scheme works, then there exists at least one residue curve connecting R and a point of $\mathcal{T}_B$, because this residue curve represents the composition profile of the entrainer recovery column. Also, P must be connected to a point of $\mathcal{T}_A$ (here, P_A) by a residue curve. We obtain therefore the necessary conditions for separability in a two-column sequence (figure 3.15):

- At least one residue curve Γ connects R to a point of $\mathcal{T}_B$ (here, P_B).
- Let Γ_B be the part of Γ contained in $\mathcal{T}_B$ and S the convex hull of the set formed by Γ_B and R. Then, at least one residue curve connects one point of $S \backslash (\{R\} \bigcup \mathcal{T}_B)$ (here, P) and a point of $\mathcal{T}_A$ (here, P_A).

These conditions are also sufficient: If a residue curve Γ connects R to a point P_B of $\mathcal{T}_B$, these two points can be obtained as products of a packed column operated at infinite reflux, and Γ represents its composition profile. So the entrainer recovery column can perform its duty. By definition of a convex hull, $S \backslash (\{R\} \bigcup \mathcal{T}_B)$ contains all the points that can be separated into R and a point P_B of Γ_B. So if a residue curve connects one point P of $S \backslash (\{R\} \bigcup \mathcal{T}_B)$ and one point P_A of $\mathcal{T}_A$, a packed column operated at infinite reflux can yield them as products. Therefore, the extractive

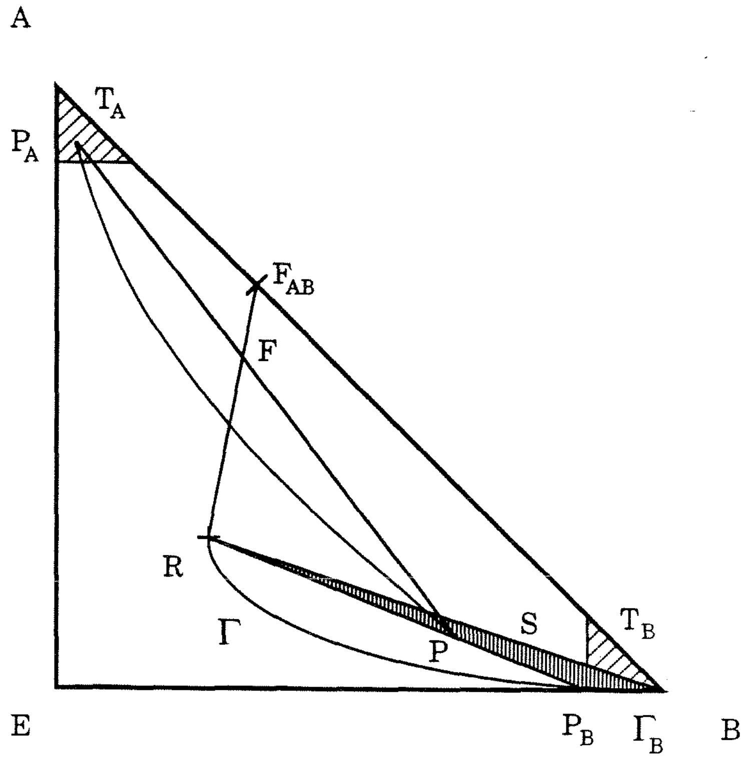
Fig. 3.14: The two-column separation sequence



column can perform its duty. Note that R is excluded because it cannot be separated in the second column into R and something else, while $\mathcal{T}_B$ is excluded because separation would be feasible with only one column otherwise. P is then fed to the second column, which we have already examined. Finally, we see that by construction (see figure 3.15) the material balance line of the extractive column intersects RF_{AB} (the line connecting the recycle to the azeotropic feed), so we can obtain the proper overall feed F by mixing adequate amounts of R and F_{AB}. As a conclusion, we see that if the two aforementioned conditions are satisfied, separation is feasible with a two-column sequence. These results are summarized in the following theorem:

Theorem 3.4 *Given a binary azeotrope A-B which we want to separate into products*

Fig. 3.15: Separation is feasible with two columns

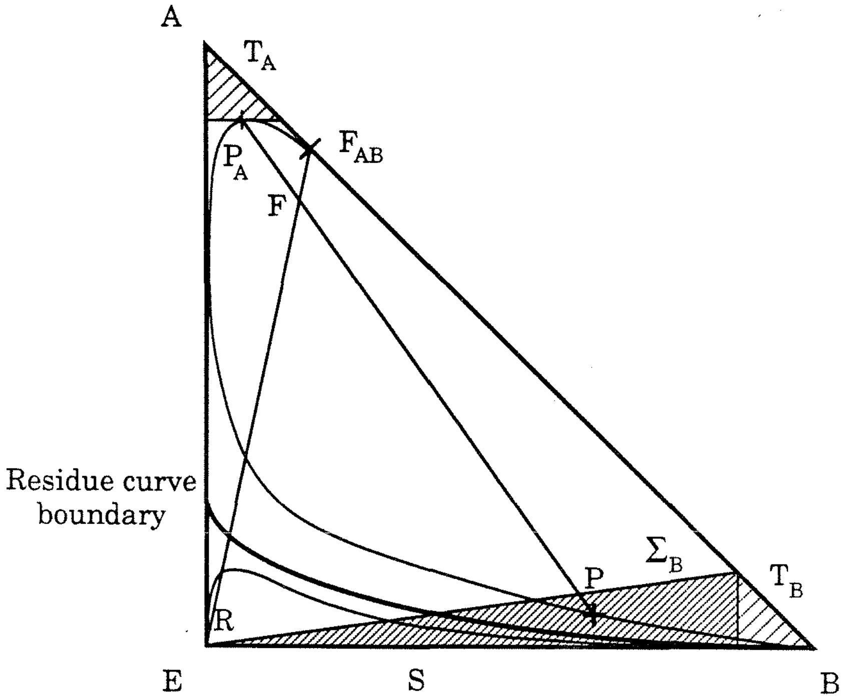


of given purities, a candidate entrainer E makes separation feasible in a sequence of two packed columns operated at total reflux where A is recovered first if and only if:

- *At least one residue curve connects the chosen recycle composition R and* $\mathcal{T}_B$.
- *At least one residue curve connects* $\mathcal{T}_A$ *and* $S\backslash(\{R\}\bigcup\mathcal{T}_B)$.

In practice, checking this condition is rather cumbersome, because the set S depends on the residue curve chosen during the first step. Because Γ_B is included in $\mathcal{T}_B$ (by definition), we obtain a much more convenient condition by considering Σ_B, the convex hull of the set formed by $\mathcal{T}_B$ and R, instead of S. Indeed, Σ_B no longer depends on Γ_B, so the resulting condition is quickly checked. Replacing S by Σ_B gives

Fig.3.16: The conditions of theorem 5 are only necessary



us a condition that is no longer sufficient, however, because the point P of Σ_B cannot always be separated into R and a point P_B located on a residue curve connected to R. Figure 3.16 illustrates this point with a mixture of the 401 type (using the graphical classification of Doherty & Caldarola (1985)). If we try to recycle essentially pure entrainer, we see that the extractive column can separate the combined feed F into a product P_A and a product P. P does belong to Σ_B (the finely hatched area), but not to S (here, S is essentially the BE edge): P cannot be separated into a product P_B contained in $\mathcal{T}_B$ and R. A necessary condition for separability is:

Theorem 3.5 *A candidate entrainer E can make the desired separation feasible only if:*

- *At least one residue curve connects the chosen recycle R and $\mathcal{T}_B$.*
- *At least one residue curve connects $\mathcal{T}_A$ and $\Sigma_B \backslash (\{R\} \bigcup \mathcal{T}_B)$.*

Note: Because residue curves are well-behaved curves, a whole set of residue curves satisfies either of these conditions if one residue curve satisfy it. These two theorems enable us to screen potential entrainers through the following procedure:

- Step 1: Pick a candidate entrainer.
- Step 2: Draw the corresponding residue curve diagram using accurate thermodynamic data.
- Step 3: Draw the areas corresponding to the desired specifications. These areas are usually triangles. We will refer to them as $\mathcal{T}_A$ and $\mathcal{T}_B$.
- Step 4: Pick the recycle composition. Candidate recycle compositions are:
    - The entrainer.
    - A binary azeotrope between the entrainer and one of the azeotropic components.
    - A ternary azeotrope.

  Note that the recycle composition need not be any of these points. For instance, in the acetone - heptane - benzene case, the recycle can contain significant fractions of either acetone or heptane. As we will later see in the case studies, the analysis of the points just mentioned (pure entrainer, binary azeotropes, ternary azeotrope) indicates what the recycle composition can be when it can differ from all of them. According to our experience, checking these points is enough: When separation is not feasible with any of these points, we have found that it is not feasible with any other point of the composition space. Thus we only have to check a very small number of points.

- Step 5: Examine whether the recycle is connected by residue curves to at least one azeotropic component, *i.e.* whether at least one residue curve joins R to a point of $\mathcal{T}_B$. If not, then we can discard this recycle composition and try another one; if all special points (pure entrainer and azeotropes) have been examined, then we can discard this candidate entrainer.

- Step 6: If the recycle is connected by residue curves to only one azeotropic constituent (say B), then this component must be recovered in the second column. Because the conditions of theorem 3.5 are more readily checked, we first examine if they are satisfied. At this point, we know that R and $\mathcal{T}_B$ are connected, so we check if $\mathcal{T}_A$ and $\Sigma_B \backslash (\{R\} \bigcup \mathcal{T}_B)$ are connected. If not, then we can discard this recycle composition and go back to step 4. If so, then we check if the second condition of theorem 3.4 is satisfied. If so, separation is feasible. If not, then we can discard this recycle composition and go back to step 4. Note that if R is connected by residue curves to both $\mathcal{T}_B$ and $\mathcal{T}_A$, then we must go through this step twice, once for each component.

Despite its apparent complexity, this screening procedure becomes fairly easy to use with a bit of experience. The major advantage of this method is that it indicates all possible separations, including some unusual feasible separation sequences, as the following case studies demonstrate.

3.1.5 Case studies

The 020 case

The 020 case (using the classification of Doherty & Caldarola (1985)) is obtained when the candidate entrainer has a lower boiling point than the azeotrope we want to separate and when it introduces no new azeotrope. The ethanol - water - methanol mixture is an example of this situation: Figure 3.17 shows that all residue curves start from the methanol corner and end either at the ethanol apex or the water apex; a residue curve boundary runs from the entrainer (methanol) to the minimum boiling azeotrope (of ethanol and water). Boundaries are never straight lines in the mathematical sense. In the 020 case, we have observed that they tend to bend always in the same direction, *i.e.* they do not contain inflexion points. Therefore, we have two possibilities, depicted in figure 3.18 and figure 3.19. We examine here the first case (represented in figure 3.18) according to the procedure described earlier; the analysis of the other case is exactly identical once we have reversed the roles of A and B:

- Step 1: The candidate entrainer has been chosen.
- Step 2: We plot the residue curve diagram of the ternary mixture (figure 3.20).
- Step 3: The acceptable product regions are added to the residue curve diagram (figure 3.21).
- Step 4: Because the entrainer introduces neither binary nor ternary azeotropes, the recycle composition choice is clear: We should recycle the entrainer.
- Step 5: Since all residue curves start from the entrainer corner and end at pure components (A or B), the recycle is connected to both azeotropic components.
- Step 6: Since R is connected to both A and B, we must consider the recovery of both components from the second column:
  - B: We draw Σ_B in the residue curve diagram (figure 3.22). We immediately see that the residue curves that go through $\mathcal{T}_A$ reach Σ_B only at point R (here, the entrainer). Therefore, we cannot meet the second condition of theorem 3.5, and separation is infeasible this way.

Fig. 3.17: Ethanol - water - methanol residue curve diagram

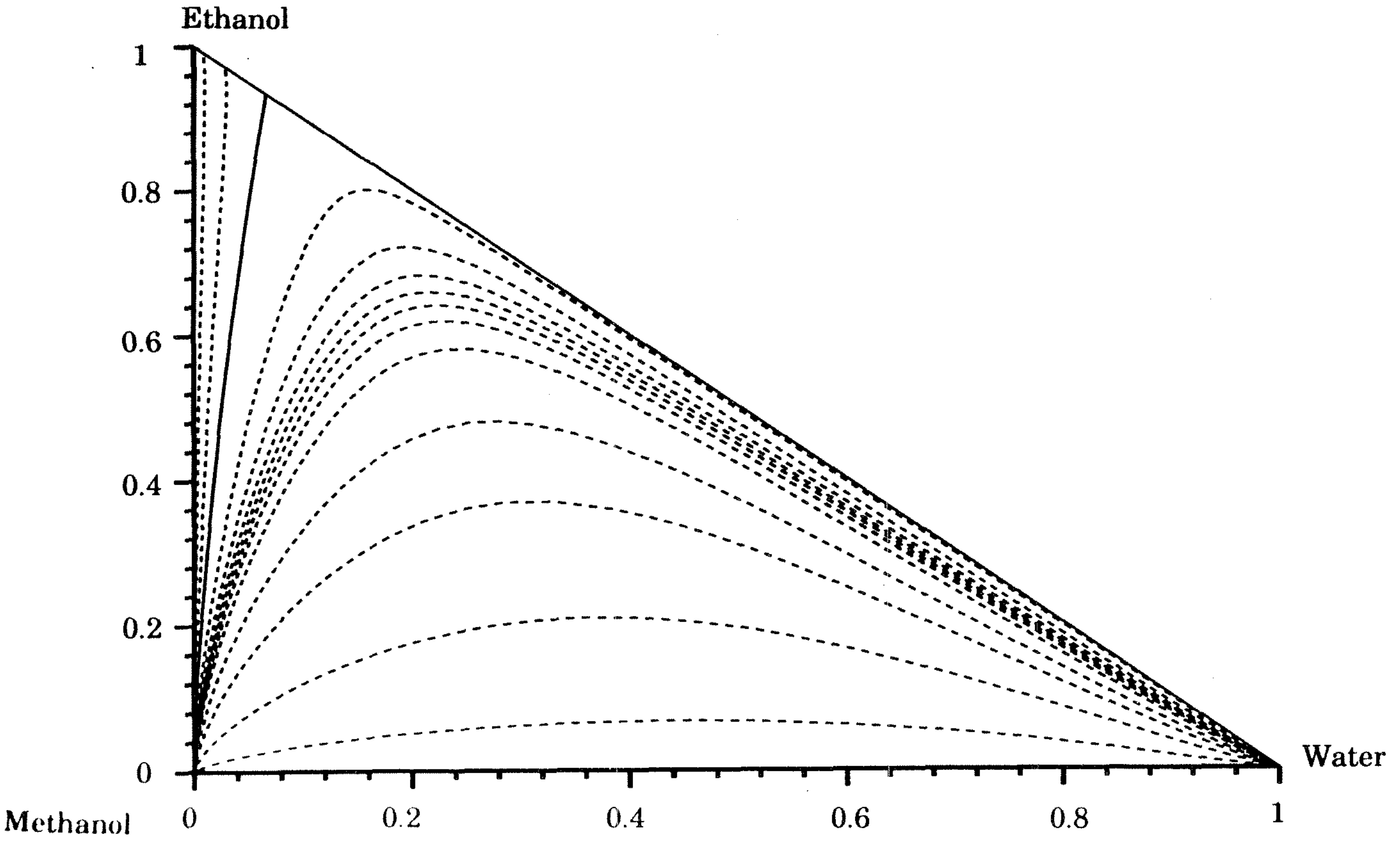


Fig. 3.18: B is located on the convex side of the residue curve boundary

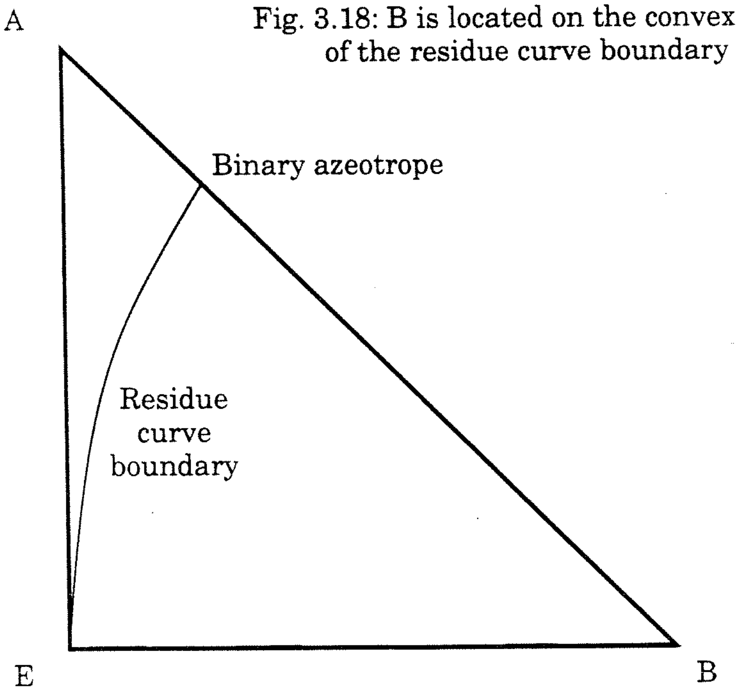


Fig. 3.19: A is located on the convex side of the residue curve boundary

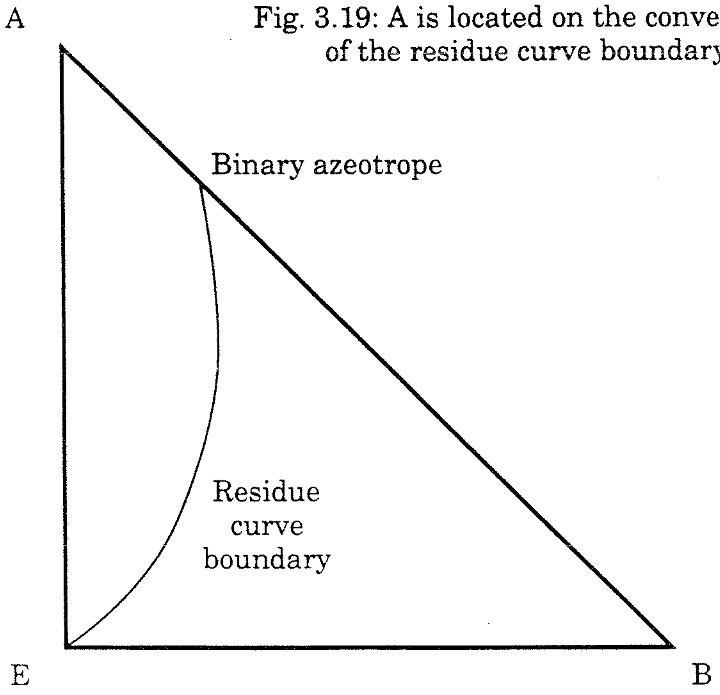


Fig. 3.20: Typical 020 residue curve diagram

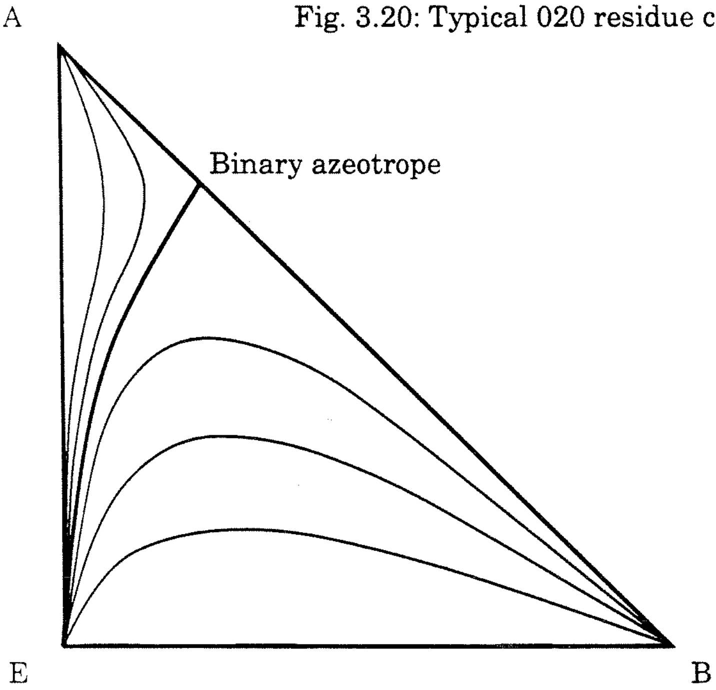


Fig. 3.21: Specification areas are added to the residue curve diagram

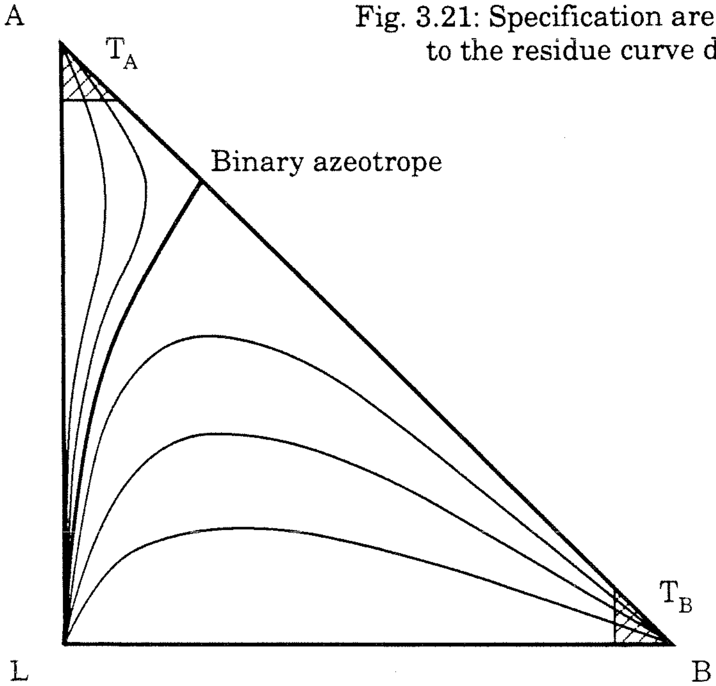
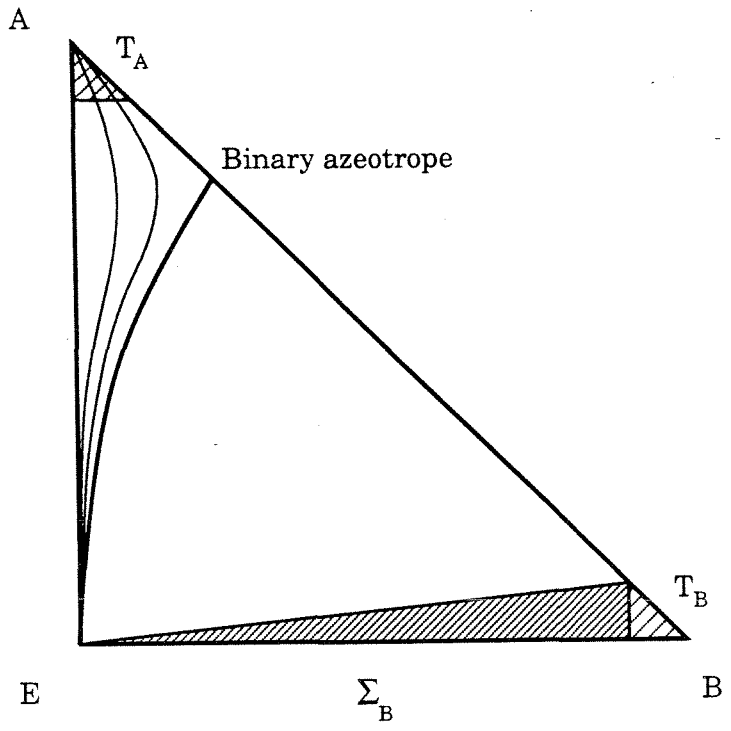
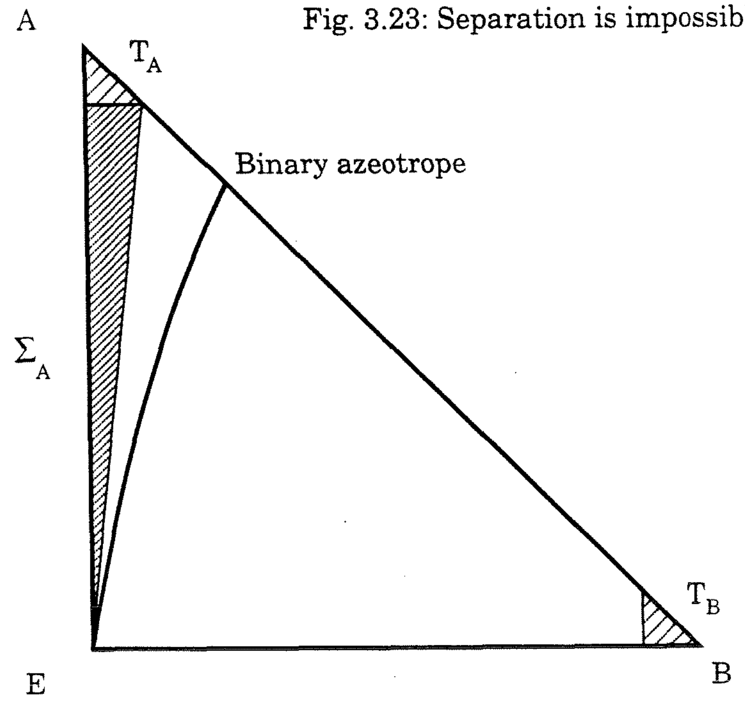


Fig. 3.22: Separation is impossible



- A: We draw Σ_A in the residue curve diagram. In this case, because the residue curve boundary bends towards Σ_A, two situations are possible:
  - The residue curve boundary does not intersect Σ_A (figure 3.23). Separation is then infeasible this way. This candidate entrainer does not make separation feasible at infinite reflux.
  - The residue curve boundary intersects Σ_A (figure 3.24). All residue curves in region 1 end at B, so the residue curves that go through the intersection of Σ_A and region 2 also cross $\mathcal{T}_B$. The necessary conditions of theorem 3.5 are therefore satisfied. By considering residue curves in region 1 that come close to the boundary, we see that every point in ($\Sigma_A \bigcap$ region 2) can be separated into R and a point of $\mathcal{T}_A$ (figure 3.24).

Fig. 3.23: Separation is impossible



Therefore, separation is feasible in this case, and the feasible separation sequence is depicted on figure 3.25. Note that separation is always feasible if the residue curve boundary is tangent to EA.

This analysis indicates that the recycle does not have to be pure to make separation feasible. Indeed, separation remains feasible as long as the the recycle composition lies in the hatched area of figure 3.26. This area is determined in the following manner:

- The recycle cannot lie in region 2, because points of region 2 are not connected to A. Recycles located in region 2 cannot be obtained as distillates of the second column.
- If the recycle point lies above the line joining the binary azeotrope to the intersection P of the residue curve boundary with Σ_A, separation becomes infeasible because we cannot avoid carrying too much B into the extractive column bottom product, which in turn prevents the second column from meeting its specifica-

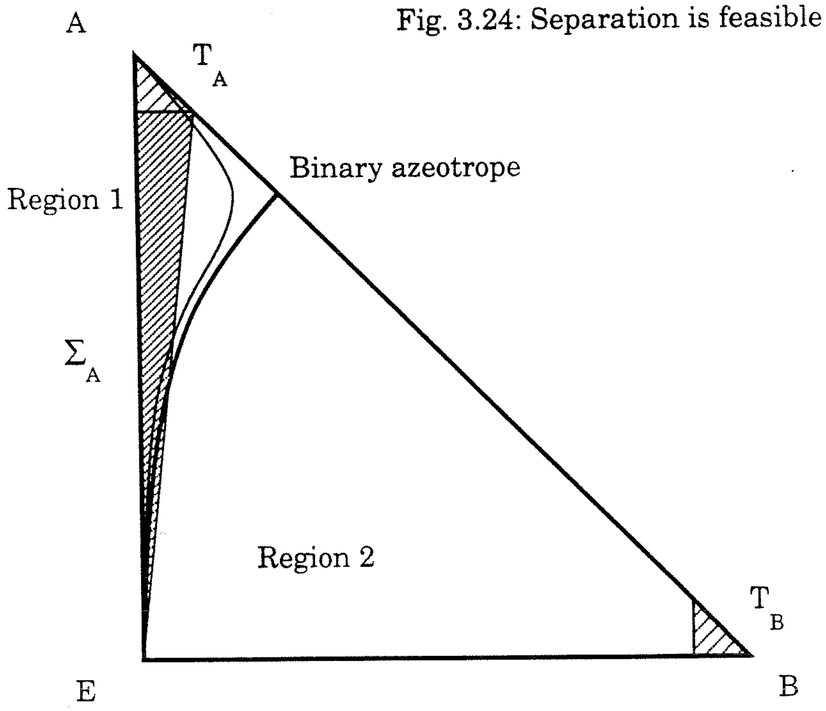


Fig. 3.24: Separation is feasible

tions.

Thus, we obtain a different situation from the one reported by Knight & Doherty (1989) in the ethanol - water - ethylene glycol case. In that case, the impurities contained in the recycle prevent the first column from meeting its specification. Here, separation fails because the second column cannot perform its assigned task.

If we apply this analysis to the ethanol (I) - water (H) - methanol (L-E) example, we see that methanol does not enable the separation of the ethanol - water azeotrope at infinite reflux. Indeed, figure 3.27 shows that the residue curve boundary does not intersect Σ_E.

The 222-m case

This situation takes place when the candidate entrainer forms minimum boiling azeotropes with both azeotropic constituents and introduces a minimum boiling

Fig. 3.25: The separation sequence obtained when separation is feasible with a light entrainer

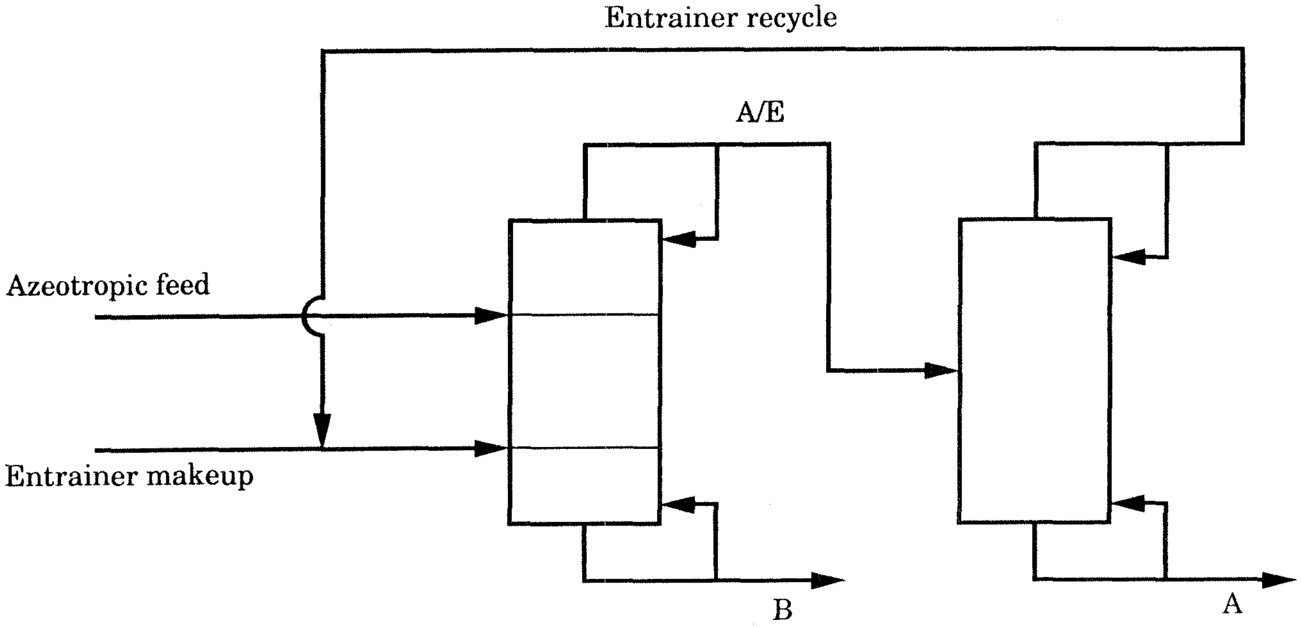
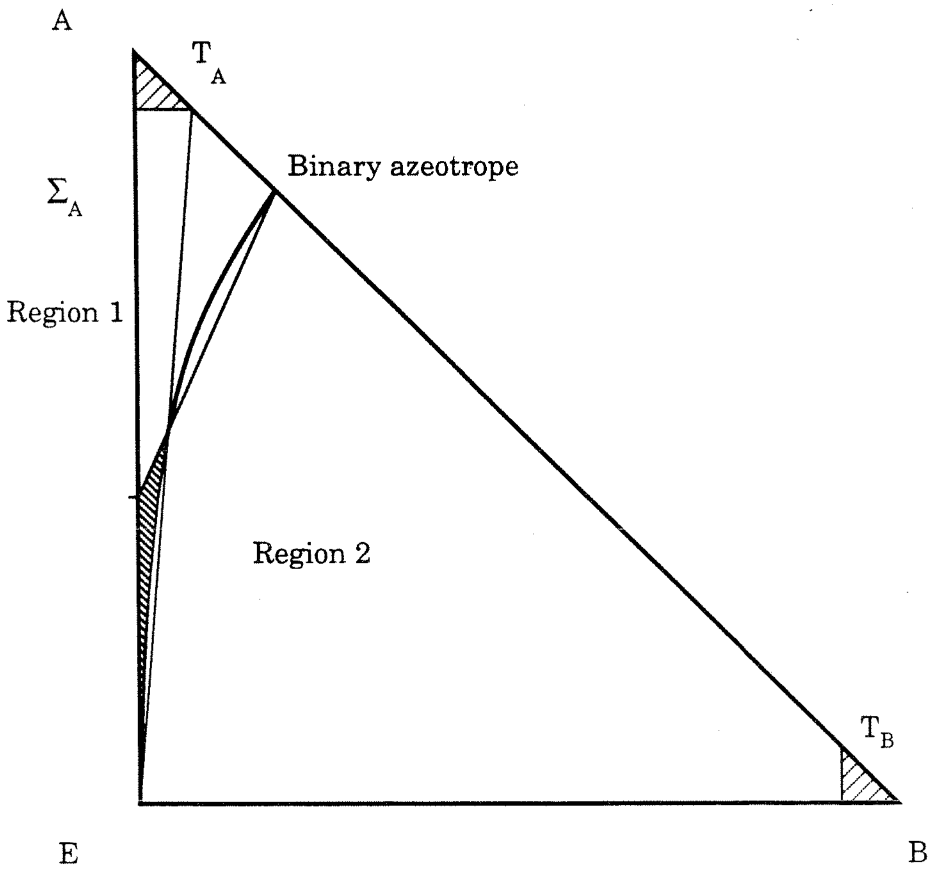


Fig. 3.26: Possible recycle compositions



ternary azeotrope. The hexane - methanol - methyl acetate mixture (we use again the regular solution equation) is a typical example of this situation (figure 3.28). Since there are three binary azeotropes, we can look at this mixture from three different points of view:

- We can use hexane as entrainer for the methanol - methyl acetate azeotrope.
- We can use methanol as entrainer for the hexane - methyl acetate azeotrope.
- We can use methyl acetate as entrainer for the hexane - methanol azeotrope.

Fig. 3.27: Separation is infeasible in the ethanol - water - methanol case

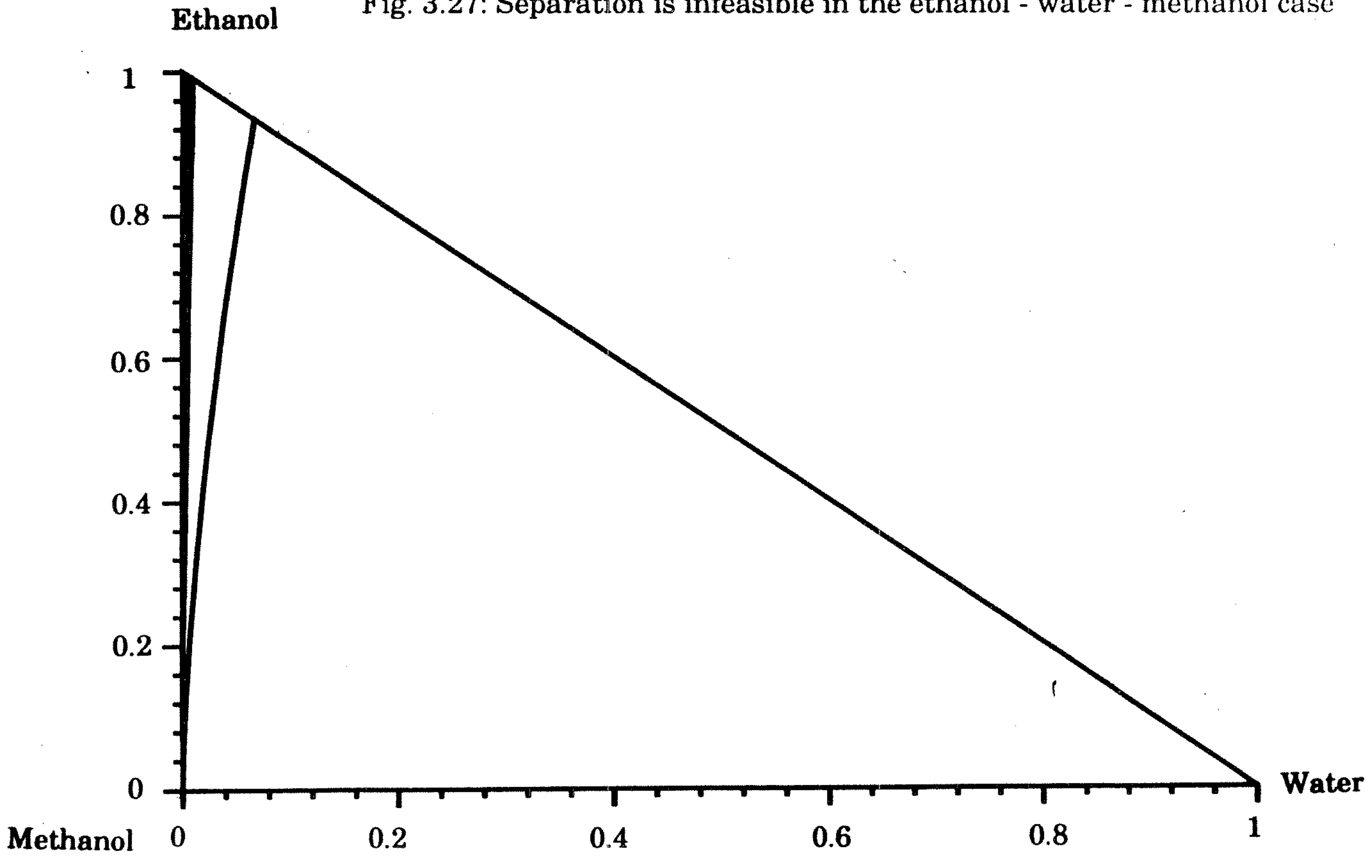
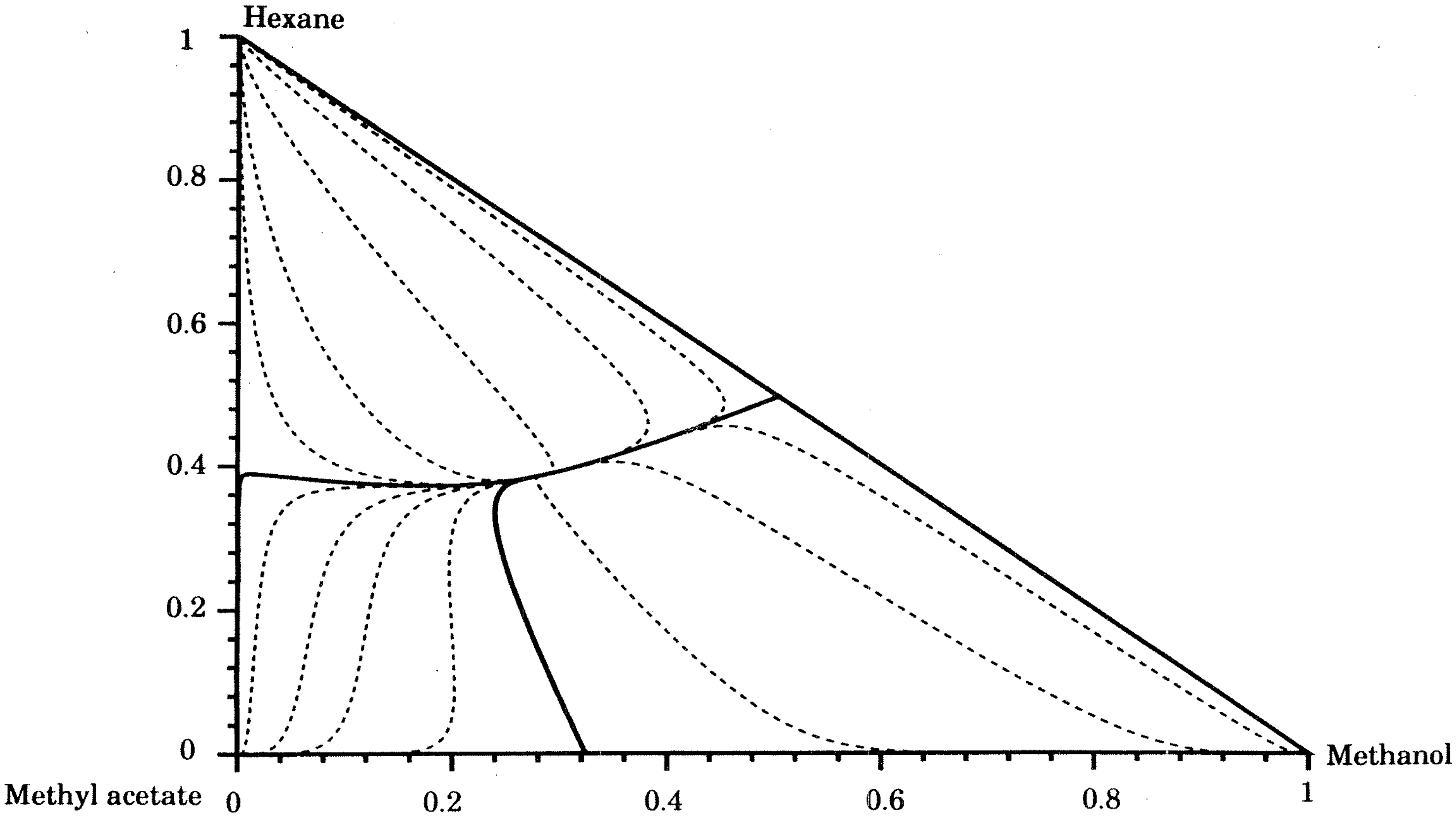


Fig. 3.28: The methyl acetate - methanol - hexane residue curve diagram



We will look here at the first two cases only; the third case can be examined in a completely similar fashion. Let us apply the screening procedure to the case where hexane is used as entrainer for the methanol - methyl acetate azeotrope:

- Step 1: The candidate entrainer has been chosen.

- Step 2: The residue curve diagram is plotted on figure 3.28.

- Step 3: The acceptable product regions, $\mathcal{T}_M$ and $\mathcal{T}_{MA}$, are added to the residue curve diagram (figure 3.29).

- Step 4: There are here four possible recycle compositions: Pure hexane, hexane - methanol azeotrope, hexane - methyl acetate azeotrope and ternary azeotrope.

- Step 5: At this point, we can eliminate pure hexane as recycle, because it is connected by residue curves neither to methanol nor to methyl acetate. The hexane - methanol azeotrope is connected only to methanol while the hexane - methyl acetate azeotrope is connected only to methyl acetate. The ternary azeotrope is connected to both methanol and methyl acetate.

- Step 6: The hexane - methanol azeotrope is connected only to methanol, so methanol must be recovered in the entrainer recovery column. Figure 3.30 shows the corresponding Σ_M region. Since the residue curves that go through $\mathcal{T}_{MA}$ are limited to region 2, they cannot reach Σ_M. Therefore, the hexane - methanol azeotrope cannot be used as recycle. The same arguments, where methanol and methyl acetate are exchanged, hold for the hexane - methyl acetate azeotrope.

  The ternary azeotrope is connected to both azeotropic components, so we can try indifferently to remove methanol or methyl acetate in the second column. If we try to remove methanol in the entrainer recovery column, we see that Σ_M is entirely contained in region 1. Since residue curves that go through $\mathcal{T}_{MA}$ are limited to region 2, this separation is impossible (figure 3.31). However,

Fig. 3.29: The specification areas are added to the residue curve diagram

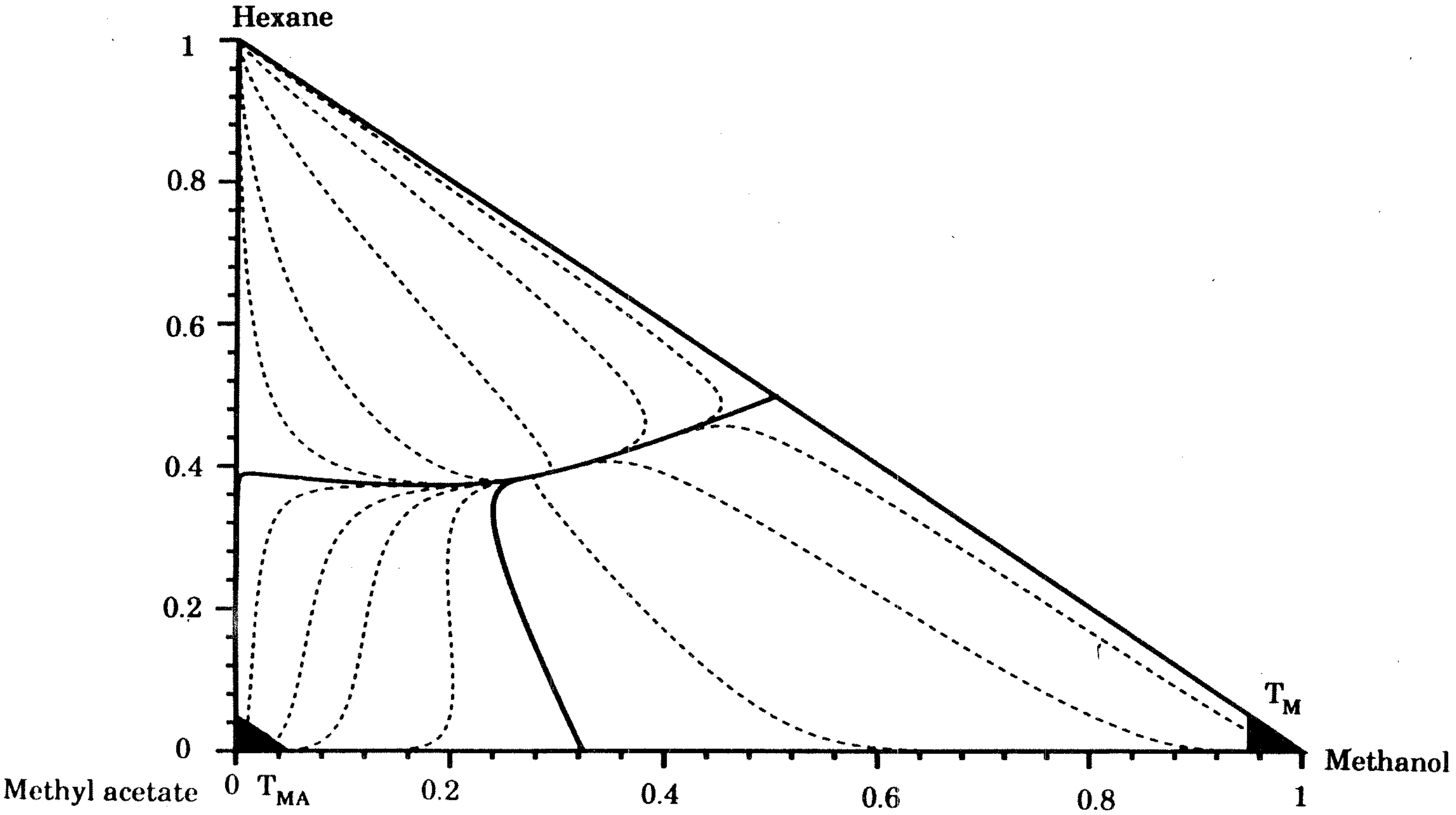
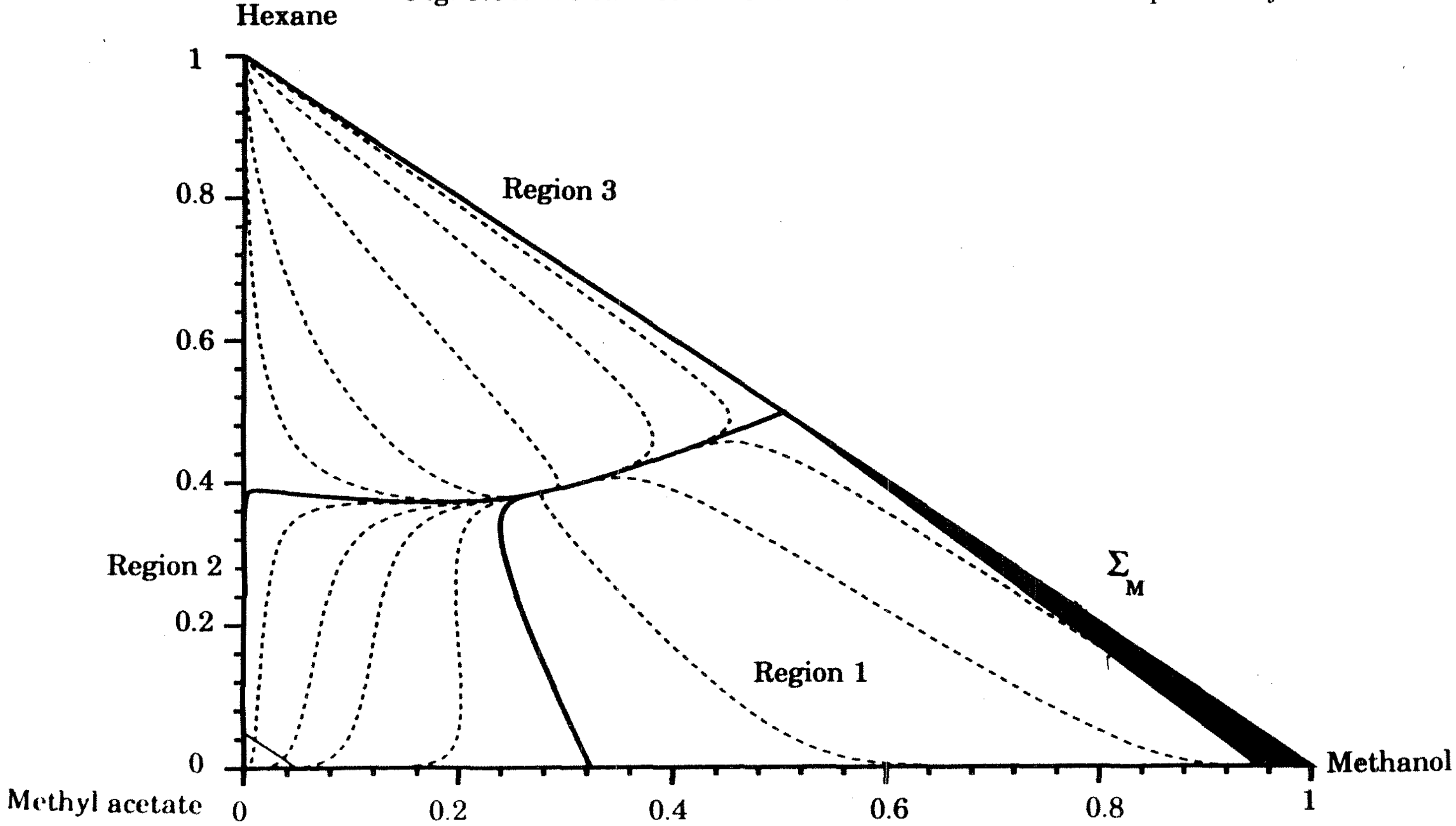


Fig. 3.30: We cannot use the hexane - methanol azeotrope as recycle



when we try to recover methyl acetate in the second column, we see that Σ_{MA} intersects region 1 (figure 3.32). Because all residue curves in region 1 reach $\mathcal{T}_M$ eventually, the second condition of theorem 3.4 is also satisfied, and separation is feasible.

We see that hexane makes the separation of the methyl acetate - methanol azeotrope feasible. The corresponding separation sequence is depicted by figure 3.33. Figure 3.34, figure 3.35 and figure 3.36 show the composition profiles of the two columns.

Let us now examine the case where we try to use methanol as entrainer for the hexane - methyl acetate azeotrope. Following the same procedure, we obtain:

- Step 1: The candidate entrainer has been chosen.
- Step 2: The residue curve diagram is unchanged.
- Step 3: The acceptable product regions are added to the residue curve diagram (figure 3.37).
- Step 4: Again, there are four possible recycle compositions: Pure methanol, methanol - hexane azeotrope, methanol - methyl acetate azeotrope and ternary azeotrope.
- Step 5: Pure methanol cannot be used as recycle because it is not connected by residue curves to either azeotropic components. The methanol - hexane azeotrope is connected only to hexane, while the methanol - methyl acetate azeotrope is connected only to methyl acetate. The ternary azeotrope is connected to both hexane and methyl acetate.
- Step 6: The methanol - hexane azeotrope cannot be used as recycle because the extractive column cannot yield a product that contains only a small fraction of methyl acetate. For a similar reason, the methanol - methyl acetate azeotrope cannot be used as recycle. If we use the ternary azeotrope as recycle and try

Fig. 3.31: We cannot recover methanol second

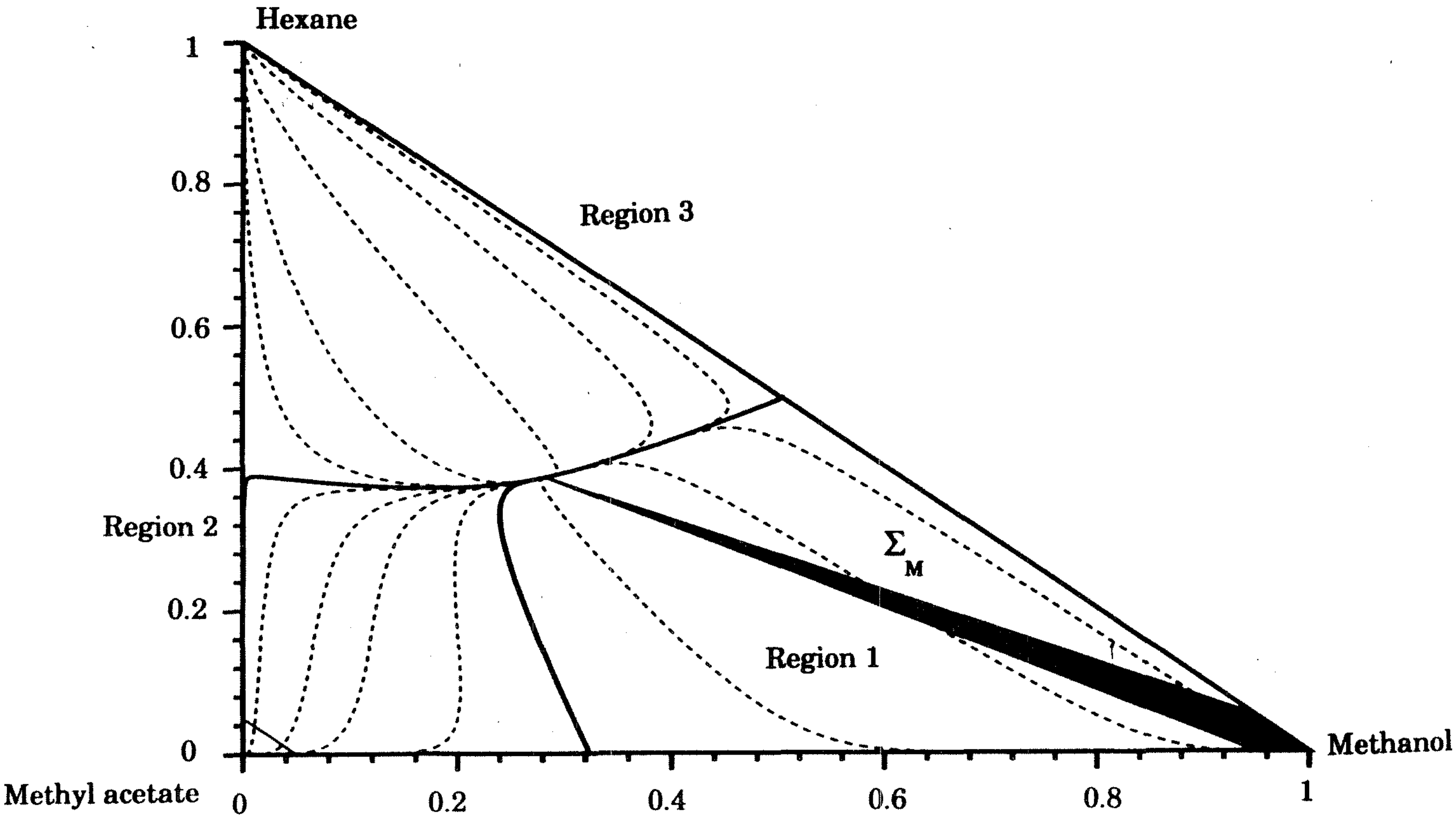
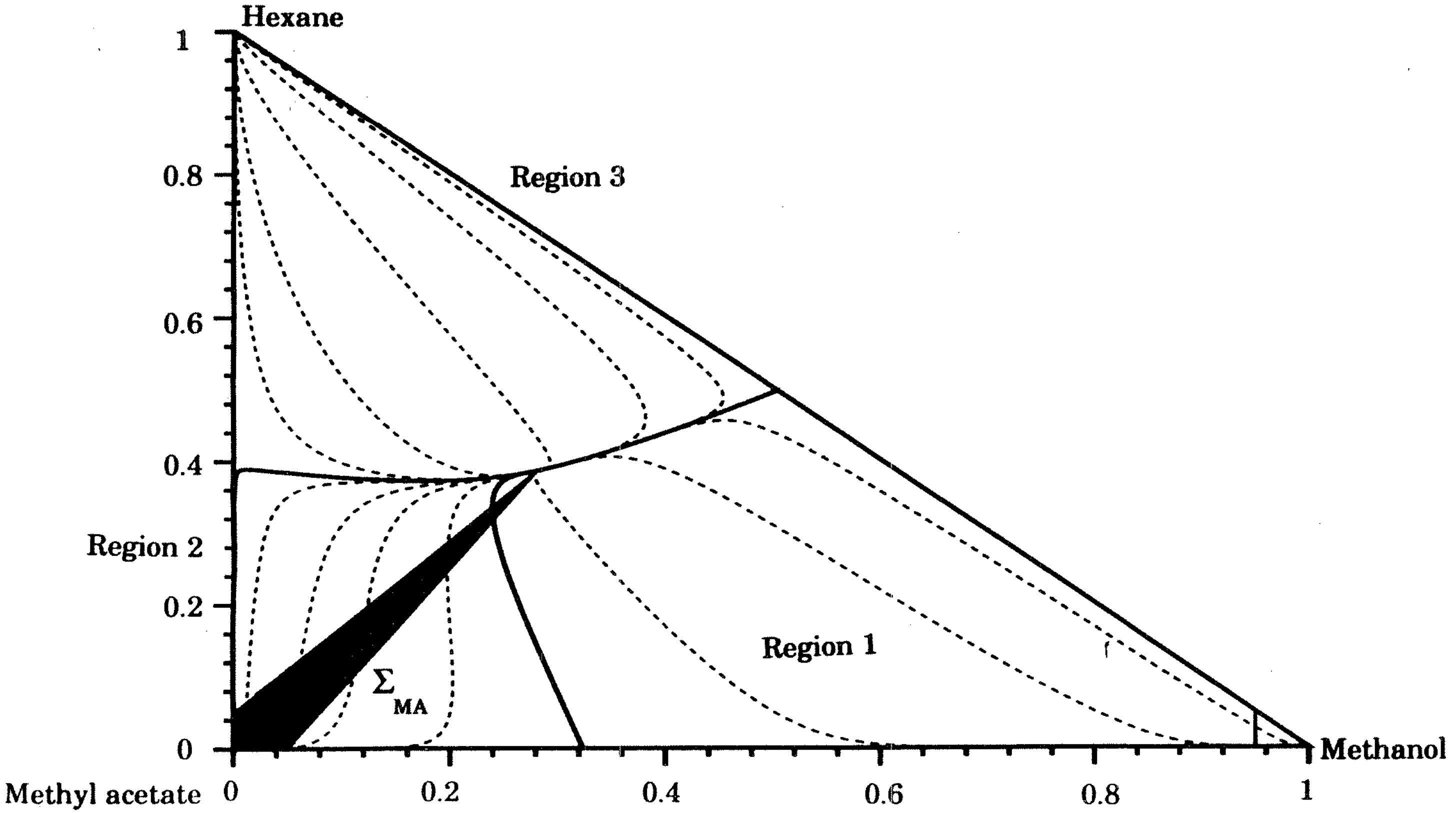


Fig. 3.32: Separation is feasible if we recover methyl acetate second



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)	0.281	0.324	0.251	0.996	0.282	0.002
Hexane (H)	0.386	0.0	0.344	0.0	0.386	0.0

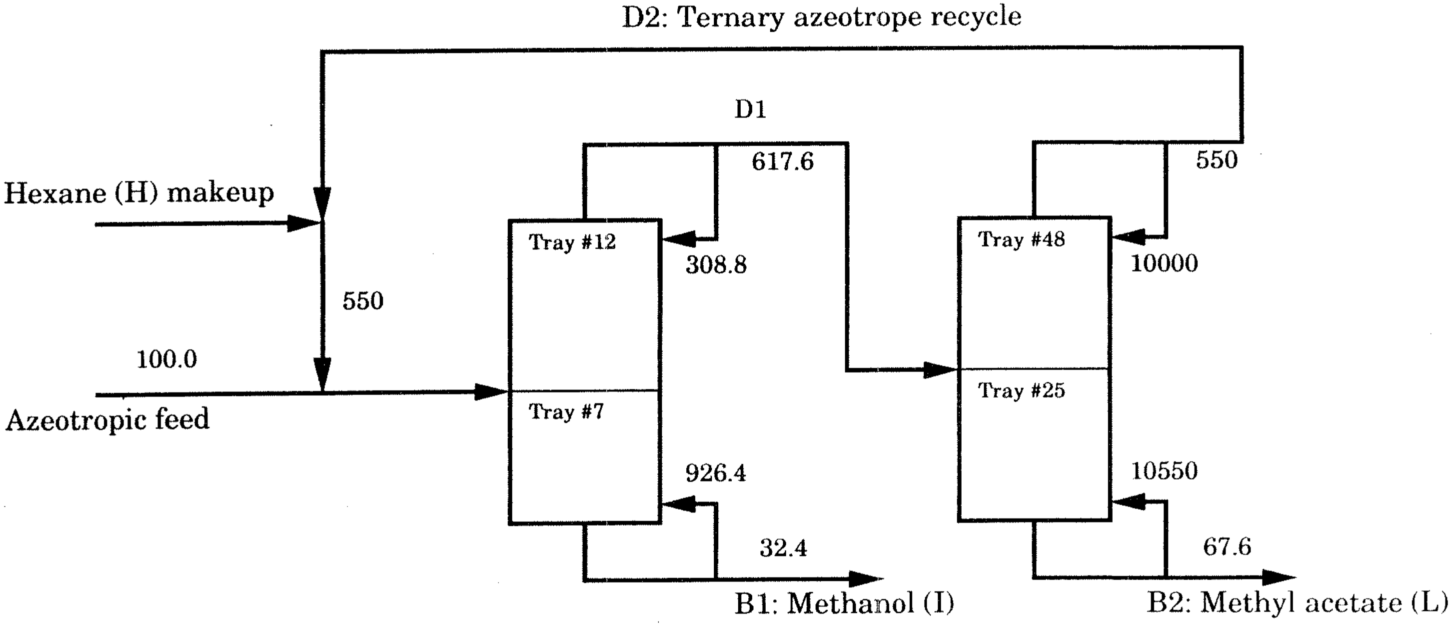


Fig. 3.33: The methanol - methyl acetate - hexane separation sequence

Fig. 3.34: Hexane (1) - methanol (2) - methyl acetate (3) extractive column composition profile

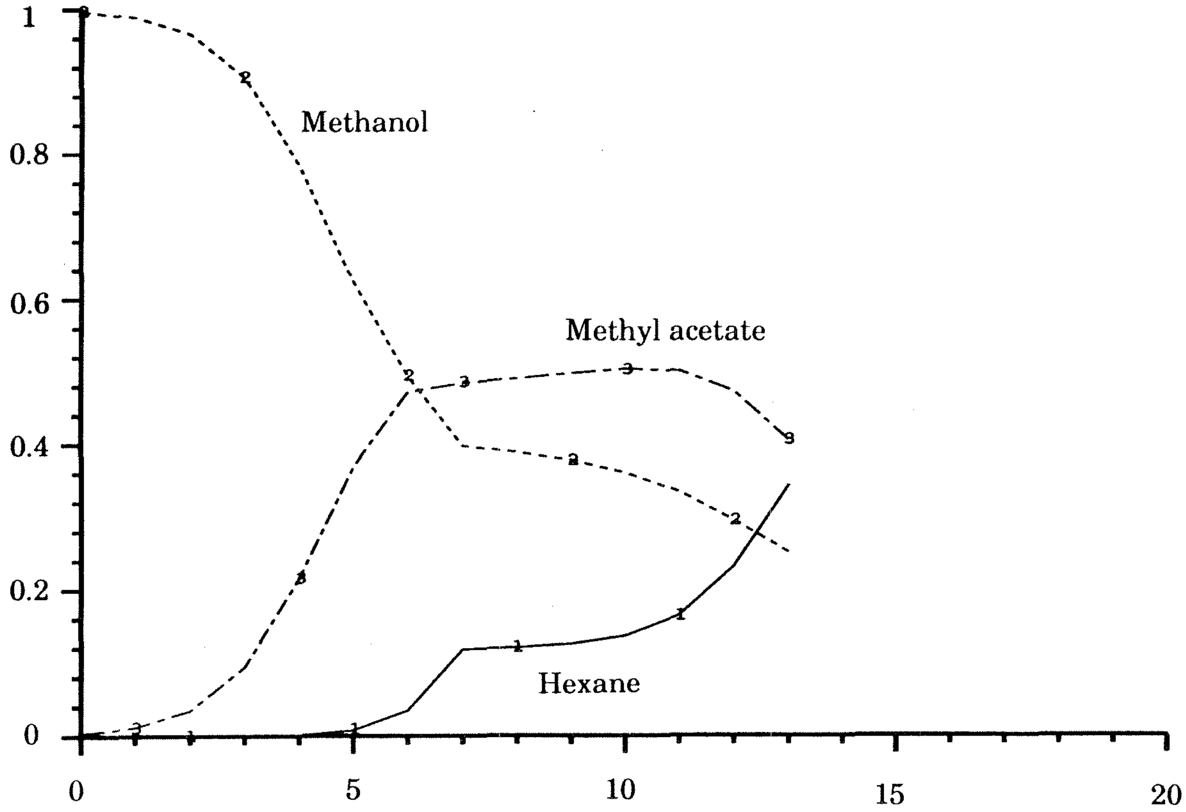


Fig. 3.35: Hexane (1) - methanol (2) - methyl acetate (3) entrainer recovery column composition profile

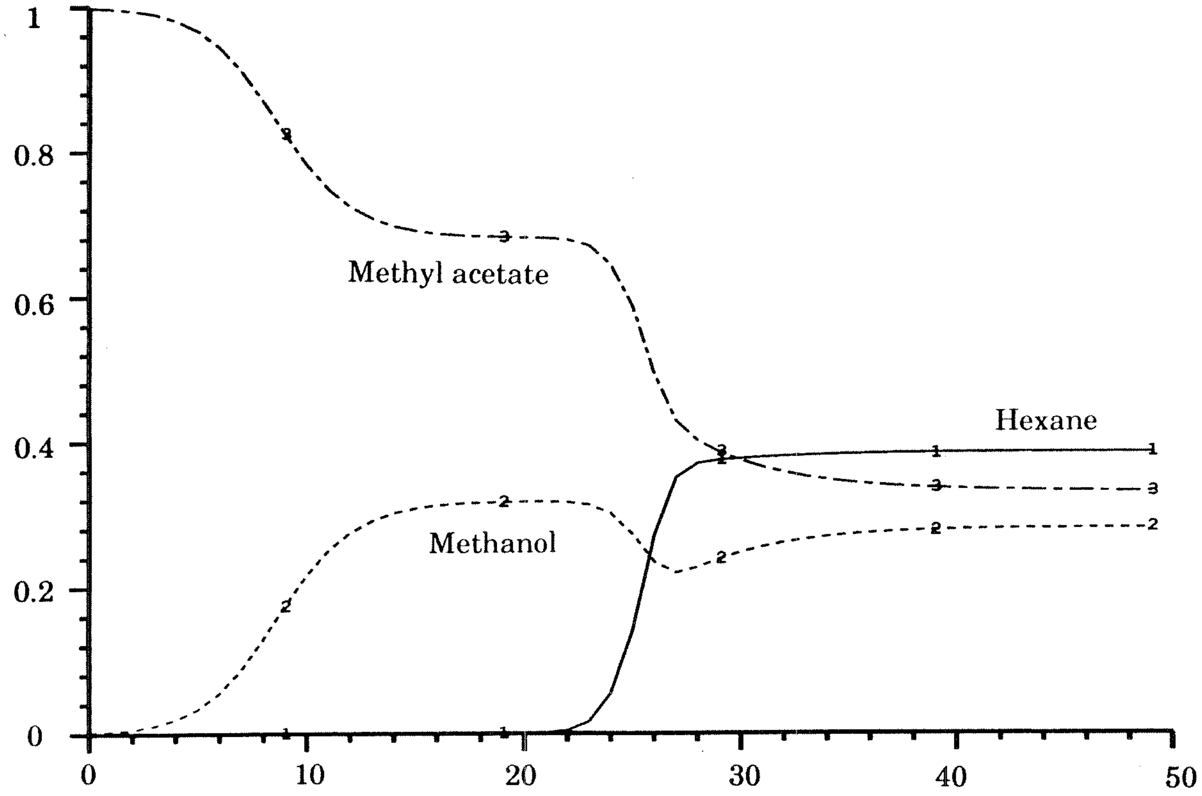


Fig. 3.36: Hexane - methanol - methyl acetate residue curve diagram and column composition profiles

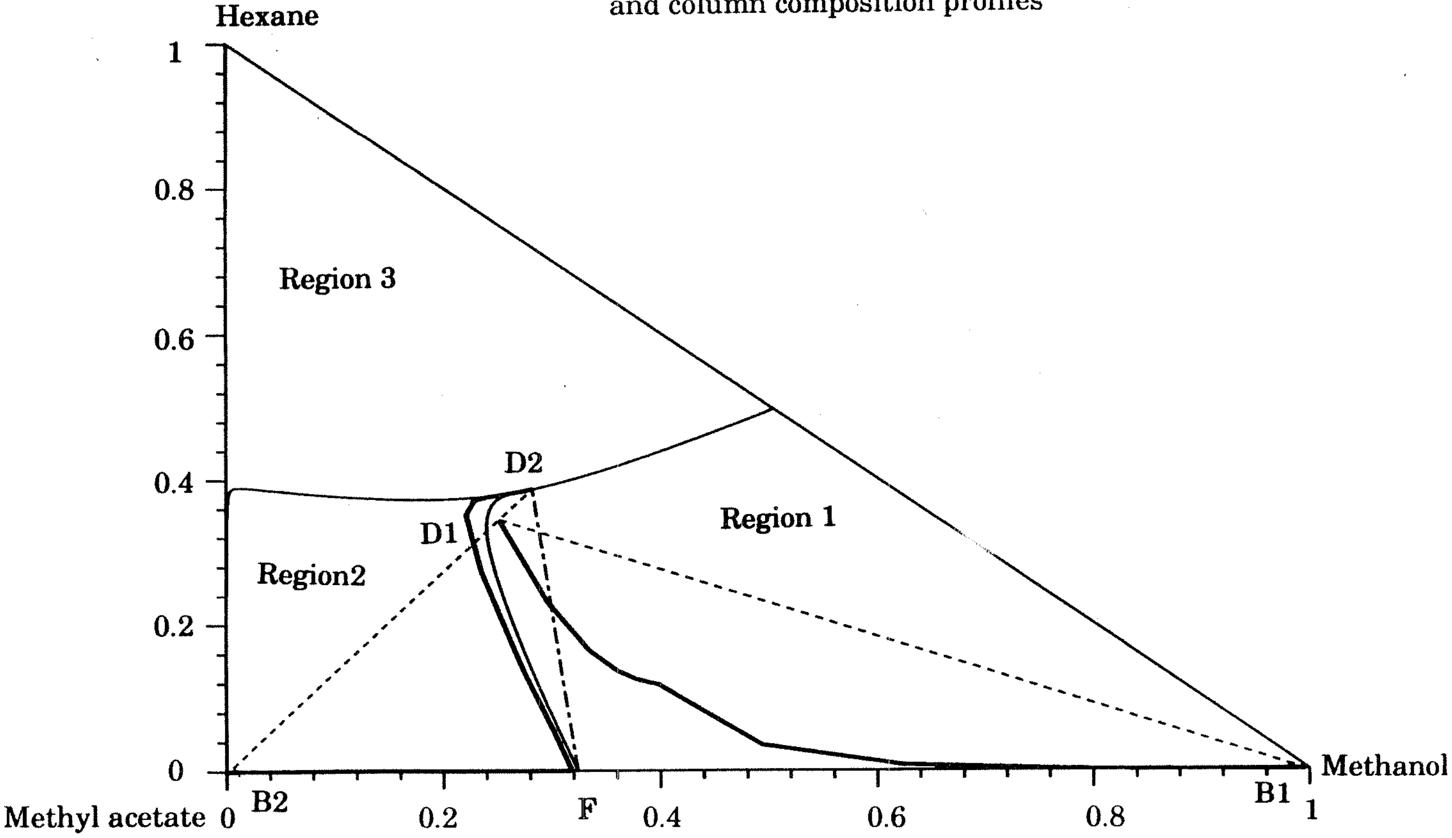
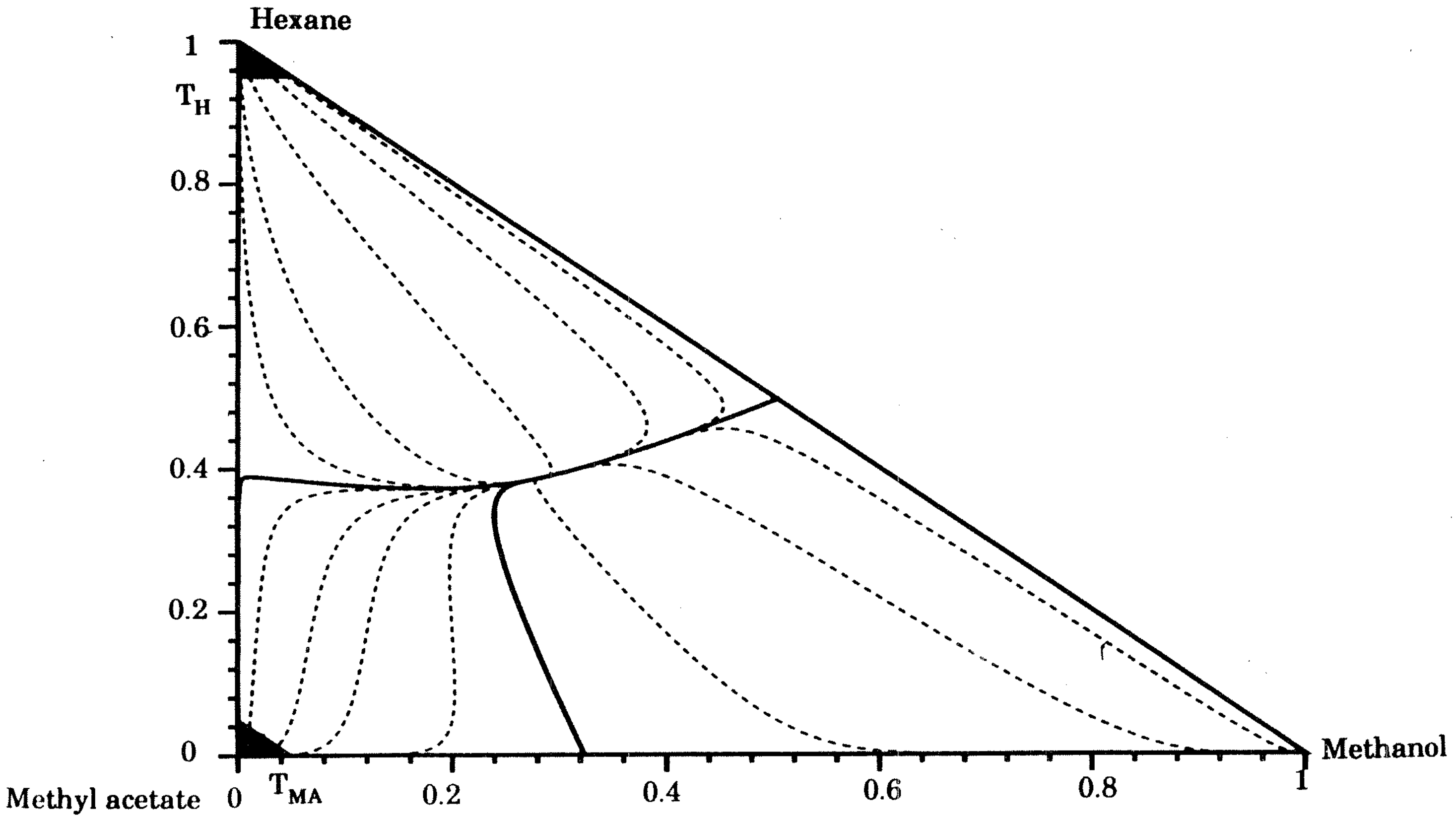


Fig. 3.37: The specification areas are added to the residue curve diagram



to recover hexane in the second column, we see that the corresponding set Σ_H does not cross the residue curve boundary that separates region 3 and region 2, so we cannot achieve separation this way (figure 3.38). We obtain the same result if we try to recover methyl acetate in the entrainer recovery column.

In summary:

- Because of the high curvature of the boundary joining the methanol - methyl acetate azeotrope to the ternary azeotrope, we can use hexane as entrainer for the methanol - methyl acetate azeotrope if we recycle the ternary azeotrope.
- Because the boundary joining the hexane - methyl acetate azeotrope to the ternary azeotrope is too close to a straight line, we cannot use methanol as entrainer to separate the hexane - methyl acetate azeotrope.

3.1.6 Separation flowsheet

The screening procedure described previously has one important additional benefit: We immediately know the qualitative flowsheet of each feasible separation sequence. Indeed, we first determine during this procedure the recycle composition and the component removal order. We can also determine for both columns an approximate composition for each product from the residue curve orientations, because residue curves go from the distillate to the bottom. Finally, we can determine a range of feasible feed ratios (entrainer feed to azeotropic feed flow rate) from the mass balance of the extractive column; for instance, in the 020 example shown in figure 3.39, we see that the feed ratio must be above $\frac{F_{AB}P}{PE}$ for separation to be feasible.

Note that the resulting flowsheet may be sometimes surprising. There are many cases where the only feasible separation sequence first yields the intermediate component as pure product. This screening procedure predicts such situations and provides an explanation for the unusual behavior of homogeneous azeotropic distillation de-

Fig. 3.38: We cannot use the ternary azeotrope as recycle

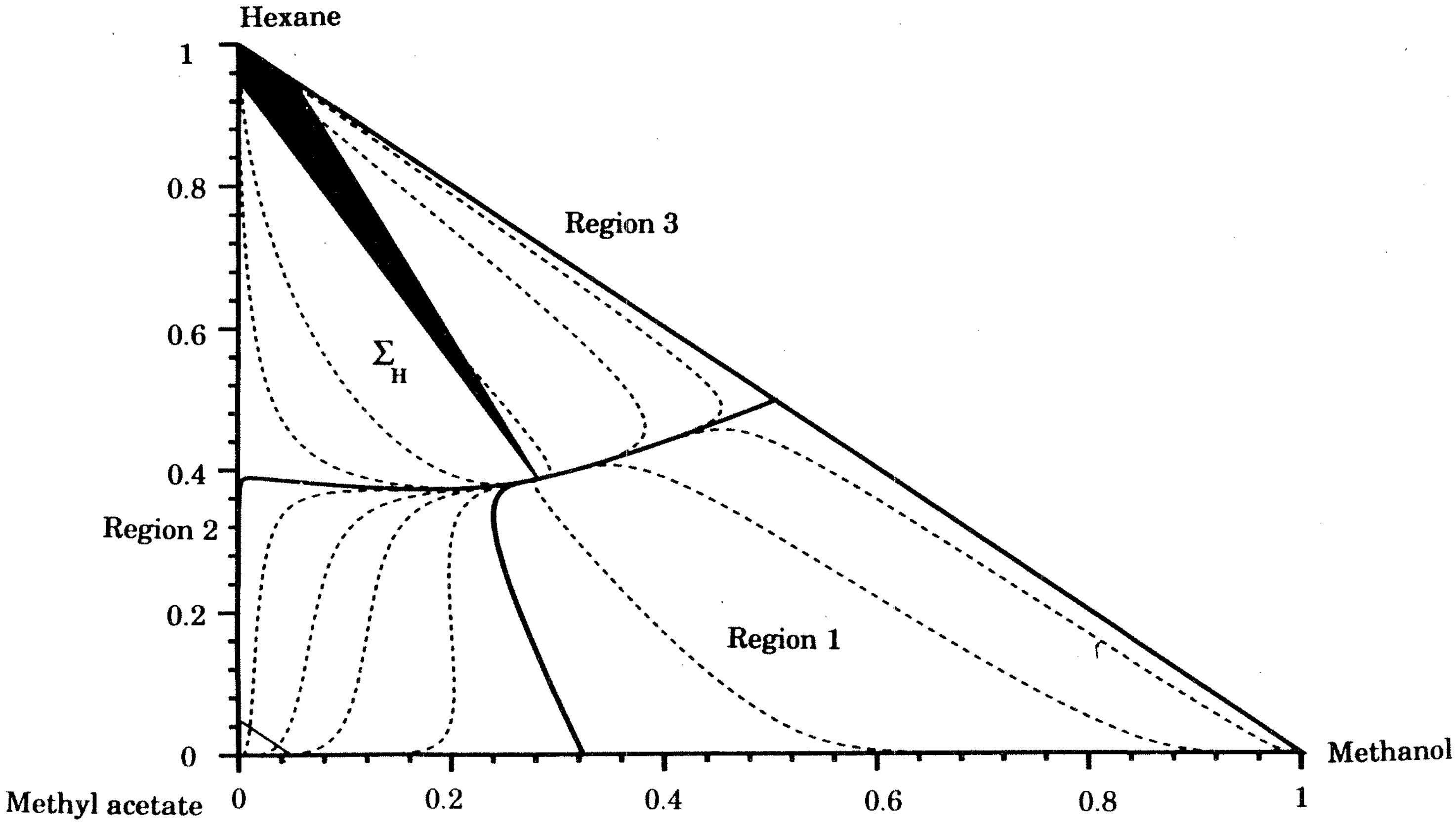
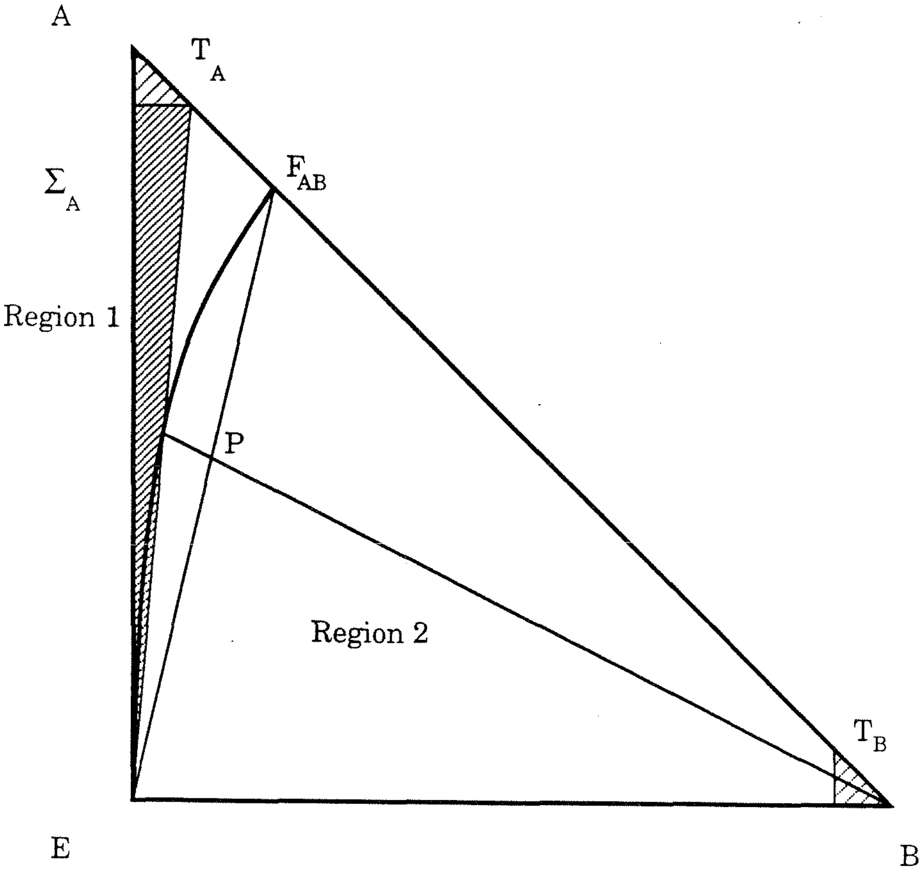


Fig. 3.39: **Separation is infeasible if the feed ratio is below $\frac{PF_{AB}}{PE}$**



scribed in chapter 2.

This insight is very useful at the next stage, *i.e.* the design of the separation sequence. Indeed, even when the existing screening criteria correctly predict separability, they do not indicate how this separation should be performed. Note, for example, that the separation sequence proposed by Stichlmair *et al.* (1989) does not work because its mass balance cannot be closed (chapter 2). Thus we have to search by trial and error for the component removal order. Therefore, knowing the approximate compositions and flow rates of the various streams before starting the separation sequence design is most beneficial. This is particularly true when we deal with complex mixtures such as hexane - methanol - methyl acetate or when we need good initial estimates to obtain convergence (as is usually the case with commercial simulators).

3.1.7 Separating a binary azeotrope with three columns

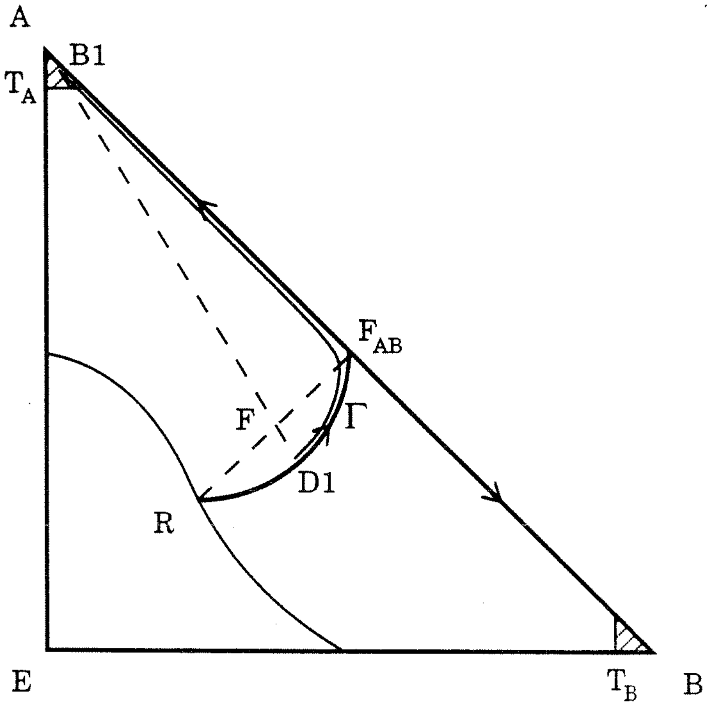
Often, the crude feed is brought to the azeotropic composition by a preconcentrator (Knight & Doherty 1988, Knapp & Doherty 1990). Thus, the complete separation sequence actually contains three columns. In this section, we show that separation is very often feasible in a three-column sequence, even when it is impossible with just two columns. More precisely:

Theorem 3.6 *We can separate a minimum-boiling binary azeotrope A-B into two products of any given purity in a separation sequence of three packed columns operated at infinite reflux using E as entrainer if:*

- *A and B are located in adjacent distillation regions.*
- *The residue curve boundaries separating these two regions does not contain any inflexion point and is oriented towards the A-B azeotrope.*

These two conditions are sufficient, but they are by no means necessary: For instance, we can use three columns to separate the acetone - heptane azeotrope using benzene as entrainer; yet in this case acetone and heptane belong to the same distillation region. In practice, we have found that these conditions are very often satisfied. For example, they are satisfied for almost light entrainers that do not add azeotropes, because, in that case, the two azeotropic components are in adjacent distillation regions, the boundary is oriented towards the binary azeotrope and almost never contains any inflexion point. A survey of more than 250 mixtures has shown that about 140 of them satisfy these assumptions.

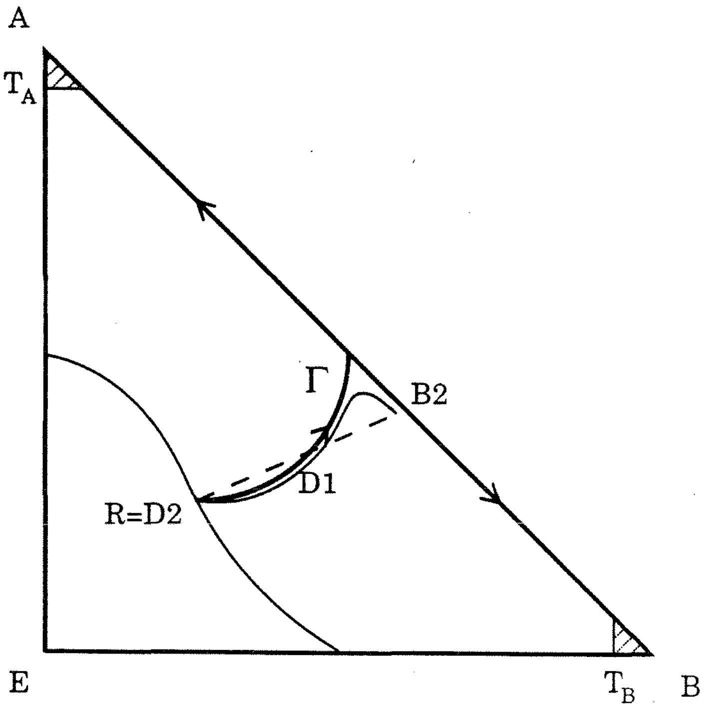
Fig. 3.40: First column profile and material balance



The proof of this theorem is graphical and can be seen on figure 3.40, figure 3.41 and figure 3.42. Let Γ be the boundary separating the two distillation regions that contain A and B. Γ must start or end at the azeotrope formed by A and B while its other extremity can be a ternary azeotrope of A, B and E, a binary azeotrope of either A and E or B and E, or the entrainer E. We denote this point by R. Because Γ does not contain any inflexion point, its curvature is always in the same direction; let us assume that A is on the convex side of Γ. Then separation can be done in the following manner (figure 3.43):

- The first column is fed with the binary A-B azeotrope and R. We can recover some A as bottom product (located within T_A) while the top product is located

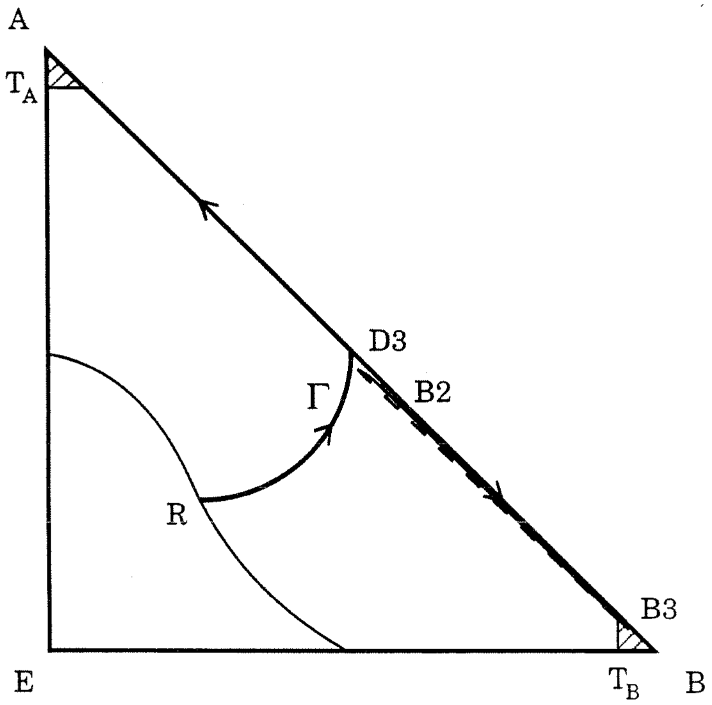
Fig. 3.41: Second column profile and material balance



very close to Γ, between the A-B azeotrope and R. A residue curve does connect these two points: It runs from the distillate along Γ to the A-B azeotrope, then along the A-B edge to $\mathcal{T}_A$ (figure 3.40).

- The second column is fed with the distillate of the first column. Because of the curvature of Γ, we can recover R as top product while the bottom product is located very close to the A-B edge, *between B and the A-B azeotrope.* This separation is feasible because a residue curve runs from R to the distillate: It starts from R, follows Γ up to the A-B azeotrope, then follows the A-B edge up to the distillate. We cross Γ within this column, not by recycle but because of its curvature (figure 3.41).

Fig. 3.42: Third column profile and material balance

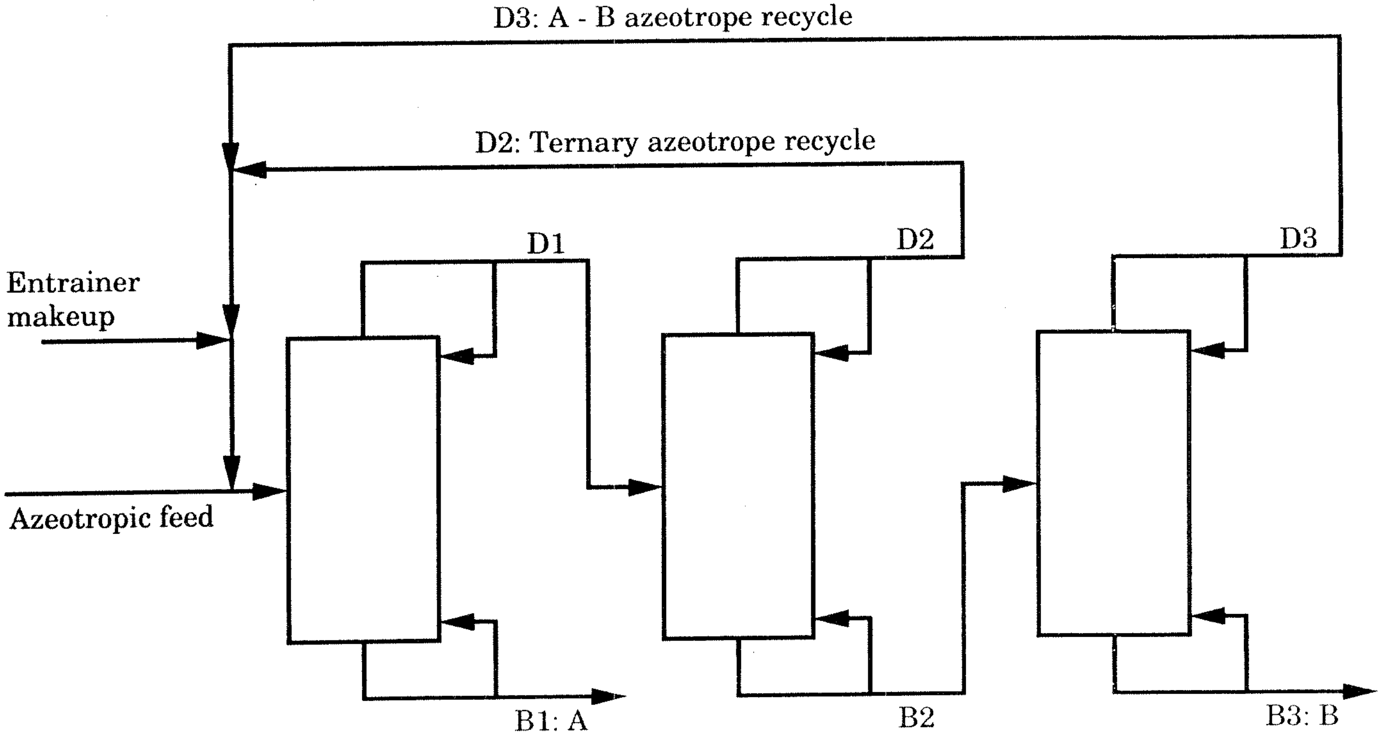


- The third column performs essentially a binary separation between A and B, because its feed contains very little E. Its bottom product lies within $\mathcal{T}_B$, while its top product is the A-B azeotrope (figure 3.42).

Depending on its composition, the crude A-B feed is introduced either in the first column or in the third column. If it contains more B than the A-B azeotrope, then it should be fed to the third column, while it should be introduced in the first column if it contains more A than the A-B azeotrope. Therefore, no preconcentrator is required.

These separation sequences would seem less attractive economically, because there is one more column and more recycle. However, we must keep in mind that the fresh feed is often brought to the azeotropic composition by a preconcentrator (Knight

Fig. 3.43: The three-column separation sequence



& Doherty 1988, Knapp & Doherty 1990). Because either the first or the third column acts as preconcentrator, only the azeotrope material recycle is added to the standard two-column sequence with preconcentrator. Obviously, whether this scheme is economically viable or not depends on the specifics of the problem. In particular, this scheme becomes all the more attractive as Γ displays more curvature. Indeed, the higher the curvature, the more A and B we can recover per pass and the less A-B azeotrope we have to recycle. Obviously, if its curvature is high enough, then we can achieve separation with only two columns.

This separation technique is illustrated by figure 3.44 to figure 3.46 in the methyl acetate (L) - methanol (I-E) - hexane (H) case. We have already shown that methanol does not make feasible the separation of the hexane - methyl acetate azeotrope in a two-column sequence. However, separation is feasible in a three-column sequence. The first column splits the overall feed (binary azeotrope and ternary azeotrope) into pure hexane and a product D_1. The second column then separates D_1 into the ternary azeotrope, which is recycled, and a product D_2. Note that, because D_2 contains very little methanol, we separate it in a binary column that produces the hexane - methyl acetate azeotrope and pure methyl acetate. The fresh hexane - methyl acetate feed would be introduced in the third column if it were richer in methyl acetate than the hexane - methyl acetate azeotrope, and in the first column if it were richer in hexane than the azeotrope. The distillation boundary is not crossed by recycle, but because of its curvature: The feed of the second column (here, D_1) lies in one distillation region while its composition profile is contained in another region.

3.1.8 Separability and residue curve diagram classes

Residue curve diagrams and boundaries represent an essential tool in this study, but residue curve diagram classes, as defined by Doherty & Caldarola (1985), do not contain the information necessary to determine separability. Separability often depends

Concentration	**Entrainer feed**	**Azeotropic feed**	**D1**	**B1**	**D2**	**B2**	**D3**	**B3**
Methyl acetate (L)	0.332	0.607	0.435	0.01	0.332	0.660	0.606	0.99
Methanol (I)	0.282	0.0	0.194	0.0	0.282	0.002	0.002	0.00
Hexane (H)	0.386	0.393	0.371	0.99	0.386	0.338	0.392	0.01

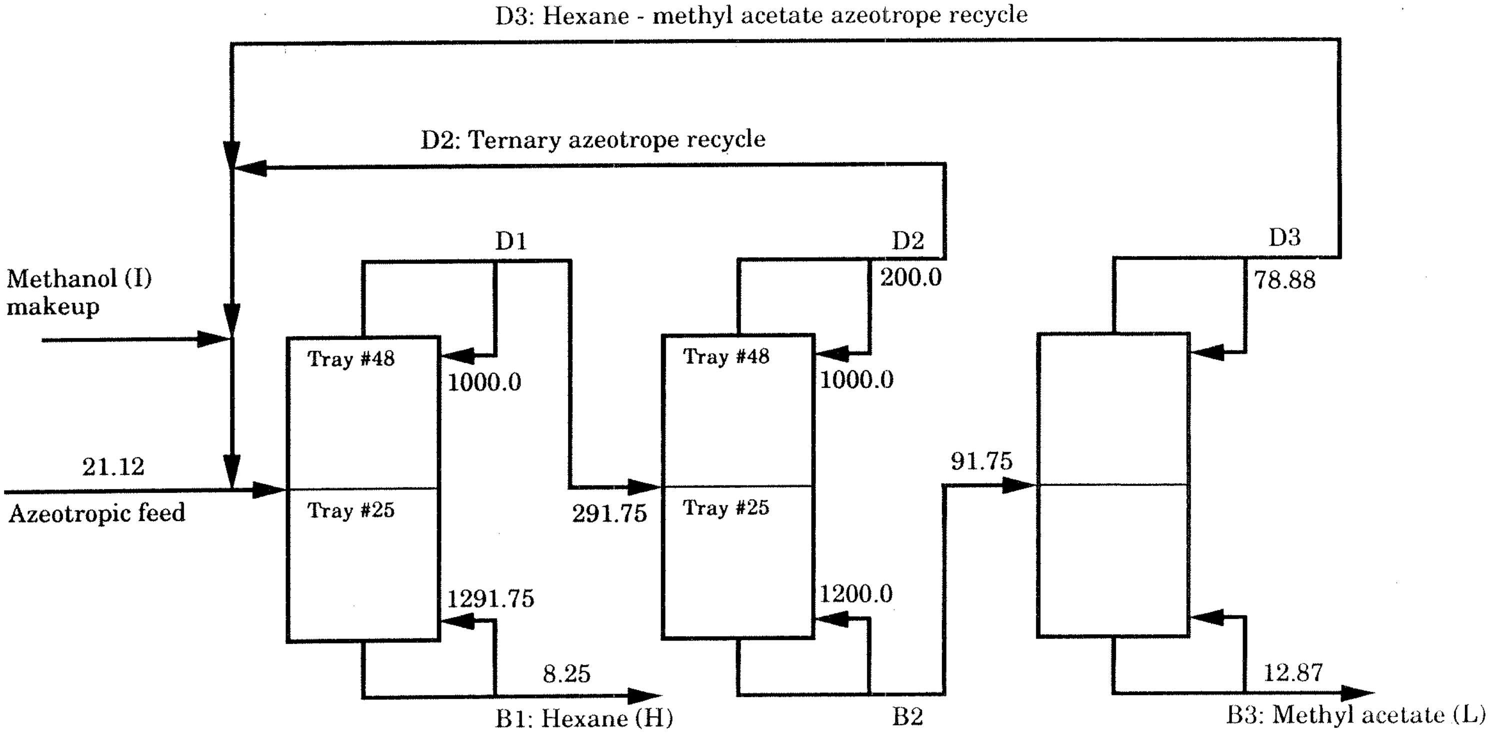


Fig. 3.44: The methyl acetate - hexane - methanol three-column separation sequence

Fig. 3.45: Methanol (1) - methyl acetate (2) - hexane (3)
first column composition profile

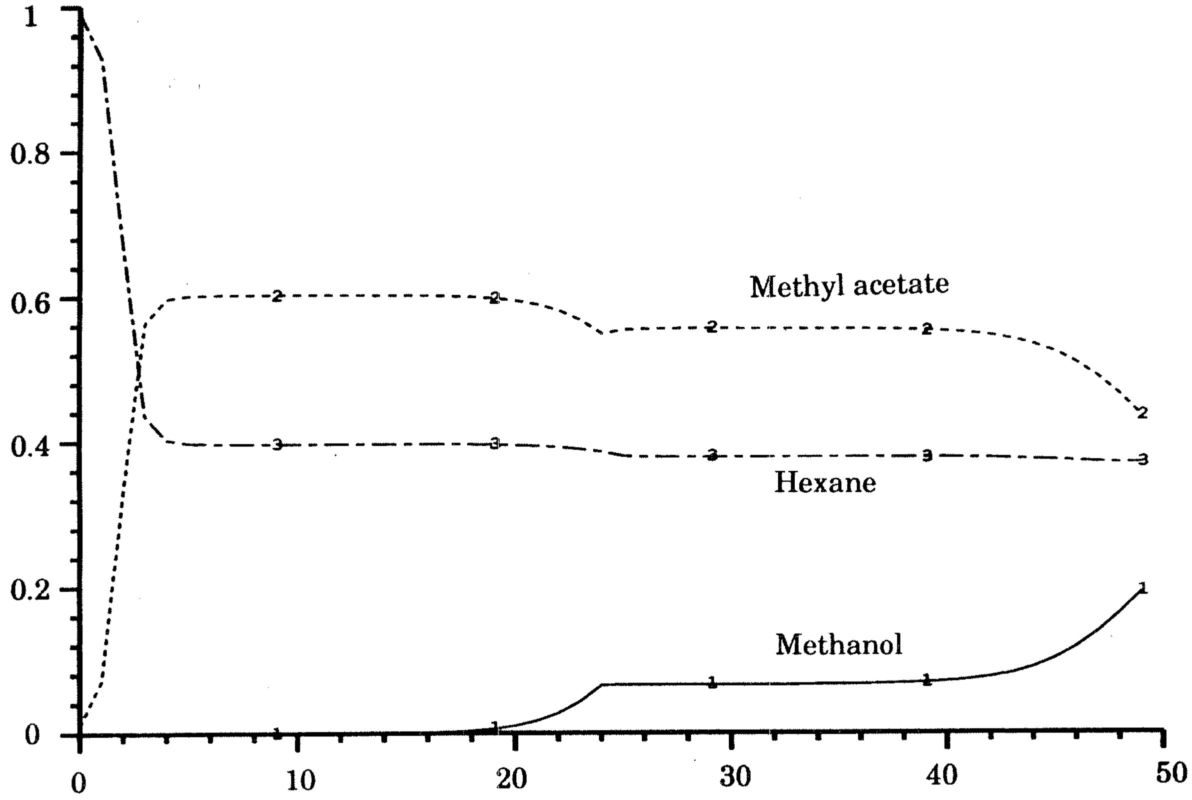


Fig. 3.46: Methanol (1) - methyl acetate (2) - hexane (3) second column composition profile

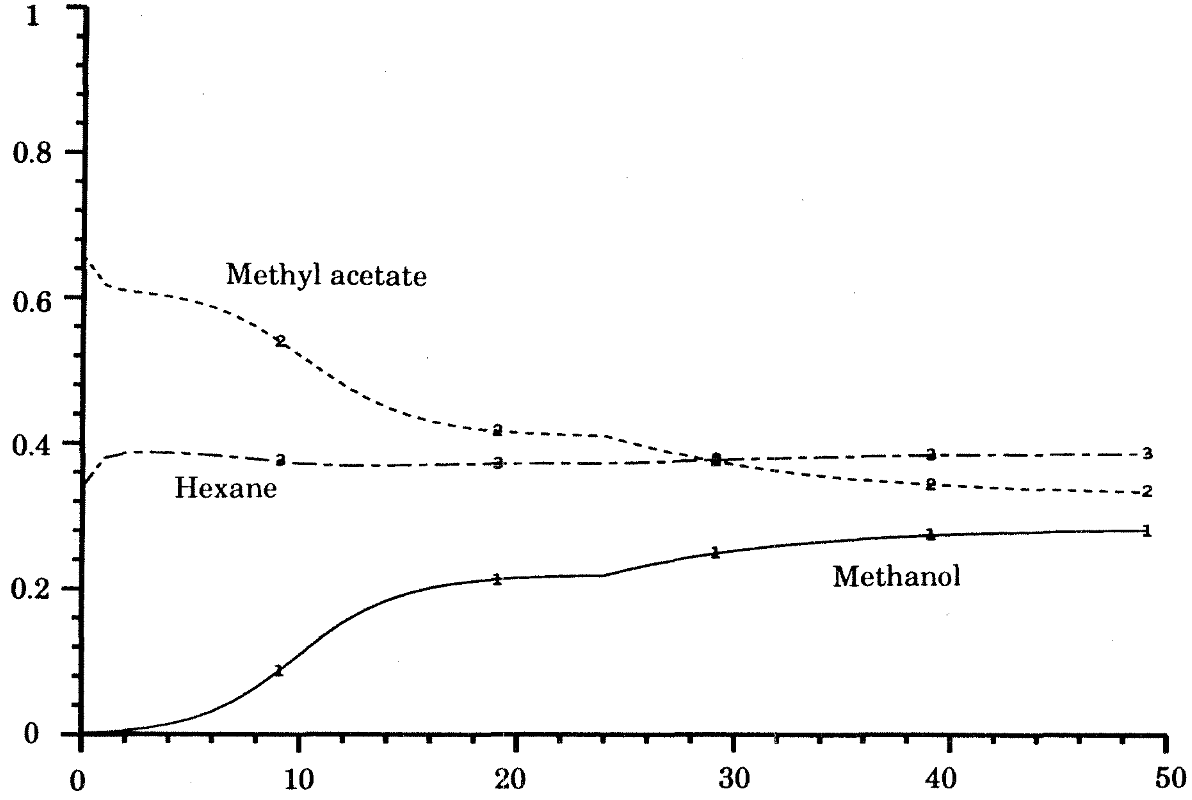


Fig. 3.47: Hexane - methanol - methyl acetate residue curve diagram and first column composition profile

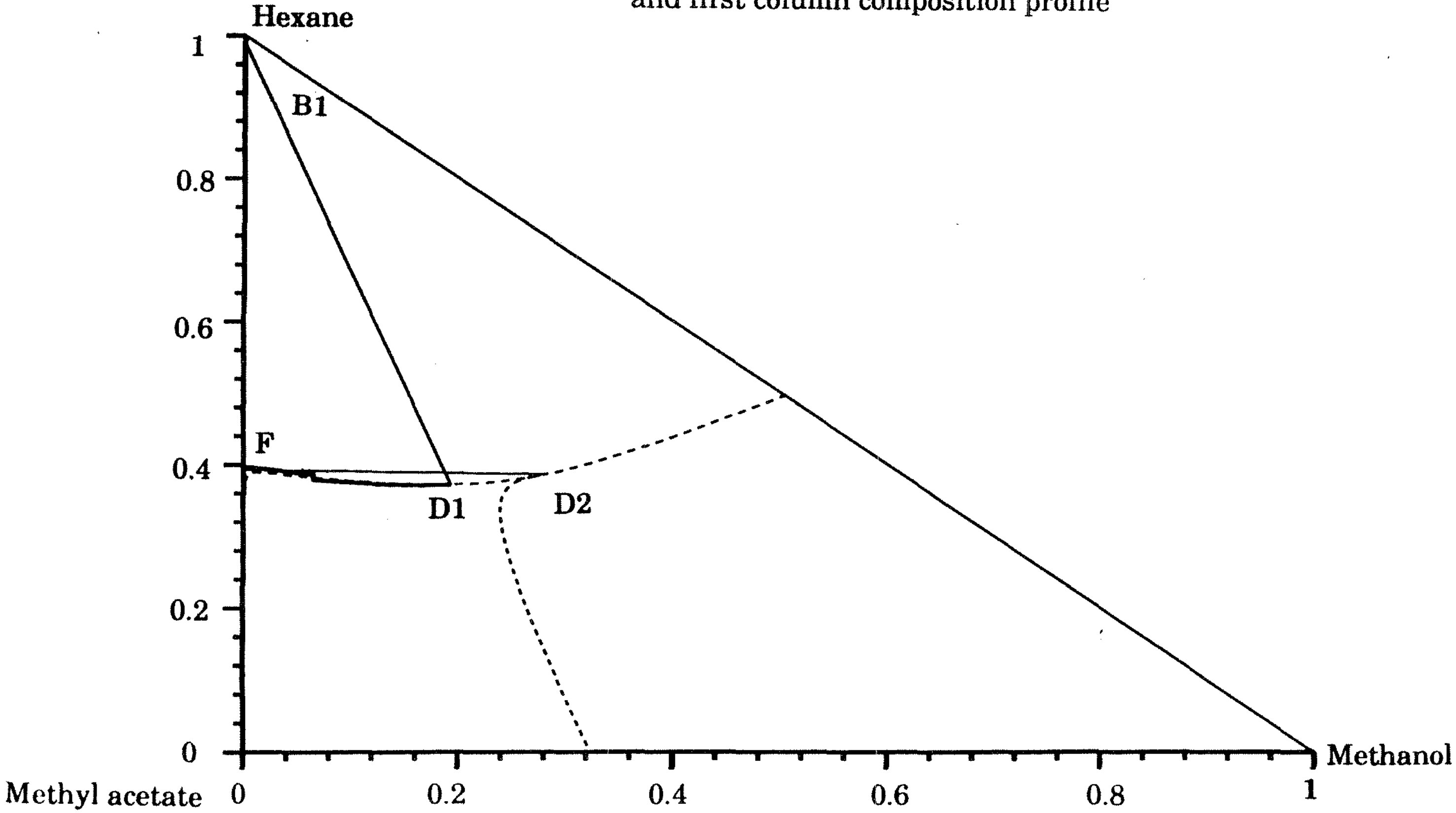
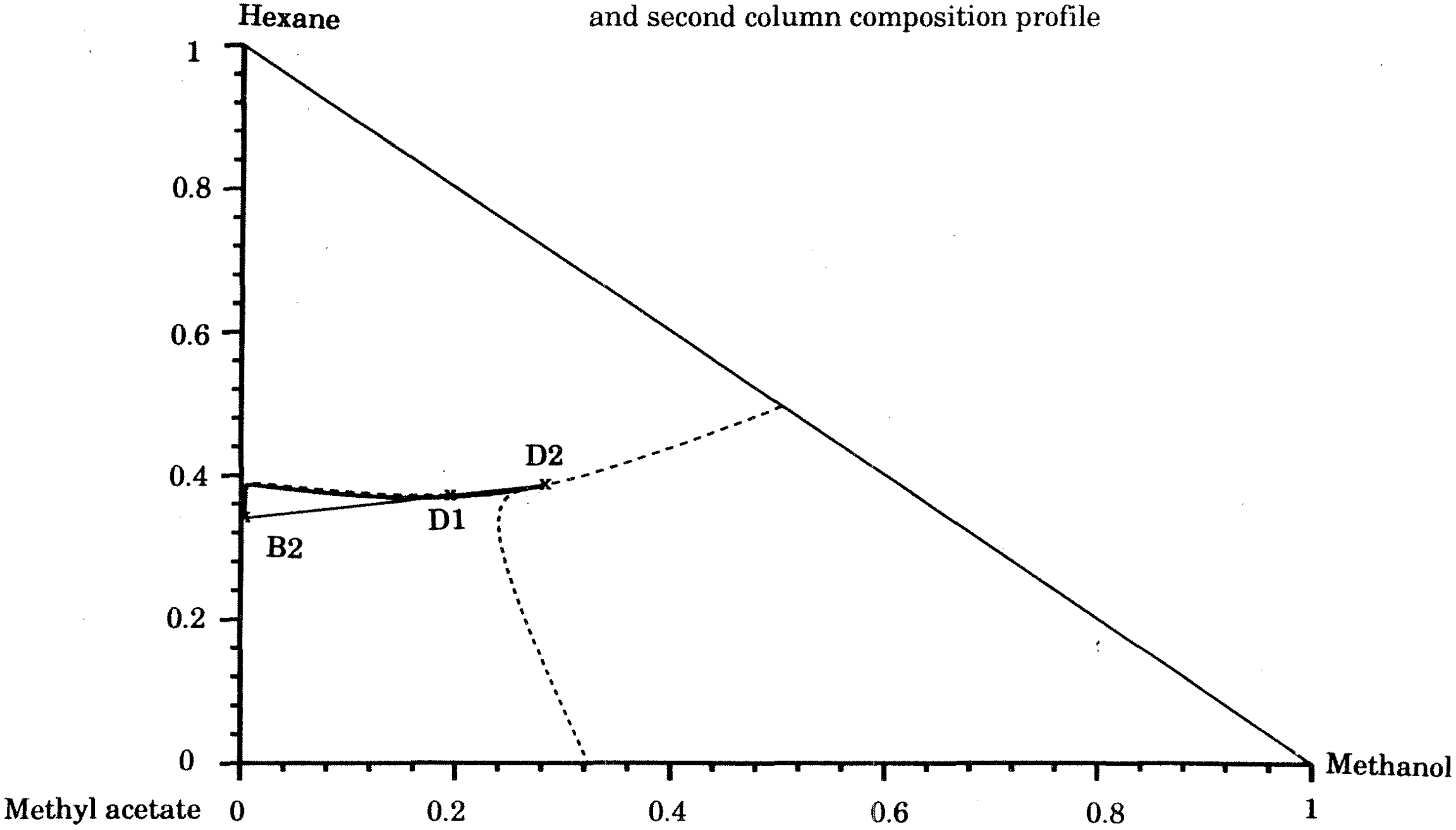


Fig. 3.48: Hexane - methanol - methyl acetate residue curve diagram and second column composition profile



on the exact location of residue curve boundaries. When separation is feasible, the number of columns required to perform this separation often depends on the curvature of a given boundary, as we have shown in the hexane - methanol - methyl acetate case. In the same manner, drawing a sketch of the residue curve diagram with straight residue curve boundaries does not give enough information. In the 020 case, separation will always be considered impossible if the residue curve boundary is represented by a straight line in the mathematical sense. Obtaining accurate thermodynamic data and, in particular, knowing the precise position and shape of the residue curve boundaries is essential for correct separability prediction and flowsheet synthesis.

3.1.9 Summary

In this section, we have established the following points:

- Separating a feed F into a distillate D and a bottom B in a packed column operated at infinite reflux is possible if and only if D, F and B are aligned and a residue curve connects D to B.

- We have found that the separation of a binary azeotrope into two pure products is sometimes possible with only one column, and we have given a necessary and sufficient condition for separability with only one column.

- Through a new screening procedure, we can determine whether a candidate entrainer makes the desired separation feasible in a sequence of two packed columns operated at infinite reflux. This procedure is illustrated with a couple of case studies. In particular, we obtain an unusual separation sequence in the case of the hexane - methanol - methyl acetate mixture, since we use a ternary azeotrope to break a binary azeotrope.

- This screening procedure can be generalized to sequences with more than two columns. We show that separation is always feasible in a three-column sequence if:
  - The two azeotropic components are located in adjacent distillation regions.
  - The boundary separating these regions does not contain any inflexion point and ends at the binary azeotrope we want to separate.

  For instance, we showed that methanol cannot act as entrainer for the hexane - methyl acetate azeotrope if we use only two columns, but makes this separation feasible in a three-column sequence.

- These conditions simplify the separation sequence design by indicating the flowsheet of the feasible separation sequence(s) and the approximate stream flow rates and compositions.

- Mixtures within the same residue curve class can give different separability results: Some might be separable while others might not. In many cases, we cannot pass a judgement on separability if we only know the residue curve diagram class; we need the exact position of the residue curve boundaries in order to determine separability correctly.

3.2 Separability in practice

Two considerations make judgements on separability quite complicated in practice:

- Firstly, distillation columns are operated at finite reflux. Because separability at infinite reflux implies separability at finite reflux, the entrainers selected by the method described in the previous section should be considered in practice. But we cannot reject the components that do not make separation feasible at infinite reflux. We show here two situations where separation is feasible at finite reflux but not at infinite reflux.

- Secondly, the determination of separability at infinite reflux requires the knowledge of the exact location of residue curve boundaries. Therefore, we need an accurate description of the vapor-liquid equilibrium data of the ternary mixture.

3.2.1 Separability and distillation boundary curvature

We have seen in the previous section that separability at infinite reflux often results from the curvature of residue curve boundaries. For instance, we can use hexane as entrainer for the methanol - methyl acetate azeotrope because the boundary joining the ternary azeotrope and the methanol - methyl acetate azeotrope bends significantly. Also, separation is feasible with two columns operated at infinite reflux in the 020 case if and only if the residue curve boundary is sufficiently curved to intersect Σ_A or Σ_B.

These boundaries are exact boundaries only for columns operated at infinite reflux. At finite reflux, composition profiles can cross distillation boundaries, as several separation sequences shown in chapter 2 bear witness. Because separation at finite reflux depends on whether there is one single feed or several separate feeds, and on their relative locations when there are more than one (chapter 2), the notion of finite reflux boundaries is not uniquely defined. By examining single feed columns only, Van Dongen (1982) has derived a procedure that estimates the location of these boundaries. Our observations in the double feed case agree with the conclusions of Van Dongen & Doherty (1985) for single feed columns: Regardless of how we define them, finite reflux boundaries always display higher curvatures than infinite reflux boundaries. In other words, we can achieve more separation at finite reflux than at infinite reflux. Therefore, separations that are impossible at infinite reflux may be feasible at finite reflux, because the infinite reflux boundaries are not sufficiently curved while the finite reflux boundaries are. Figure 3.49, figure 3.50 and figure 3.51 illustrate this fact in the ethanol (I) - water (H) - methanol (L-E) case: Although the distillation boundary curvature prevents separation from being feasible at infinite reflux in a two-column sequence, separation is feasible at finite reflux with only two columns. Note that the ethanol - water - methanol residue curve diagram belongs to the 020 class. In practice, we have found that light entrainers that introduce no new azeotrope almost always make separation feasible in a two-column sequence.

3.2.2 Heavy entrainers

There is another situation where separation is infeasible at infinite reflux but feasible at finite reflux, namely the 100 case, which is most common in industry. We obtain a residue curve diagram that belongs to this class when we use as entrainer a heavy component that adds no azeotrope. Because Andersen *et al.* (1990) have extensively studied the 100 case at finite reflux, we use their results here and refer the reader to their article for details. They have shown that separation decreases when reflux is increased beyond a certain point in a homogeneous azeotropic distillation column, because this action dilutes the entrainer in the extractive section. At infinite reflux, the entrainer concentration is essentially null except on a few trays of the bottom section. From the residue curve diagram, we can predict that separation is infeasible at infinite reflux, as figure 3.52 illustrates in the case of ethanol - water - ethylene glycol. By applying theorem 3.2, we see that a feed located between the binary azeotrope (azeotropic feed) and the ethylene glycol corner (entrainer feed) cannot be separated into a distillate that is almost pure ethanol and a bottom that contains very little ethanol, because the residue curves that come close to the pure ethanol corner stay close to the ethanol - ethylene glycol edge and away from the water - ethylene glycol edge. These residue curves do not interesect the distillate - feed line, so the material balance cannot be satisfied.

Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethanol (I)	0.0	0.9334	0.1345	0.01
Water (H)	0.0	0.0666	0.0006	0.99
Methanol (L)	1.0	0.0	0.8649	0.00

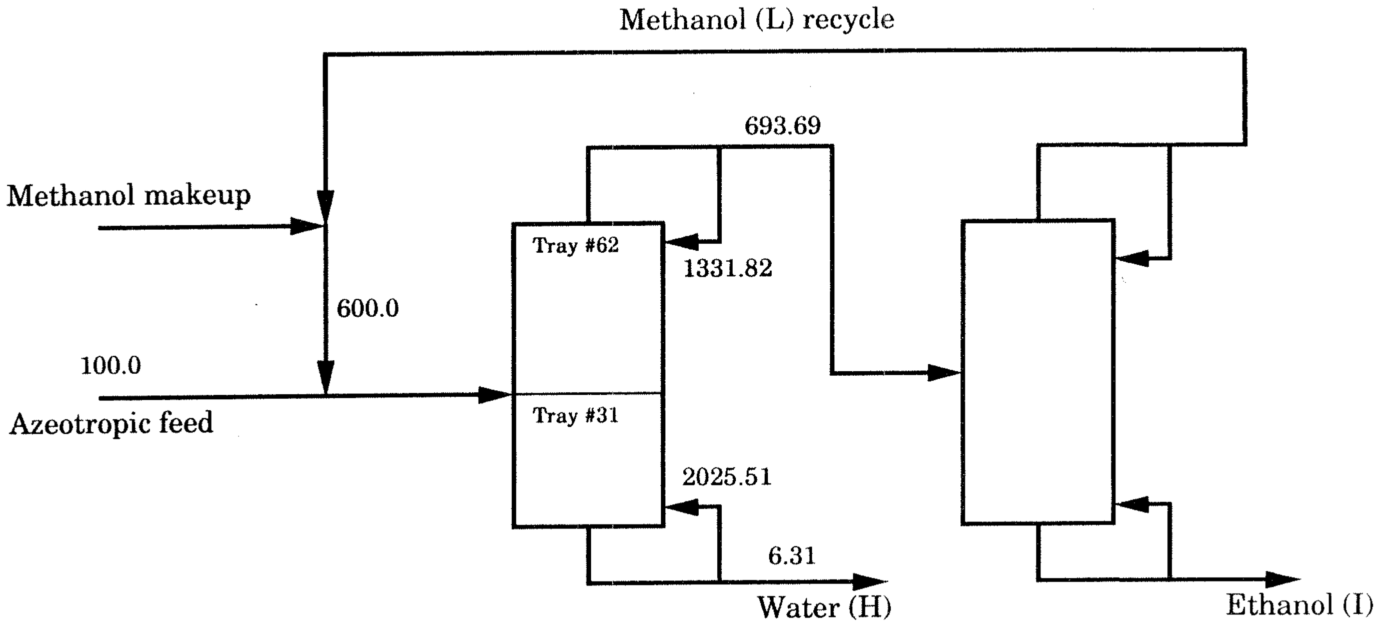


Fig. 3.49: The ethanol - water - methanol separation sequence

Fig. 3.50: Ethanol (1) - water (2) - methanol (3) extractive column composition profile

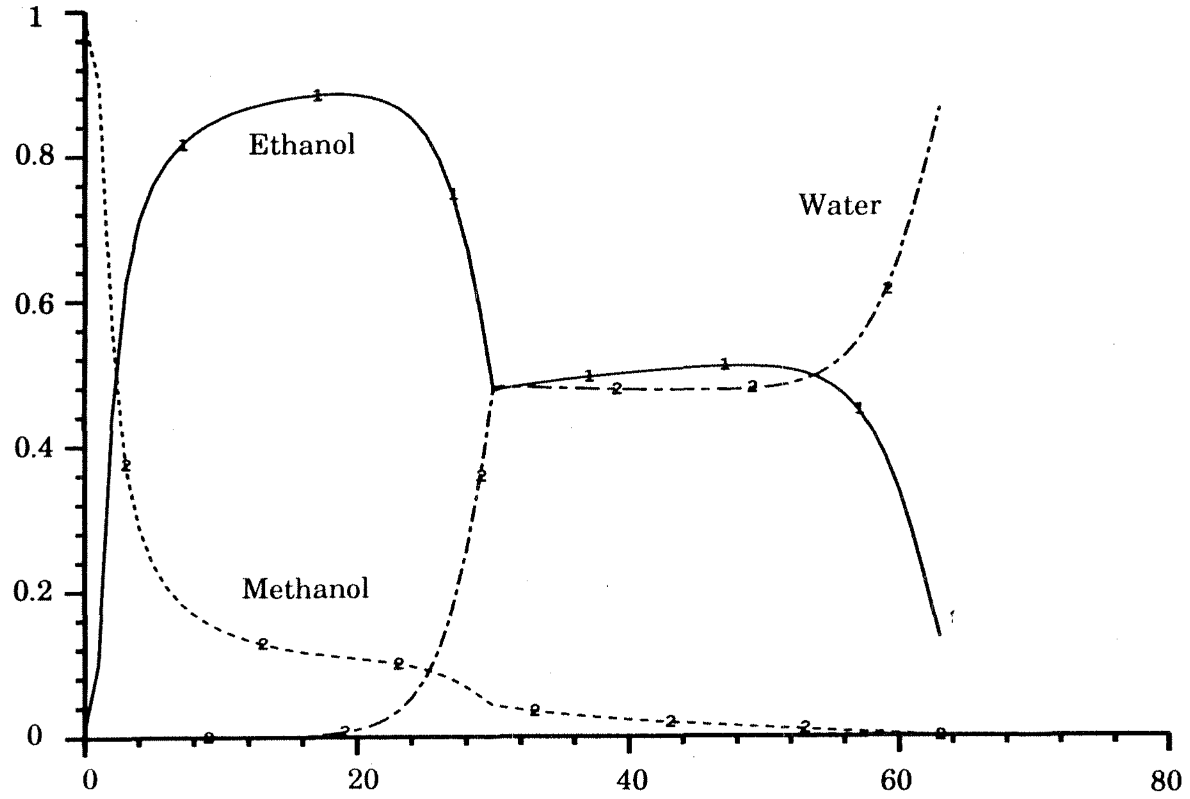
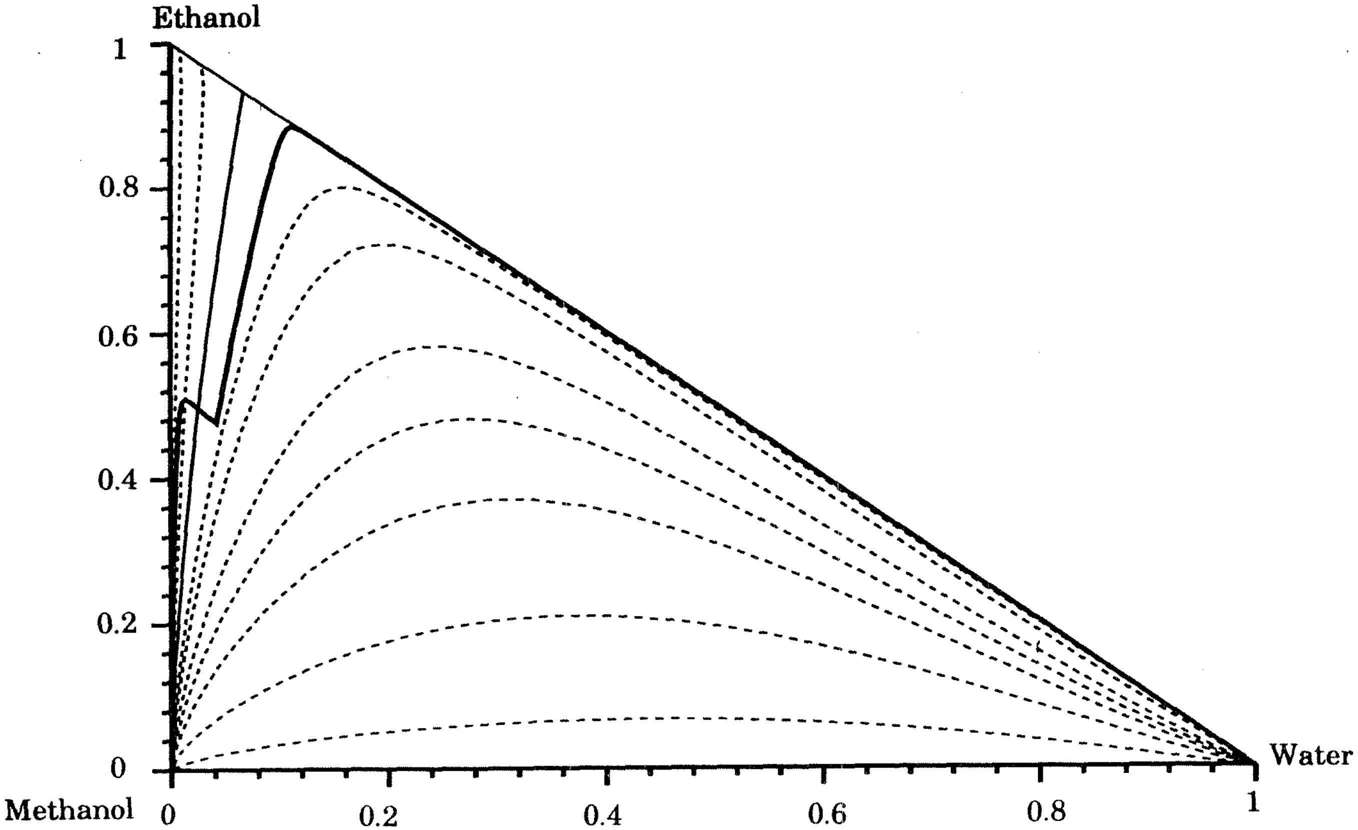


Fig. 3.51: Ethanol - water - methanol residue curve diagram
and extractive column composition profile



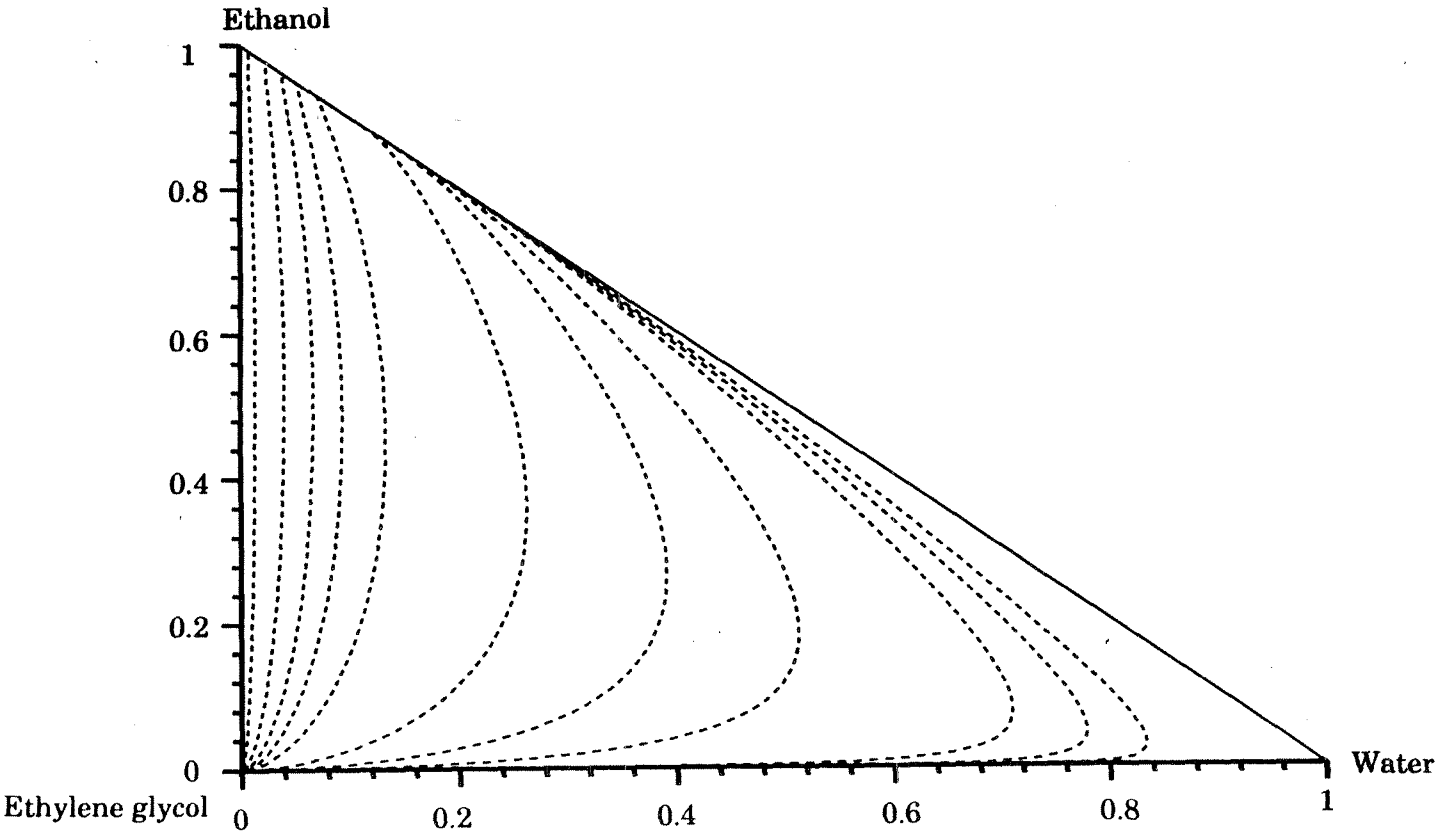


Fig. 3.52: Ethanol - water - ethylene glycol residue curve diagram

This result is general and applies to all mixtures of the 100 class: Separation is never feasible at infinite reflux. Yet separation is almost always feasible at finite reflux. This point emphasizes the danger of drawing conclusions based on the infinite reflux situation only.

3.2.3 The importance of good thermodynamic data

Throughout this article, we have assumed perfect knowledge of the mixture thermodynamics. Such an assumption can never be satisfied in practice. When is our conclusion on separability affected by small errors in the thermodynamic parameters? We do not know. Cases where separability depends on the curvature of a boundary would seem particularly sensitive to thermodynamic data uncertainty, since the shape and location of this boundary may change when we change the thermodynamic parameter. For example, methanol makes the separation of the ethyl ethanoate - ethanol azeotrope feasible if we use the Van Laar equation to represent the liquid phase activity coefficients (figure 3.53, figure 3.54 and figure 3.55), but not if we use the Wilson equation. In practice, we have often found that separability is easier to obtain with the Van Laar equation than with the Wilson equation. We have also observed that, when separation is feasible with both equations, the Van Laar equation usually leads to lower feed ratios, lower reflux ratios and smaller columns. For instance, ethylene glycol appears to be a much better entrainer for the ethanol water azeotrope with the Van Laar equation than with the Wilson equation (*cf.* Knapp & Doherty 1990).

As we have shown in chapter 2, sensitivity to thermodynamic data uncertainty may occur even in the case of heavy entrainers that add no azeotropes, a case which is usually considered as insensitive: In the ethyl ethanoate - methyl ethyl ketone - toluene case, slight changes in one liquid activity coefficient parameter can lead to dramatic changes in the separation sequence flowsheet. For some values of this parameter, toluene enables the recovery of ethyl ethanoate as pure distillate of the

Concentration	**Entrainer feed**	**Azeotropic feed**	**Distillate**	**Bottoms**
Ethyl ethanoate (I)	0.3056	0.5656	0.31202	0.01
Ethanol (H)	0.0	0.4344	0.00005	0.99
Methanol (L)	0.6944	0.0	0.68793	0.00

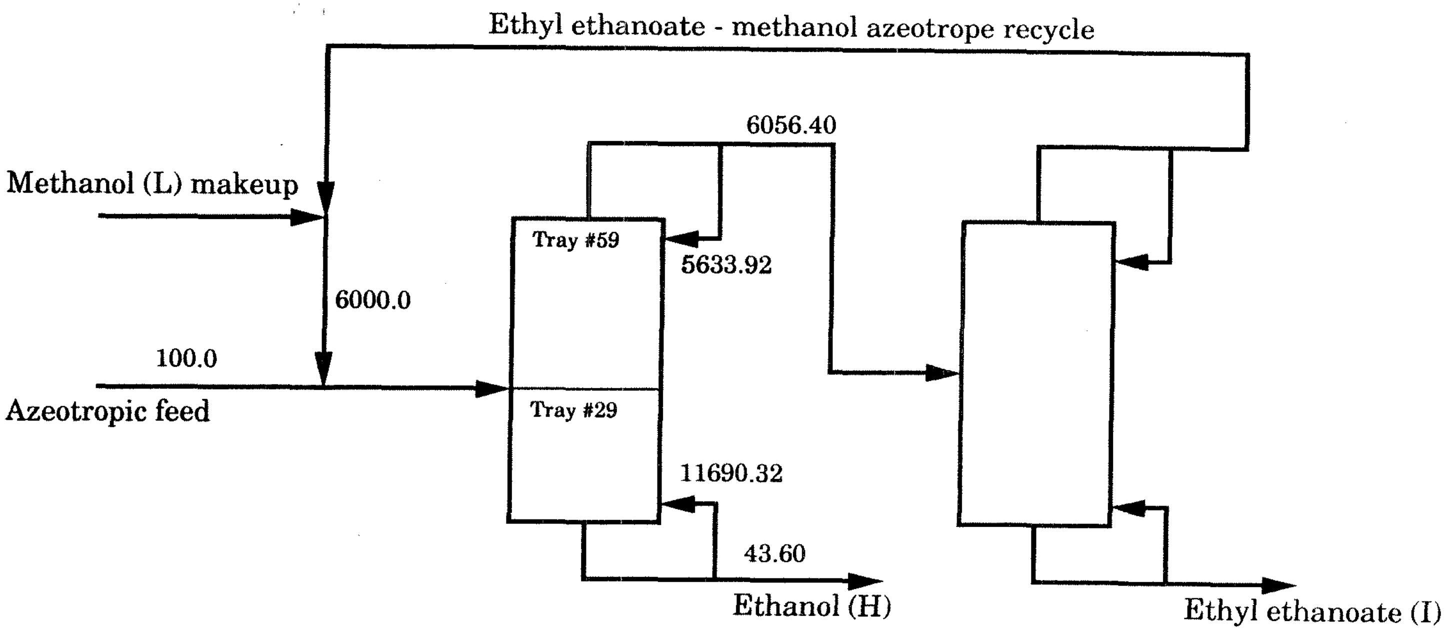


Fig. 3.53: The ethyl ethanoate - ethanol - methanol separation sequence

Fig. 3.54: Ethyl ethanoate (1) - ethanol (2) - methanol (3) extractive column composition profile

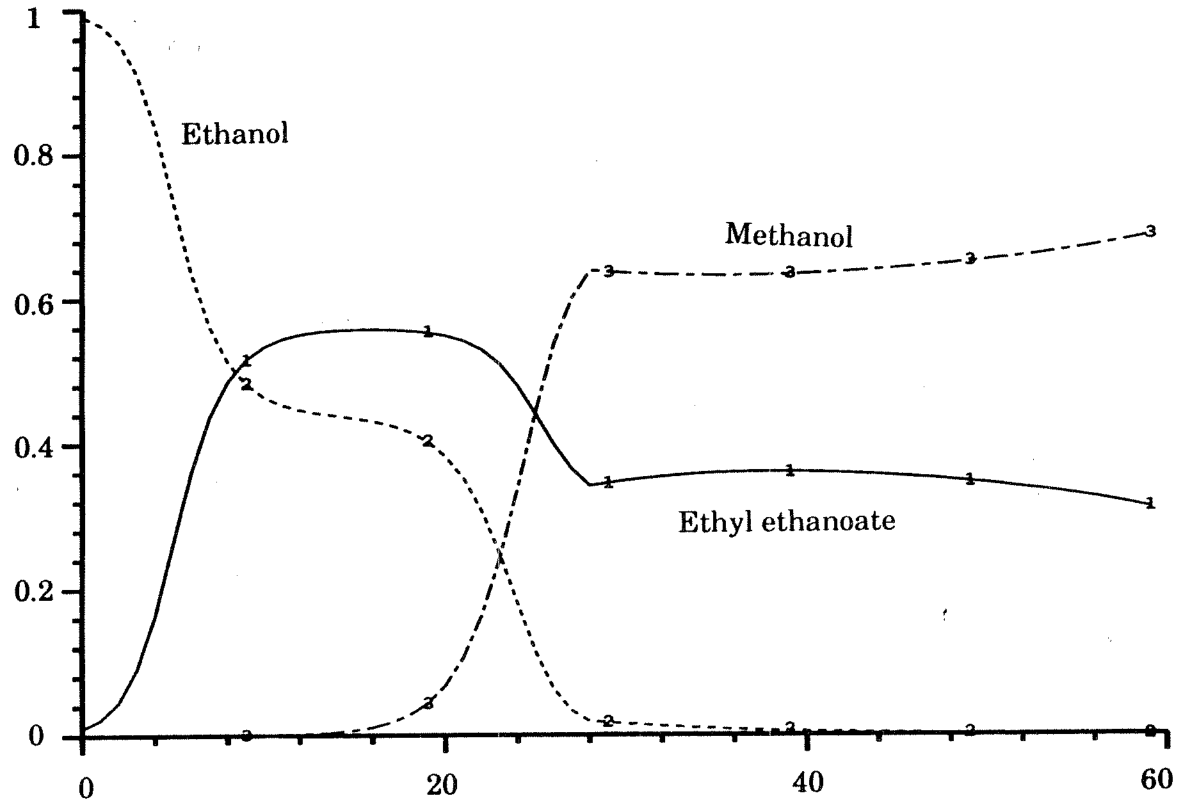
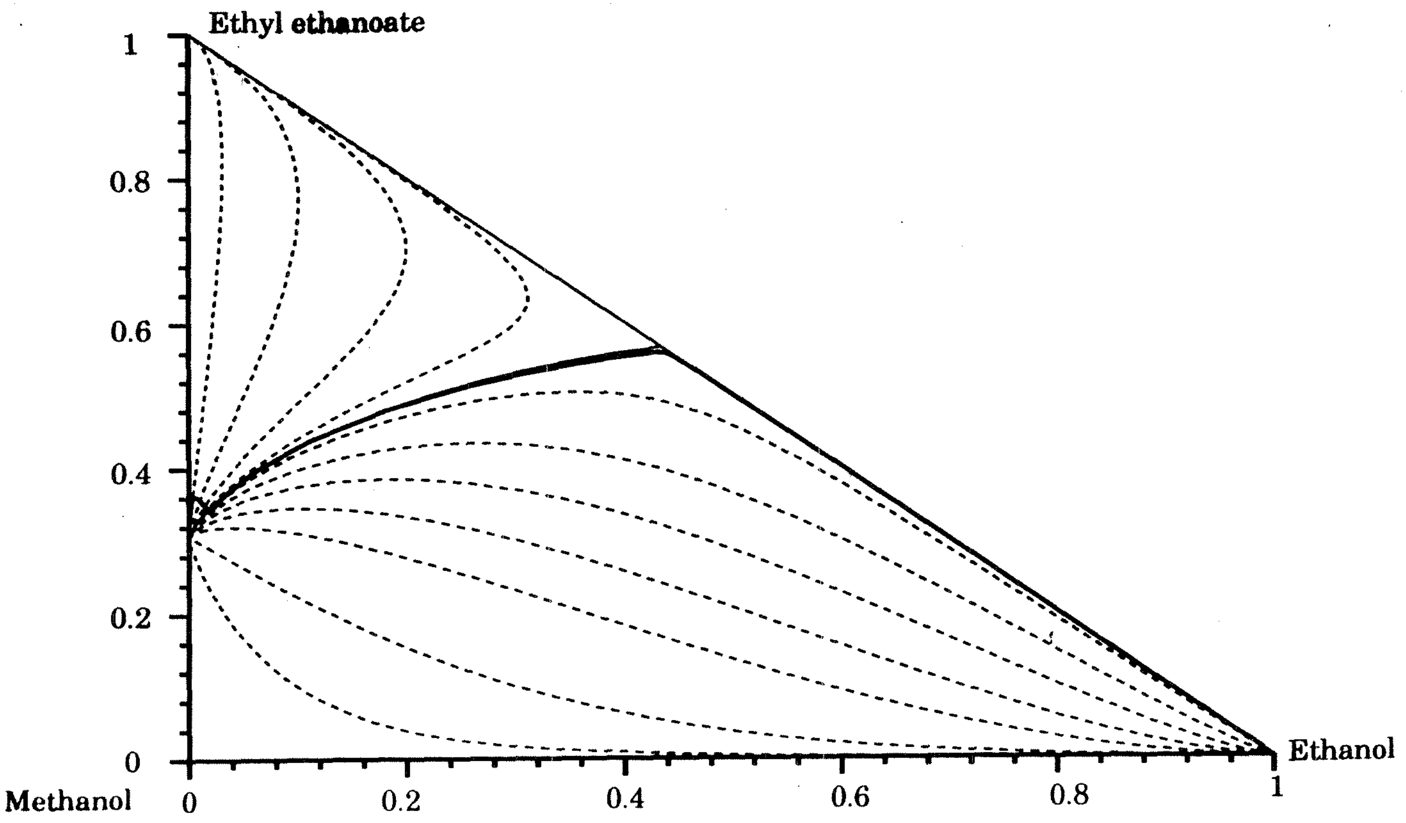


Fig. 3.55: Ethyl ethanoate - ethanol - methanol residue curve diagram and extractive column composition profile



extractive column while it enables the recovery of methyl ethyl ketone as distillate for other values.

At this point, it seems that the correct determination of separability requires an accurate description of the vapor-liquid equilibrium. Although a more robust entrainer selection criterion method would be desirable, we have not yet identified which cases are sensitive to thermodynamic data uncertainty and which are not.

3.2.4 Summary

In this section, we have focused on the practical aspects of separability:

- In practice, distillation columns are operated at finite reflux. Although separability at infinite reflux implies separability at finite reflux, there are cases where separation is feasible at finite reflux but not at infinite reflux. We have identified two cases where this situation occurs:
    - Finite reflux boundaries display more curvature than the corresponding infinite reflux boundaries; the finite reflux boundary may be curved enough while the infinite reflux boundary is not.
    - When the entrainer is a heavy component that introduces no azeotrope, increasing reflux dilutes the entrainer in the extractive section, and separation becomes impossible above a certain value. Yet, separation is almost always possible at finite reflux.
- In order to correctly predict separability, we often need to know the exact location and shape of a residue curve boundary. This position may change with the representation of the vapor-liquid equilibrium data we choose, so cases where separability depends on boundary curvature might be sensitive to thermodynamic data uncertainty. But such sensitivity can occur even for heavy entrainers that do not add azeotropes. When is our conclusion on separability robust

to thermodynamic data uncertainty? We do not know.

Chapter 4

Extractive Distillation Entrainers Comparison

4.1 A few new concepts

4.1.1 Considered entrainers

In chapter 3, we have discussed in detail the issue of separability. One important fact has emerged from this study: Usually, the correct determination of separability at infinite reflux requires the knowledge of the exact location and shape of the residue curve boundaries. Without accurate data, the screening procedure presented in chapter 3 becomes less reliable: Separations that appear feasible with one vapor-liquid equilibrium description may be impossible in practice because the actual distillation boundary location differs from the predicted position. Therefore, we could design a separation sequence that could not perform its task in practice. As we have demonstrated in the ethyl ethanoate - methyl ethyl ketone - toluene case (chapter 2), this situation can occur even in the case of heavy entrainers that add no azeotrope (the most common case in industry). Homogeneous azeotropic distillation can be very sensitive to thermodynamic data uncertainty.

However, we can partially avoid this problem by considering only components that add no azeotropes. Indeed, such components make separation almost always feasible:

- Heavy entrainers (*i.e.* entrainers that have a higher boiling point than both azeotropic components) usually lead to separation (Benedict & Rubin 1945).

- Intermediate entrainers (*i.e*,. entrainers that have a boiling point located between those of the two azeotropic constituents) have been discovered by Hoffman (1964). As we demonstrate later in this article, these entrainers provide much flexibility: Separation is feasible with only one column (chapter 3), as well as with the direct sequence and the indirect two-column sequence.
- Light entrainers (*i.e.* entrainers which have a lower boiling point than both azeotropic components) almost always make separation feasible in a two-column sequence (chapter 2), even though they introduce a residue curve boundary between the two azeotropic constituents.

These entrainers have another important advantage: They do not add complexity to an already-complicated situation. Therefore, although many other types of entrainers lead to separability as well, we restrict our investigations to components that add no azeotropes. We assume throughout the rest of this article that the ternary mixture azeotropic component #1 - azeotropic component #2 - entrainer exhibits only one azeotrope, namely the binary azeotrope we are trying to separate.

We now introduce a few concepts and definitions which we will use repeatedly in our comparison of entrainers.

4.1.2 Equivolatility and isovolatility curves

As equipotential lines are defined as curves along which potential is constant, we define equivolatility curves as the curves along which the relative volatility of two components is constant. More precisely:

Definition 4.1 *The* α_o*-equivolatility curve* $\Gamma_{\alpha_o}^{AB}$ *of components A and B is the set of points where the relative volatility of A and B is equal to* α_o : $\alpha_{AB} = \frac{y_A}{y_B} / \frac{x_A}{x_B} = \alpha_o$.

The equivolatility curves have the following properties:

- In the case of a multicomponent mixture containing N species, the composition space is a hyperplane of dimension N-1. The equation $\alpha_{AB} = \alpha_o$ defines a surface of dimension N-2. In the case of ternary mixtures, this equality defines curves; as an example, figure 4.1 shows the 2.0-equivolatility curve of acetone and methanol in the acetone (L) - methanol (I) - water (H) system.

- Because x_A and y_A (x_B and y_B respectively) are both null on BC (AC respectively), α_{AB} is defined everywhere in the composition space $\mathcal{T}$ except AC and BC. Since we only consider homogeneous azeotropic distillation, we exclude liquid - liquid separation, so α_{AB} is a "smooth" function of the liquid composition (x_A, x_B). By assuming that α_{AB} is uniformly continuous in its domain, we can extend it to the whole composition space and its extension is uniformly continuous. The definition of $\Gamma_{\alpha_o}^{AB} = \{P \in \mathcal{T} / \alpha_{AB}(P) = \alpha_o\}$ implies that $\Gamma_{\alpha_o}^{AB}$ is compact. In theory, $\Gamma_{\alpha_o}^{AB}$ may therefore contain several branches and/or closed curves. In practice, the equivolatility curves we obtain with mixtures containing only one azeotrope do not contain closed curves. This would not necessarily be the case if we considered very complex mixtures like methylcyclohexane - hexafluorobenzene - benzene (Wade & Taylor 1973, Doherty & Perkins 1978). We have found cases where equivolatility curves contain more than one branch; for instance, the 1.1-equivolatility curve of ethyl ethanoate and methyl ethyl ketone in the ethyl ethanoate (I) - methyl ethyl ketone (H) - acetone (L) mixture contains two separate branches (figure 4.2).

- Equivolatility curves divide the composition space in two (or more) separate regions. Because α_{AB} is a continuous function that yields real values, the relative volatility of A and B is always on the same side of α_o within one of these regions. Figure 4.2 illustrates this point in the ethyl ethanoate (I) - methyl ethyl ketone (H) - acetone (L) case: The relative volatility of ethyl ethanoate and methyl

Fig. 4.1: The 2.0-equivolatility curve of acetone and methanol in the acetone (L) - methanol (I) - water (H) case

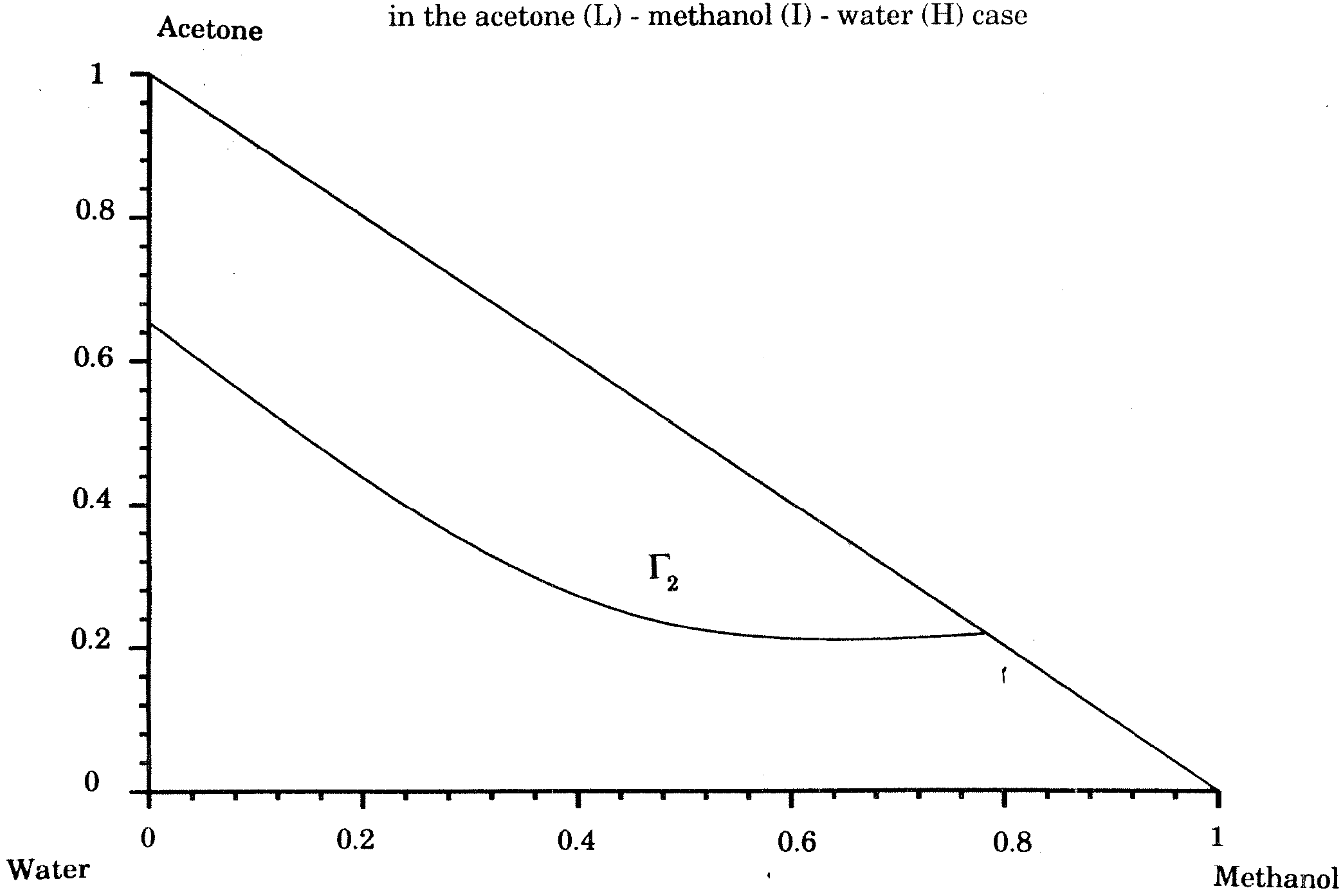
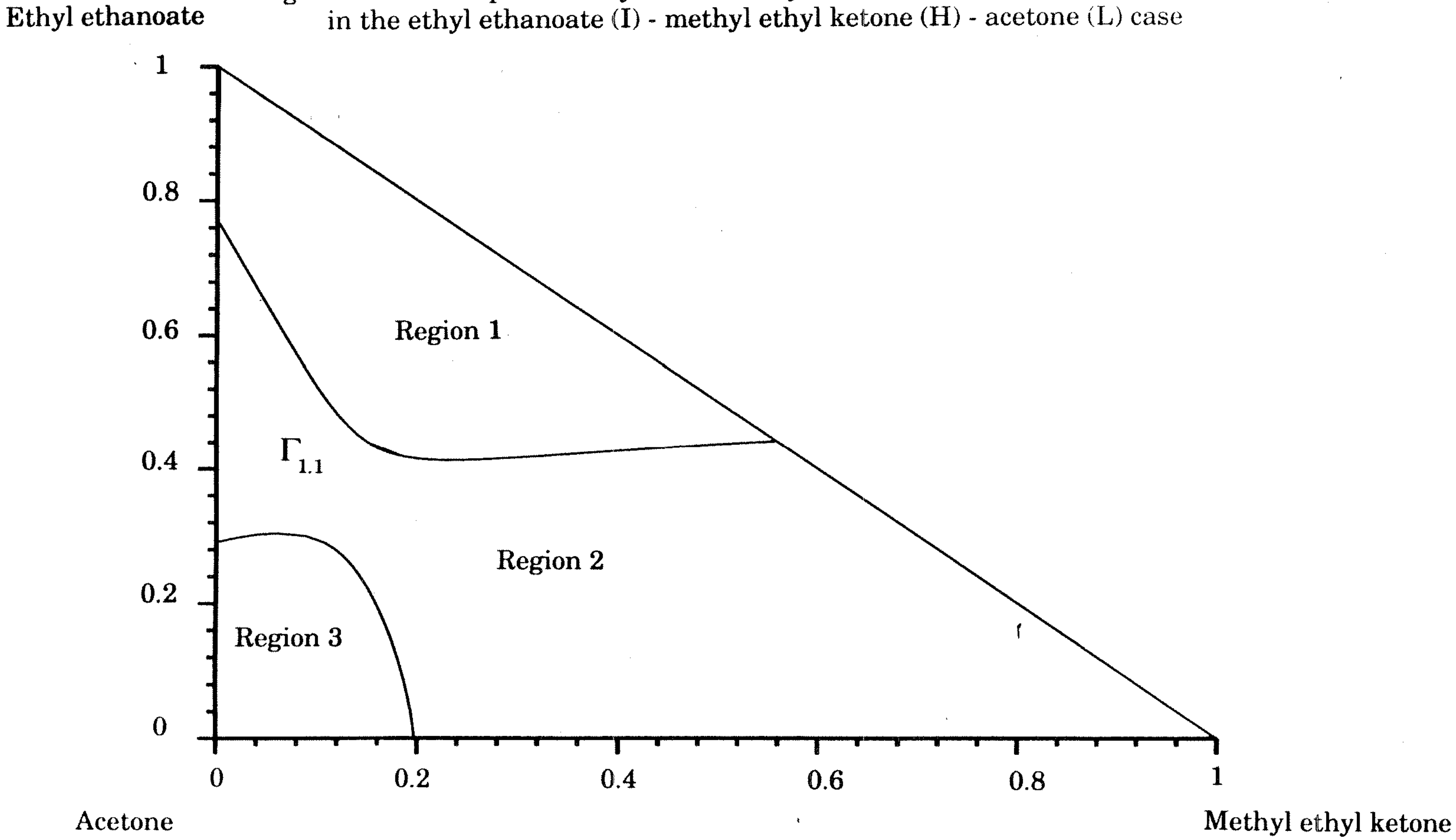


Fig. 4.2: The 1.1-equivolatility curve of ethyl ethanoate and methyl ethyl ketone in the ethyl ethanoate (I) - methyl ethyl ketone (H) - acetone (L) case



ethyl ketone is larger than 1.1 in region 2 and lower than 1.1 in both regions 1 and 3.

In the set of equivolatility curves of two components, the 1.0-equivolatility curve stands out. Because A is as volatile as B at every point of this curve, we call it the isovolatility curve of A and B:

Definition 4.2 *The isovolatility curve Σ_{AB} of components A and B is the set of points where the relative volatility of A and B is equal to 1.*

Isovolatility curves have interesting properties, which we use repeatedly in the next sections:

- Because isovolatility curves are special equivolatility curves, they have the same properties as equivolatility curves. However, we have observed in all eighty cases we examined that isovolatility curves are made of only one branch that connects one edge of the composition space to another edge and divides the composition triangle in two separate regions. We assume in the remainder of this article that isovolatility curves contain only one branch.

- If A and B form a binary azeotrope, then Σ_{AB} includes this azeotrope. When there is a ternary azeotrope, then the isovolatility curves Σ_{AB}, Σ_{AC} and Σ_{BC} all exist and intersect at the ternary azeotrope.

- The isovolatility curve of two components can exist even when these two components form no azeotrope; for example, figure 4.3 shows the isovolatility curve of benzene and heptane in the acetone (L) - heptane (H) - benzene (I) system. This curve does not intersect the benzene - heptane edge, because benzene and heptane form no azeotrope. This mixture exhibits only one azeotrope, namely the acetone - heptane azeotrope.

Fig. 4.3: The isovolatility curve of heptane and benzene in the acetone (L) - heptane (H) - benzene (I) case

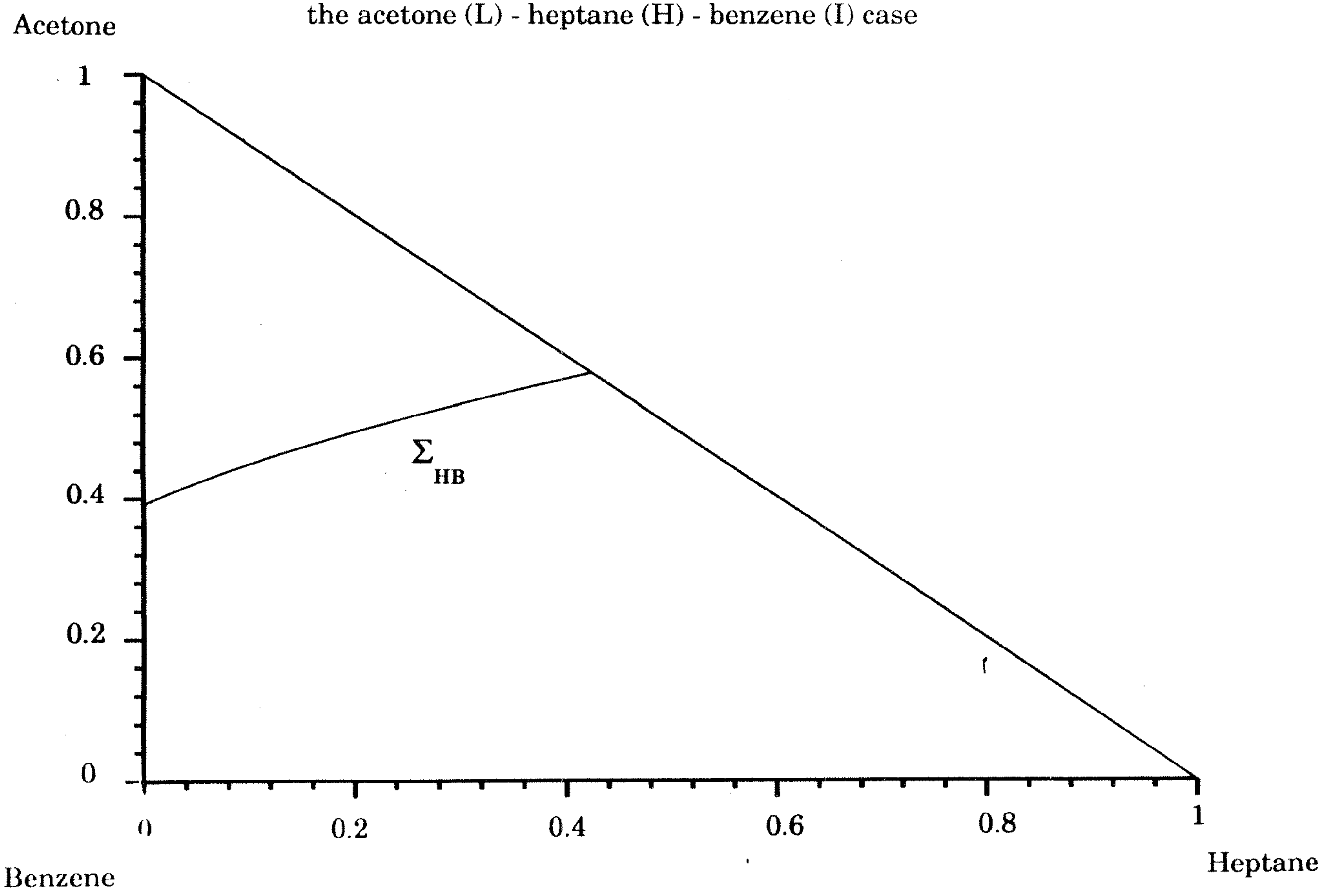
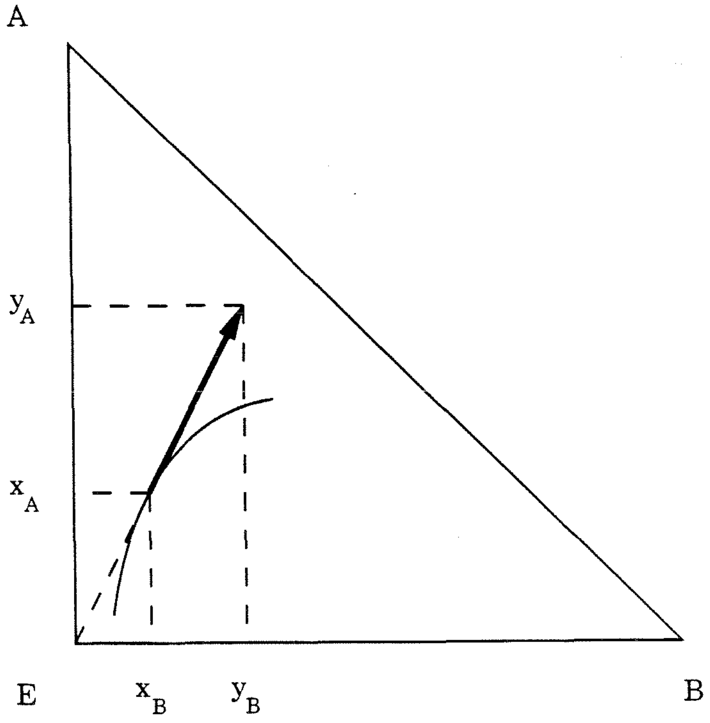


Fig. 4.4: The tie line contains E when the relative volatility of A and B is equal to 1



- Isovolatility curves can be derived from residue curves (Van Dongen 1982). Indeed, the points E, (x_A, x_B) and (y_A, y_B) are aligned if and only if $\frac{y_A}{y_B}/\frac{x_A}{x_B} = \alpha_{AB} = 1$. Therefore, the tie line (which joins the liquid composition (x_A, x_B) to the vapor composition (y_A, y_B)) contains point E if and only if the relative volatility of A and B is equal to 1 at that point (figure 4.4). Since tie lines are tangent to residue curves, Σ_{AB} can also be defined as the set of points where the residue curve tangent contains point E.

In practice, we determine the position of an equivolatility curve through the following algorithm:

- Step 1: Pick an initial point.
- Step 2: Pick a search direction.
- Step 3: Find the point where $\alpha_{AB} - \alpha_o = 0$ along the perpendicular to the search direction. This is easily done with a standard Newton-Raphson one-dimensional search.
- Step 4: Step by a given amount in the search direction.
- Step 5: Go back to step 3.

Program interruption comes from two sources: When the perpendicular to the search direction does not contain any zero of $(\alpha_{AB} - \alpha_o)$, or when we step out of the composition triangle during our move along the search direction. Isovolatility curves are obtained with the same method by setting α_o equal to 1.

By plotting a set of equivolatility curves for components A and B, we obtain a graphical representation of the spatial distribution of α_{AB}. We define the resulting diagram as the equivolatility curve diagram:

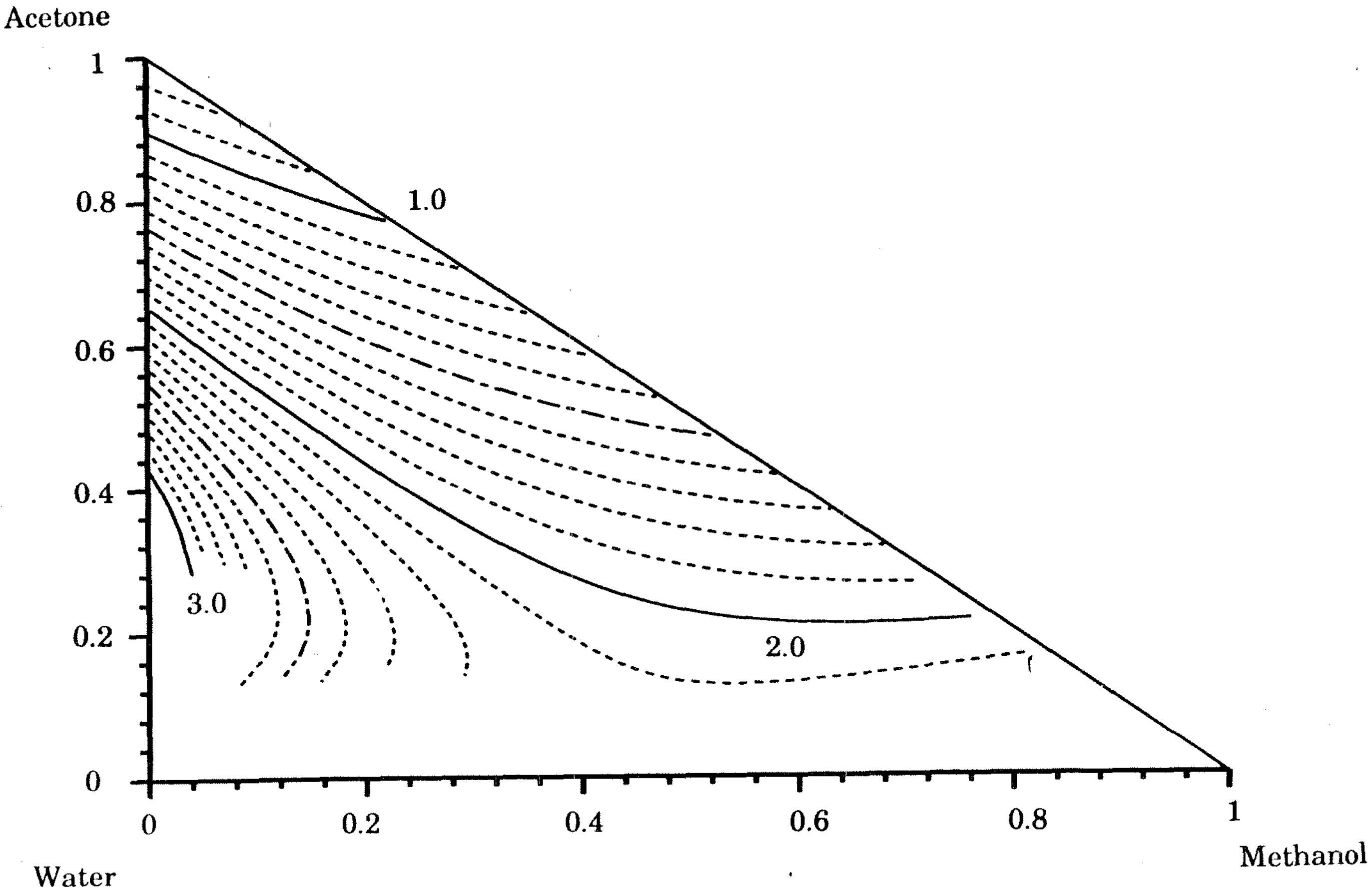
Definition 4.3 *The equivolatility curve diagram of two components A and B displays a representative set of equivolatility curves of A and B. In particular, if the isovolatility curve of A and B exists, it is shown on the equivolatilty curve diagram.*

Figure 4.5 represents the equivolatility curve diagram of acetone and methanol in the acetone (L) - methanol (I) - water (H) case.

4.1.3 Local Volatility Order

In the zeotropic case, the boiling point order coincides with the volatility: If the boiling point of A is lower than the boiling point of B, then A is more volatile than B.

Fig. 4.5: The equivolatility curves of acetone and methanol in the acetone (L) - methanol (I) - water (H) case



The situation becomes different for azeotropic mixtures: The volatility order depends on the considered point in the composition space. For instance, if A and B have a minimum boiling azeotrope, A is more volatile than B for mixtures richer in A than the azeotrope and B is more volatile than A on the other side of the azeotrope. We therefore introduce here a notion of local volatility order:

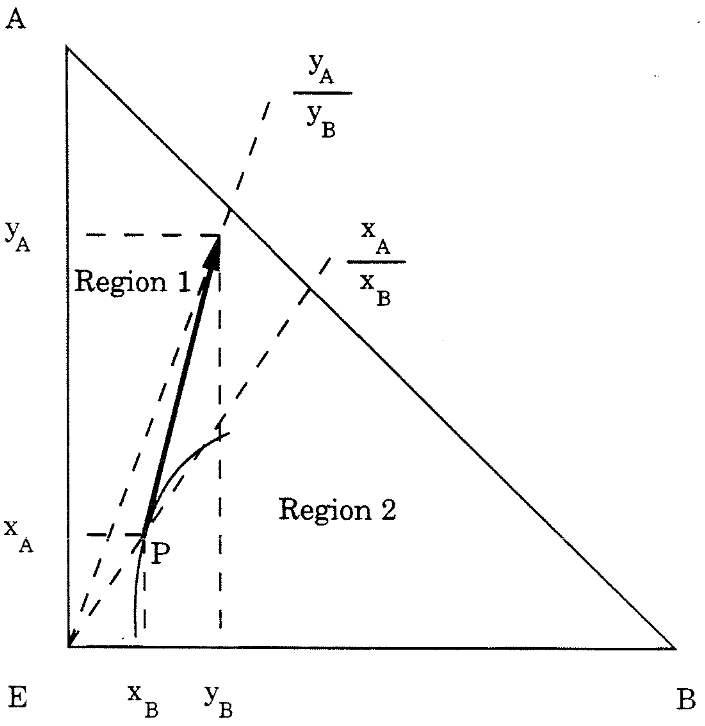
Definition 4.4 *A is more volatile than B in a region $\mathcal{R}$ of the composition space if it is more volatile than B at every point of $\mathcal{R}$. We denote this by "A>B."*

We have already seen that isovolatility curves divide the composition space in two separate regions: In one of them, A is more volatile than B, while B is more volatile than A in the other. Identifying where A is more volatile than B can also be done from residue curves. Indeed, A is more volatile than B if and only if $\alpha_{AB} > 1$, or equivalently if and only if $y_A/y_B > x_A/x_B$. Graphically, we see that A is more volatile than B if and only if the point representing the vapor in equilibrium with P is located above EP (figure 4.6). Because of the orientation of residue curves and of the tangency of tie lines and residue curves, this condition becomes equivalent to: A is more volatile than B at P if and only if the residue curve that contains P crosses EP from region 1 to region 2. By continuity, if A is more volatile than B at P, then it is more volatile than B in the whole region that contains P. Once we have found the location of Σ_{AB}, we can determine the volatility order of A and B at every point in the composition space by checking just one point. We can further simplify this procedure by choosing a point P located on the AB edge, because the determination of the volatility order of A and B is very simple there.

4.1.4 Volatility order diagram

In a ternary mixture, there are at most three isovolatility curves (one for each pair of components). Note that there can be less: In the acetone (L) - methanol (I) - water (H) case, both acetone and methanol are always more volatile than water, so this

Fig. 4.6: A is more volatile than B



mixture displays only one isovolatility curve (figure 4.7). By combining all existing isovolatility curves in one diagram, we obtain the volatility order diagram. More precisely:

Definition 4.5 *The volatility order diagram of a ternary mixture is a graphical representation of:*

- *All existing isovolatility curves.*
- *The volatility order of the three components in each subregion of the composition triangle.*

Fig. 4.7: The acetone (L) - methanol (I) - water (H) volatility order diagram

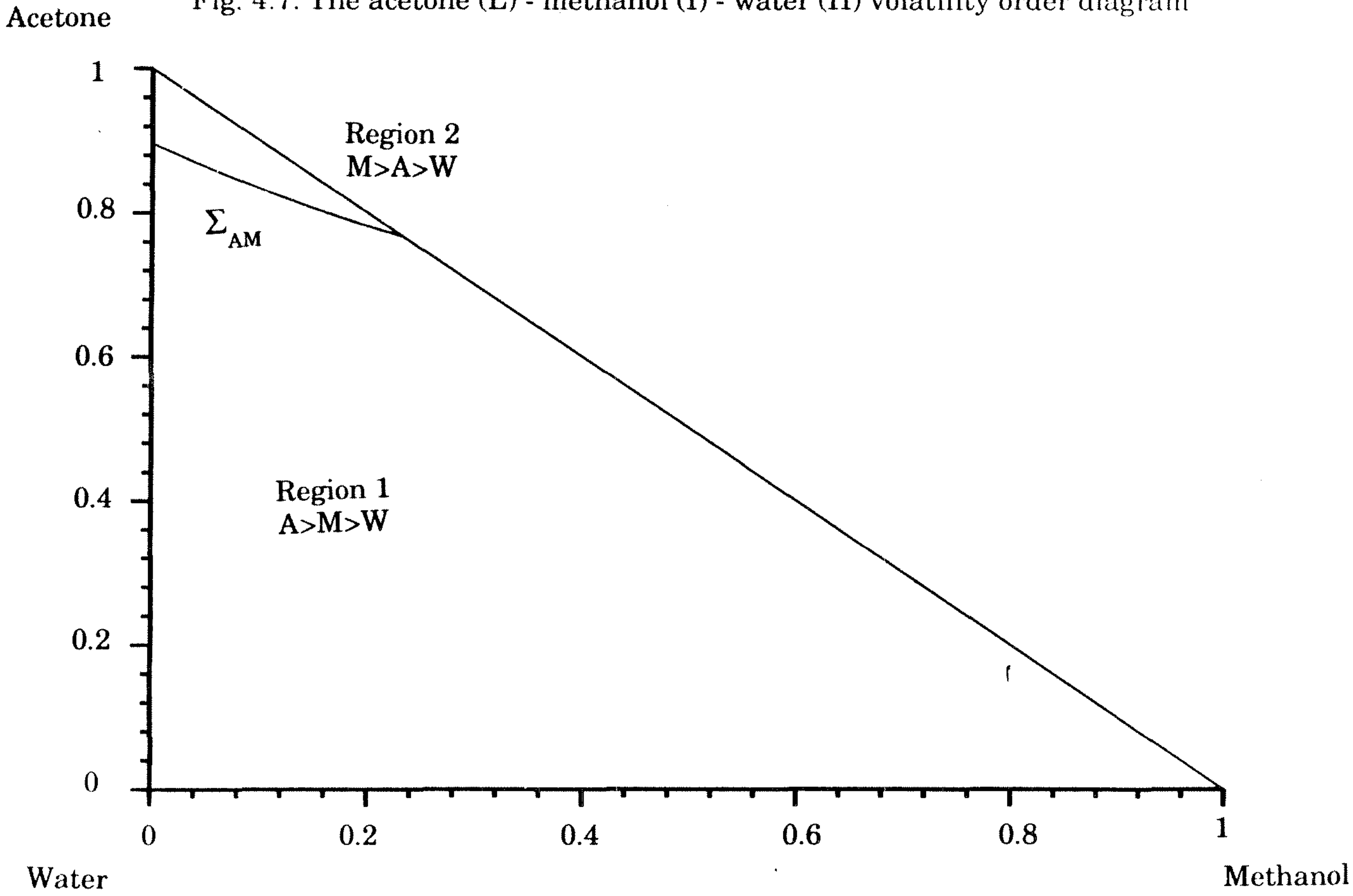


Figure 4.7 displays the volatility order diagram of the acetone (L) - methanol (I) - water (H) mixture: The composition triangle is divided into two regions. In region 1, the local volatility order is acetone > methanol > water while in region 2, methanol is more volatile than acetone and the local volatility order becomes methanol > acetone > water. Acetone is the most volatile component in region 1, while methanol is the most volatile in region 2. In the next section, we show how we can deduce the separation sequence flowsheet from the volatility order diagram of the ternary mixture azeotropic component #1 - azeotropic component #2 - entrainer.

4.2 Flowsheet

4.2.1 Heavy entrainers

Heavy entrainers represent the most common type of entrainers in industry. Such entrainers are extensively used in industry to isolate valuable chemicals, such as benzene (Berg 1983), isoprene (Enomoto 1971) and butadiene (Buell & Boatright 1947, Bannister & Buck 1969, Asatani & Hayduk 1983), from hydrocarbon mixtures. Another important industrial application is the separation of the water - ethanol azeotrope using various heavy entrainers such as glycols, glycerin, and heavy alcohols (Black & Distler 1972, Black 1980, Lee & Pahl 1985, Yeh 1986, Knight & Doherty 1989, Knapp & Doherty 1990). Because of their economic significance, these entrainers have been extensively studied by numerous authors in both industry and academia. In particular, the separation flowsheet is well-established: The entrainer is fed close to the top of the extractive column and is recovered at the bottom of the entrainer recovery column. Both azeotropic components are recovered as distillates.

For a long time, finding which azeotropic constituent is recovered first could only be done by trial and error (Knapp & Doherty 1990). Yeh (1986) discovered that the entrainer carries down the extractive column the azeotropic component for which it has more affinity, freeing the other component and enabling its recovery as distillate.

Affinity can be measured by comparing the polar interaction and hydrogen bonding of the candidate entrainer with the polar interactions and hydrogen bondings of the two azeotropic constituents. Yeh's method has the advantage of using only pure component data, but can make erroneous predictions: DMFA seems to have more affinity for acetone, yet it carries down methanol in the bottom product of an extractive column. Yeh's method is also limited to heavy entrainers.

Let us analyze the fundamental behavior of an extractive column separating a minimum boiling azeotrope of components A and B (where A has a lower boiling point than B) using component E as entrainer. Let us assume that A is recovered as pure distillate. The key separation is performed in the extractive section: By feeding the entrainer above the azeotrope, we ensure that the entrainer concentration remains high enough on each tray of the middle section to make A more volatile than B. The rectifying section separates the entrainer from A; the concentration of B is very small, so this section essentially performs a binary separation. The separation between A and B must be completed below the entrainer feed, because the entrainer concentration decreases quickly in the rectifying section and the azeotropic behavior reappears: B becomes more volatile than A, since the distillate is richer in A than the azeotrope. The stripping section depletes the liquid phase of its content of A. From this analysis, we conclude that A is the most volatile component in the bottom and middle sections, while B is the most volatile component in at least the top of the rectifying section. Because the concentration of B vanishes below the entrainer feed, we see that for small mole fractions of B:

- A is more volatile than B when the mole fraction of E is significant.
- B is more volatile than A when the mole fraction of E is negligible.

In other words, the local volatility order of A and B changes along the A - E edge. This implies that the isovolatility curve of A and B intersects the A - E edge. We conclude that a necessary condition for the recovery of azeotropic component A as distillate of the extractive column is that the isovolatility curve of A and B intersects the A - E edge.

In the case of a heavy entrainer, the volatility order diagram contains only one isovolatility curve, namely the isovolatility curve of the two azeotropic components, because the entrainer is the least volatile component everywhere. Because Σ_{AB} must start at the A - B azeotrope and end on another edge, it must intersect either the A - E edge or the B - E edge; the situation where it ends precisely at E is singular and does not occur in practice, since slight changes in any parameter bring us back to one of the two considered situations. Let us assume that Σ_{AB} intersects the B - E edge, for instance. Then B is the most volatile component in a region that contains part of the B - E edge. If we introduce enough entrainer in the column to obtain a significant entrainer concentration in the extractive column, then B is more volatile than A throughout this section. We can then separate A from B in the extractive section if the number of trays in this section is sufficient. The stripping section can remove B from the liquid phase, because B remains more volatile than A in that section. Finally, the rectifying section can separate the entrainer from B, since E is the least volatile component. We obtain the following result:

Proposition 4.1 *We can determine the flowsheet of the feasible separation sequence from the volatility order diagram:*

- *If the isovolatility curve of A and B intersects the A - E edge, A is recovered as distillate of the extractive column while B is recovered as distillate of the entrainer recovery column.*
- *If the isovolatility curve of A and B intersects the B - E edge, B is recovered as distillate of the extractive column while A is recovered as distillate of the entrainer recovery column.*

This result is illustrated by figure 4.7 and figure 4.8 with the acetone - methanol azeotrope and two different heavy entrainers, water and chlorobenzene. In the acetone (L) - methanol (I) - water (H) case, the isovolatility curve of acetone and methanol intersects the water - acetone edge: Acetone is recovered as top product of the extractive column (figure A.10.) In the acetone (L) - methanol (I) - chlorobenzene (H) case, the isovolatility curve of acetone and methanol intersects the chlorobenzene - methanol edge: Methanol is recovered as top product of the extractive column (figure A.13).

4.2.2 Light entrainers

In chapter 3, we have shown that light entrainers make separation feasible at infinite reflux when the residue curve boundary that joins the entrainer corner to the binary azeotrope is sufficiently curved. When separation is possible at infinite reflux, the procedure presented in that article shows that the feasible separation flowsheet depends on which side the boundary bends[1]:

- When the residue curve boundary bends as in figure 4.9, the separation sequence yields B as pure bottom product of the extractive column and A as pure bottom product of the entrainer recovery column. The entrainer is fed below the azeotrope and recovered at the top of the entrainer recovery column (figure 4.10).

- When the residue curve boundary bends as in figure 4.11, the separation sequence yields A as pure bottom product of the extractive column and B as pure bottom product of the entrainer recovery column. Again, the entrainer is fed below the azeotrope and recovered at the top of the entrainer recovery column

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[1] We assume that this boundary always bends in the same direction and never displays inflexion points. In practice, we have found that such is indeed the case in all the cases we examined but one; only the isopropanol (I) - water (H) - acetone (L) mixture does not satisfy this assumption.

Fig. 4.8: The acetone (L) - methanol (I) - chlorobenzene (H) volatility order diagram

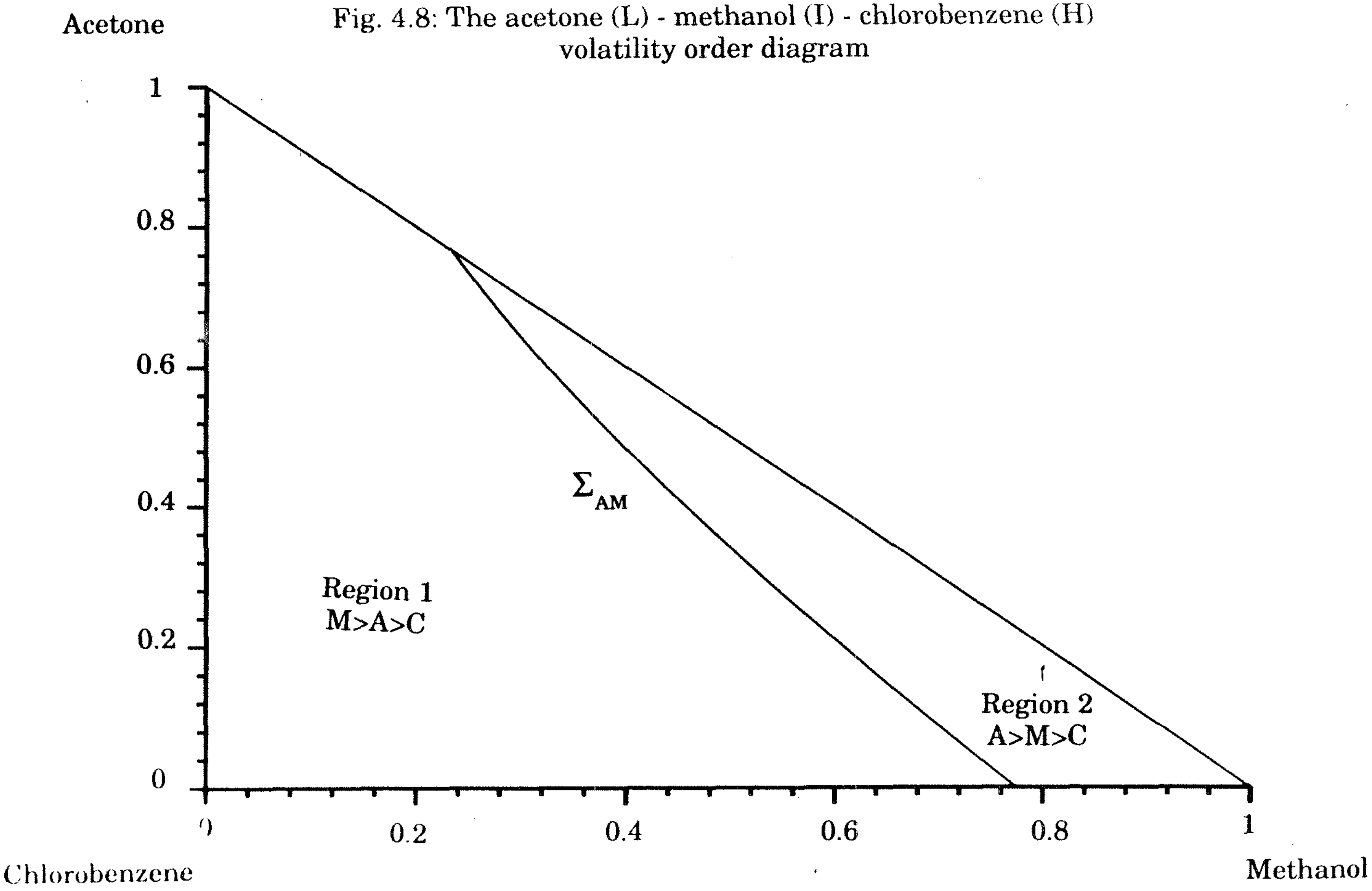


Fig. 4.9: B is located on the convex side of the residue curve boundary

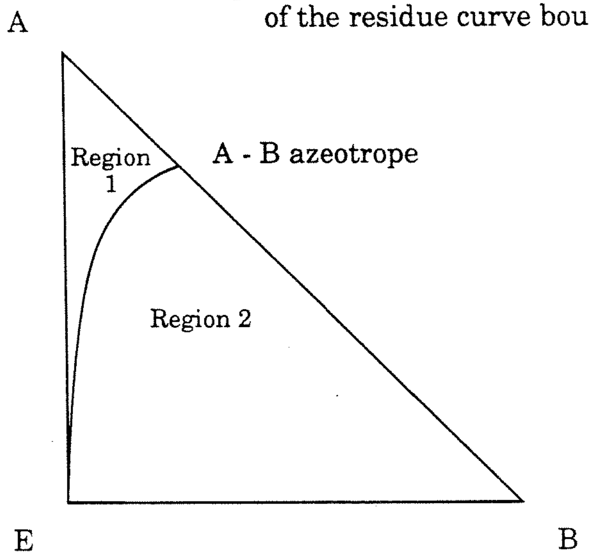


Fig. 4.10: Separation sequence obtained when B is on the boundary convex side

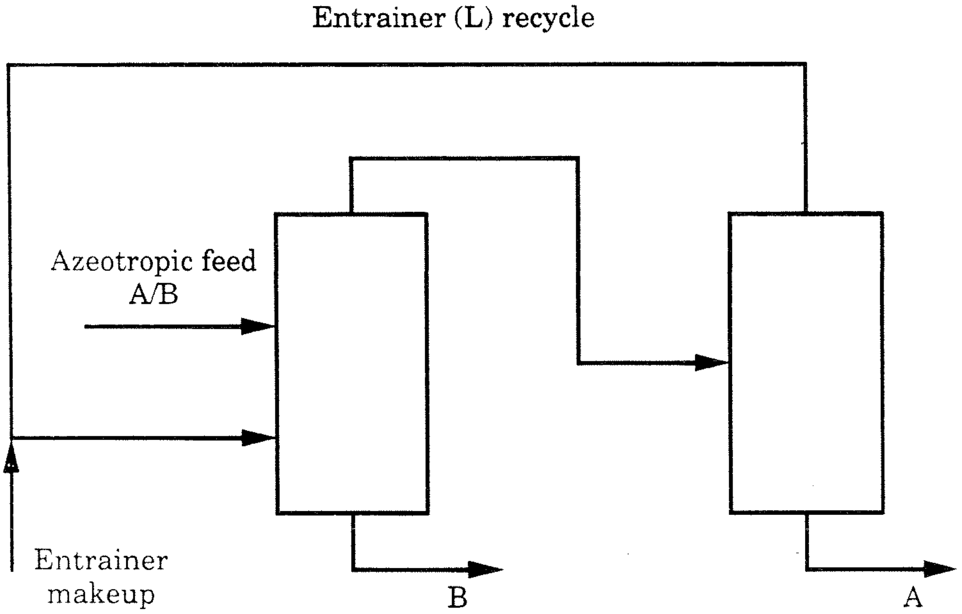
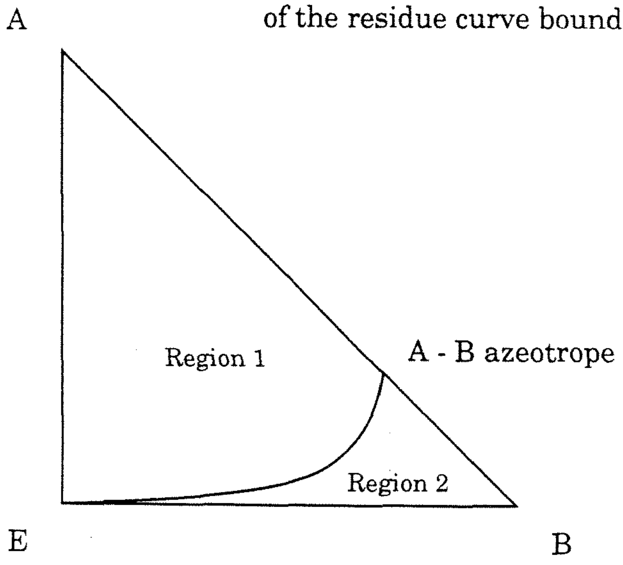


Fig. 4.11: A is located on the convex side of the residue curve boundary

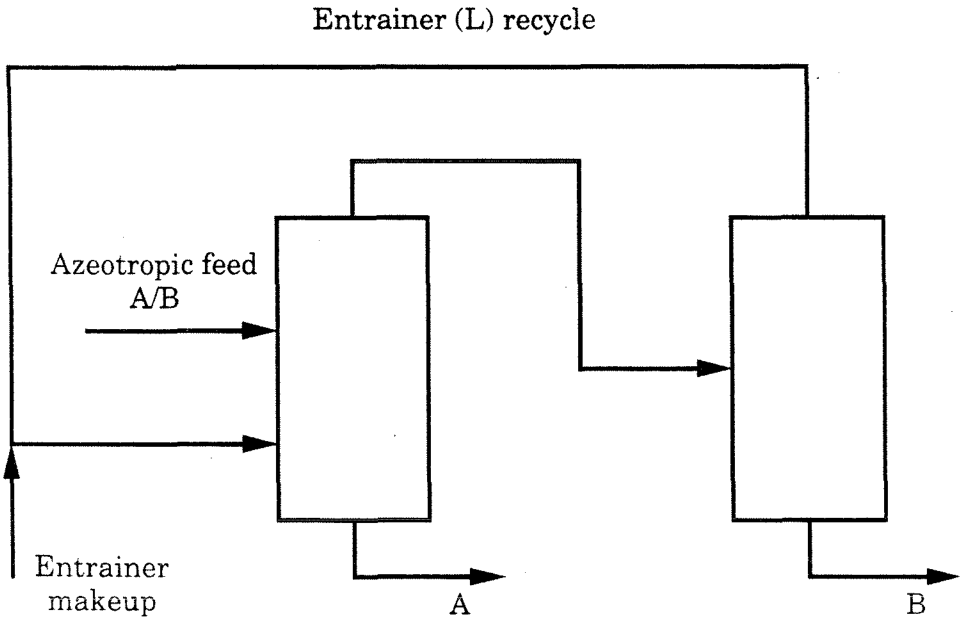


(figure 4.12).

Because residue curve boundaries are never straight lines in the mathematical sense, they always show some curvature, but this curvature may not be large enough to make separation feasible at infinite reflux. In practice, we have found that we can achieve more separation at finite reflux than at infinite reflux. In particular, we have found that separation is actually almost always feasible at finite reflux, even when the boundary almost looks like a straight line (chapter 3). Although their precise locations are difficult to determine, finite reflux boundaries always display more curvature than infinite reflux boundaries. This implies that we can apply the rule expressed above to determine which separation sequence is feasible at finite reflux.

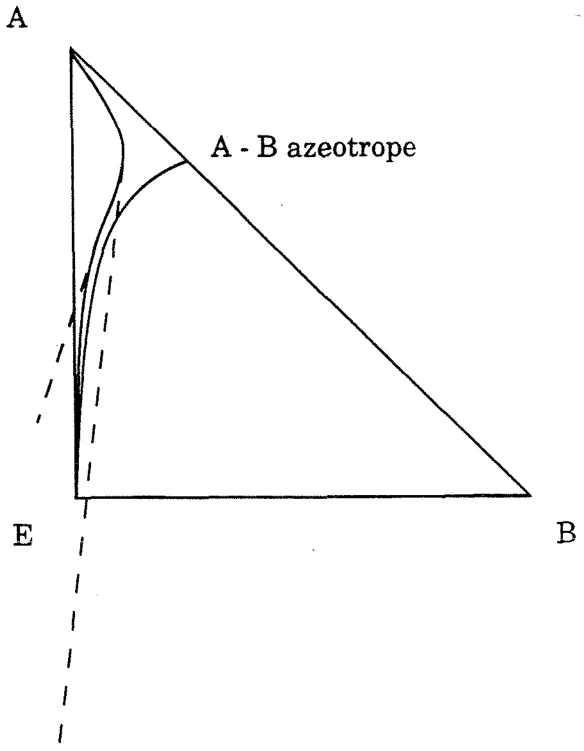
This rule can also be interpreted in terms of volatility order diagrams. Indeed, let us consider figure 4.9. Because of the boundary curvature, the residue curves tangents of points in region 1 close to the entrainer corner must intersect the vertical axis above

Fig. 4.12: Separation sequence obtained when A is on the boundary convex side



the entrainer while the tangents of points located in region 1 close to the A corner must intersect the vertical axis below the entrainer (figure 4.13). Therefore, there are points in region 1 where the residue curve tangent contains the entrainer corner. This implies that the isovolatility curve of A and B is located in region 1 and goes from the A - B azeotrope to the A - E edge. There is usually only one isovolatility curve in this case: The entrainer is the most volatile component everywhere (later in this paper we examine the case where the entrainer is not the most volatile component.) The volatility order diagrams corresponding to figure 4.9 and figure 4.11 are shown on figure 4.14 and figure 4.15 respectively. We see that, in figure 4.14, B is the least volatile component in a region that reaches the A - E edge. Therefore, if we introduce enough entrainer in the extractive column, the whole composition profile is contained in this region: B is the least volatile component throughout the column and can be recovered as pure bottom product, while we recover at the top of the column a binary mixture of A and E. In figure 4.15, A is the least volatile component in a region

Fig. 4.13: Tie lines in the light entrainer case



that contains part of the B - E edge. By using enough entrainer, we can operate a column that has its composition profile entirely within this region. A is then the least volatile component throughout the column and can be recovered as bottom product. We obtain the following results:

Proposition 4.2 *From the volatility order diagram, we can determine the flowsheet of the feasible separation sequence:*

- *If the isovolatility curve of A and B intersects the A - E edge, B is recovered as bottom product of the extractive column while A is recovered as bottom product of the entrainer recovery column.*

Fig. 4.14: Volatility order diagram when B lies on the boundary convex side

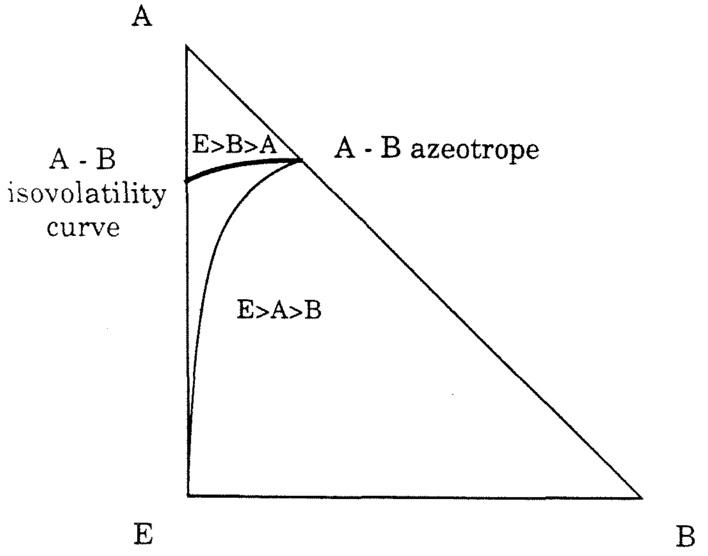
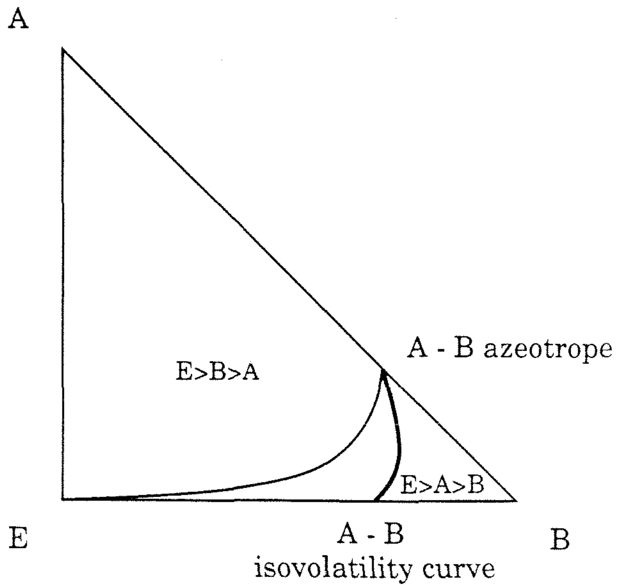


Fig. 4.15: Volatility order diagram when A lies on the boundary convex side



- *If the isovolatility curve of A and B intersects the B - E edge, A is recovered as bottom product of the extractive column while B is recovered as bottom product of the entrainer recovery column.*

Figure 4.16 and figure 4.17 illustrate these two cases with the ethanol (I) - water (H) - acetone (L) and methyl ethyl ketone (I) - water (H) - acetone (L) mixtures. When we use acetone as entrainer for the ethanol - water azeotrope, we obtain water at the bottom of the extractive column (figure A.7); here, water has the highest boiling point. When we use acetone as entrainer for the methyl ethyl ketone - water azeotrope, we obtain methyl ethyl ketone as bottom product (figure 2.28). Note that methyl ethyl ketone is the intermediate boiling component in this case.

In a couple of cases, namely ethanol (I) - water (H) - methanol (L) and ter-butanol (I) - water (H) - methanol (L), we have observed that the entrainer, methanol in both cases, is not the most volatile component over the whole composition space. For large water concentrations, methanol becomes less volatile than ethanol or ter butanol. The corresponding volatility order diagrams are shown on figure 4.18 and figure 4.19: We now have two isovolatility curves. However, we see that the region where water is the least volatile component covers most of the composition space and reaches the methanol - ethanol or methanol - ter butanol edge. Therefore, we can recover water as extractive distillation bottom product in both cases; the sequence separating ethanol and water using methanol as entrainer can be found in chapter 2.

4.2.3 Intermediate entrainers

Intermediate entrainers differ from heavy and light entrainers by the flexibility they give to the designer: While only one separation sequence can perform the desired separation in the case of heavy or light entrainers, separation can be achieved in three ways with an intermediate entrainer:

Fig. 4.16: The ethanol (I) - water (H) - acetone (L)
volatility order diagram

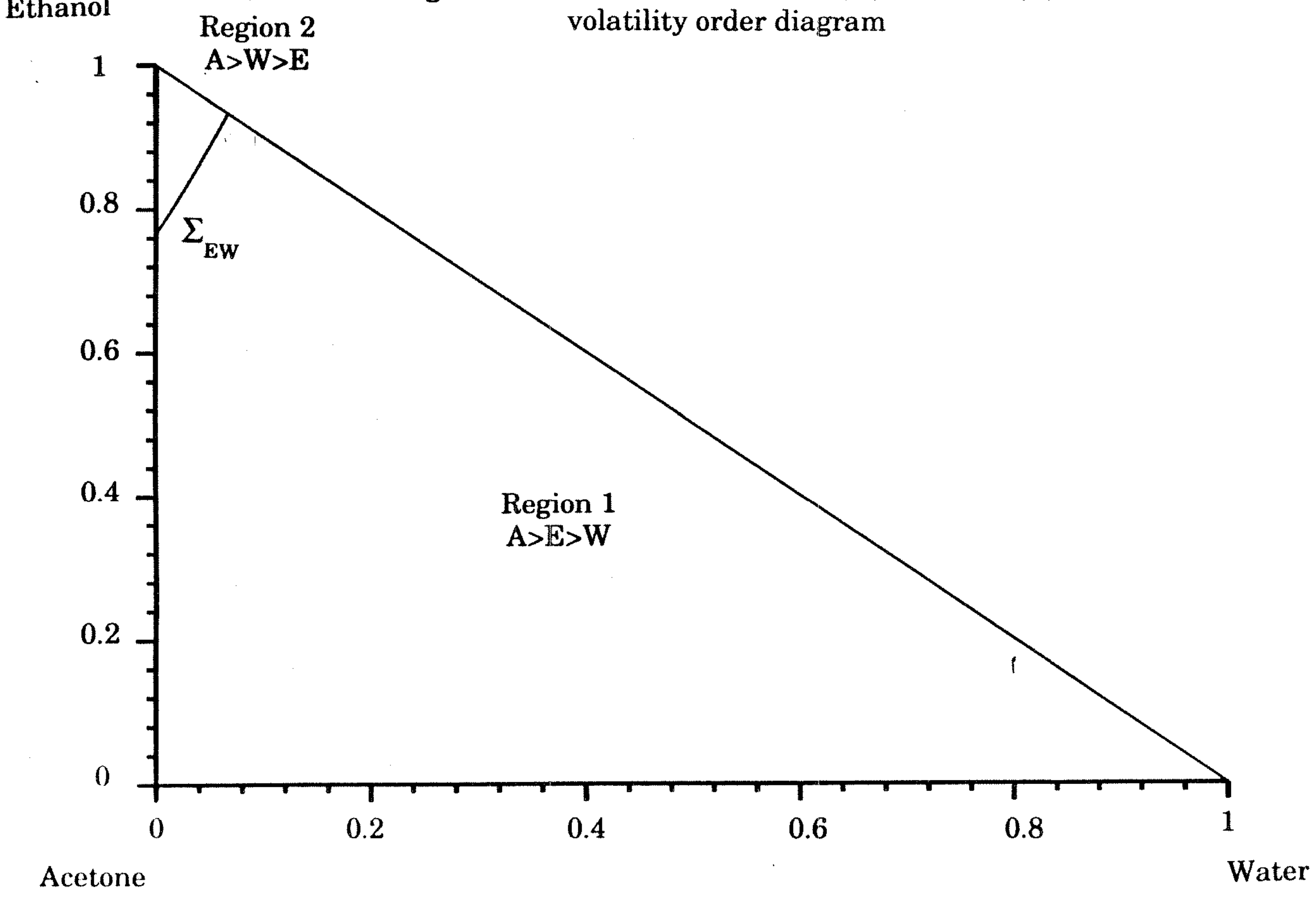


Fig. 4.17: The methyl ethyl ketone (I) - water (H) - acetone (L) volatility order diagram

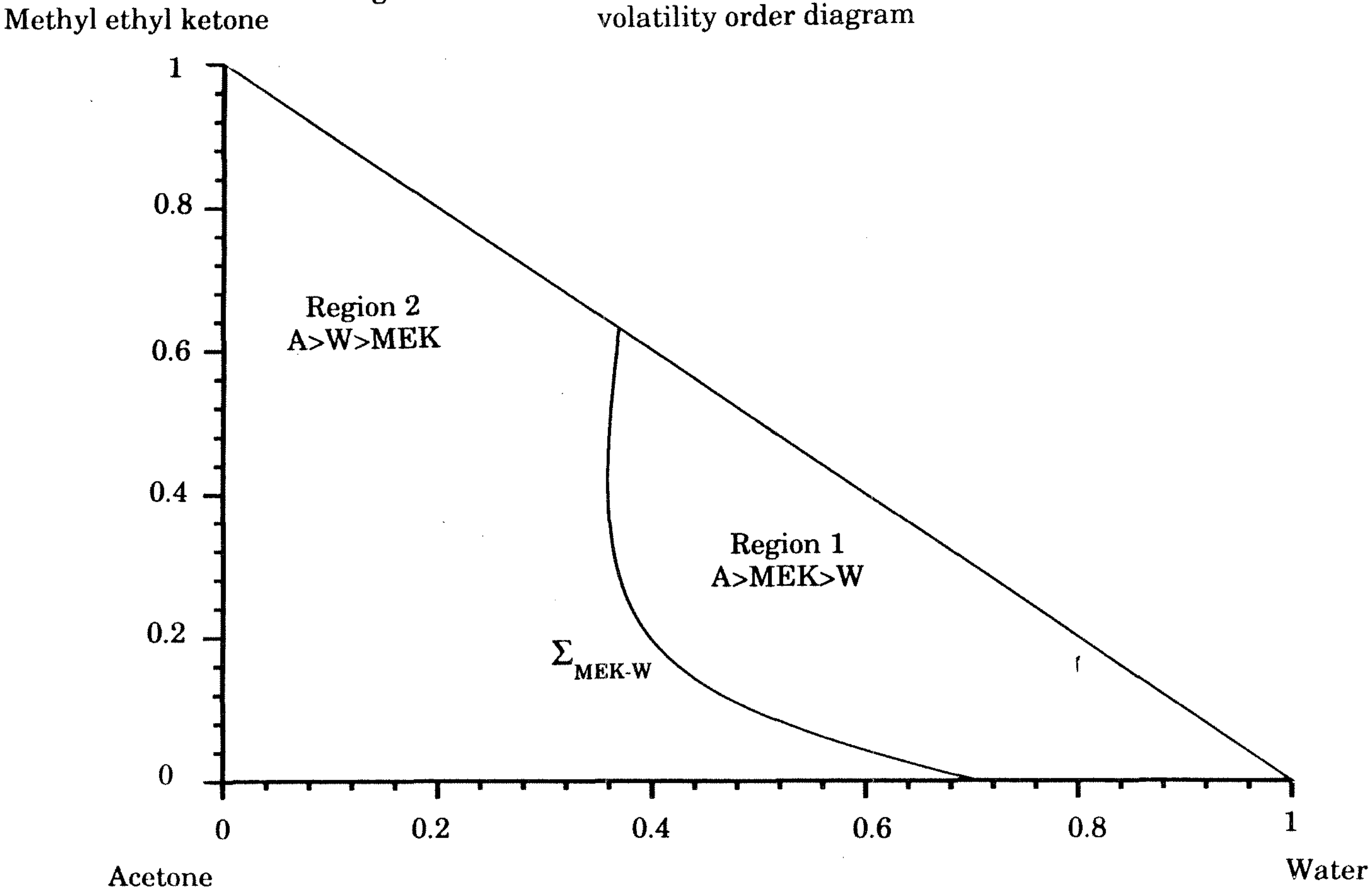


Fig. 4.18: The ethanol (I) - water (H) - methanol (L) volatility order diagram

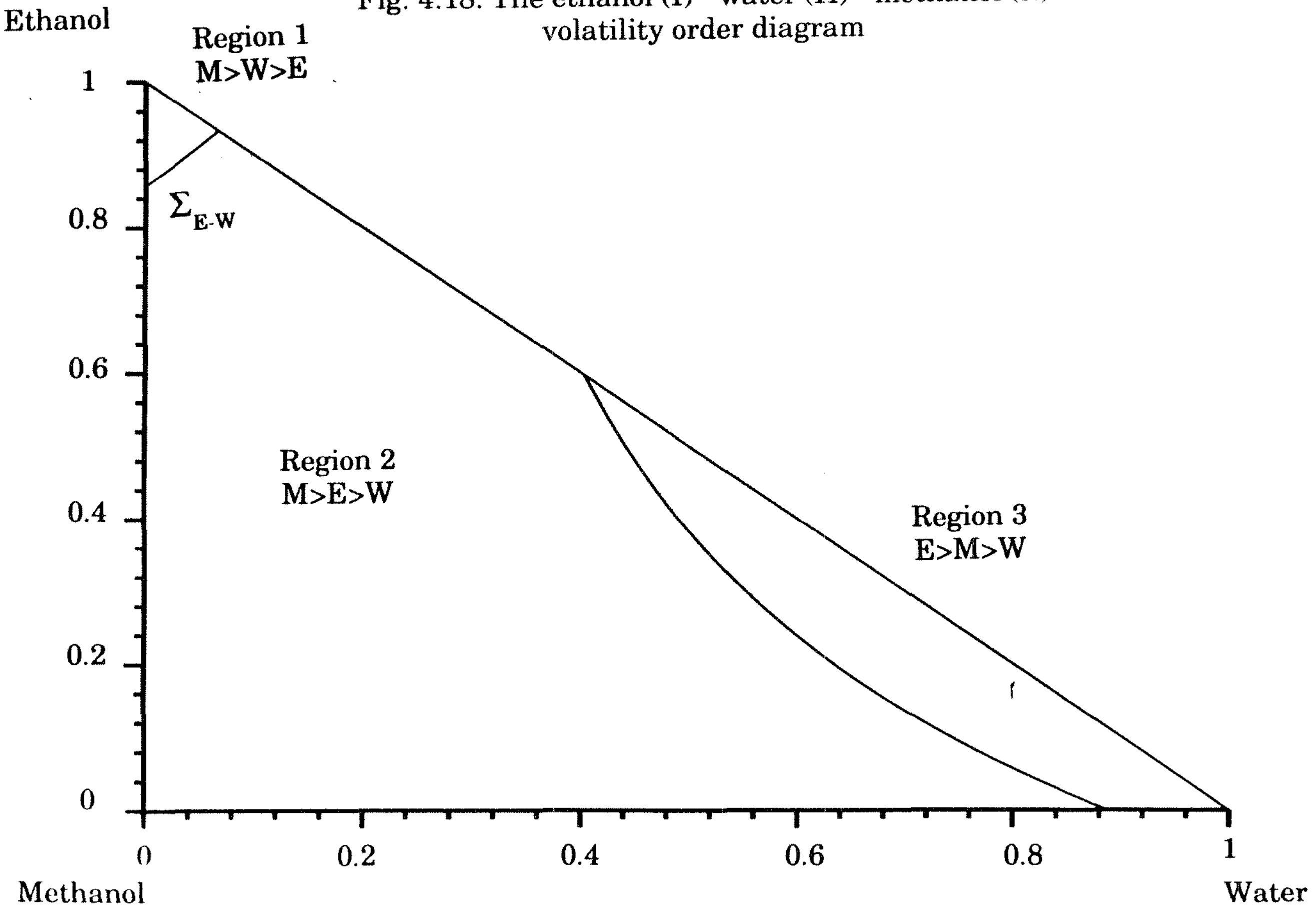
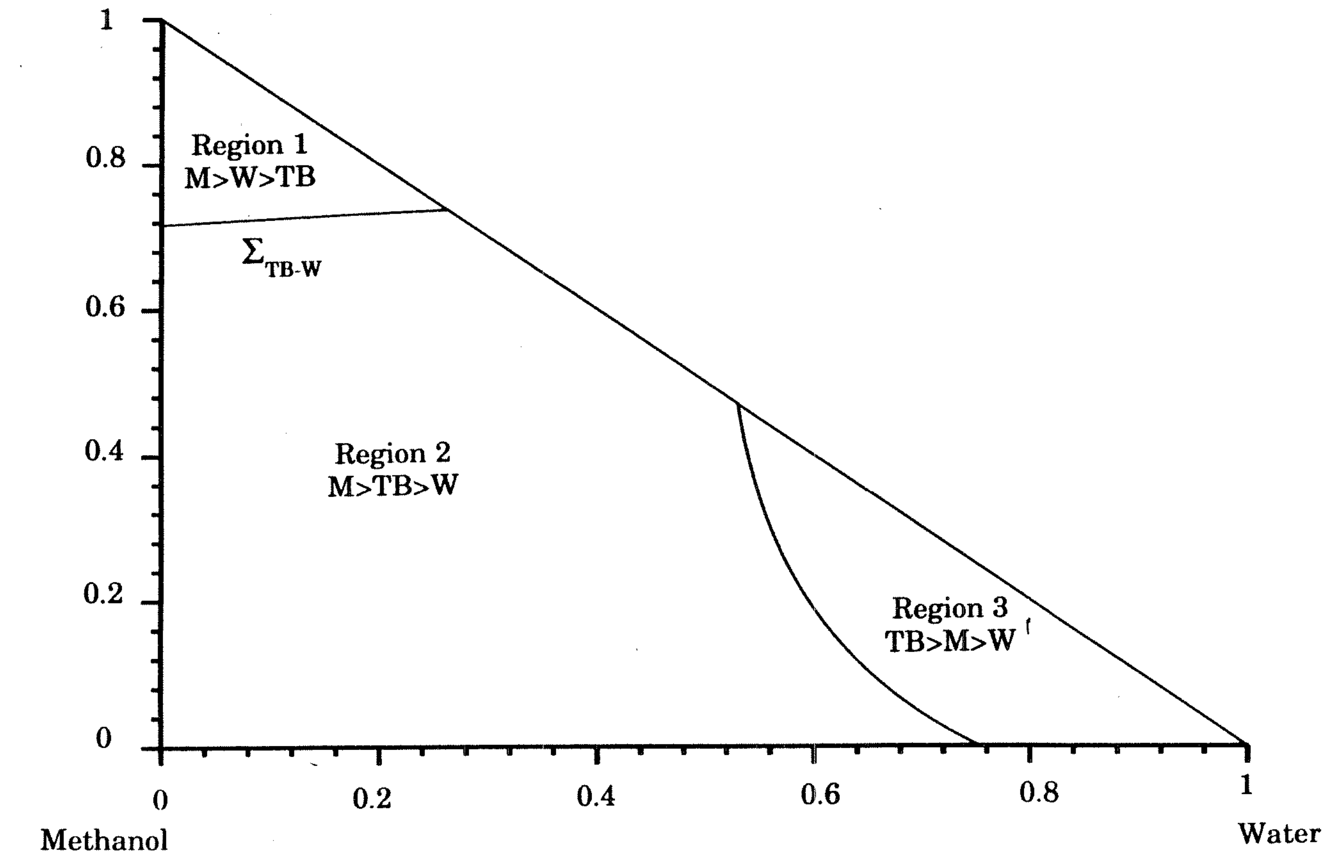


Fig. 4.19: The ter-butanol (I) - water (H) - methanol (L)
volatility order diagram

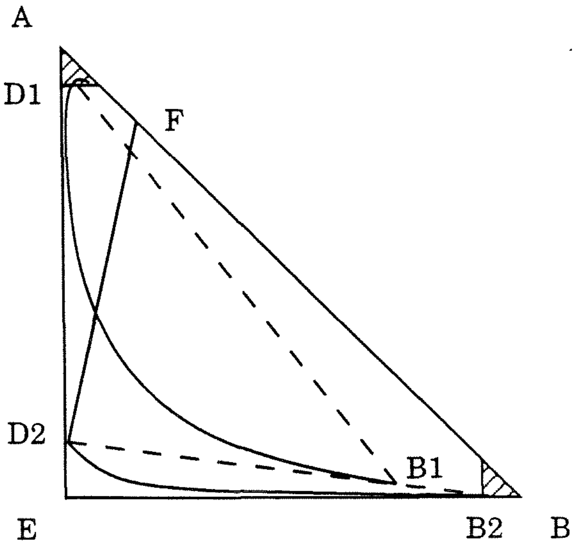


- We can use one column only (chapter 3). Because the entrainer is not recovered, the entrainer comes off the column as product impurity. Therefore, the amount of entrainer we can add is limited by the amount of impurity we tolerate in the product streams. The purer the products, the less entrainer we can use. A small amount of entrainer still makes separation feasible: Because of its boiling point, we can accumulate entrainer in the middle of the column by using a column that contains many stages. When the entrainer concentration is significant, the ternary mixture behaves like a normal ternary mixture: The boiling point order coincides with the volatility order. So we can send A to the top of the column and B to the bottom. This way of separating binary azeotropes has several advantages: It requires only one column, and only a very small amount of entrainer, so the diameter of the column can be small. On the other hand, it requires a column with many trays, and the entrainer is lost. Obviously, these advantages and disadvantages must be weighed against one another in each case to determine if this scheme is economically interesting. This method remains one feasible alternative that does not exist with other entrainers and should be considered when available.

- The direct sequence is always feasible; in other words, we can always recover A as top product of the extractive column and B as bottom product of the entrainer recovery column. This result can be obtained in two ways: We can apply the procedure described in chapter 3, or examine the volatility order diagram:

    - The results of the procedure described in chapter 3 are displayed in figure 4.20. Because all the residue curves that come close to the entrainer corner end at B, the second column can perform its duty, namely separate B from the entrainer. Because the residue curves that are close to A along

Fig. 4.20: The direct sequence is possible



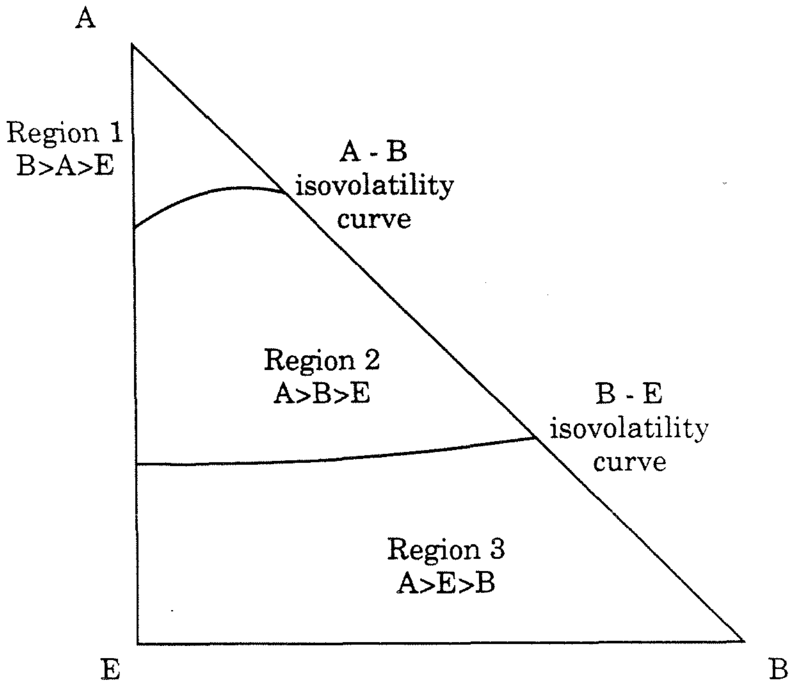
the A - E edge move along this edge and then along the B - E edge to finally reach B, we can find a residue curve that comes close to A and intersects the mass balance line of the second column. Therefore, the first column can perform its duty, namely to produce pure A at the top and a binary mixture B1 of B and E at the bottom. Because the infinite reflux situation is the limit of high reflux ratio, this separation is also feasible at finite reflux.

- In the case of an intermediate entrainer, the volatility order diagram always looks like figure 4.21. Close to corner A, residue curves move from the A - B azeotrope towards A; therefore, the local volatility order in that region is B>A>E. The order of A and B changes when we cross the isovolatility curve of A and B; it becomes A>B>E. Finally, close to the entrainer corner, the local volatility order coincides with the boiling point order, *i.e.*

A>E>B. This implies that the volatility order diagram contains an isovolatility curve for B and E; since B and E do not form any azeotrope, this curve cannot intersect the B - E edge. The composition space is therefore divided in three different regions, and A is the most volatile component in both regions 2 and 3. By adding enough entrainer or using a large enough column (the entrainer concentrates in the middle of the column and reaches higher mole fractions with a larger column), we can bring the column profile in the regions where A is the most volatile component and separate it from B. The top of the column essentially performs a binary separation between the entrainer and A. The mechanism of this separation is very similar to the one obtained with a heavy entrainer, but because the entrainer is more volatile than the second azeotropic component, we do not have to feed the entrainer separately. Also, obtaining high entrainer concentrations can be achieved by increasing the number of trays rather than using large amounts of entrainers.

- The indirect sequence is always feasible too: We can always recover B as bottom product of the extractive column and A as top product of the entrainer recovery column. We can reach this result in a completely similar fashion:
  - The results of the procedure described in chapter 3 are displayed in figure 4.22. Because the residue curves that are close to A along the A - E edge move along this edge and come close to the entrainer corner, the entrainer recovery column can perform its duty and separate a binary mixture of A and E. Because the residue curves that come close to the A - E edge eventually end at B, B can be recovered as bottom product B1 while the distillate D1 is a binary mixture of A and E. Again, because the infinite reflux situation is the limit of high reflux ratio, this separation is

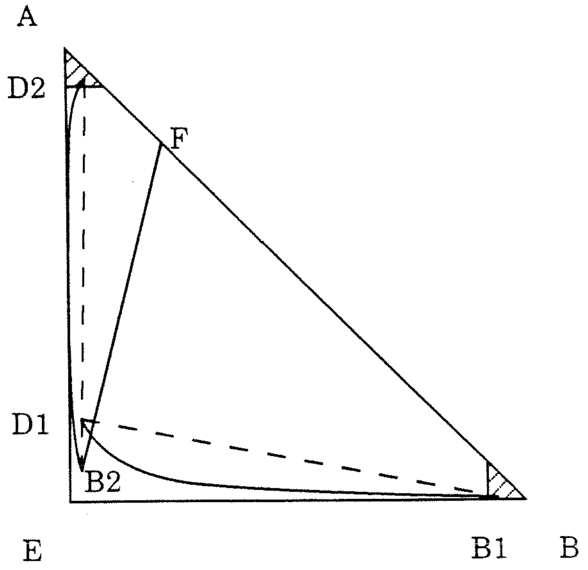
Fig. 4.21: **Volatility order diagram in the intermediate entrainer case**



also feasible at finite reflux.

- From the volatility order diagram, we see that B is the least volatile component in region 3. By feeding enough entrainer to the column or by using a large enough column, we can obtain high entrainer concentration in the middle of the column and bring the column profile within region 3. B becomes then the least volatile component throughout the column and can be recovered as pure bottom product. The distillate is a binary mixture of A and E which can be separated easily in the second column. The mechanism of this separation is very similar to the one obtained with a light entrainer, but because the entrainer is less volatile than the first

Fig. 4.22: The indirect sequence is possible



azeotropic component, we do not have to feed the entrainer separately. We can again obtain high entrainer concentrations by increasing the number of trays rather than using large amounts of entrainers.

We obtain the following results:

Proposition 4.3 *Three different separation sequence flowsheets are possible in the case of intermediate entrainers; separation can be achieved with:*

- *Only one column.*
- *The direct sequence.*
- *The indirect sequence.*

These three possible separation sequences have been illustrated in previous chapters with the acetone - heptane - benzene example.

4.2.4 Summary

In this section, we have shown how the volatility order diagrams can be used to determine the flowsheet of the feasible separation sequence. We have obtained the following results:

- When we use a heavy boiler, we recover A as distillate of the extractive column and B as distillate of the entrainer recovery column if the isovolatility curve of A and B intersects the A - E edge; we recover B first and A second if this isovolatility curve intersects the B - E edge.
- When we use a light boiler, we recover A as bottom product of the extractive column and B as bottom product of the entrainer recovery column if the isovolatility curve of A and B intersects the B - E edge; we recover B first and A second if this isovolatility curve intersects the A - E edge.
- When we use an intermediate boiler, we can choose from three separation sequences: We can use one column only, the direct sequence or the indirect sequence.

4.3 Entrainer comparison

4.3.1 The minimum trade-off curve

In order to be able to compare entrainers, we need to define a measure of entrainer performances. Clearly, the best entrainer for a given azeotrope is the entrainer that minimizes the total annualized cost to separate this azeotrope into pure products[1]. Thus, an obvious measure of entrainer performance is the total annualized cost of the corresponding separation sequence. But designing the feasible separation sequences

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[1] The total annualized cost combines capital investments and operating expenses (Douglas 1988, Knapp & Doherty 1990).

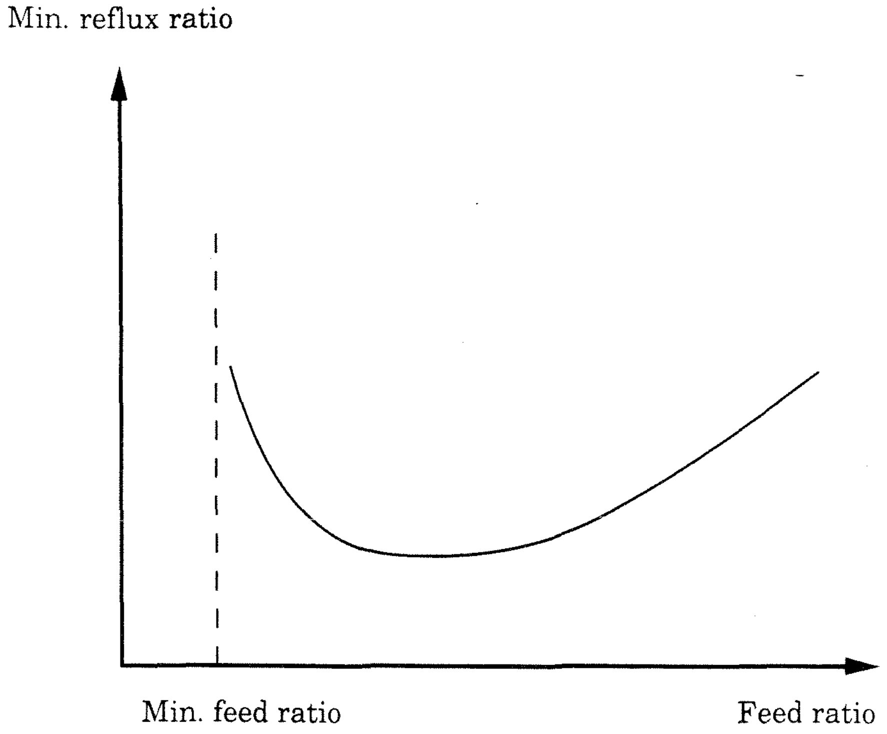
for each entrainer is time-consuming. By examining the detailed cost study of the ethanol (L) - water (I) - ethylene glycol (H) homogeneous azeotropic distillation sequence performed by Knight & Doherty (1989) and revised by Knapp & Doherty (1990), we show that we can relate this cost to the minimum trade-off curve:

Definition 4.6 *The minimum trade-off curve represents the minimum reflux ratio needed to achieve separation (defined as the minimum reflux flow rate divided by the azeotropic feed flow rate) as a function of the entrainer-to-azeotrope feed ratio.*

Indeed, because we consider only saturated azeotropic feeds, the main optimization variable for the two-column separation sequence is the feed ratio, *i.e*,. the ratio of the entrainer feed flow rate to the azeotropic feed flow rate. Knight & Doherty have shown that the separation sequence found by determining the other design variables through reasonable heuristic rules and optimizing only the feed ratio comes very close to the true optimum. The detailed cost analysis they performed on a slightly suboptimal sequence (see table 2 of Knight & Doherty 1989) reveals that the operating expenses, *i.e*,. steam and cooling water, account for about half of the sequence total annualized cost. We also see from their figures 2 and 6 that the total annualized cost does not depend much on the heuristic rule used for the reflux ratio: Setting the reflux ratio at 1.15, 1.2 or 1.3 times the minimum does not make much difference. The minimum reflux ratio needed to achieve separation at a given feed ratio determines the operating expenses. We should therefore try to minimize this minimum reflux ratio as a function of feed ratio.

Typically, minimum trade-off curves are similar to the curve represented on figure 4.23. Except in the intermediate entrainer case, separation is impossible when the feed ratio is too low. Above this threshold, separation is always feasible. The typical shape of minimum trade-off curves results from the competition of two effects. Adding entrainer increases the entrainer concentration inside the column; this usually increases the relative volatility of the azeotropic components and therefore

Fig. 4.23: Typical minimum trade-off curve



lowers the value of the minimum reflux ratio needed to achieve separation. However, adding entrainer also increases the column load, leading to a minimum reflux ratio increase. The overall result depends on the operating point: For low feed ratios, the relative volatility improvement dominates the load increase while, for high feed ratios, the load increase takes over the relative volatility improvement. Minimum trade-off curves display a minimum, which we use here as our entrainer performance measure: We define the corresponding feed ratio (minimum reflux ratio respectively) as the optimum feed ratio (optimum minimum reflux ratio resp.).

We compute minimum trade-off curves by calculating the minimum reflux ratio corresponding to each value of the feed ratio; minimum reflux ratio calculations are carried out with the exact algorithm described in Levy & Doherty (1986). In order to compare entrainers on an equitable basis[2], we assume in all cases that:

- The composition of the feed we want to separate is that of the azeotrope at atmospheric pressure.
- The entrainer feed contains only pure entrainer.
- We set the purity specifications on both azeotropic component products at 0.998.
- We specify a value of 1000 for the ratio of the azeotropic component mole fractions in the entrainer recovery column feed (this ratio usually limits the achievable product purity in the entrainer recovery column (Andersen *et al.* 1989)).

We therefore compare entrainers by comparing their minimum trade-off curves. The best entrainer is the entrainer that yields the lowest optimum feed ratio and minimum reflux ratio. These two properties can sometimes conflict, as the acetone (L) - methanol (I) - water (H) and acetone (L) - methanol (I) - chlorobenzene (H) examples show (figure 4.24). Both water and chlorobenzene can be used as entrainers to separate the acetone - methanol azeotrope and we see from the corresponding minimum trade-off curves that separation with chlorobenzene requires a lower minimum reflux than with water, but the optimum feed ratio is higher in the case of chlorobenzene than of water. Whether chlorobenzene is a better entrainer than water for the acetone - methanol azeotrope depends on the relative costs of energy and of capital: High energy costs would favor chlorobenzene, while low energy costs favor water.

A fair entrainer comparison requires the reflux ratio to be defined with respect to the azeotropic feed and not to the distillate flow rate, as would commonly be the

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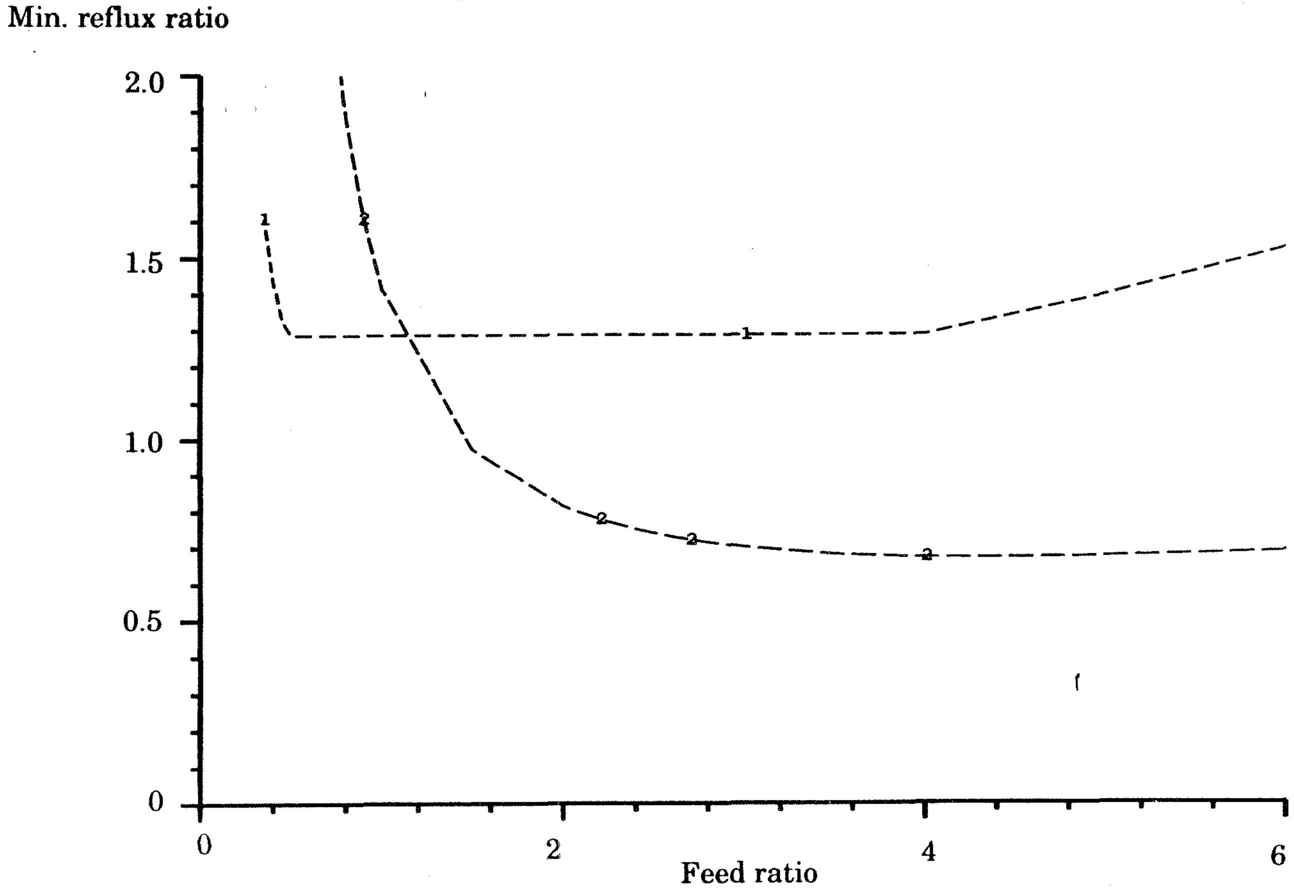
[2] As we show later in this section, the minimum trade-off curve enables us to compare only entrainers of the same kind; we cannot fairly compare entrainers that belong to different classes.

Fig. 4.24: The minimum trade-off curves of acetone and methanol using water (1) and chlorobenzene (2) as entrainers



case. Indeed, the usual definition of the reflux ratio would bias the comparison towards entrainers that yield the highest distillate flow rate. For instance, chlorobenzene sends methanol to the top while water sends acetone to the top of the extractive column. Because the azeotrope contains three times more acetone than methanol, dividing the minimum reflux flow rate by the distillate flow rate makes water artificially appear as a much better entrainer than chlorobenzene: Reflux flow rates are identical for both entrainers if we use a feed ratio of 1.1, yet the usual reflux ratio definition makes water look much better than chlorobenzene at that point.

4.3.2 Comparing heavy entrainers

In the case of heavy entrainers, the position of the minimum trade-off curve can be easily related to the equivolatility curve diagram obtained with this entrainer. Indeed, let A be the component recovered at the top of the extractive column. Separation can be achieved only when the entrainer concentration in the extractive section is large enough to make A more volatile than B throughout the middle section. We have to introduce enough entrainer in the column so that the entrainer concentration in the extractive section exceeds x_E. Although the connection is not direct since reflux and boilup have to be taken into account, the larger x_E is, the more entrainer we need to add to "break" the azeotrope and to make the azeotropic component recovered overhead more volatile than the other in both the extractive and the stripping sections. Therefore, lower values of x_E imply lower x-coordinates for the points of the minimum trade-off curve. A comparison of figure 4.25 and figure 4.26 illustrates this point in the case of the acetone (L) - methanol (I) azeotrope, using water, ethanol and isopropanol as heavy entrainers. In all three cases, the corresponding equivolatility curve diagrams show that acetone is recovered as distillate of the extractive column, since the resulting isovolatility curve of acetone and methanol intersects the acetone - entrainer edge. The resulting values of x_E are: 0.10 for water, 0.20 for ethanol and

0.29 for isopropanol. The minimum trade-off curves show the same trend: Operating the separation sequence at the feed ratio optimum requires less entrainer when we use water as entrainer than when we use ethanol, and less entrainer when we use ethanol as entrainer than when we use isopropanol.

The y-coordinates of the minimum trade-off curve points are the minimum reflux ratio obtained for the given feed ratio. In all distillation columns, there is a direct connection between minimum reflux ratio and relative volatility. In the case of homogeneous azeotropic distillation, minimum reflux ratio is intimately connected to the relative volatility of the two azeotropic components: The higher the achievable relative volatility is, the easier the separation and the lower the minimum reflux ratio. This relation is particularly true when the entrainer can be readily separated from the two azeotropic constituents, which is the most common case. In that case, the separation between the two azeotropic components is the factor that limits separation. A comparison of figure 4.27, figure 4.28 and figure 4.29 illustrates this point, using again the acetone - methanol azeotrope and water, ethanol and isopropanol as entrainers. We see that water is again the best entrainer, because we can obtain a higher relative volatility between acetone and methanol. We also see that isopropanol is better than ethanol in terms of minimum reflux ratio: Indeed, we can achieve relative volatilities higher than 2.5 with isopropanol, while we are limited to about 2.1 with ethanol. The minimum trade-off curves reflect these facts: We achieve separation with a lower minimum reflux ratio when we use water as entrainer than when we use either ethanol or isopropanol, while isopropanol leads to lower minimum reflux ratios than ethanol.

In the case of heavy entrainers, the most difficult separation is performed in the extractive section: If the entrainer sends A to the top of the extractive column, this section removes B from the ternary mixture. Because the extractive section composition profile then lies close to the A - E edge, we should compare entrainers that send A to the top by comparing the relative volatility of A and B close to the A -

Fig. 4.25: The minimum trade-off curves of acetone and methanol using ethanol (1), isopropanol (2) and water (3) as entrainers

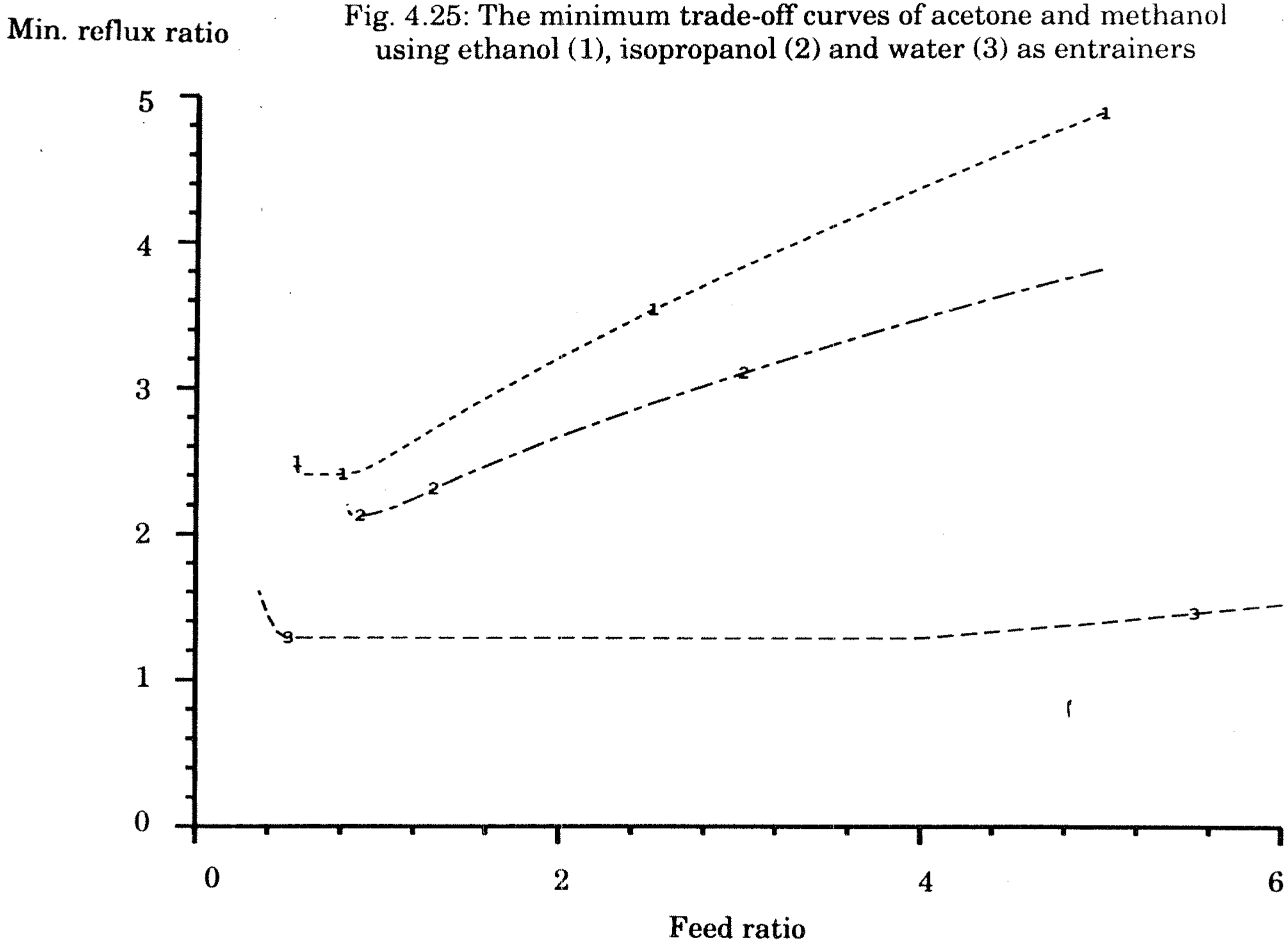


Fig. 4.26: The isovolatility curves of acetone and methanol using ethanol (1), isopropanol (2) and water (3) as entrainers

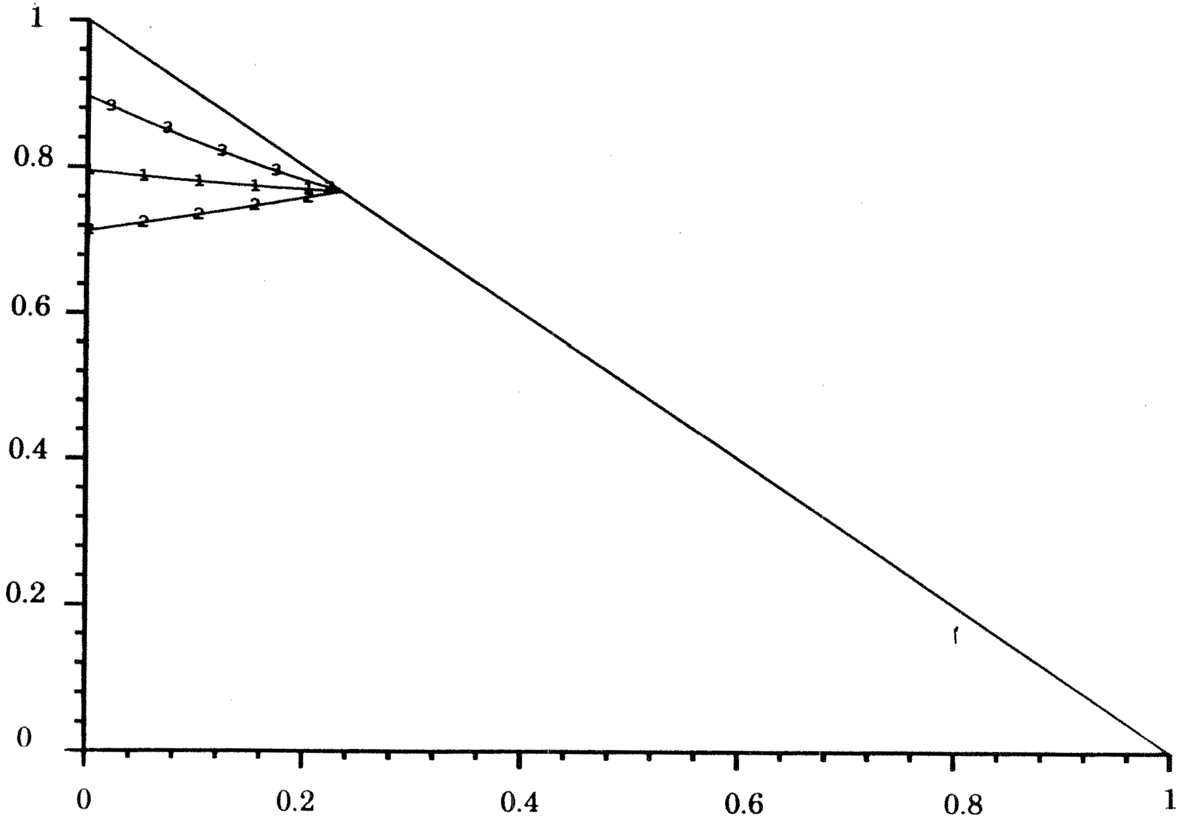


Fig. 4.27: The equivolatility curves of acetone and methanol in the acetone (L) - methanol (I) - ethanol (H) case

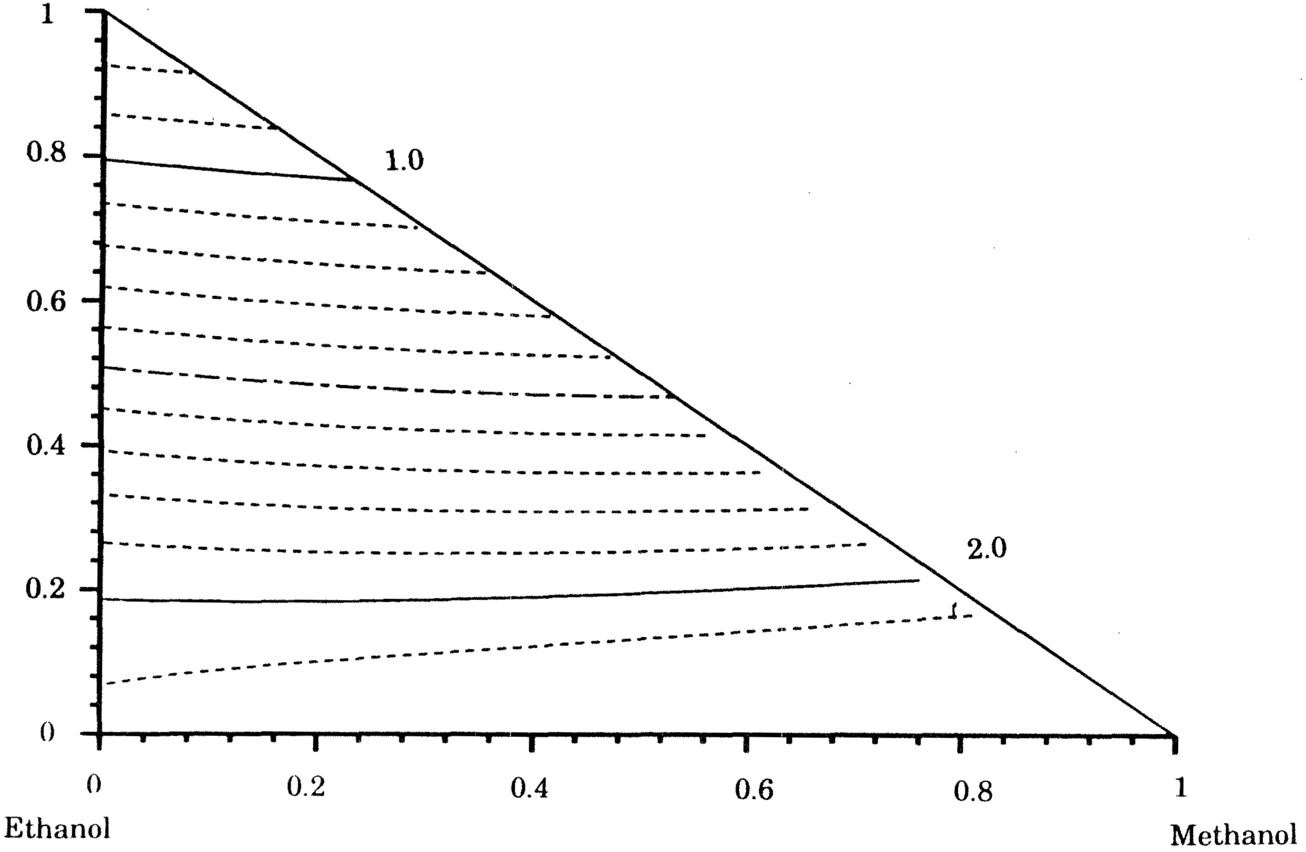


Fig. 4.28: The equivolatility curves of acetone and methanol in the acetone (L) - methanol (I) - isopropanol (H) case

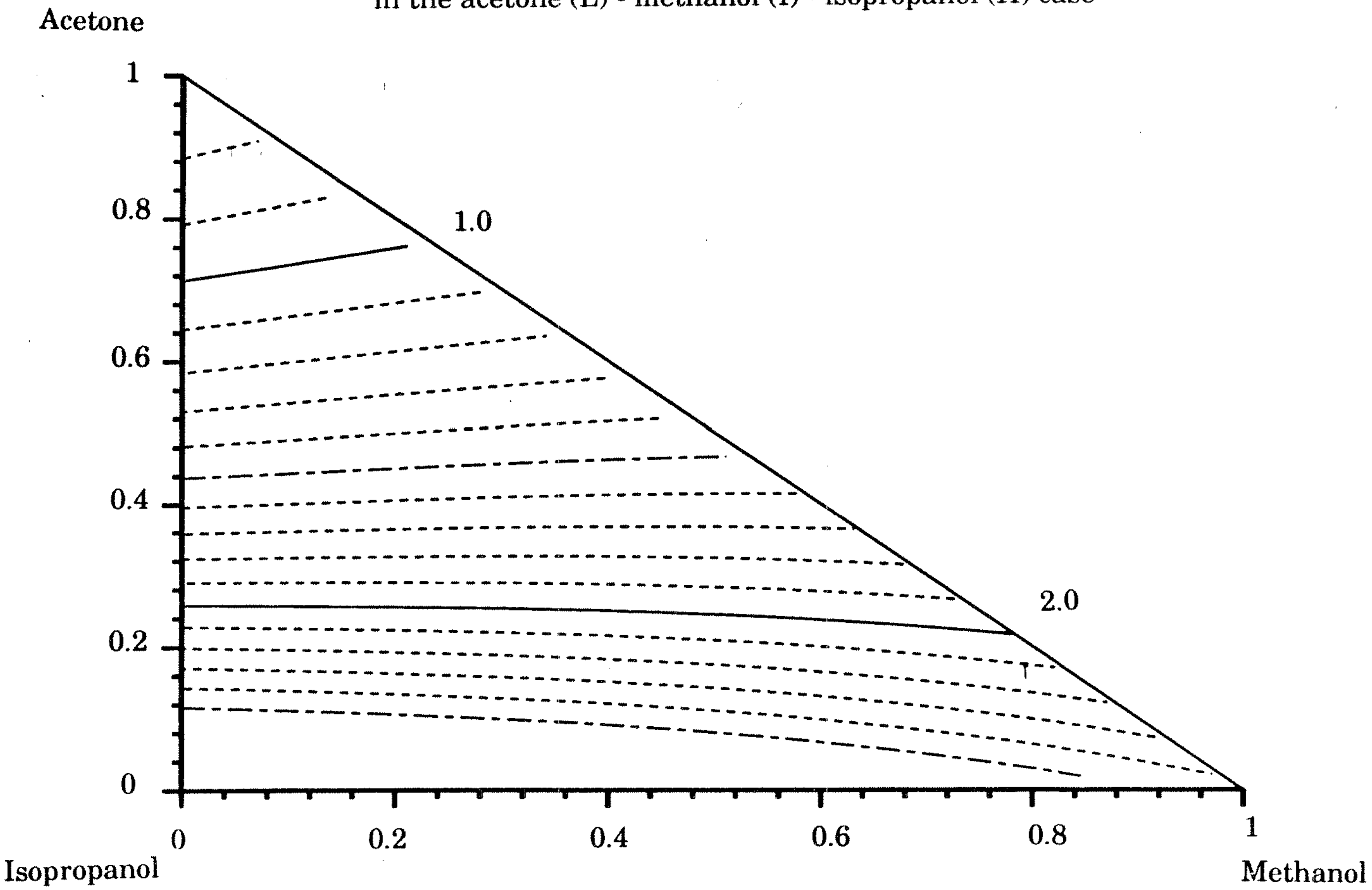
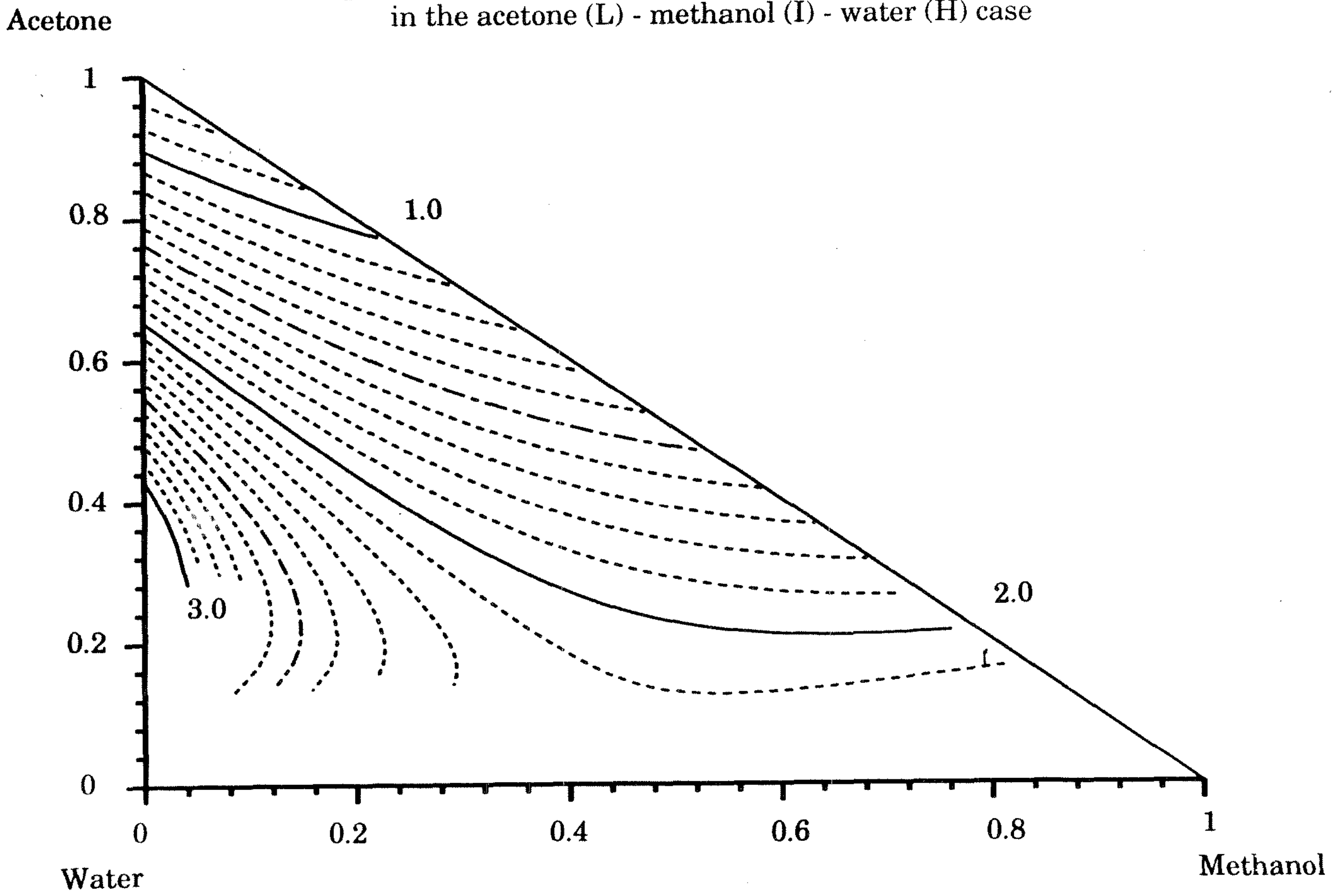


Fig. 4.29: The equivolatility curves of acetone and methanol in the acetone (L) - methanol (I) - water (H) case



E edge. Similarly, we should compare entrainers that send B to the top by comparing the relative volatility of A and B close to the B - E edge, because the extractive section composition profile is then located in that region.

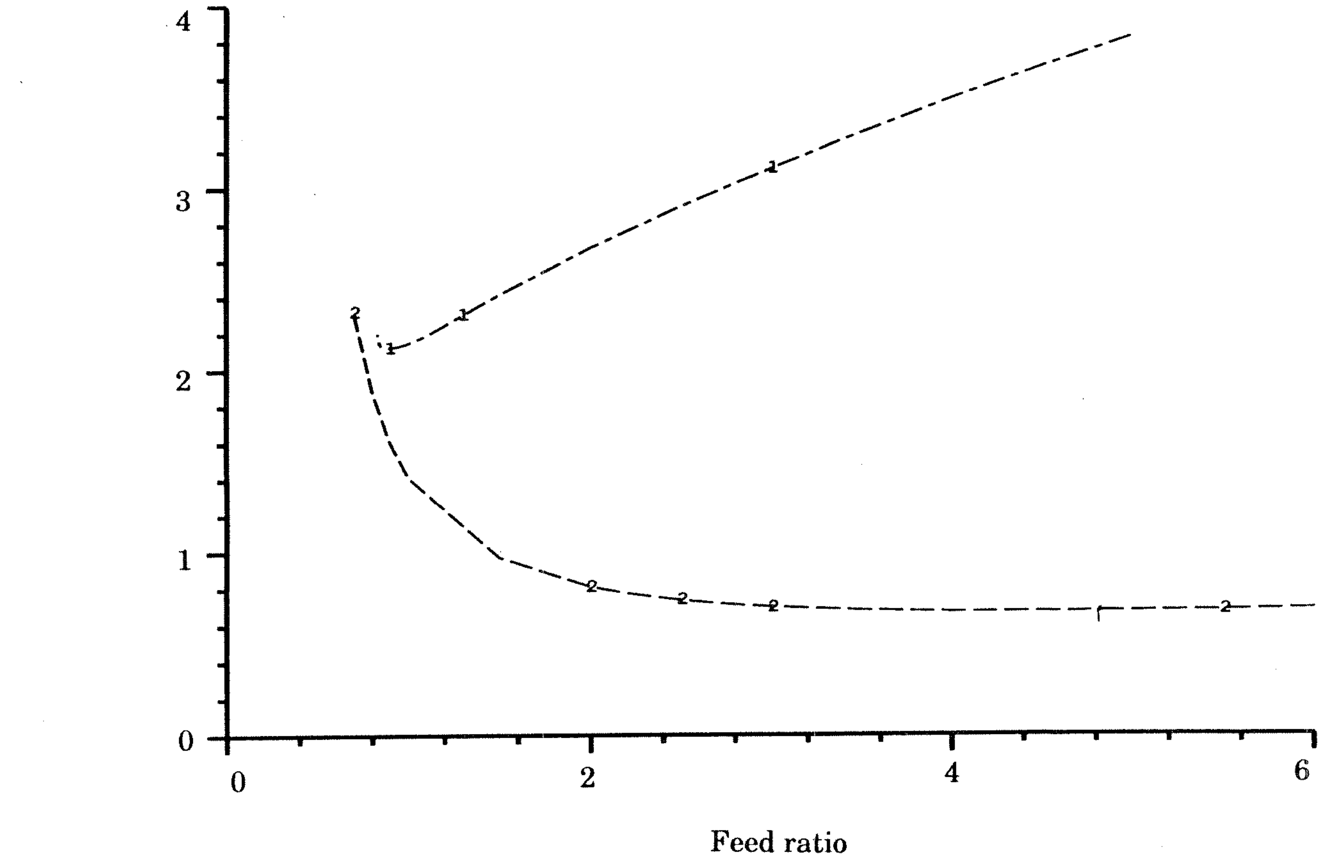
The comparison of entrainers that send different azeotropic components to the top of the extractive column based on their equivolatility curve diagrams is less meaningful and less reliable in practice than the comparison of entrainers that send the same azeotropic component to the top of the extractive column. Indeed, let us consider the acetone (L) - methanol (I) azeotrope, using isopropanol and chlorobenzene as heavy entrainers. With isopropanol, we recover acetone as distillate of the extractive column, while we recover methanol as top product of the extractive column if we use chlorobenzene. Therefore, chlorobenzene must increase the methanol concentration from 0.248 to 0.998, while isopropanol only has to increase the acetone concentration from 0.752 to 0.998. Therefore isopropanol has an advantage over chlorobenzene, which distorts the comparison we obtain from the equivolatility curve diagrams. We see that x_E is equal to 0.29 for isopropanol (figure 4.28) and 0.23 for chlorobenzene (figure 4.8). Chlorobenzene should yield a lower optimum feed ratio, but we see from figure 4.30 that such is not the case. Therefore we should separately compare entrainers that send A to the top of the extractive column and entrainers that send B to the top of the extractive column.

Proposition 4.4 *We can compare heavy entrainers for a given binary azeotrope by examining the corresponding equivolatility curve diagrams:*

- *The lower x_E is, the lower the optimum feed ratio.*
- *The higher the relative volatility is, the lower the optimum minimum reflux ratio.*

Note that we should compare in this manner only entrainers that do not send the same azeotropic component to the top of the extractive column.

Fig. 4.30: The minimum trade-off curves of acetone and methanol using isopropanol (1) and chlorobenzene (2) as entrainers



A good entrainer should easily "break" the azeotrope we want to separate. In practice, we have found that separation becomes very difficult and requires very large feed ratios when the value of x_E exceeds 0.7. We illustrate this point with a couple of examples:

- Normal butanol can act as a heavy entrainer for the methanol (L) - methyl ethyl ketone (I) azeotrope. Figure 4.31 shows the corresponding isovolatility curve of methanol and methyl ethyl ketone. We see that x_E is equal to 0.89. We have found that separation is not feasible for feed ratios below 20.
- Sec-butanol can act as a heavy entrainer for the ethanol (L) - methyl ethyl ketone (I) azeotrope. Figure 4.32 shows that x_E is equal to 0.81 in this case; we have found that separation is impossible for feed ratios below 25.

A good entrainer should also yield high relative volatilities between the two azeotropic components. In practice, we have found that separation becomes very difficult when the relative volatility of the two azeotropic constituents always remains below 1.1 in the region that would contain the extractive section composition profile. For example, toluene can act as a heavy entrainer for the ethyl ethanoate (L) - methyl ethyl ketone (I) azeotrope. Yet the relative volatility of ethyl ethanoate and methyl ethyl ketone never exceeds 1.1 (figure 4.33); we have found that the optimum reflux ratio is over 25.

We can now explain the example presented in chapter 2 where we altered the value of the Wilson interaction parameter of toluene and ethyl ethanoate in the ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) mixture. We noted that, for values of a_{T-EE} below 0.77, we must recover ethyl ethanoate first, whereas we must recover methyl ethyl ketone first for values of a_{T-EE} above 0.89. We found that separation is infeasible for feed ratios below 50 if the value of a_{T-EE} is between 0.77 and 0.89. We also noted that changing the value of a_{T-EE} from 0.6 to 1.0 does not affect the binary equilibrium of toluene and ethyl ethanoate significantly. The

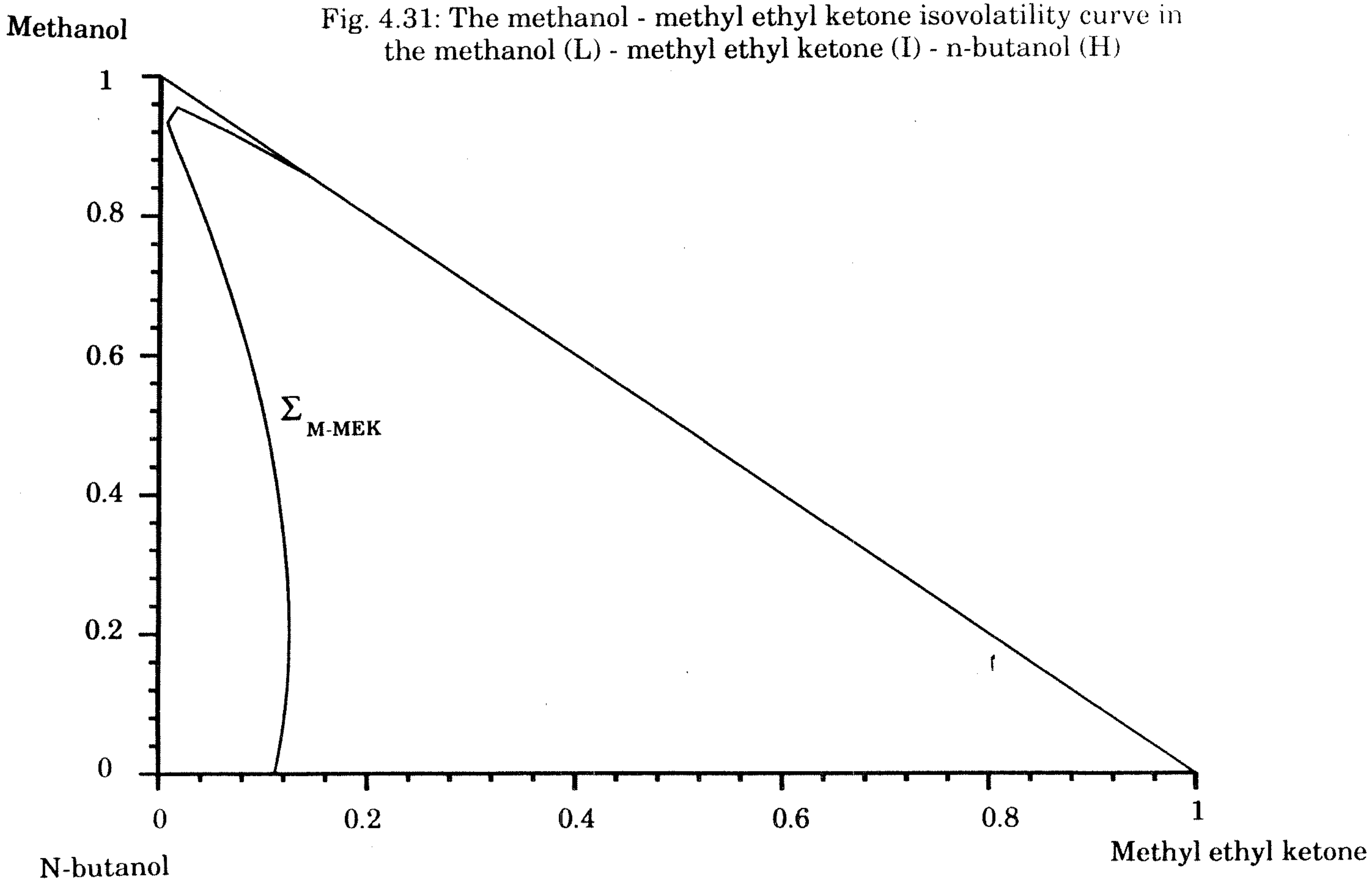
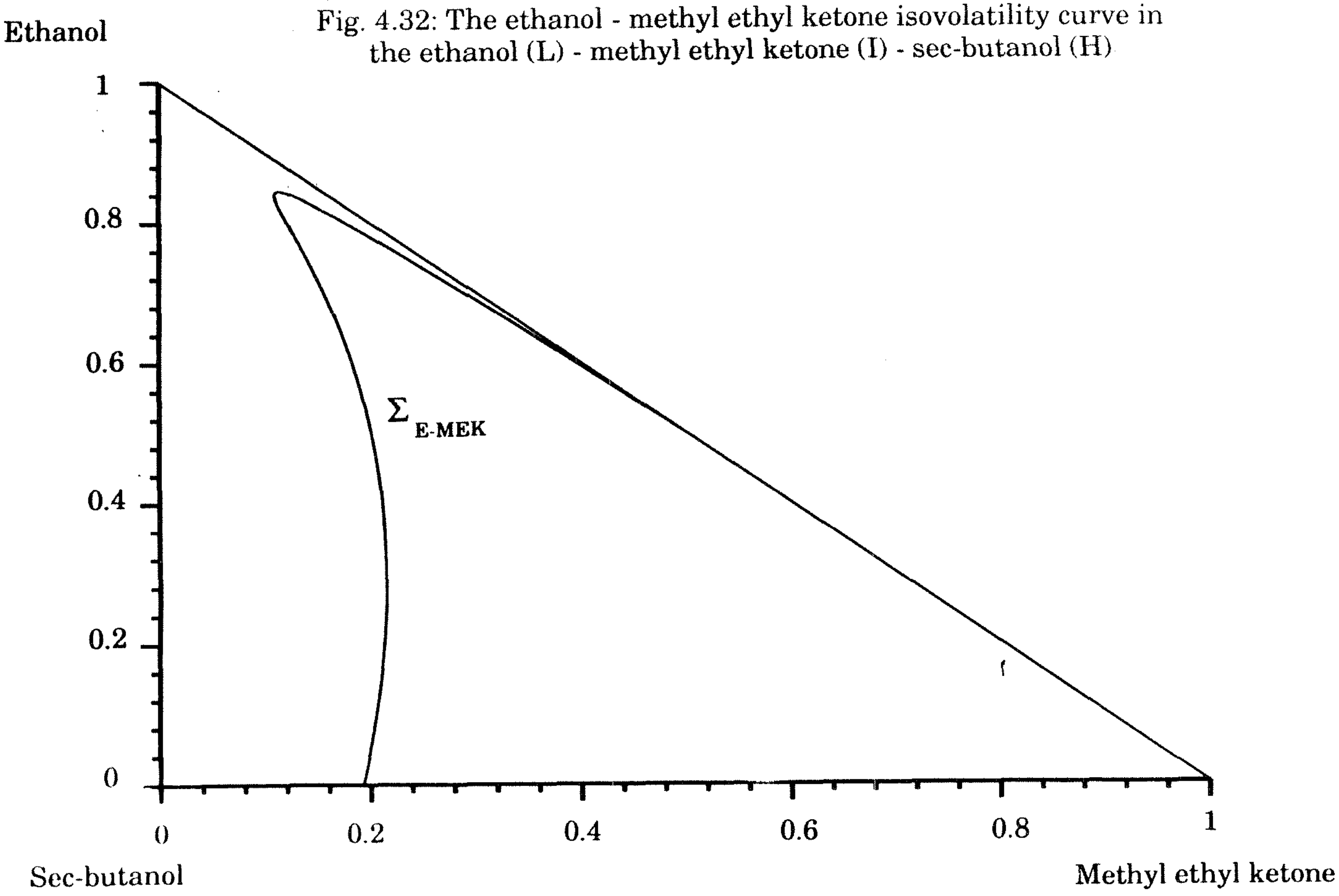


Fig. 4.31: The methanol - methyl ethyl ketone isovolatility curve in the methanol (L) - methyl ethyl ketone (I) - n-butanol (H)

Fig. 4.32: The ethanol - methyl ethyl ketone isovolatility curve in the ethanol (L) - methyl ethyl ketone (I) - sec-butanol (H)



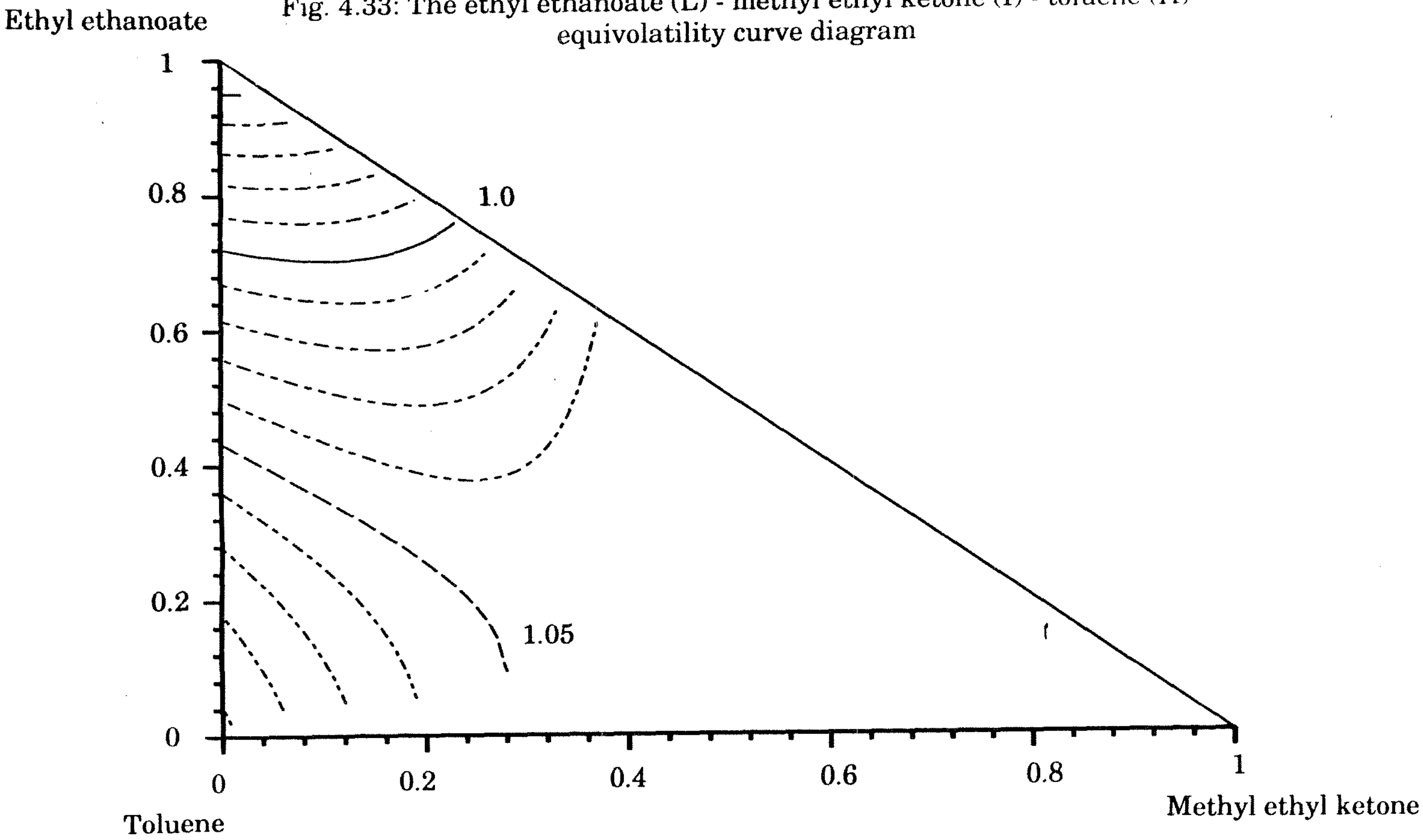


Fig. 4.33: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

set of equivolatility curve diagrams shown in figure 4.34 to figure 4.38 enables us to explain this behavior. At first, as we increase a_{T-EE}, the isovolatility curve end point moves along the ethyl ethanoate - toluene edge towards toluene; for values of a_{T-EE} up to 0.84, ethyl ethanoate must be recovered first. As we increase a_{T-EE} from 0.6 to 0.84, the relative volatility of ethyl ethanoate and methyl ethyl ketone in the extractive column decreases; figure 2.53 shows that, for a constant feed ratio of 50, there is an increase in the minimum feed ratio necessary to achieve separation. Separation actually becomes infeasible when a_{T-EE} exceeds 0.77. When a_{T-EE} goes above 0.84, the isovolatility curve end point is now located on the methyl ethyl ketone - toluene edge, so we can recover methyl ethyl ketone first (figure 4.39). But because the relative volatility of methyl ethyl ketone and ethyl ethanoate remains very low, separation remains infeasible at first. Separation becomes feasible at a feed ratio of 50 only when a_{T-EE} exceeds 0.89. Since the relative volatility of methyl ethyl ketone and ethyl ethanoate increases as we increase a_{T-EE}, separation becomes easier and requires lower minimum reflux ratios when a_{T-EE} goes from 0.89 to 1.0.

We have applied these rules of thumb to several azeotropes, examining several entrainers for each of them, and we show the corresponding results in appendix C. We have found that comparing entrainers can be done very reliably in all cases, except when one entrainer cannot be easily separated from one of the azeotropic components.

4.3.3 Light entrainers

We obtain very similar results with light entrainers: The position of the minimum trade-off curve can be related to the equivolatility curve diagram in a completely analogous manner. Indeed, as in the case of heavy entrainers, good entrainers should yield low values of x_E, because less entrainer is required to "break" the azeotrope and make the component recovered as bottom product the least volatile component throughout the column. Thus lower values of x_E imply lower x-coordinates for the

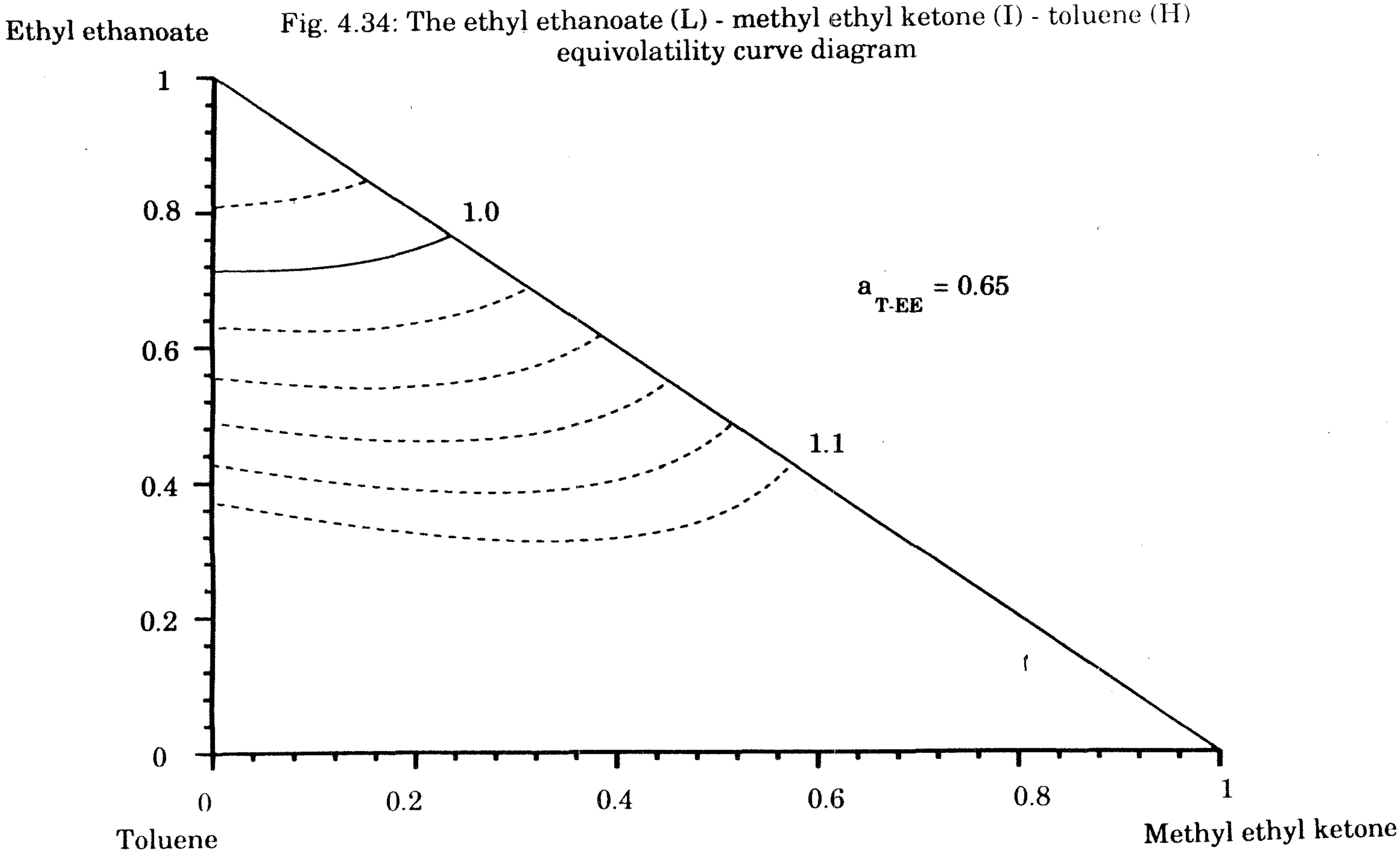


Fig. 4.34: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

Fig. 4.35: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

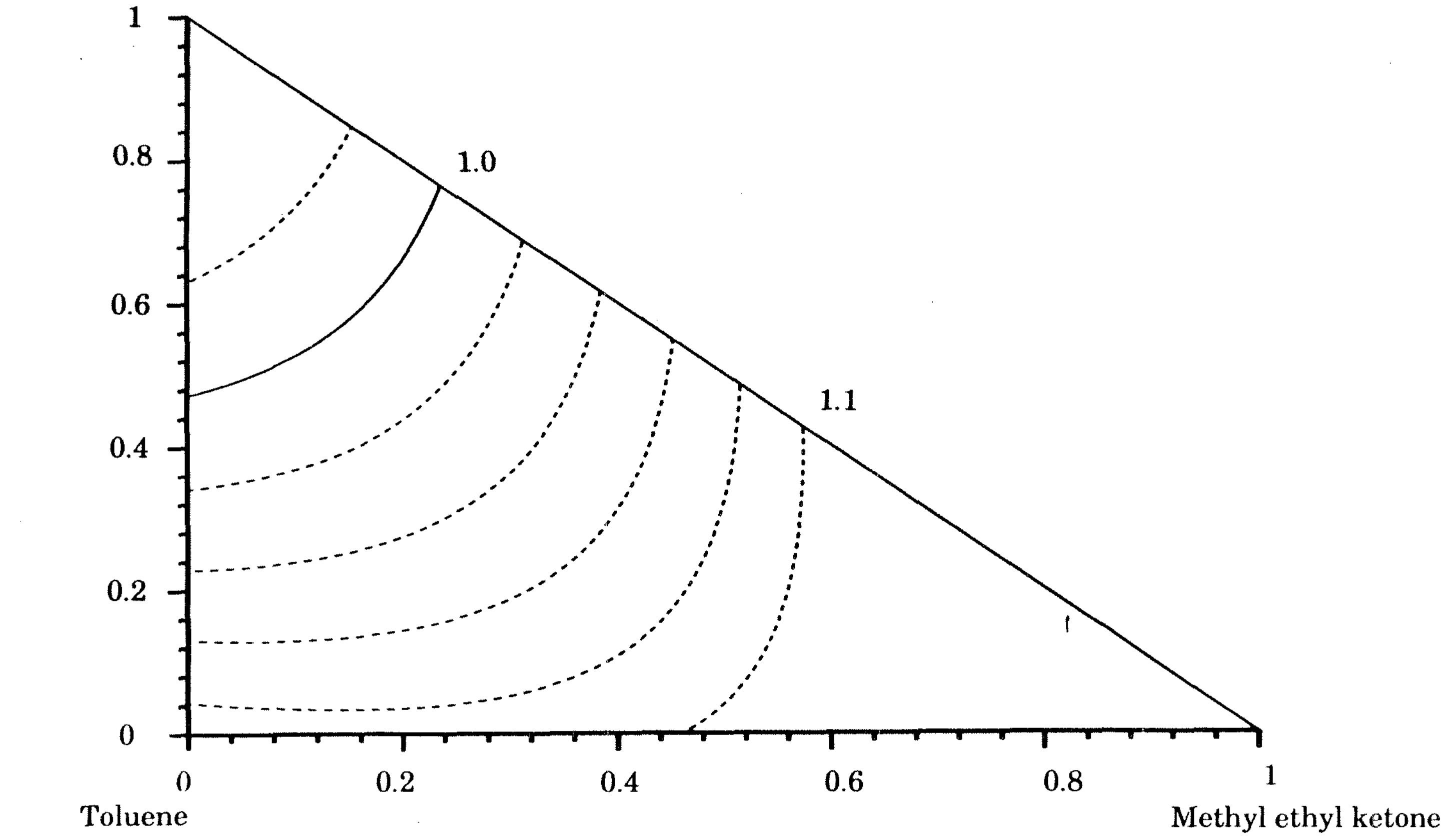


Fig. 4.36: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

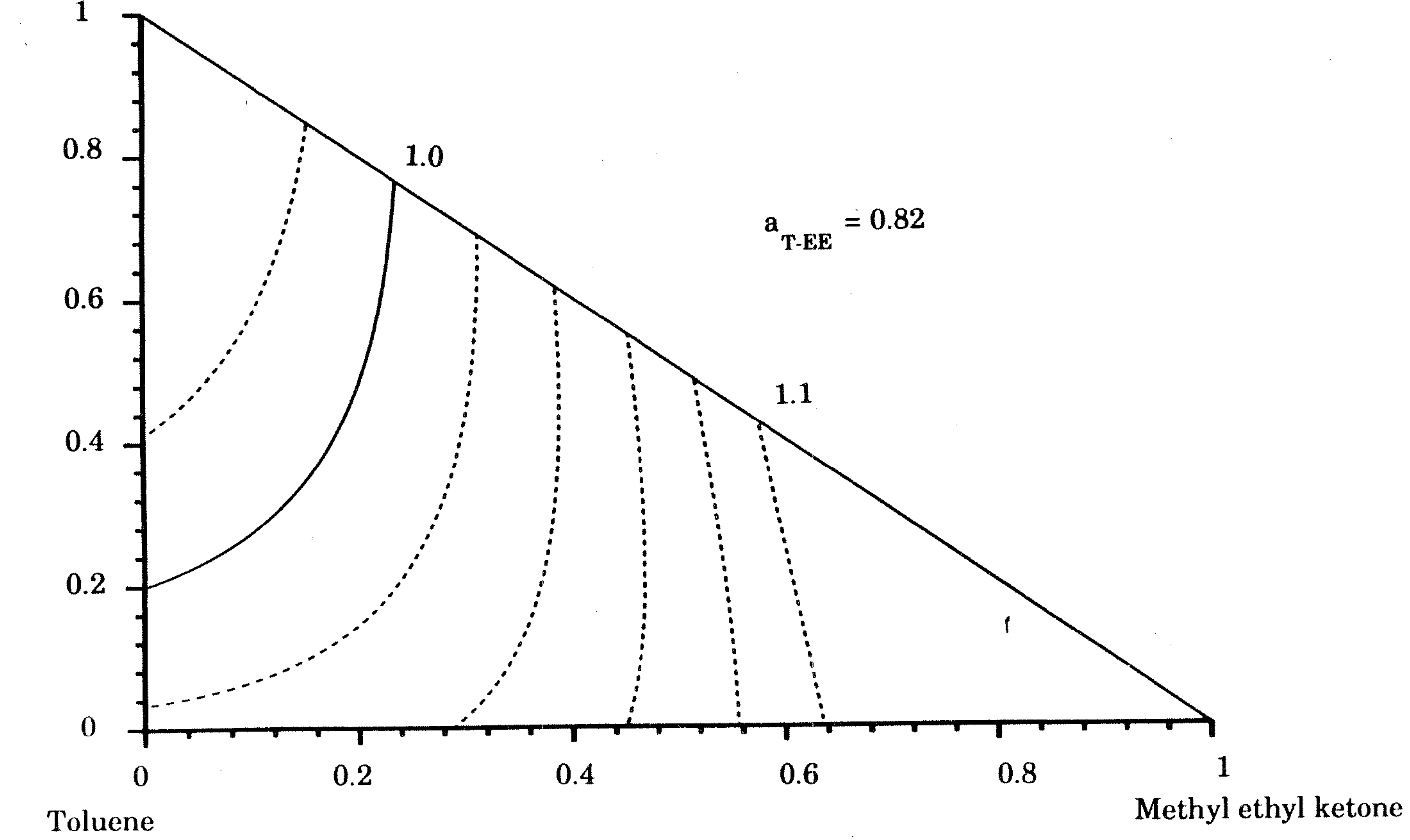


Fig. 4.37: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

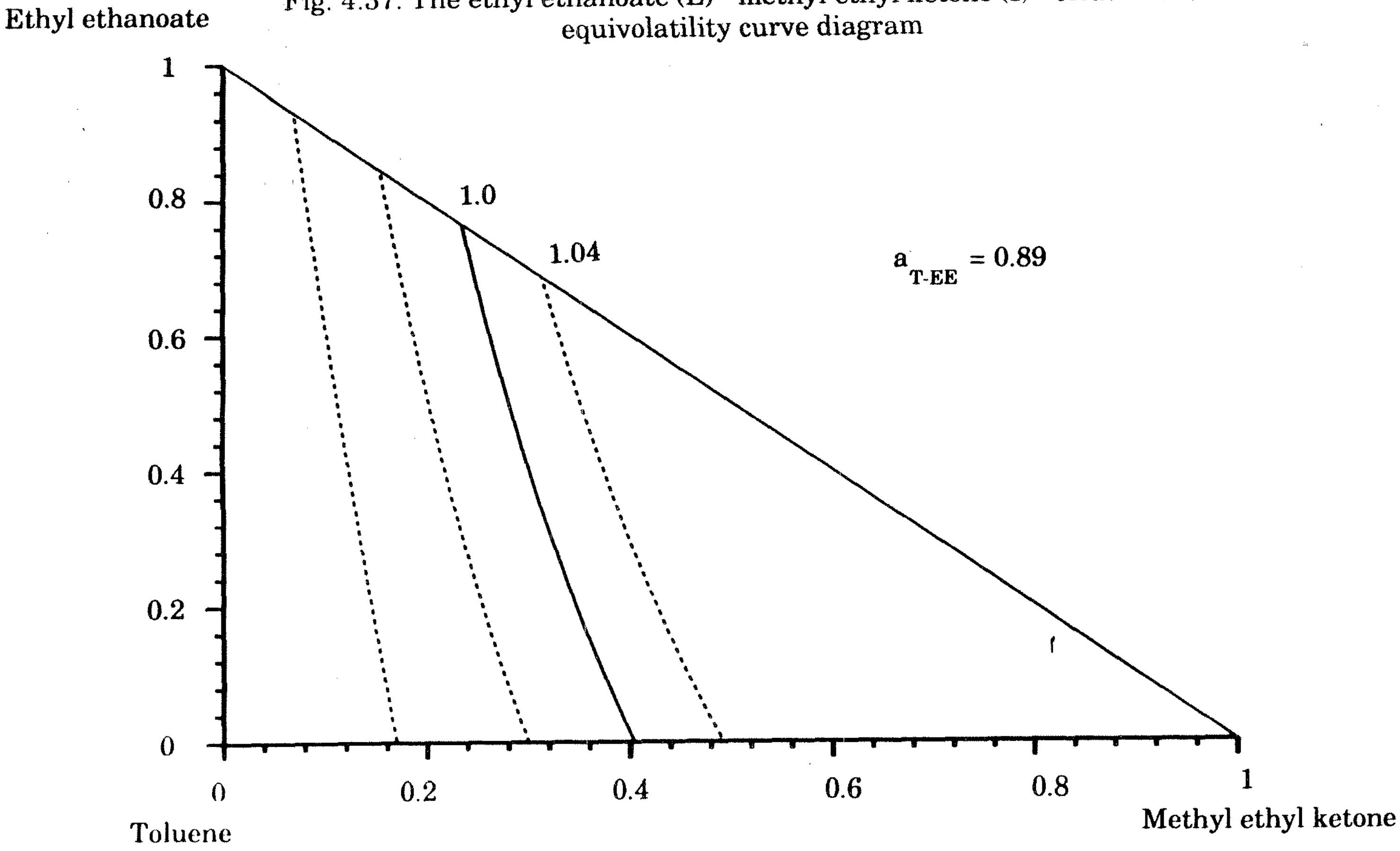


Fig. 4.38: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

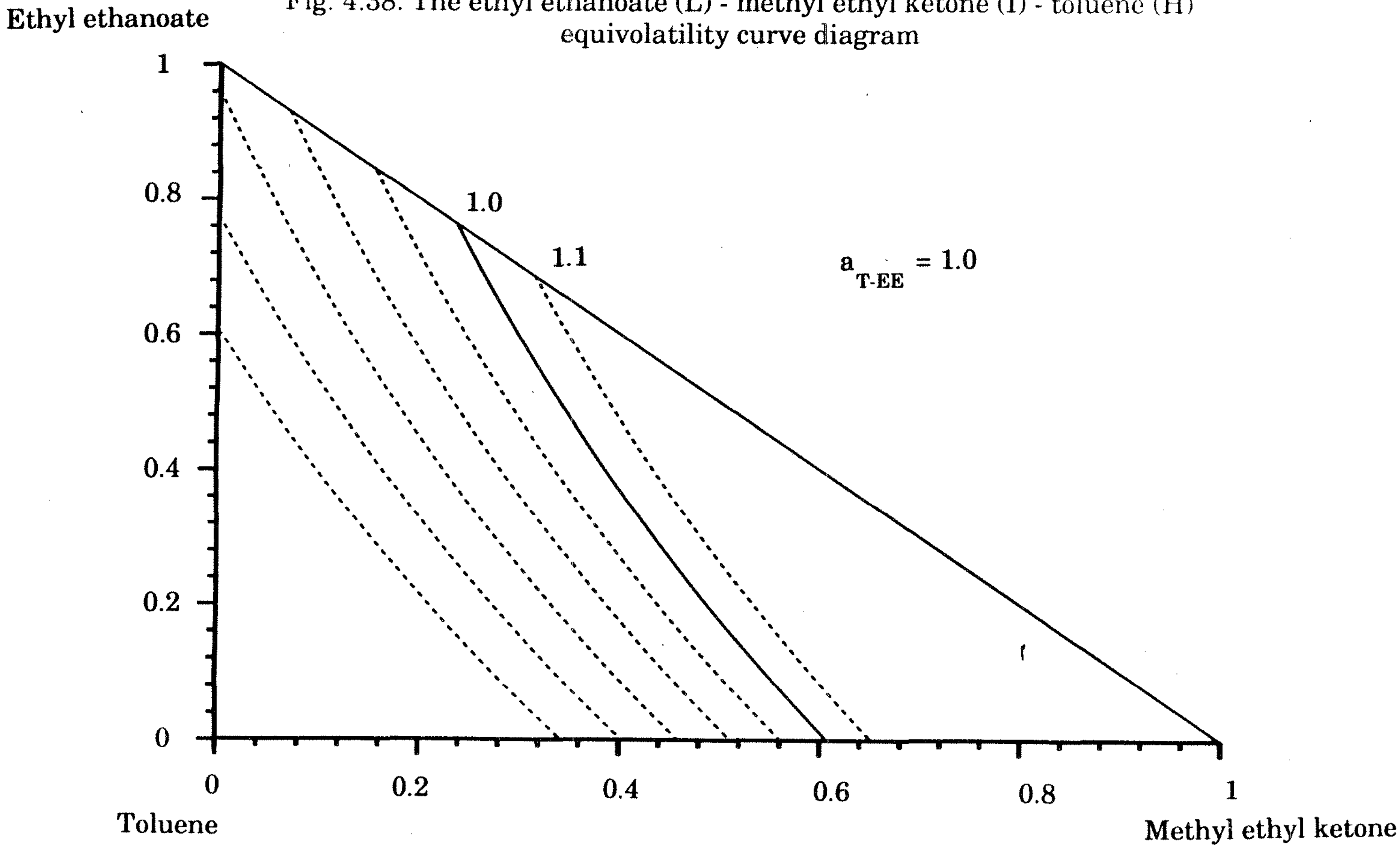
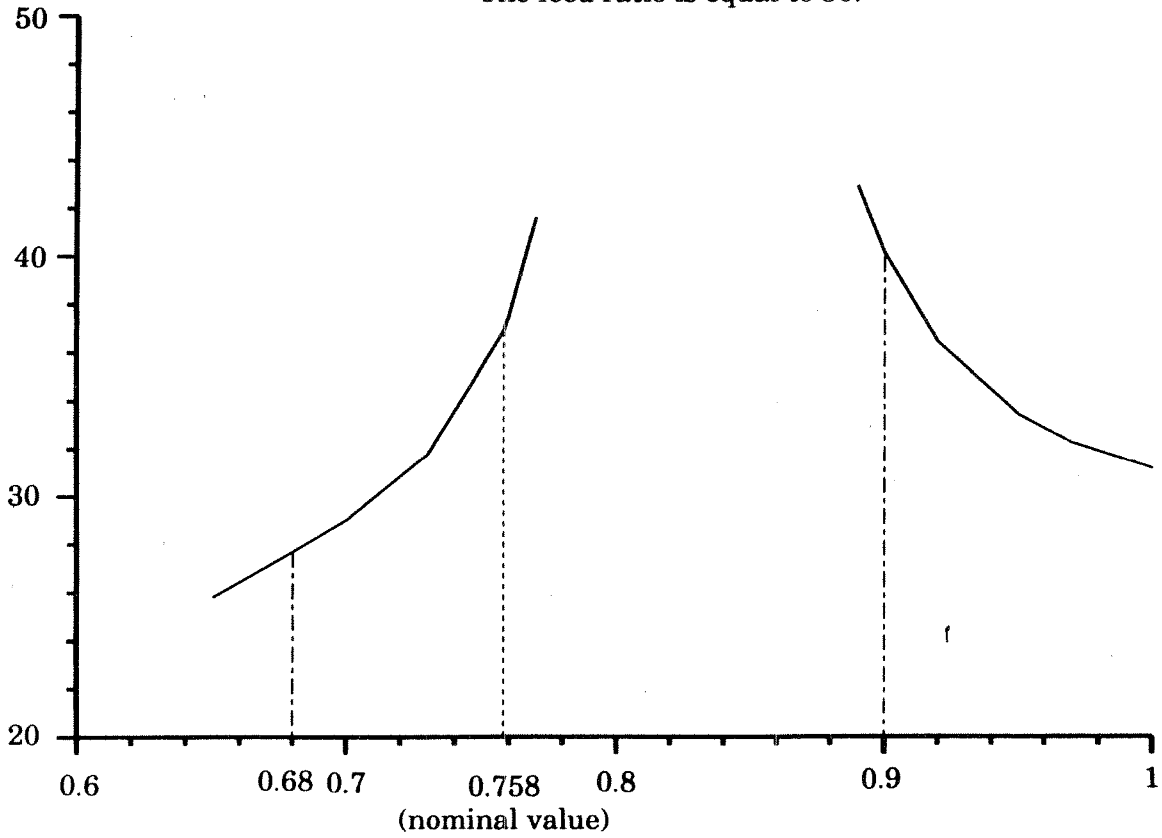


Fig. 4.39: Minimum reflux ratio for varying ethyl ethanoate-toluene Wilson parameters.
The feed ratio is equal to 50.



points of the minimum trade-off curves. This point is illustrated by figure 4.40 and figure 4.41 using the ethanol (I) - water (H) azeotrope and ethanol and acetone as light entrainers. Both entrainers enable the recovery of water as bottom product of the extractive column: The isovolatility curve of ethanol and water intersects the ethanol - entrainer edge in both cases. Methanol yields a lower x_E value than acetone; the comparison of the two minimum trade-off curves shows that the optimum feed ratio is lower when we use methanol than when we use acetone.

As in the case of heavy entrainers, the relative volatility of the two azeotropic constituents is the key factor determining the necessary minimum reflux ratio (unless the entrainer is very difficult to separate from one of the two azeotropic constituents). A high relative volatility implies an easy separation. Figure 4.42 and figure 4.43 show that we can achieve a much higher relative volatility between ethanol and water with methanol than with acetone; figure 4.40 confirms that the optimum minimum reflux ratio is much lower with methanol than with acetone.

As in the heavy entrainer case, the relative volatility of the two azeotropic components inside the composition triangle measures entrainer performance. In the case of light entrainers, the most difficult separation is performed in the top section of the column; without the entrainer presence, the component recovered in the bottom product would be more volatile than the other azeotropic component, and separation would stop. So good light entrainers should make the relative volatility of the two azeotropic constituents as high as possible in this section. If A is recovered at the bottom, the composition profile of the rectifying section is located close to the B - E edge. As in the heavy entrainer case, we expect the comparison of entrainers that send different azeotropic components to the top of the extractive column based on their equivolatility curve diagrams to be less meaningful and less reliable in practice than the comparison of entrainers that send the same azeotropic component to the top of the extractive column.

Fig. 4.40: The minimum trade-off curves of ethanol and water using acetone (1) and methanol (2) as entrainers

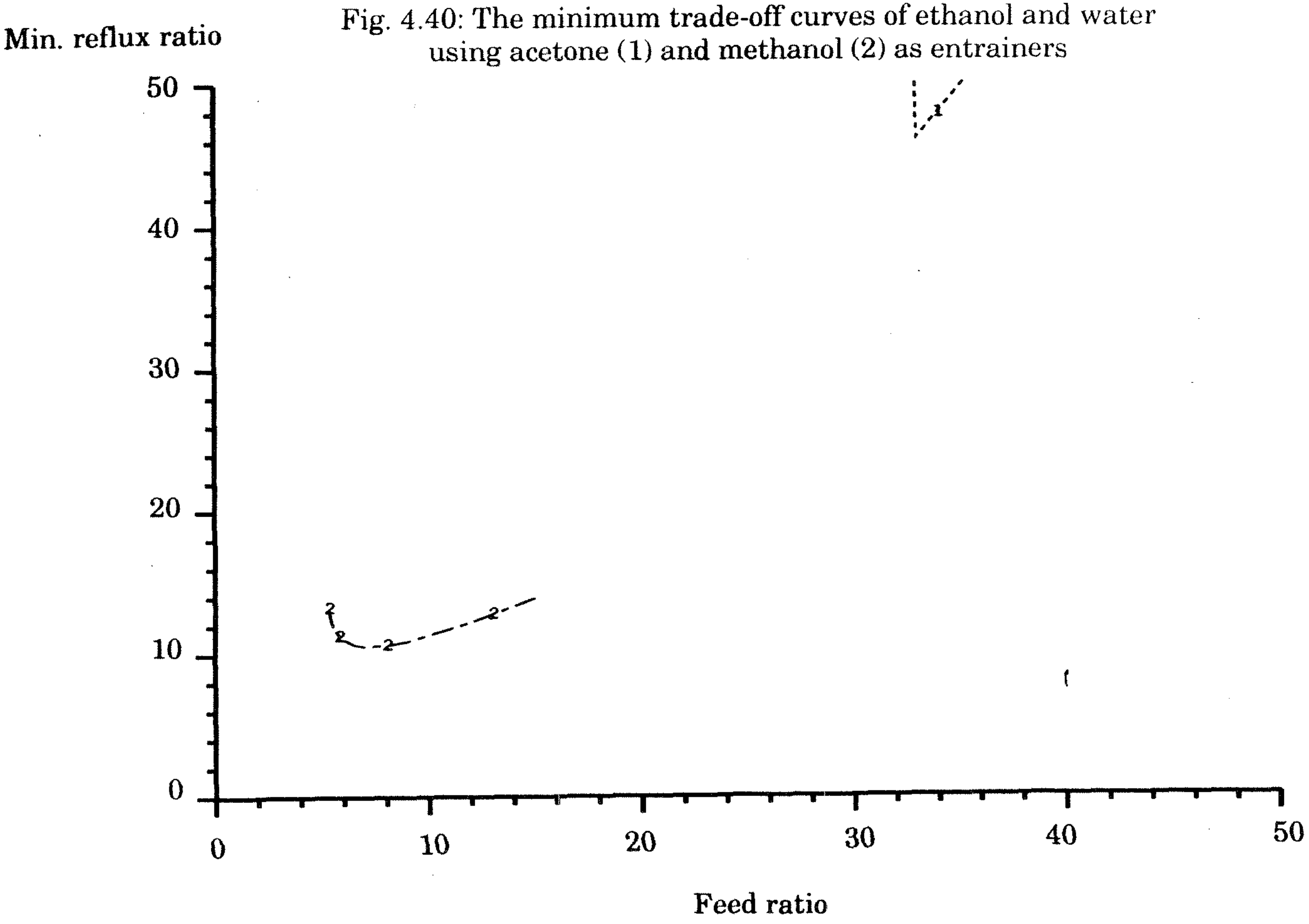


Fig. 4.41: The isovolatility curves of ethanol and water using acetone (1) and methanol (2) as entrainers

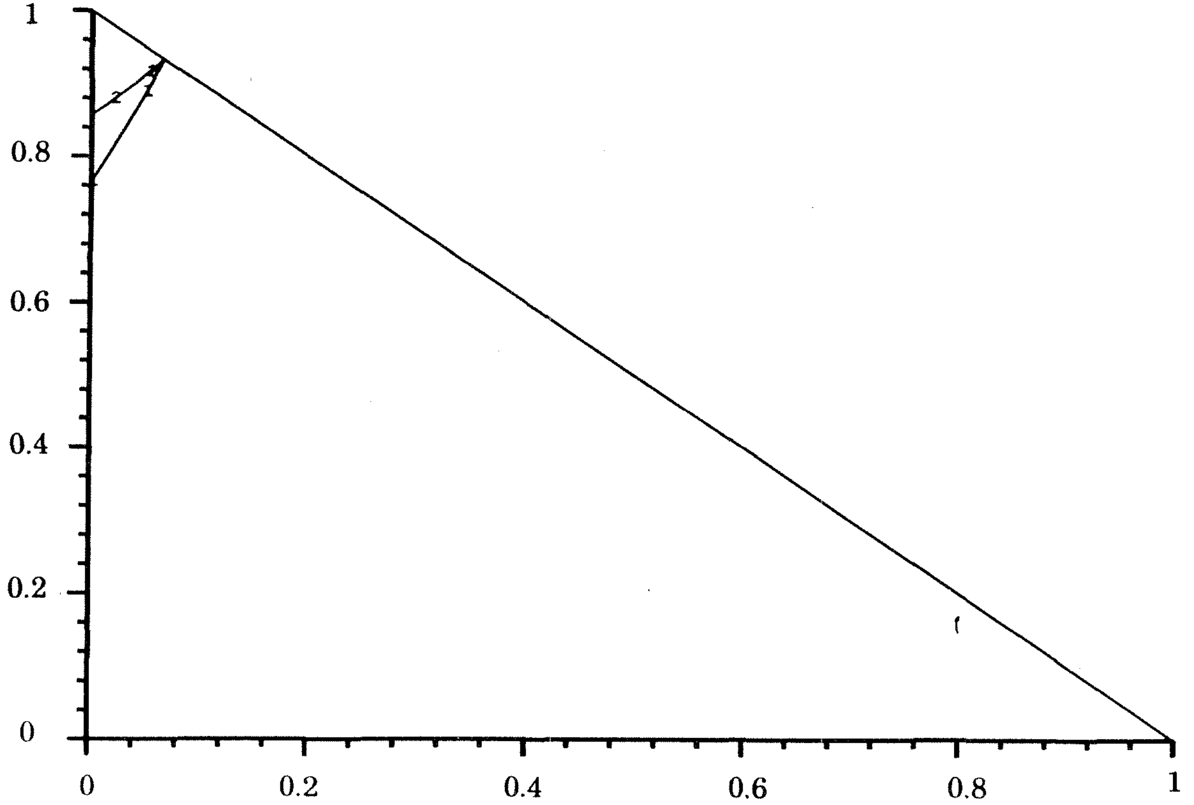
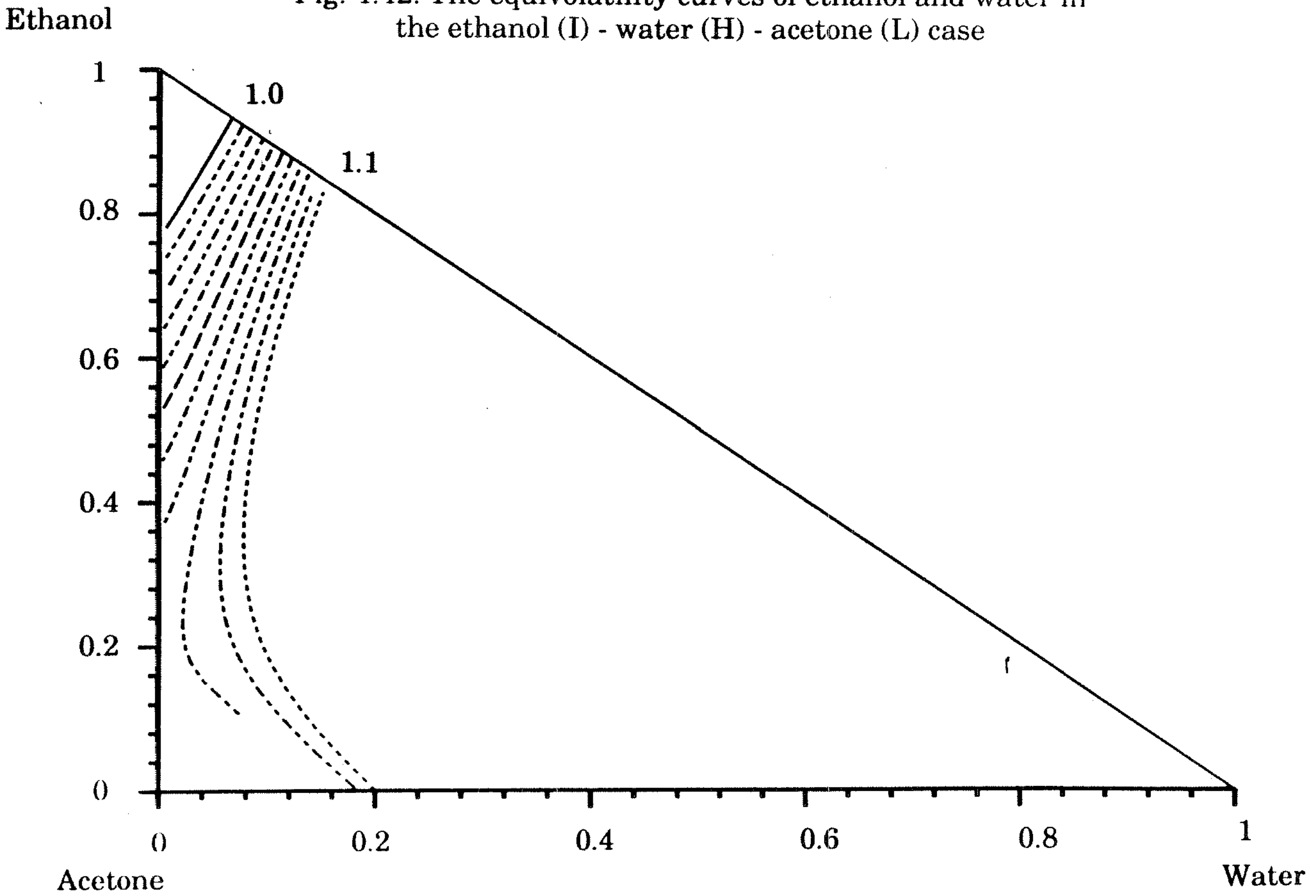


Fig. 4.42: The equivolatility curves of ethanol and water in the ethanol (I) - water (H) - acetone (L) case



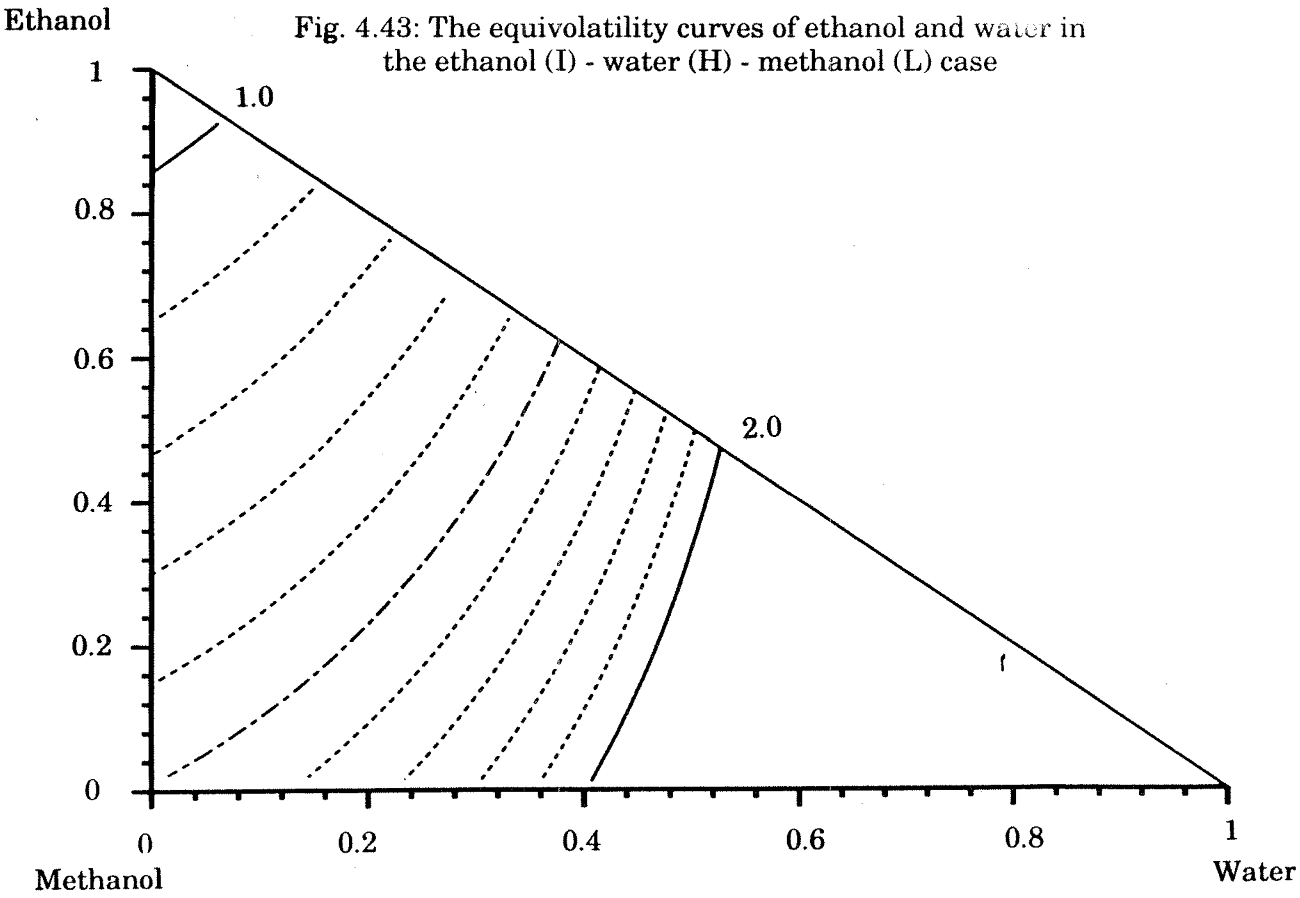


Fig. 4.43: The equivolatility curves of ethanol and water in the ethanol (I) - water (H) - methanol (L) case

Proposition 4.5 *We can compare light entrainers for a given binary azeotrope by examining the corresponding equivolatility curve diagrams:*

- *The lower x_E is, the lower the optimum feed ratio.*
- *The higher the relative volatility is, the lower the optimum minimum reflux ratio.*

Note that only entrainers that do not send the same azeotropic component to the bottom of the extractive column should be compared in this manner.

The value of x_E should be low for a good entrainer. In practice, we have found that separation again becomes very difficult when x_E exceeds 0.7. The following examples demonstrate this point:

- Acetone can act as a light entrainer for the isopropanol (I) - water (H) azeotrope by enabling the recovery of isopropanol as extractive distillation column bottom product. Because x_E is equal to 0.78 (figure 4.44), separation requires high feed ratios: We have found that separation can be achieved only when the feed ratio exceeds 30.
- The isovolatility curve of isopropanol and water in the isopropanol (I) - water (H) - methanol (L) system indicates that water can be recovered as extractive column bottom product. Yet, because x_E is equal to 0.82 (figure 4.45), we have been unable to synthesize a column performing this separation.

A good entrainer should also yield high relative volatilities between the two azeotropic components. In practice, we have observed that separation is difficult and requires high minimum reflux ratios when this relative volatility does not exceed 1.1 in the region that would contain the stripping section of the extractive column. This point is illustrated by figure 4.42 in the ethanol (I) - water (H) - acetone (L) case: The relative volatility of ethanol and water remains below 1.1 close to the ethanol - acetone edge.

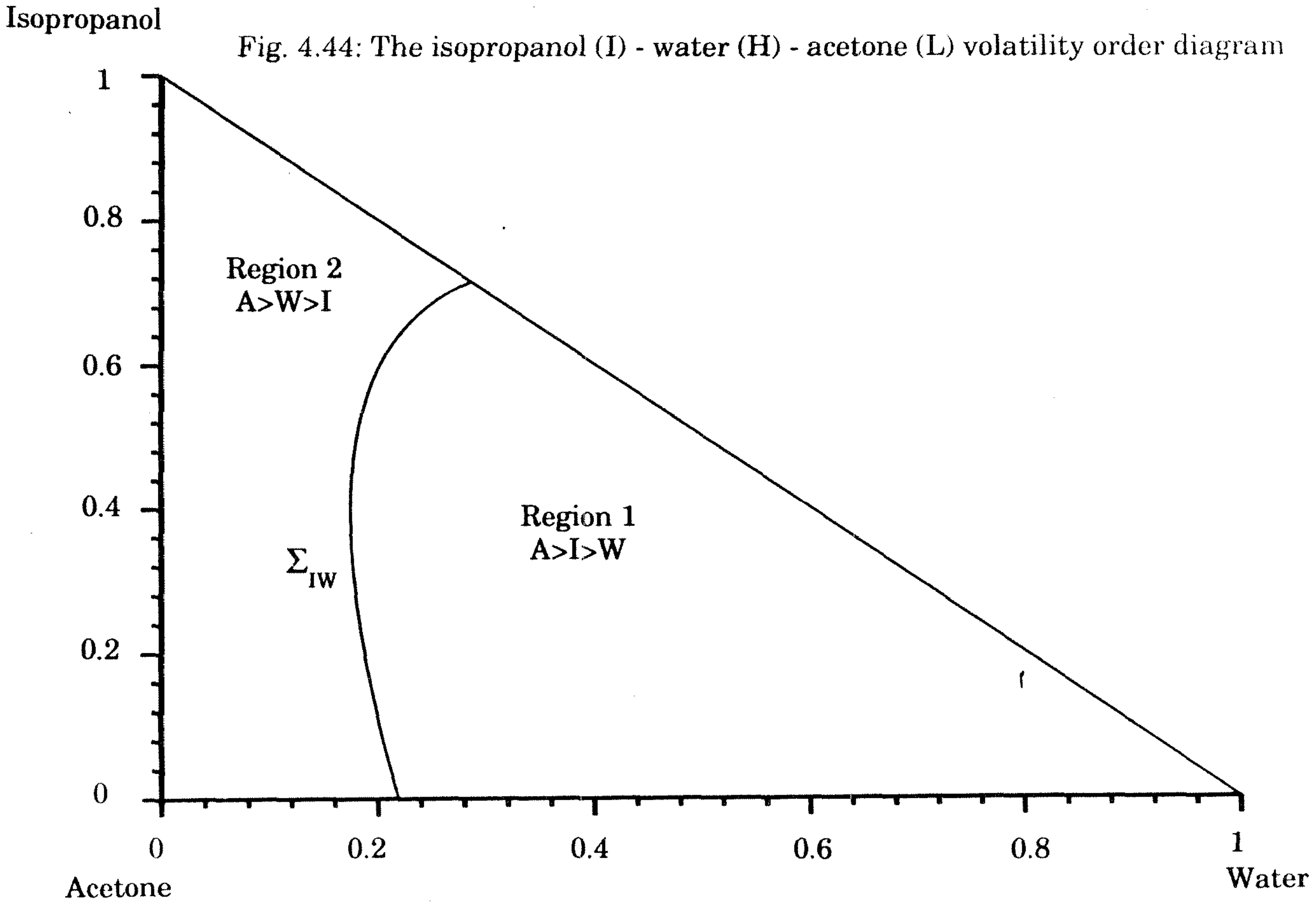


Fig. 4.44: The isopropanol (I) - water (H) - acetone (L) volatility order diagram

Fig. 4.45: The isopropanol (I) - water (H) - methanol (L) volatility order diagram

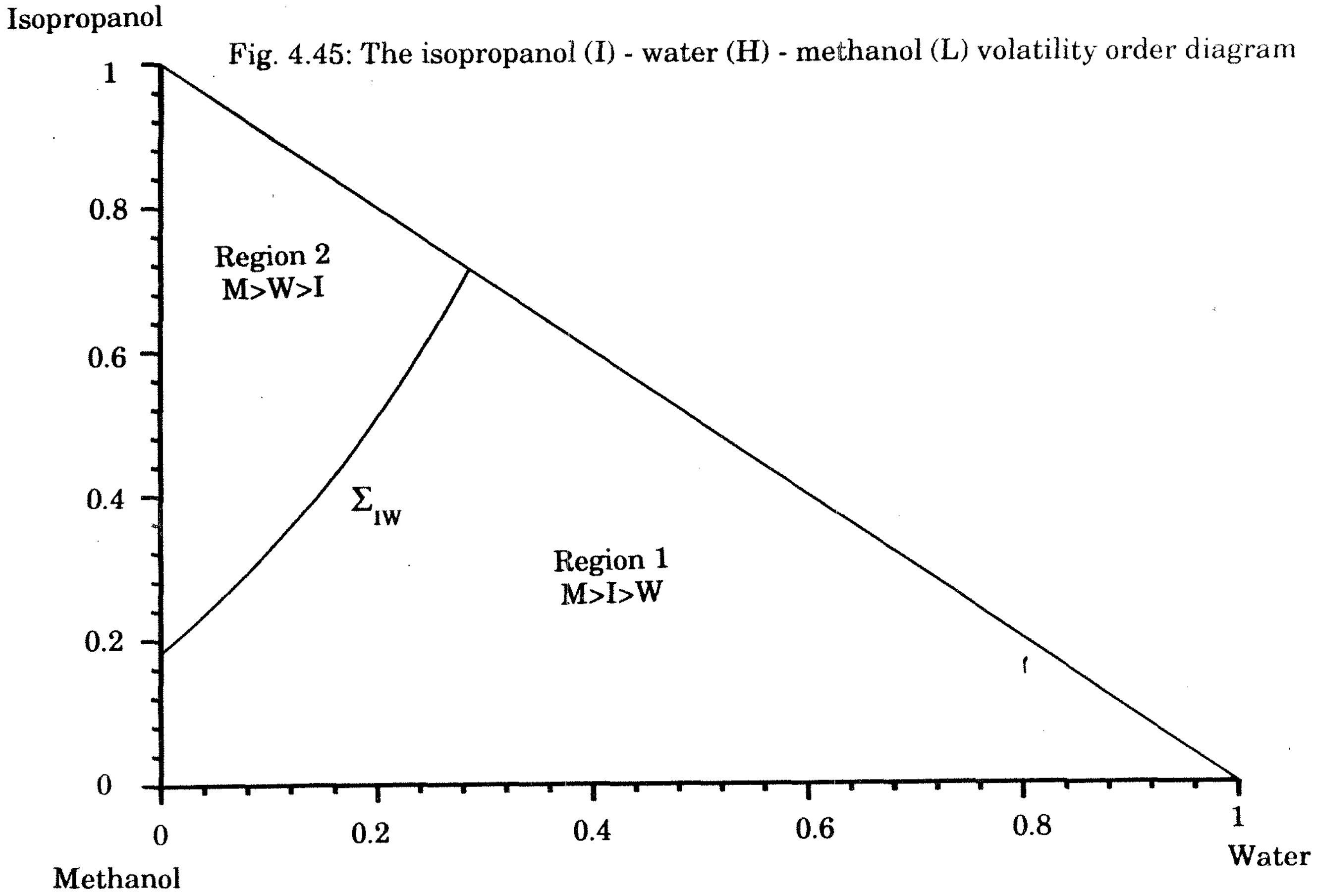


Figure 4.40 shows that separation is feasible, but requires a minimum reflux ratio in excess of 45.

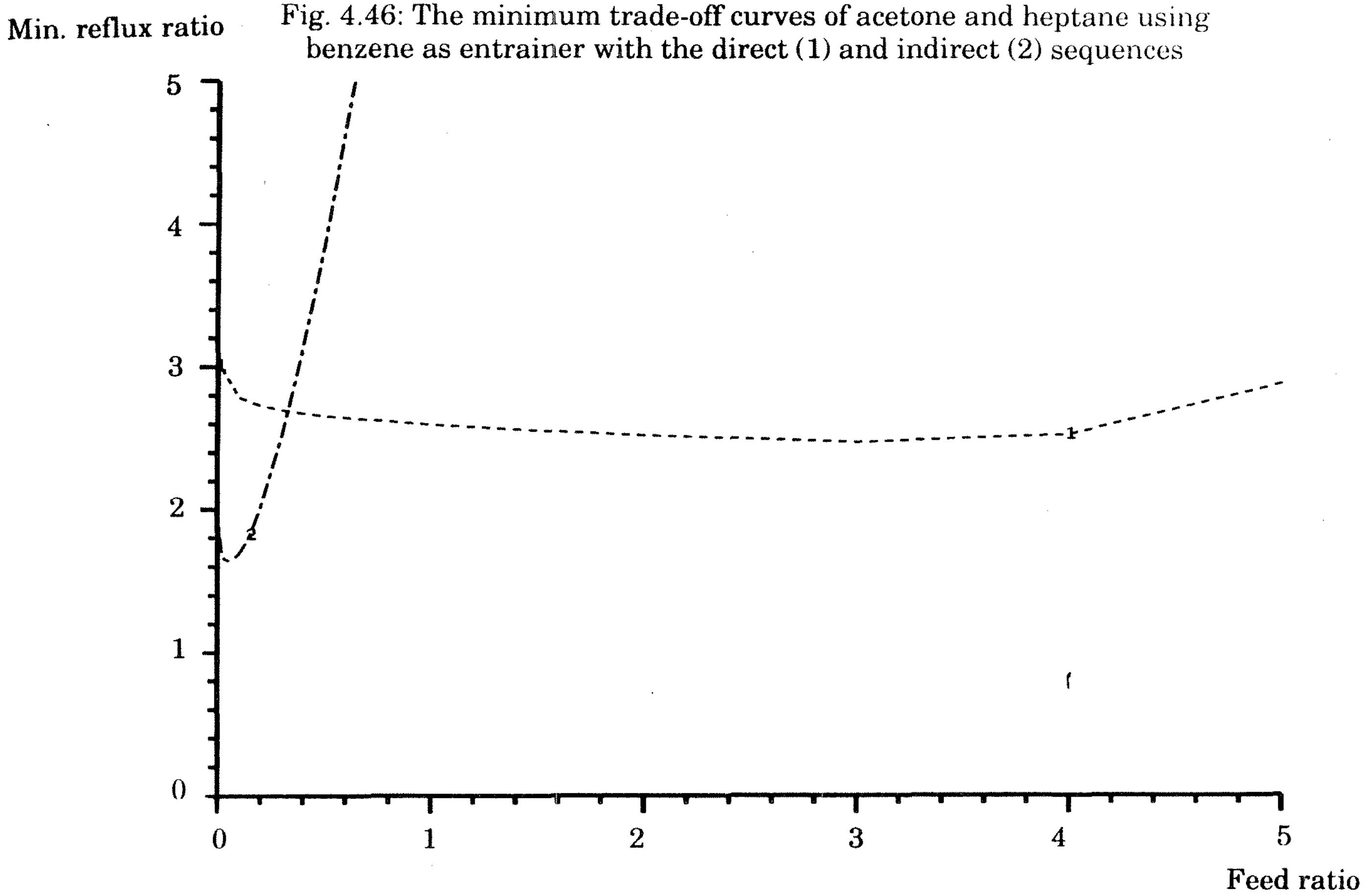
4.3.4 Intermediate entrainers

As in the case of heavy and light entrainers, we achieve separation only when the entrainer concentration inside the column is high enough to "override" the azeotropic behavior. But contrary to heavy and light entrainers, obtaining a significant entrainer concentration does not necessarily require large feed ratios. Because of the mixture volatility order, we can concentrate the entrainer inside the column by using a large number of trays and/or high reflux. There is no direct correlation between the isovolatility curve location and the x-coordinates of the minimum trade-off curve point. Contrary to the light and heavy entrainer case, there is no minimum feed ratio below which separation becomes infeasible; the minimum trade-off curve points abscissa span the whole positive real axis. Figure 4.46 illustrates this point for both the direct and indirect sequences, using acetone - heptane - benzene as an example.

When we use an intermediate entrainer, we essentially substitute for the separation of the two azeotropic constituents two separations: On one hand, we split the lighter azeotropic component and the entrainer, while on the other hand, we separate the entrainer from the heavier azeotropic component. These two separations are independent, and can be performed in any order (direct or indirect sequence) or in the same column at different levels. Therefore, the degree of difficulty of these two separations determines the efficiency of an intermediate entrainer. The relative volatility of the two azeotropic components becomes less important in this case than in the case of light or heavy entrainers, so we cannot use the equivolatility curve diagram of the two azeotropic components to measure the performances of intermediate entrainers.

Note that, because intermediate entrainers are far less common than light or heavy entrainers, obtaining an efficient comparison method for this type of entrainer is not

Fig. 4.46: The minimum trade-off curves of acetone and heptane using benzene as entrainer with the direct (1) and indirect (2) sequences



as important. In practice, we have only found one example of intermediate entrainer, namely the acetone (L) - heptane (H) - benzene (I) mixture, out of a total list of 250 ternary mixtures.

4.3.5 Overall comparison

We have shown in the previous section that the mechanisms by which heavy, intermediate and light entrainers lead to separability differ from one another. In particular, the corresponding separation sequences have different characteristics, different advantages and different bottlenecks. Some of these differences are:

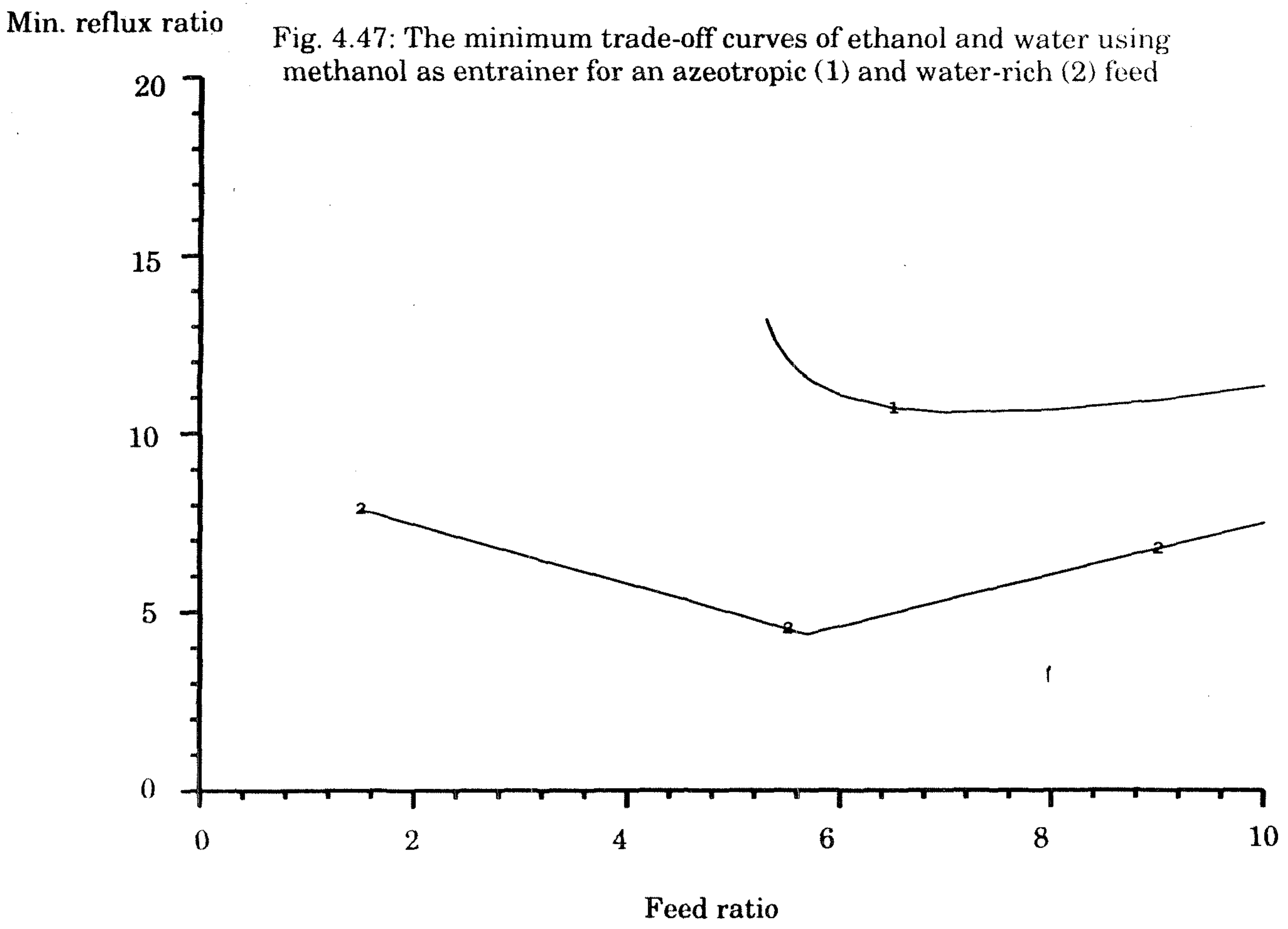
- Recycle purity: Knight & Doherty (1989) have shown that heavy entrainers require high purity entrainer recycles, because any impurity contained in this stream automatically contaminates one of the separation sequence products, namely the extractive column distillate. In the light entrainer case, we have shown (chapter 3) that separation does not require high purity entrainer recycles; for instance, in the ethanol (I) - water (H) - methanol (L) case, we can achieve separation with up to 5% ethanol in the methanol recycle stream. In the intermediate entrainer case, there is essentially no limitation; the entrainer recycle composition is then dictated by an optimization between the cost of recycling material and the cost of separation.

- Number of columns: If we use a heavy entrainer, separation requires at least two columns. In the ethanol (L) - water (I) - ethylene glycol (H) case, the economic optimization of the separation sequence shows that a preconcentrator lowers the sequence cost (Knight & Doherty 1989), because it eliminates much of the water before the extractive column, correspondingly lowering the load and energy requirements of this column. However, a preconcentrator would be detrimental if the crude feed contained more ethanol than the azeotrope: A preconcentrator would recover some ethanol as bottom product, but its top product has a higher water concentration and is therefore more difficult to enrich via extractive distillation than the crude feed. Given a crude A - B feed that contains less A than the A - B azeotrope, a preconcentrator should help separation in the case of heavy entrainers that send A to the top of the extractive column while separation should be easier without preconcentrator in the case of heavy entrainers that send B to the top of the extractive column.

We obtain a symmetric situation when we use a light entrainer. In that case, the entrainer is needed only in the rectifying section, where its presence makes the component recovered as bottom product the least volatile component. Being the most volatile component, the entrainer tends to naturally accumulate in the rectifying section, while its concentration in the stripping section is negligible. Therefore, the stripping section of the extractive column essentially performs a binary separation between the two azeotropic constituents. If the crude I - H feed is richer in I than the I - H azeotrope, a preconcentrator is useless for light entrainers that send I to the bottom of the extractive column, because the preconcentrator would perform the same duty as the extractive column stripping section. For instance, figure 4.47 shows that preconcentrating a water-rich feed in the ethanol (I) - water (H) - methanol (L) case makes the separation performed in the extractive column more difficult. However, a preconcentrator makes separation easier for entrainers that send H to the bottom of the extractive column.

We have already examined the case of intermediate entrainers. As we demonstrated in section 2, separation can be done with one or two columns. Since the direct sequence is similar to the heavy entrainer case, a preconcentrator may lower the total separation sequence cost. Intermediate entrainers provide much flexibility, and all combinations should be examined.

Fig. 4.47: The minimum trade-off curves of ethanol and water using methanol as entrainer for an azeotropic (1) and water-rich (2) feed



- Entrainer recovery column feed purity: Andersen *et al.* (1989) have shown that, in the heavy entrainer case, the extractive column bottom product must be very pure, because any impurity contained in this stream automatically contaminates the entrainer recovery distillate. We obtain a similar situation in the light entrainer case: Here, the component recovered as extractive column bottom product is the least volatile component throughout the entrainer recovery column, so it contaminates the bottom product of this column. We avoid this problem if we use an intermediate entrainer; in that case, the entrainer presence restores the natural volatility order based on boiling points. Any impurity in the entrainer recovery column feed goes to the entrainer recycle and does not contaminate the desired product.

- Relative volatility: We can usually achieve higher relative volatilities between the two azeotropic components with heavy entrainers than with light entrainers. However, such is not always the case: Both acetone and toluene can act as entrainers for the ethyl ethanoate - methyl ethyl ketone azeotrope. Acetone is a light entrainer, while toluene is a heavy entrainer. A comparison of figure 4.48 and figure 4.49 shows that we can obtain higher relative volatilities with acetone than with toluene. As we have seen in the previous subsection, the relative volatility of the two azeotropic components is not a good performance measure for intermediate entrainers.

- Utilities: When we use a heavy entrainer, the boiling points of the two bottom products are above the boiling points of both azeotropic components. Higher reboiler temperatures often translate into higher-pressure steam, which raises the separation sequence cost, as in the ethanol - water - ethylene glycol case (Knight & Doherty 1989). The condenser temperatures, on the other hand, are the boiling points of the two azeotropic constituents. When we use a light

Fig. 4.48: The ethyl ethanoate (L) - methyl ethyl ketone (I) - toluene (H) equivolatility curve diagram

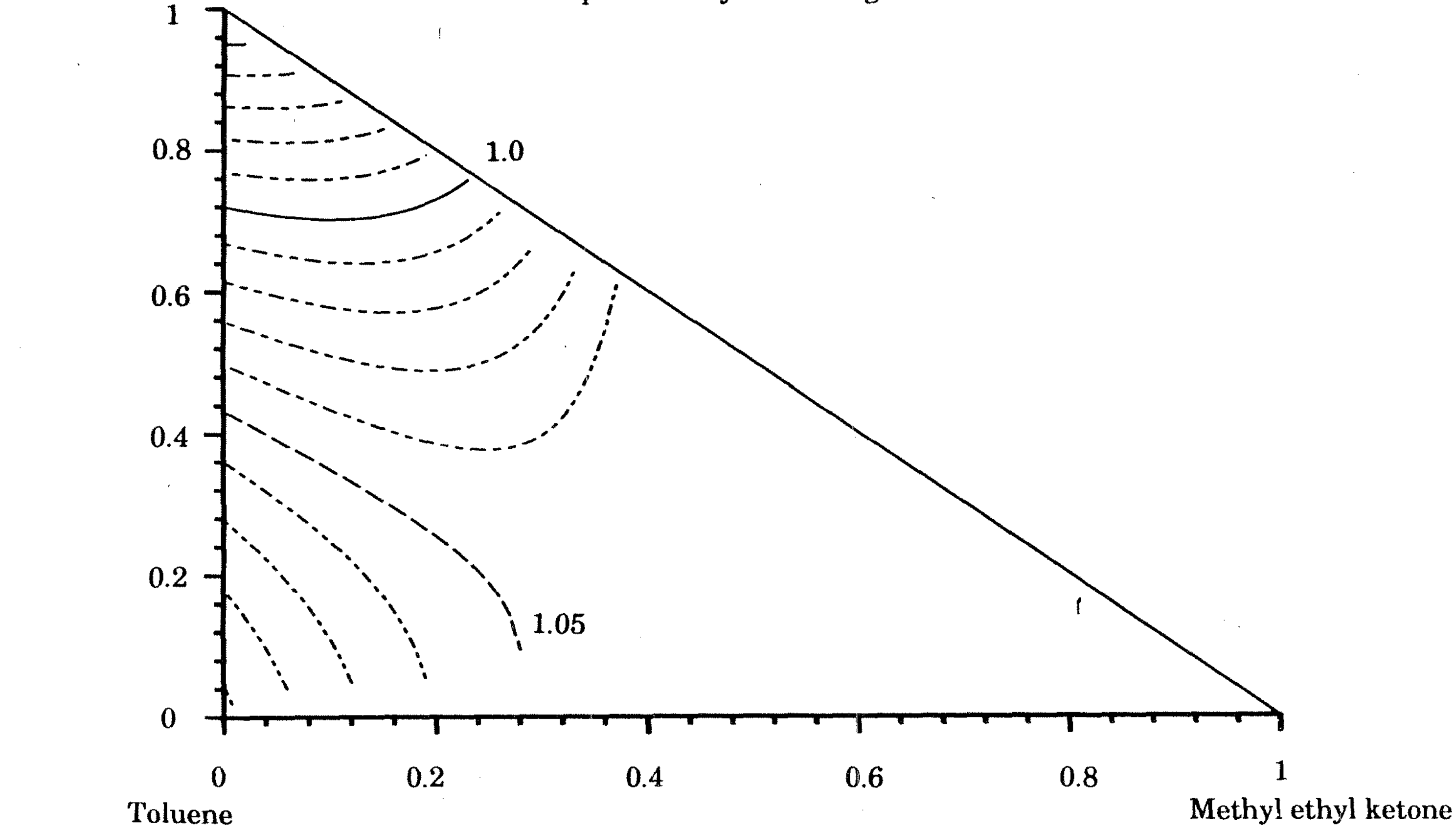
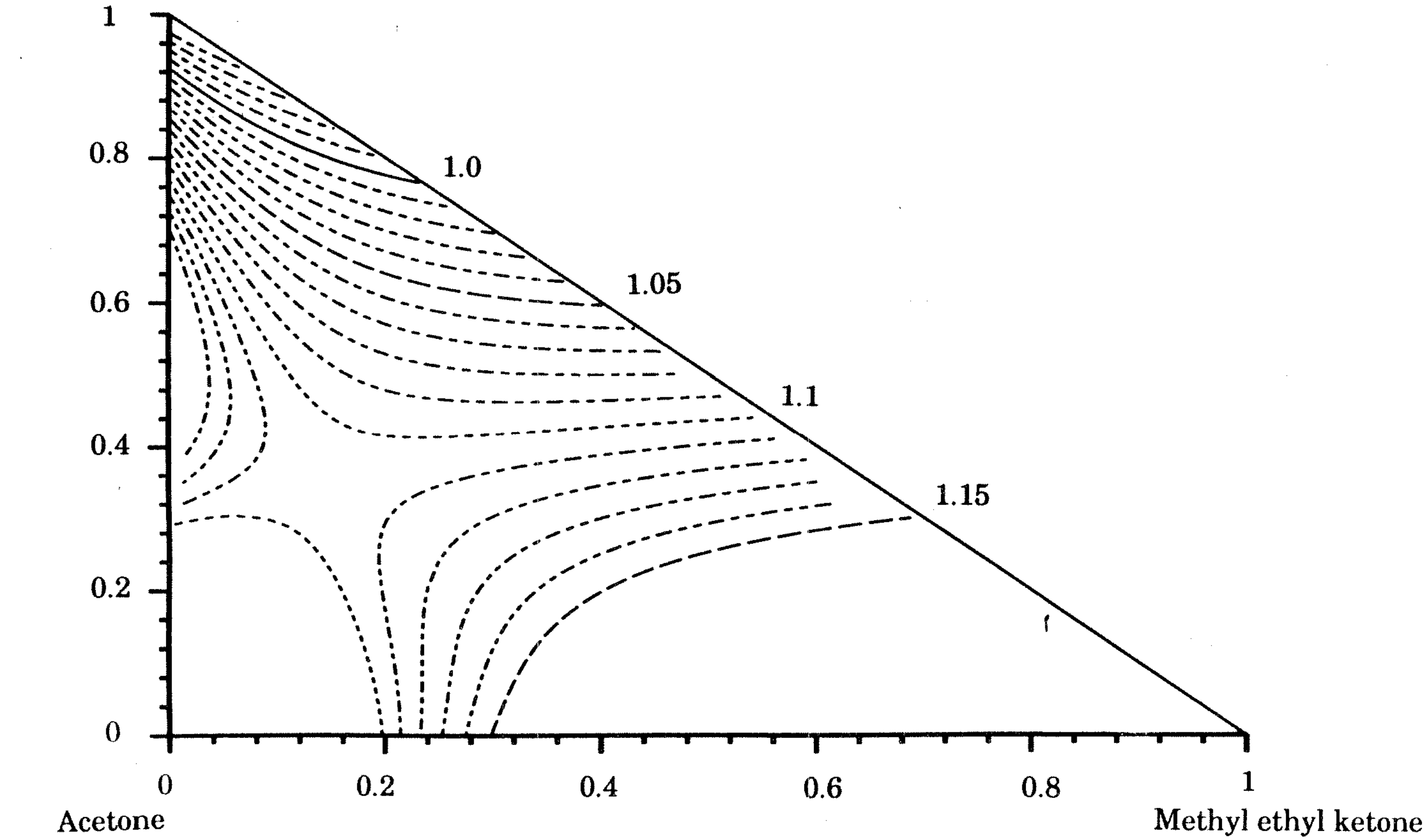


Fig. 4.49: The ethyl ethanoate (I) - methyl ethyl ketone (H) - acetone (L) equivolatility curve diagram



entrainer, the reboiler temperatures are given, but the condenser temperatures are then lowered; this may make chilled water necessary, leading to a cost increase. Note that we automatically avoid such problems with intermediate entrainers, since the temperature range is then fixed by the two azeotropic components.

By applying the previous entrainer comparison techniques to each class of entrainers, we can narrow down a long list of potential entrainers to a handful by keeping only the most promising candidates of each class. Because the corresponding separation sequences have very different characteristics, we cannot compare entrainers of different classes fairly without designing, costing and optimizing the feasible separation sequence(s) for each entrainer selected at the previous stage.

In summary, given a binary azeotrope that we want to separate into two pure products and a set of chemicals that we consider as candidate entrainers, we recommend the following entrainer selection procedure:

- Eliminate all chemicals that introduce additional azeotropes.
- By comparing the corresponding equivolatility curve diagrams, select the best (or best few) candidates in each of the following classes:
    - Heavy entrainers that send the lighter azeotropic component to the top of the extractive column.
    - Heavy entrainers that send the heavier azeotropic component to the top of the extractive column.
    - Light entrainers that send the lighter azeotropic component to the bottom of the extractive column.
    - Light entrainers that send the heavier azeotropic component to the bottom of the extractive column.

- Design, cost and optimize the feasible separation sequence(s) corresponding to the remaining candidate entrainers. The best entrainer yields the lowest total annualized cost.

Chapter 5

Conclusion

In chapter 1, we have shown that homogeneous azeotropic distillation can behave in a very unusual manner. Amongst its surprising features, we find that:

- One should sometimes decrease reflux to increase purity. In many cases, but not all, 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 are 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. Therefore, entrainer selection criteria which reject components when they do not make separation feasible at infinite reflux are fundamentally flawed. A critical review of four existing entrainer screening criteria reveals that they contradict each other and that none of them can be used reliably. Because they do not recognize the specificity of homogeneous azeotropic distillation, they exclude incorrectly a large number of entrainers. Briefly, they fail because:

- The rule of Benedict & Rubin does not take full advantage of the possibilities offered by homogeneous azeotropic distillation.
- Hoffman's rule eliminates components which do not make separation feasible at infinite reflux. As we have shown in this paper, separation may still be feasible at finite reflux.
- The rule of Doherty & Caldarola is based on the incorrect assumption that the feed and composition profile of a distillation column must lie in the same distillation region, regardless of operating conditions. Our experience shows that distillate and bottom can often lie in different distillation regions at finite reflux, because we can achieve more separation at finite reflux than at infinite reflux: Finite reflux composition profiles often cross distillation boundaries. The requirement that the feed must belong to the same region as the composition profile is superfluous, even at infinite reflux, because the composition profile can lie on the convex side of a distillation boundary while the feed lies on its concave side.
- The rule of Stichlmair, Fair and Bravo eliminates components which do not make separation feasible at infinite reflux. Again, separation may still be feasible at finite reflux.

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

Because separability at infinite reflux is not equivalent to separability at finite reflux, we must examine these two situations separately. In the second chapter, we have analyzed in detail the infinite reflux situation. In particular, we have answered the following question: Given a binary azeotrope which we want to split into two pure products, does a given candidate entrainer make this separation feasible in a sequence of columns (we consider here sequences of one, two and three columns) operated at total reflux?

We have obtained the following results:

- In some cases, a binary azeotrope may be separated into two pure products with only one distillation column. We present a necessary and sufficient condition which can identify such situations.

- Through a new screening procedure, we can determine whether a candidate entrainer makes the desired separation feasible in a sequence of two columns operated at infinite reflux. This method is illustrated with some case studies; it can predict unusual separation sequences (*cf.* the hexane - methanol - methyl acetate case).

- The procedure can be generalized to sequences which contain more than two columns. Such feature is required by some separations: For example, we see that methanol can be used as entrainer for the hexane - methyl acetate azeotrope if we use three columns, but not if we use only two. We show that separation can be very often performed in this manner.

- The separability conditions presented here have an important benefit: They directly indicate the flowsheet of the feasible separation sequence(s) and give approximate flow rates and compositions of each product stream.

- Although residue curve diagrams are very valuable tools for determining separability at infinite reflux, residue curve diagram classes cannot be used for that purpose (contrary to the assertion of Doherty & Caldarola). Mixtures which belong to the same class may yield different separability results: Some can be separated in a two-column sequence, others cannot.

Finally, we have examined two aspects of separability in practice:

- Distillation columns are operated at finite reflux; the situation obtained at finite reflux can differ significantly from the infinite reflux case. Finding a necessary and sufficient condition for separability at finite reflux is a task which remains to be accomplished. However, we have identified here two situations where separation is feasible at finite reflux but not at infinite reflux.

- The thermodynamic data used to represent the vapor-liquid equilibrium of the ternary mixture always contain some errors. This uncertainty can lead to incorrect conclusions regarding separability. Sensitivity to thermodynamic data uncertainty can be observed even in the case of heavy entrainers which add no azeotropes (the most common situation in industry). Finding a robust entrainer selection criterion remains an open issue at this point.

In chapter 3, we have analyzed in detail the mechanisms by which heavy, intermediate and light entrainers make separation feasible using the notions of equivolatility curves, isovolatility curves and local volatility order. This study shows that, in each case, we can determine the feasible separation sequence flowsheet once we have obtained the volatility order diagram of the ternary mixture azeotropic component #1 - azeotropic component #2 - entrainer:

- In the heavy entrainer case, we must examine the position of the isovolatility curve of the two azeotropic components A and B:

  - If this isovolatility curve intersects the A - E edge, we recover A as distillate of the extractive column while B is recovered as distillate of the entrainer recovery column.
  - If this isovolatility curve intersects the B - E edge, we recover B as distillate of the extractive column while A is recovered as distillate of the entrainer recovery column.

- In the light entrainer case, we must again examine the position of the isovolatility curve of the two azeotropic components A and B:
  - If this isovolatility curve intersects the A - E edge, we recover B as bottom product of the extractive column while A is recovered as bottom product of the entrainer recovery column.
  - If this isovolatility curve intersects the B - E edge, we recover A as bottom product of the extractive column while B is recovered as bottom product of the entrainer recovery column.
- In the intermediate entrainer case, separation can be achieved in three different ways:
  - We can use one column only.
  - We can use the direct sequence.
  - We can use the indirect sequence.

We have shown that the minimum trade-off curve (which represents minimum reflux ratio as a function of feed ratio) is a reliable measure of entrainer performance. A good entrainer should lead to both low feed ratios and a low reflux ratios. These two quantities can be related to the equivolatility curve diagram of the ternary mixture azeotropic component #1 - azeotropic component #2 - entrainer:

Chapter 6

Future Work

Throughout this work, we have examined the issue of separability, assuming a perfect knowledge of the mixture thermodynamics. Case studies indicate that homogeneous azeotropic distillation may be very sensitive to thermodynamic data uncertainty. By limiting our entrainer comparison (chapter 4) to entrainers that do not introduce new azeotropes, we partially avoid this difficulty. However, accurate thermodynamic data is difficult and expensive to obtain. In practice, thermodynamic data uncertainty is always present, so we need a method that accounts for such uncertainty. Important practical questions are:

- Will an entrainer that makes separation feasible for a given thermodynamic model still make separation feasible if we change the description of the vapor-liquid equilibrium data?
- In which cases do small changes in thermodynamic parameters change our conclusions on separability?
- In which cases is our entrainer comparison method sensitive to uncertainty? Does the result of a given comparison change significantly if we change the thermodynamic data description? If we change the thermodynamic parameters?

Another important issue is the issue of separability at finite reflux. We have shown here how we can determine separability at infinite reflux. But all physical columns

- In the heavy entrainer case, the location of the end point of the isovolatility curve of the two azeotropic components determines the optimum feed ratio, while the optimum minimum reflux ratio is correlated to the relative volatility between the two azeotropic constituents. We can compare heavy entrainers by examining the corresponding values of x_E (which we read directly from the equivolatility curve diagram) and the values of the relative volatility of the two azeotropic components in the region of the composition space where the extractive section composition profile would lie. In practice, we have found that separation becomes very difficult when the relative volatility of the two azeotropic components remains below 1.1 (because this leads to high reflux ratios) or when x_E exceeds 0.7 (because this implies high feed ratios). We have also found that, with these rules, we should only compare with one another entrainers which send the same azeotropic component to the top of the extractive column.

- We obtain a very similar situation in the light entrainer case. We can compare light entrainers for a given binary azeotropes by examining the values of x_E and the relative volatility of the two azeotropic components in the region of the composition triangle where the rectifying section composition profile would lie. Again, we have found that separation becomes very difficult when x_E exceeds 0.7 or when the considered relative volatility remains below 1.1. Again, we should only compare with one another entrainers which send the same azeotropic component to the bottom of the extractive column.

- Intermediate entrainers lead to a very different situation. Because we can increase the concentration of an intermediate entrainer without increasing the feed ratio (by increasing the column height), we cannot compare intermediate entrainers by examining their corresponding volatility order diagrams. Because intermediate entrainers are quite rare, this is not a major limitation.

Finally, our detailed analysis of the homogeneous azeotropic separation sequences obtained with heavy, intermediate and light entrainers has shown that they have very different strengths and weaknesses, and that we cannot directly compare entrainers of different classes. Therefore, we should compare candidate entrainers of the same class with one another using equivolatility curve diagrams, then compare the few best candidates of each class with one another by designing, costing and optimizing the corresponding feasible sequences.

operate at finite reflux. We have shown that we can often achieve more separation at finite reflux than at infinite reflux. Determining how much more separation we can perform at finite reflux than at infinite reflux would be very valuable for practitioners. Such a finite-reflux separability criterion should also be robust to thermodynamic data uncertainty.

Finally, the scope of this work has been consistently restricted to ternary mixtures. The ideal situation assumed here, where we have to separate a binary azeotrope into two pure components, is rather uncommon; the more common situation involves multicomponent, multiazeotrope mixtures. The problem of finding the optimal way of separating a multicomponent mixture into pure components is essentially solved in the ideal case. However, the analogous problem in the azeotropic case is far from a general solution.

Bibliography

Acrivos, A., N. R. Amundson, 1955. On the Steady State Fractionation of Multicomponent and Complex Mixtures in an ideal Cascade. 5. The extension to Packed Columns, *Chem. Eng. Science*, **4**, pp. 206-208.

Andersen, H. W., L. Laroche, M. Morari, 1989. Effect of Design on the Control of Homogeneous Azeotropic Distillation, AIChE Annual Meeting, San Francisco.

Andersen, H. W., L. Laroche, A. Skjellum, M. Morari, 1989. Distillation Column Simulation, Program Documentation, Version 0.3, 3/20/89, Chem. Eng. Dept. 210-41, Caltech.

Asatani, H., W. Hayduk, 1983. Solubilities of Gaseous Butadiene and Butene-2 in Possible Extractive Distillation Solvents, *Can. J. Chem. Eng.*, **61**(2), pp. 227-232.

Bannister, R. R., E. Buck, 1969. Butadiene Recovery via Extractive Distillation, *Chem. Eng. Prog.*, **65**(8), pp. 65-68.

Bastos, J. C., M. E. Soares, A. G. Augusto, 1985. Selection of Solvents for Extractive Distillation. A Data Bank for Activity Coefficients at Infinite Dilution, *Ind. Eng. Chem. Process Des. Dev.*, **24**(2), pp. 420-426.

Benedict, M., L. C. Rubin, 1945. Extractive and Azeotropic Distillation. 1. Theoretical Aspects, *Trans. AIChE*, **41**, pp. 353-370.

Berg, L., 1969. Azeotropic and Extractive Distillation - Selecting the Agent for Distillation, *Chem. Eng. Prog.*, **65**(9), pp. 52-57.

Berg, L., 1983. Separation of Benzene and Toluene from Close Boiling Nonaromatic Hydrocarbons by Extractive Distillation, *AIChE Journal*, **29**(6), pp. 961-966.

Berg, L., A. Yeh, 1985. The Unusual Behaviour of Extractive Distillation - Reversing the Volatility of the Acetone - Isopropyl Ether System. *AIChE Journal*, **31**(3), pp. 504-506.

Black, C., 1980. Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol, *Chem. Eng. Prog.*, **76**, pp. 78-85.

Black, C., D. E. Ditsler, 1972. Azeotropic and Extractive Distillation, Advances in Chemistry Series 115; R. F. Gould, Ed.; American Chemistry Society, Washington, D. C., pp. 1-15.

Buell, C. K., R. G. Boatright, 1947. Furfural Extractive Distillation for Separating and Purification of C_4 Hydrocarbons, *Ind. Eng. Chem.*, **39**, pp. 695-705.

Doherty, M. F., G. A. Caldarola, 1985. Design and Synthesis of Homogeneous Azeotropic Distillation. 3. The Sequencing of Columns for Azeotropic and Extractive Distillation, *Ind. Eng. Chem. Fundam.*, **24**, pp. 474-485.

Doherty, M. F., J. D. Perkins, 1978a. On the Dynamics of Distillation Processes. 1. The Simple Distillation of Multicomponent Non-reacting, Homogeneous Liquid Mixtures, *Chem. Eng. Science*,

Doherty, M. F., J. D. Perkins, 1978b. On the Dynamics of Distillation Processes. 2. The Simple Distillation of Model Solutions, *Chem. Eng. Science*, **33**, pp. 281-301.

Doherty, M. F., J. D. Perkins, 1979. On the Dynamics of Distillation Processes. 3. The Topological Structure of Ternary Residue Curve Maps, *Chem. Eng. Science*, **34**, pp. 1401-1414.

Douglas, J. M., 1988. Conceptual Design of Chemical Processes, McGraw-Hill, New York.

Enomoto, M., 1971. Extractive Distillation Solvents for the Separation of Isoprene, *Bull. Jap. Petrol. Inst.*, **13**(2), pp. 169-176.

Henley, E. J., J. D. Seader, 1981. Equilibrium-Stage Separation Operations in Chemical Engineering, Wiley, New York.

Hess, H. V. *et al.*, 1962. Phase Equilibrium, em AIChE Symp. Ser. 2, pp. 72-79.

Hoffman, E. J., 1964. Azeotropic and Extractive Distillation, Interscience, New York.

Hopper, M. J.(ed.), 1981. Harwell Subroutine Library, United Kingdom Atomic Energy Authority, AERE, Harwell, November 1981.

Hunek, J., S. Gal, E. Posel, P. Glavič, 1989. Separation of an Azeotropic Mixture by Reverse Extractive Distillation, *AIChE Journal*, **35**(7), pp. 1207-1210.

Jacobsen, E. W., L. Laroche, H. W. Andersen, M. Morari, 1990. Robust Control of Homogeneous Azeotropic Distillation, AIChE Annual Meeting, Chicago.

Knapp, J. P., M. F. Doherty, 1990. Thermal Integration of Homogeneous Azeotropic Distillation Sequences, *AIChE Journal*, **36**(7), pp. 969-984.

Knight, J. R., M. F. Doherty, 1986. Design and Synthesis of Homogeneous Azeotropic Distillation. 5. Columns with Nonnegligible Heat Effects, *Ind. Eng. Chem. Fundam.*, **25**, pp. 279-289.

Knight, J. R., M. F. Doherty, 1989. Optimal Design and Synthesis of Homogeneous Azeotropic Distillation Sequences, *Ind. Eng. Chem. Res.*, **28**, pp. 564-572.

Kojima, K., K. Ochi, 1974. Screening of Addition Agents for Extractive Distillation from Bubble Point Data, *J. Chem. Eng. Japan*, **7**(2), pp. 71-75.

Kovack III, J. W., W. S. Seider, 1987. Heterogeneous Azeotropic Distillation: Experimental and Simulation Results, *AIChE Journal*, **33**(8), pp. 1300-1314.

Laroche, L., N. Bekiaris, H. W. Andersen, M. Morari, 1990a. The Curious Behaviour of Homogeneous Azeotropic Distillation - Implications for Entrainer Selection, *submitted to the AIChE Journal.*

Laroche, L., H. W. Andersen, M. Morari, 1990b. Homogeneous Azeotropic Distillation: Separability and Flowsheet Synthesis, to be submitted to *Ind. Eng. Chem. Fundam.*

Laroche, L., H. W. Andersen, M. Morari, 1990c. Homogeneous Azeotropic Distillation: Comparing Entrainers, to be submitted to the *Can. J. Chem. Eng.*

Lee, F. M., R. H. Pahl, 1985, Solvent Screening Study and Conceptual Extractive Distillation Process to Produce Anhydrous Ethanol from Fermentation Broth, *Ind. Eng. Chem. Process Des. Dev.*, **24**(1), pp. 168-172.

Levy, S. G., D. B. Van Dongen, M. F. Doherty, 1985. Design and Synthesis of Homogeneous Azeotropic Distillation. 2. Minimum Reflux Calculations for Nonideal and Azeotropic Columns, *Ind. Eng. Chem. Fundam.*, **24**, pp. 463-474.

Levy, S. G., M. F. Doherty, 1986. Design and Synthesis of Homogeneous Azeotropic Distillation. 4. Minimum Reflux Calculations for Multiple-Feed Columns, *Ind. Eng. Chem. Fundam.*, **25**, pp. 269-279.

Murti, P. S., M. Van Winkle, 1957. Vapor-Liquid Equilibria and Heat of Mixing: n-Octane-Ethylbenzene-Cellosolve System, *AIChE Journal*, **3**, pp. 517-522.

Prabhu, P. S., M. Van Winkle, 1963. Effect of Polar Components on the Relative Volatility of the Binary System n-Hexane-Benzene *J. Chem. Eng. Data*, **8**, pp. 210-214.

Qozati, A., M. J. Van Winkle, 1960. Vapor-Liquid Equilibria for Ethylbenzene, Ethylcyclohexane, and Hexylene Glycol, *J. Chem. Eng. Data*, **5**, pp. 269-271.

Scheibel, E. G.,1948. Principles of Extractive Distillation, *Chem. Eng. Prog.*, **44**, pp. 927-931.

Shinskey, F. G., 1984. Distillation Control for Productivity and Energy Conservation, McGraw-Hill, New York.

Stephenson, R. W., M. Van Winkle, 1962. Modification of Relative Volatilities by Addition of Solvent, *J. Chem. Eng. Data*, **7**, pp. 510-516.

Stichlmair, J., J. R. Fair, J. L. Bravo, 1989. Separation of Azeotropic Mixtures via Enhanced Distillation, *Chem. Eng. Prog.*, **85**, pp. 63-69.

Tassios, D. P., 1970. GLC Screens Extractive Solvent, *Hydrocarbon Process. Petrol. Refiner*, **49**(7), pp. 114-118.

Tassios, D. P., 1972a. Infinite Dilution Relative Volatilities Through Gas-Liquid Chromatography, *Ind. Eng. Chem. Process Des. Dev.*, **11**, pp. 43-46.

Tassios, D. P., 1972b. Rapid Screening of Extractive Distillation Solvents, Advances in Chemistry Series 115; R. F. Gould, Ed.; American Chemistry Society, Washington, D. C., pp. 46-63.

Van Dongen, D. B., 1982. Distillation of Azeotropic Mixtures. The Application of Simple-distillation Theory to the Design of Continuous Processes, Ph. D. Dissertation, University of Massachusetts, Amherst.

Van Dongen, D. B., M. F. Doherty, 1984. On the Dynamics of Distillation Processes. 5. The Topology of the Boiling Temperature Surface and its Relation to Azeotropic Distillation, *Chem. Eng. Science*, **39**(5), pp. 883-892.

Van Dongen, D. B., M. F. Doherty, 1985. Design and Synthesis of Homogeneous Azeotropic Distillation. 1. Problem Formulation for a Single Column, *Ind. Eng. Chem. Fundam.*, **24**, pp. 454-463.

Van Winkle, M., 1976. Distillation, McGraw-Hill, New York.

Wade, J. C., Z. L. Taylor, 1973. Vapor-Liquid Equilibrium in Perfluorobenzene-Benzene-Methylcyclohexane, *J. Chem. Eng. Data*, **18**, pp. 424-427.

Yeh, A., 1986. A Study of the Reversing of Relative Volatilities by Extractive Distillation, Ph. D. Dissertation, Montana State University.

Appendix A

Feasible Separation Sequences

This appendix contains the flowsheets and composition profiles of the extractive columns for the following 11 mixtures:

- Ethyl ethanoate - ethanol azeotrope: Acetone
- Ethanol - water azeotrope: Ethylene glycol, acetone
- Acetone - methanol azeotrope: Water, chlorobenzene, ethanol, isopropanol
- Isopropanol - toluene azeotrope: Methanol, ethanol, ethyl ethanoate, acetone

The separation sequences corresponding to the remaining four mixtures described in section 2.2.2 (Ethyl ethanoate - ethanol - chlorobenzene, ethanol - water - methanol, acetone - heptane - toluene and acetone - heptane - benzene) are already included in chapter 2. These separation sequences are designed to show separability and were not optimized in any sense. Some of these separations require very high entrainer and/or reflux flow rates, and are therefore impractical, but this is beyond the scope of our argument.

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

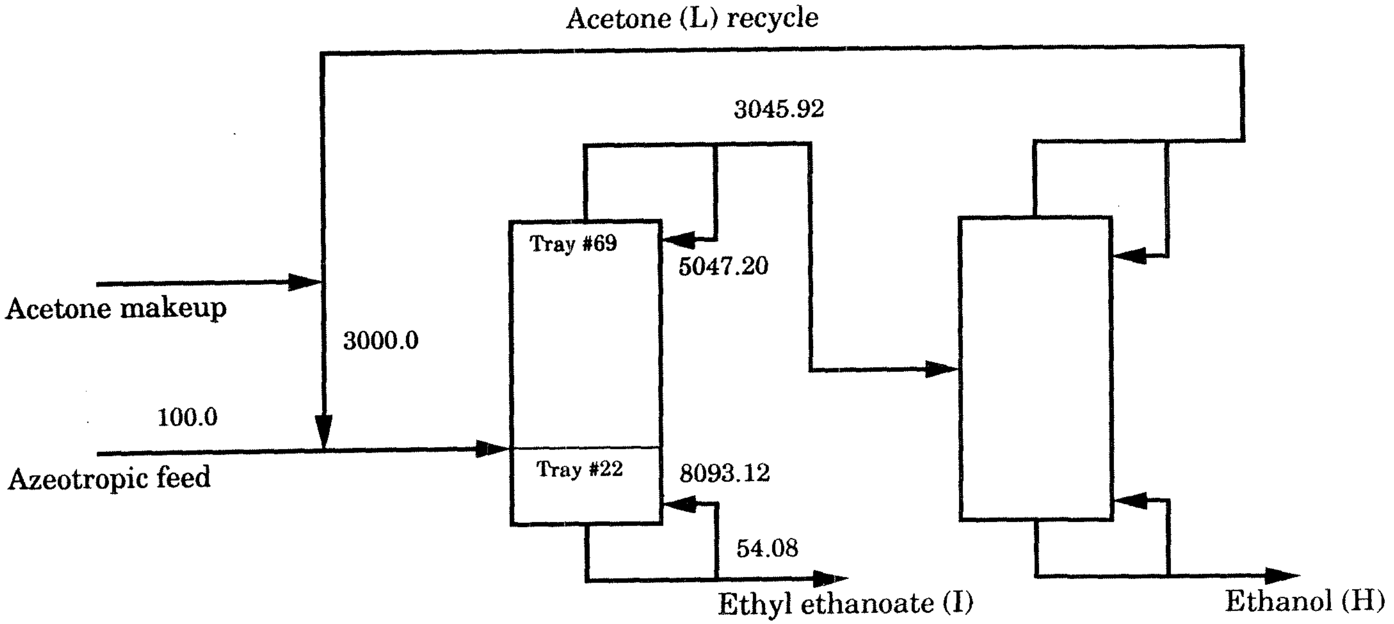


Fig. A.1: The ethyl ethanoate - ethanol - acetone separation sequence

Fig. A.2: Ethyl ethanoate (1) - ethanol (2) - acetone (3) extractive column composition profile

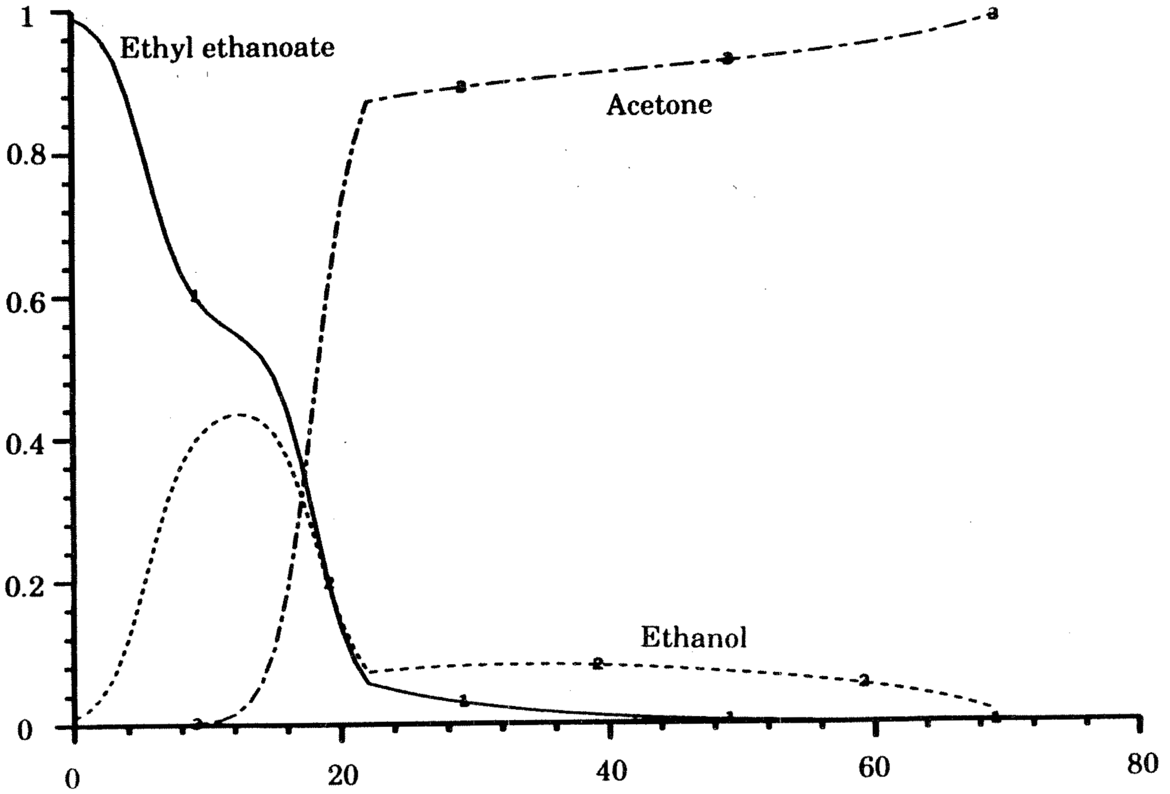
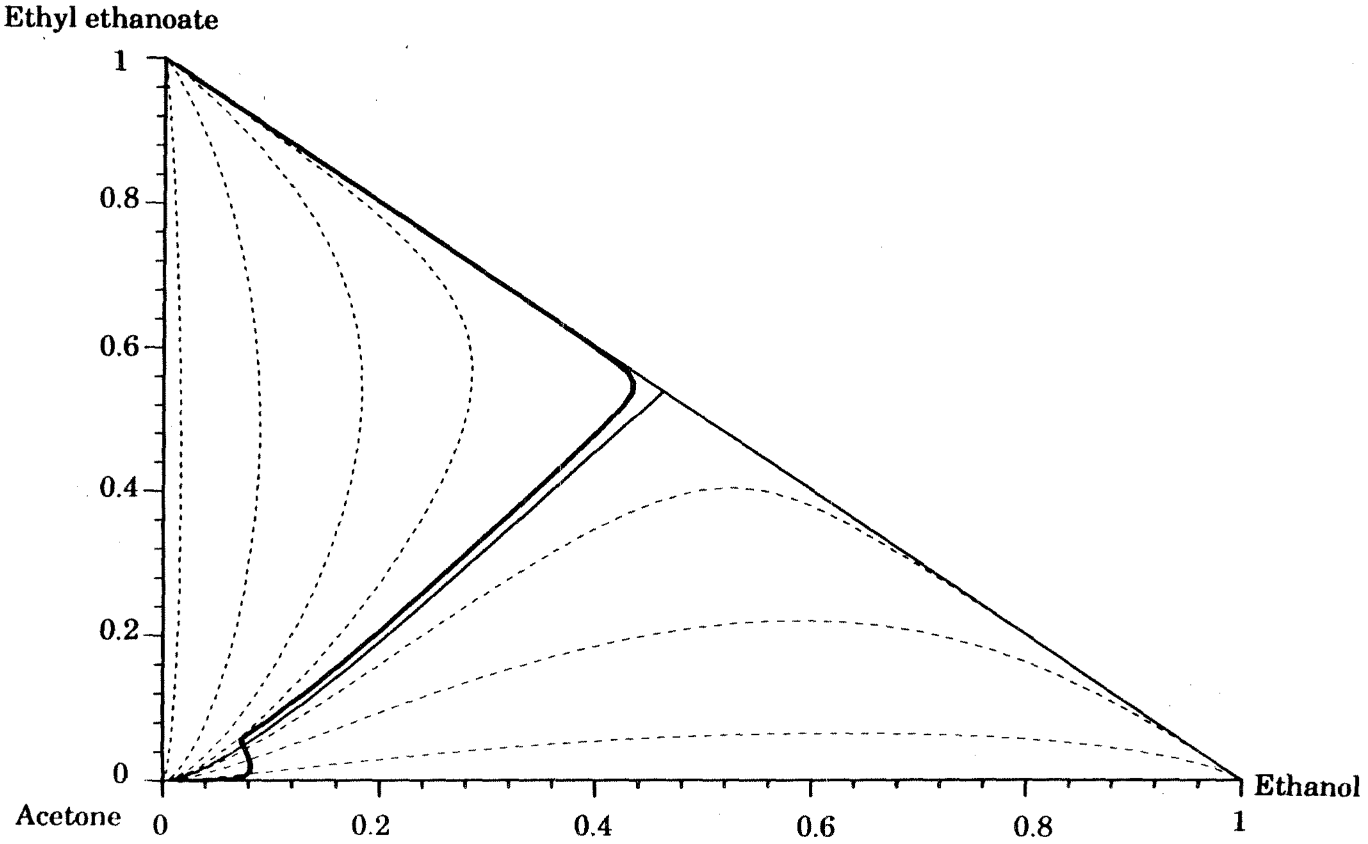


Fig. A.3: Ethyl ethanoate - ethanol - acetone residue curve diagram and extractive column composition profile



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Ethanol (L)	0.0	0.9182	0.99	0.00012
Water (I)	0.0	0.0818	0.01	0.02360
Ethylene glycol (H)	1.0	0.0	0.0	0.97628

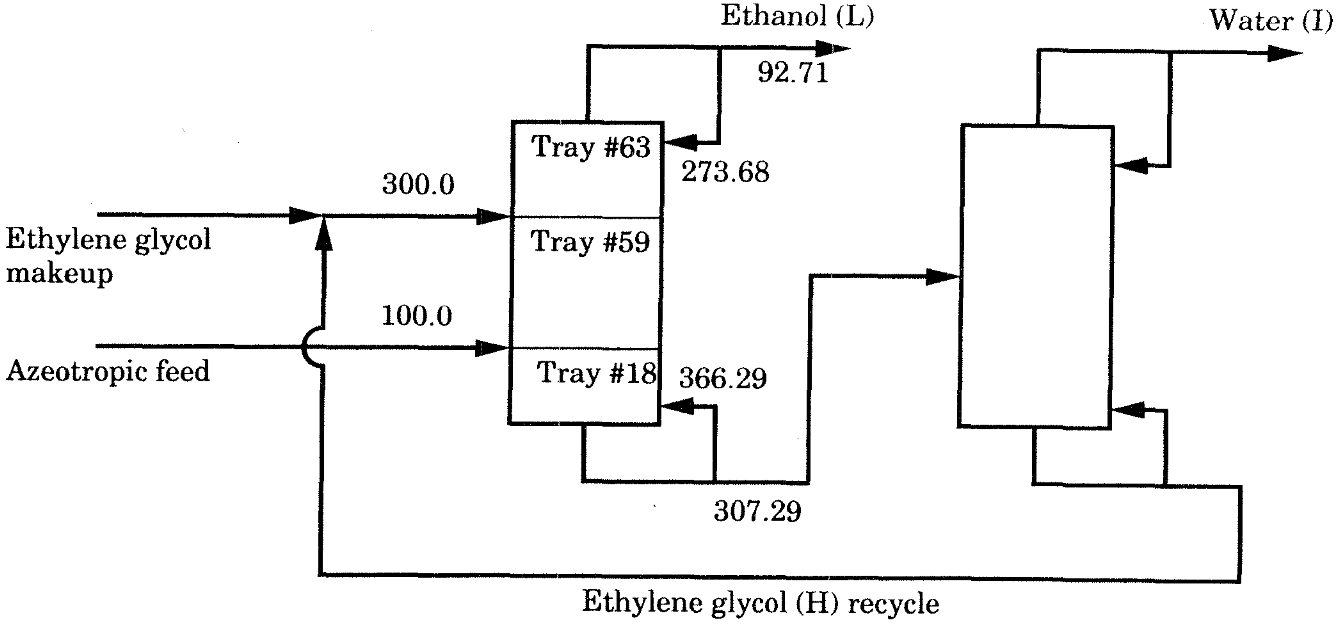


Fig. A.4: The ethanol - water - ethylene glycol separation sequence

Fig. A.5: Ethanol (1) - water (2) - ethylene glycol (3) extractive column composition profile

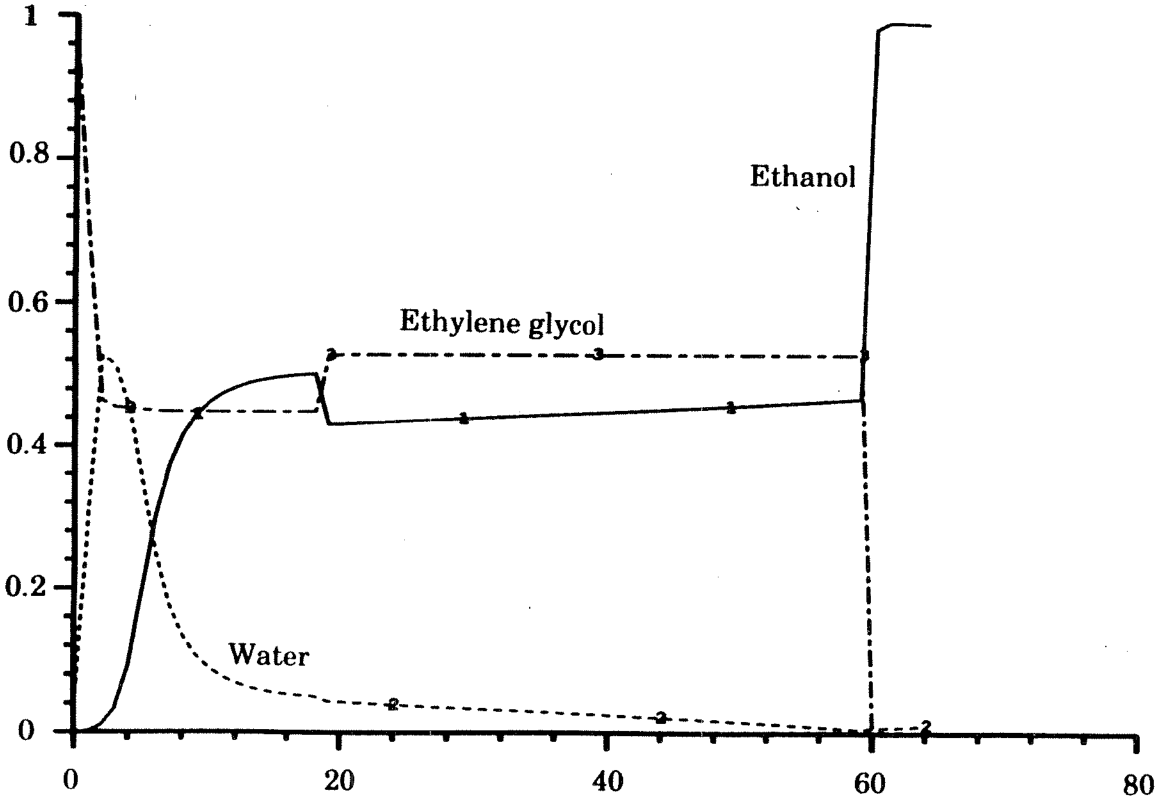
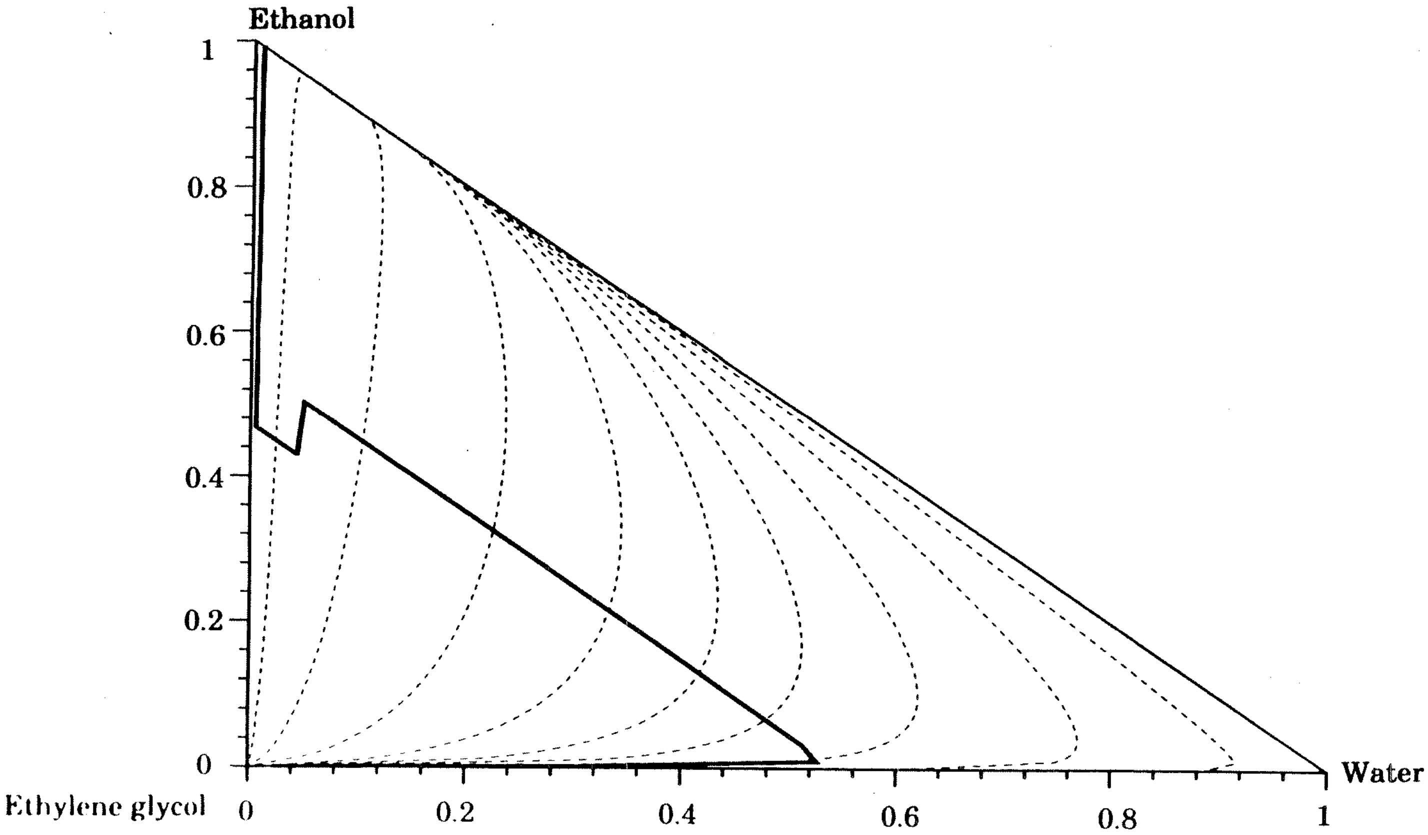


Fig. A.6: Ethanol - water - ethylene glycol residue curve diagram and extractive column composition profile



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

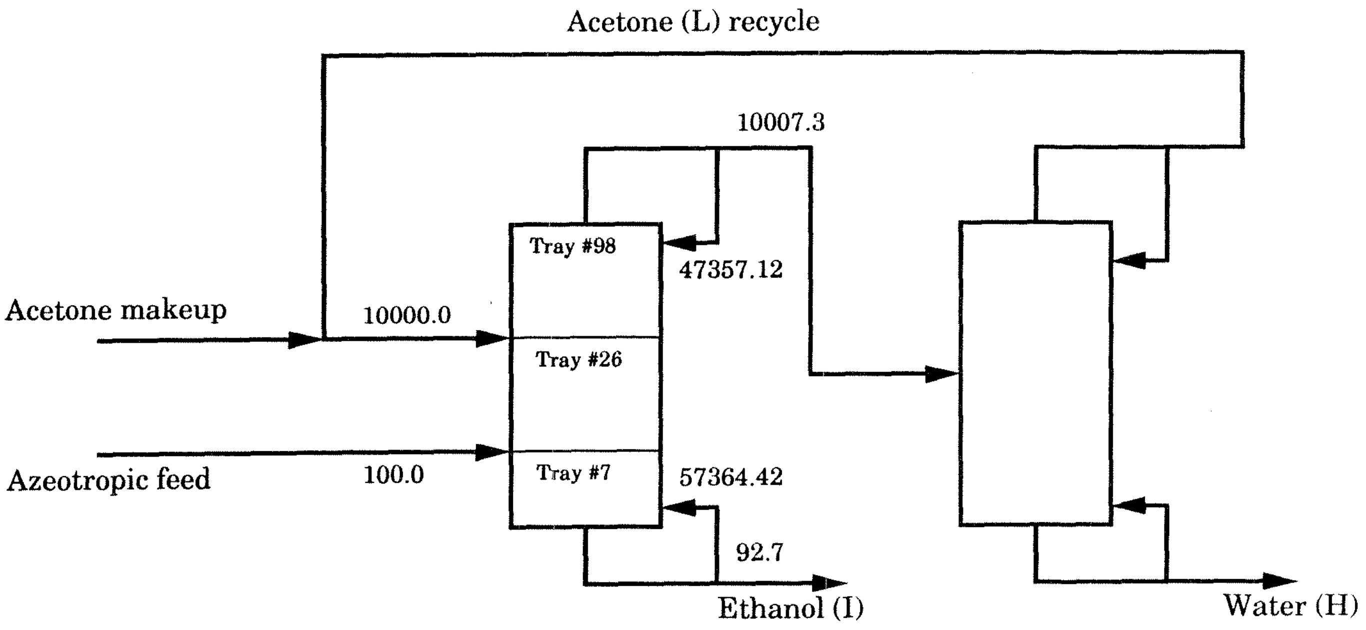


Fig A.7: The ethanol - water - acetone separation sequence

Fig. A.8: Ethanol (1) - water (2) - acetone (3) extractive column composition profile

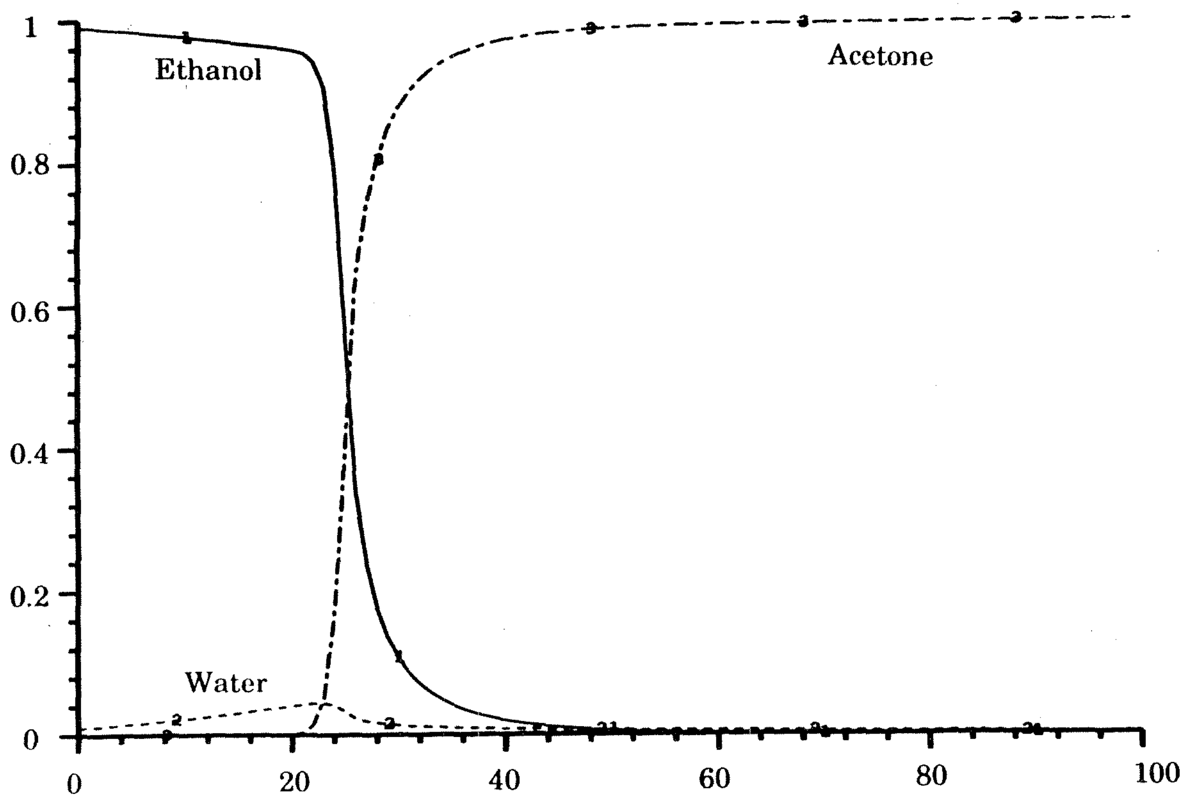
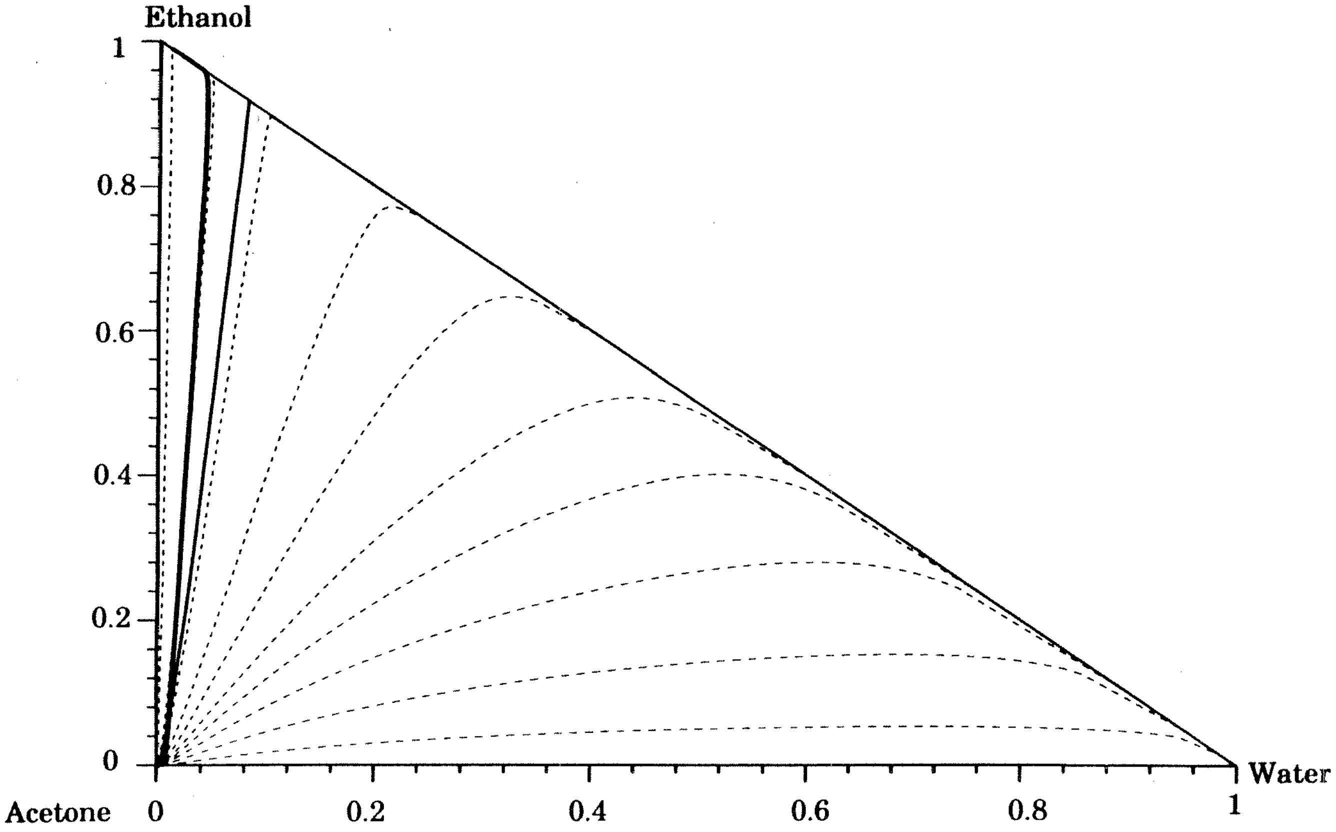


Fig. A.9: Ethanol - water - acetone residue curve diagram and extractive column composition profile



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.7480	0.9898	0.0003
Methanol (I)	0.0	0.2520	0.0002	0.1122
Water (H)	1.0	0.0	0.0100	0.8875

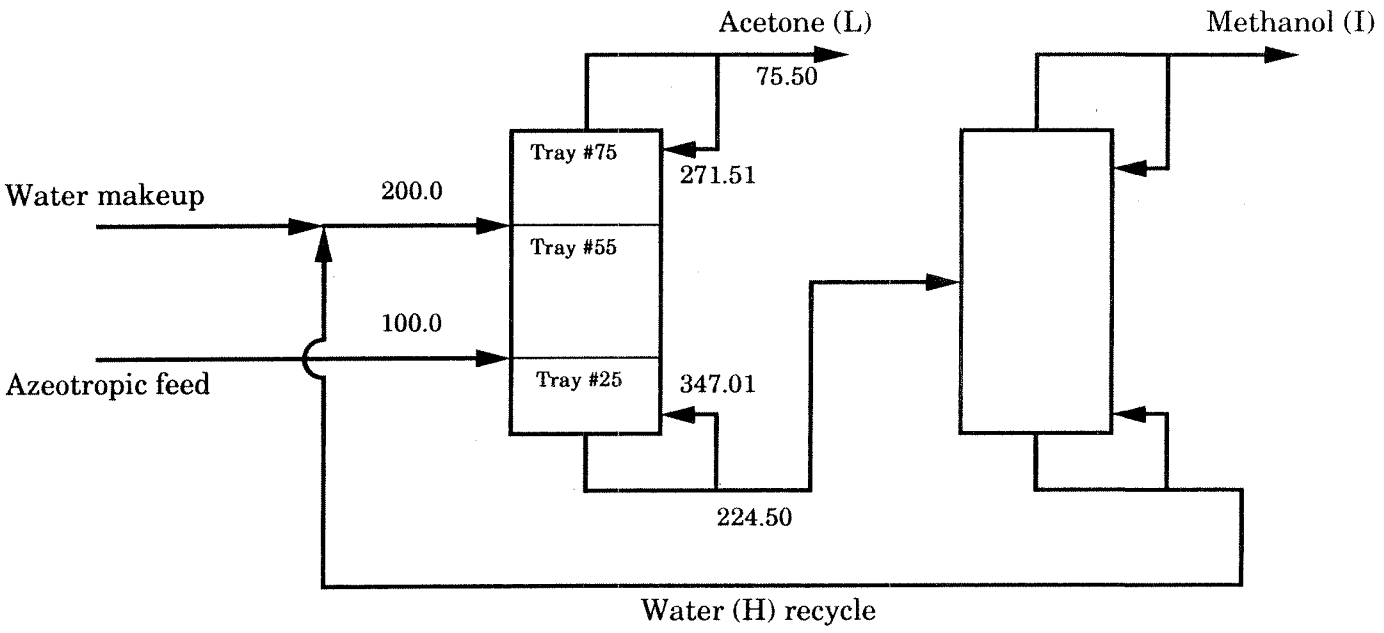


Fig. A.10: The acetone - methanol -water separation sequence

Fig. A.11: Acetone (1) - methanol (2) - water (3)
extractive column composition profile

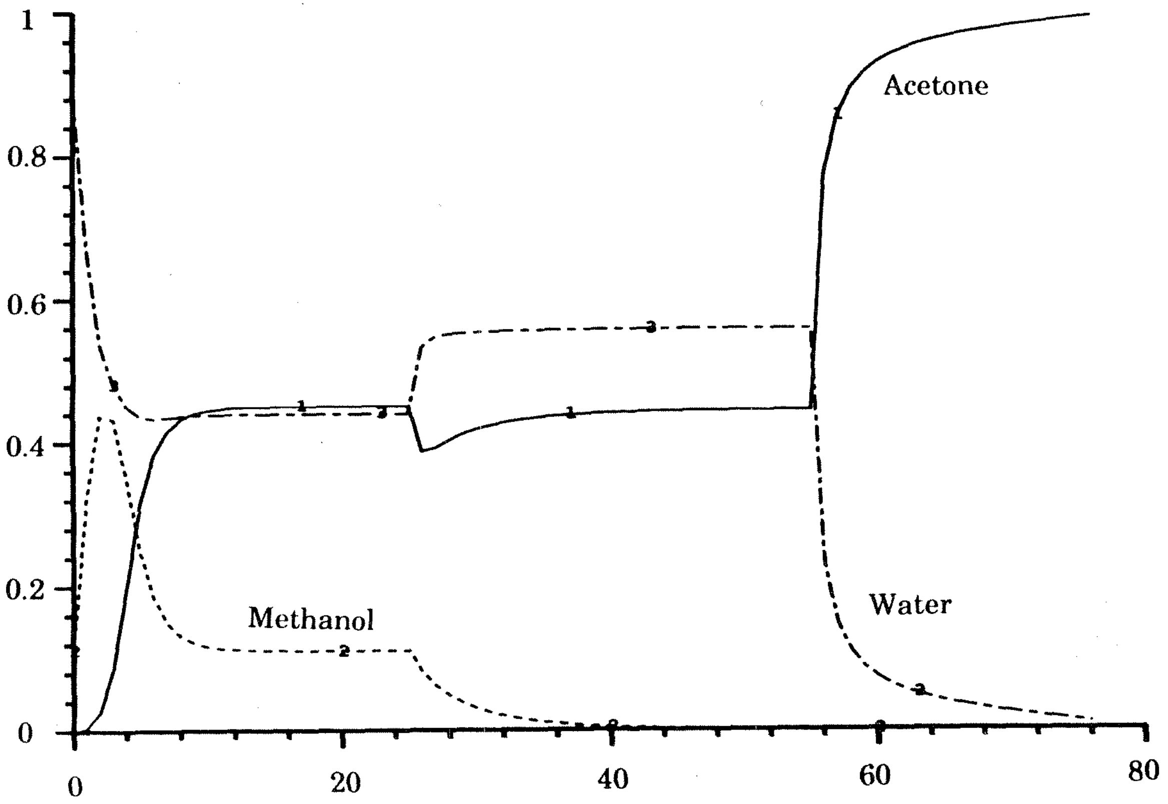
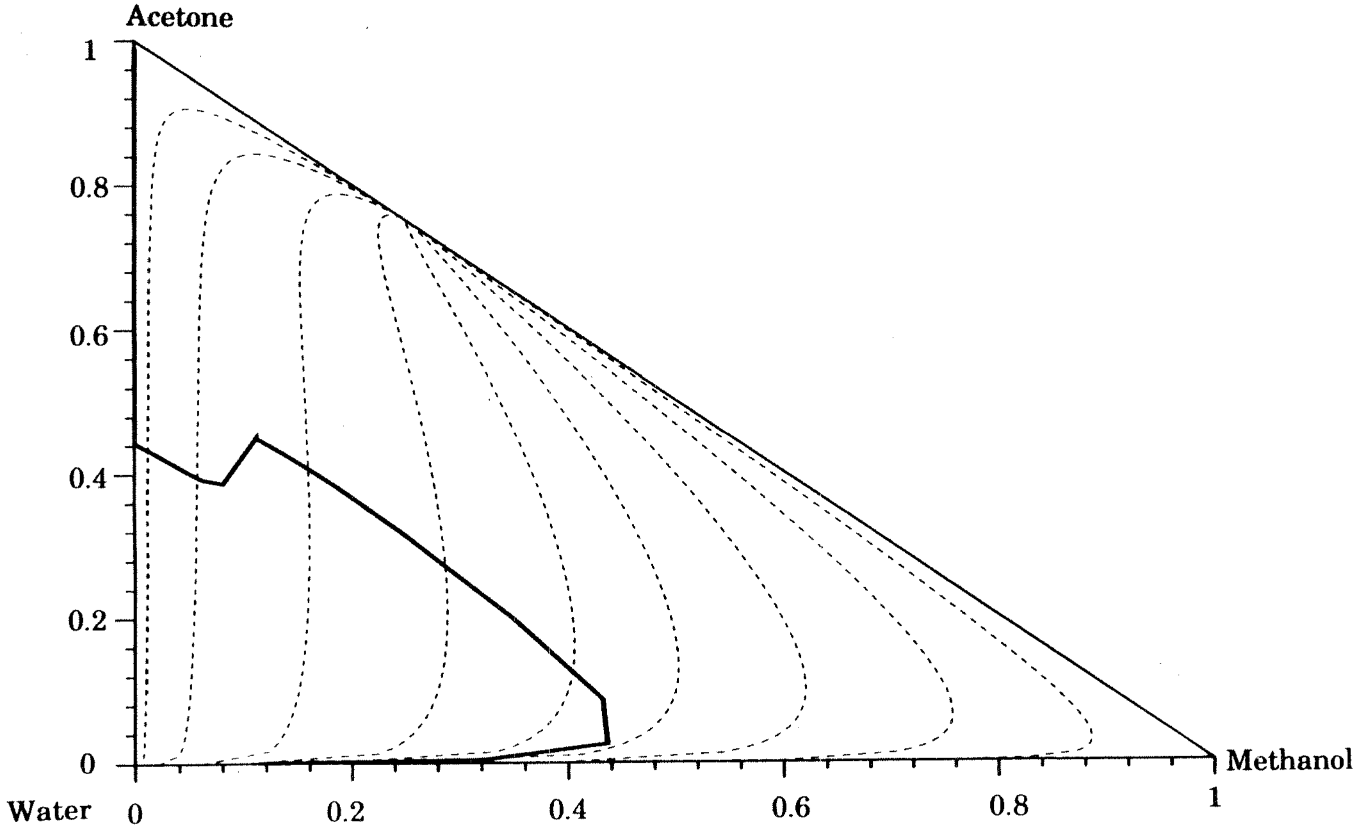


Fig. A.12: Acetone - methanol - water residue curve diagram and extractive column composition profile



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.7480	0.0006	0.13009
Methanol (I)	0.0	0.2520	0.99	0.00056
Chlorobenzene (H)	1.0	0.0	0.0094	0.86935

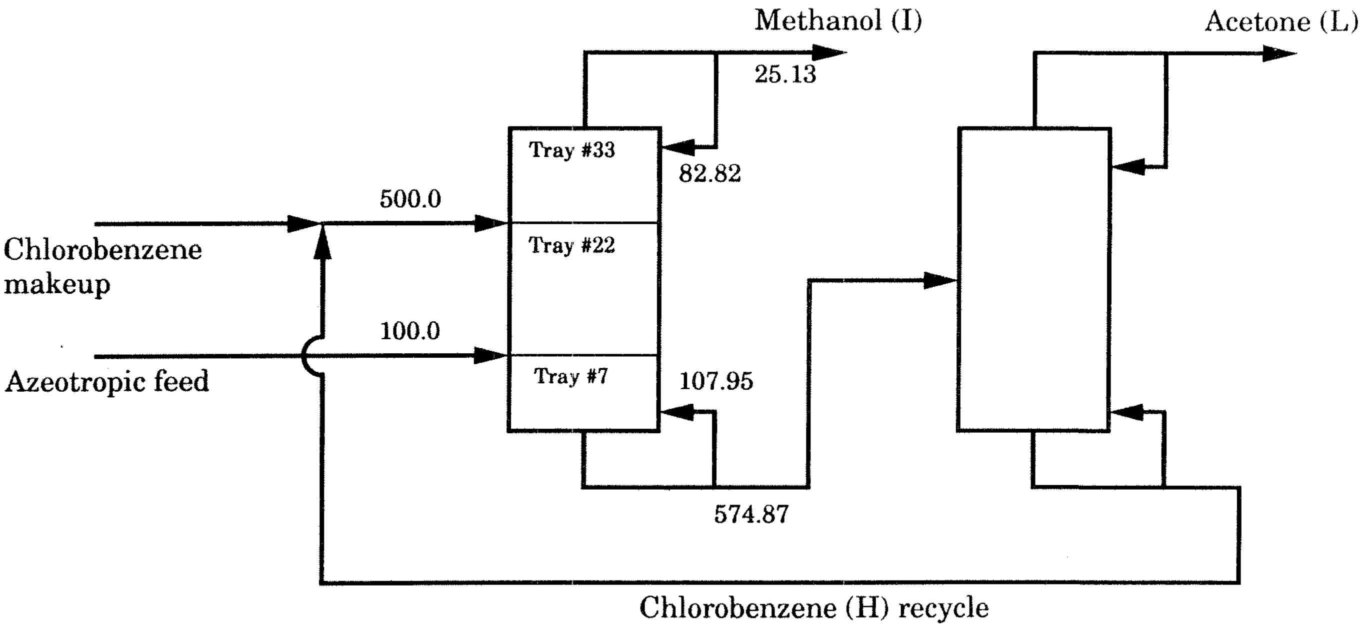


Fig. A13: The acetone - methanol - chlorobenzene separation sequence

Fig. A.14: Acetone (1) - methanol (2) - chlorobenzene (3)
extractive column composition profile

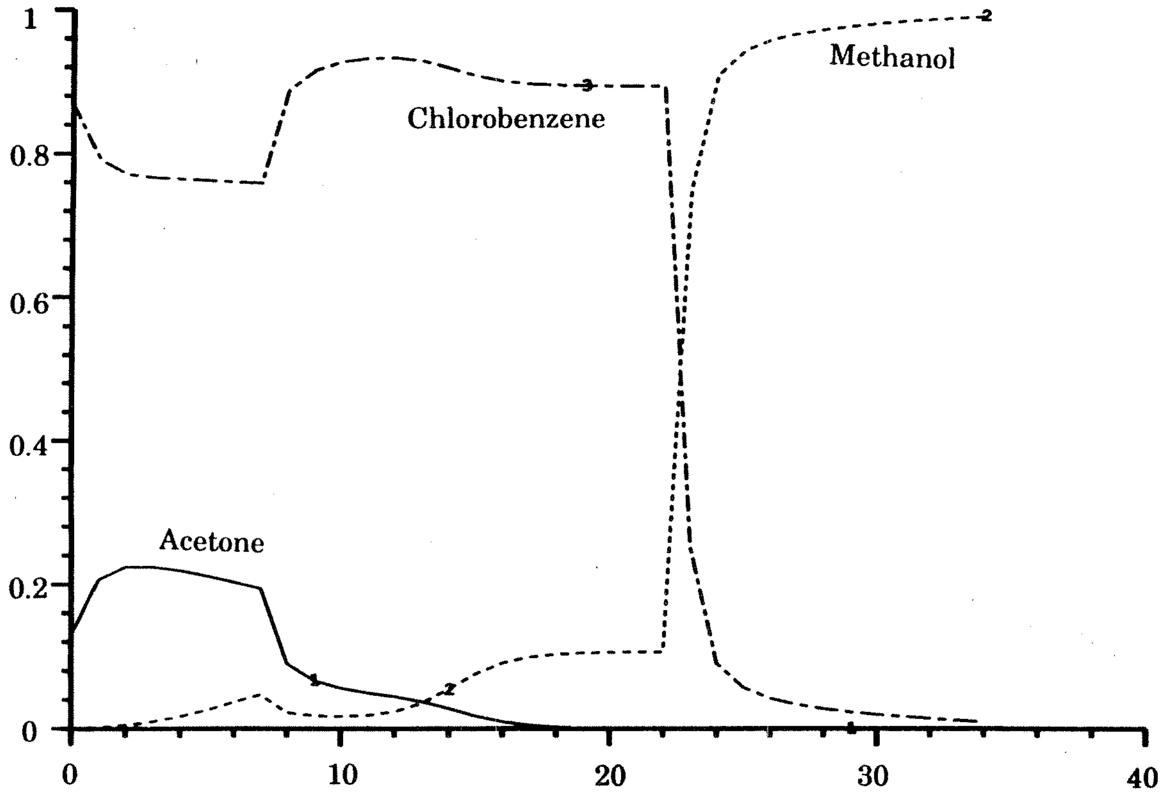
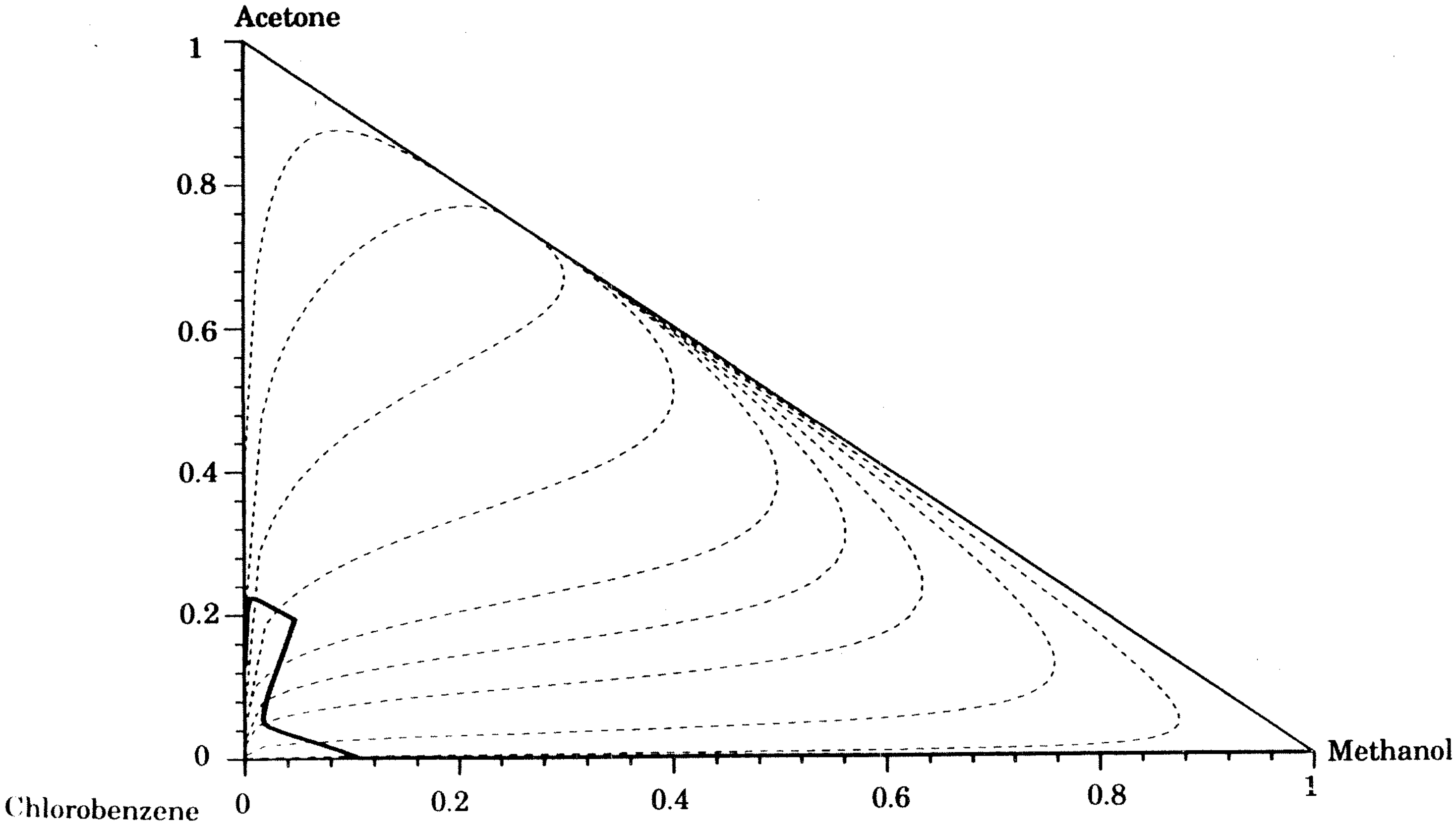


Fig. A.15: Acetone - methanol - chlorobenzene residue curve diagram and extractive column composition profile



Concentration	**Entrainer feed**	**Azeotropic feed**	**Distillate**	**Bottoms**
Acetone (L)	0.0	0.7480	0.99	0.00024
Methanol (I)	0.0	0.2520	0.0003	0.04800
Ethanol (H)	1.0	0.0	0.0097	0.95176

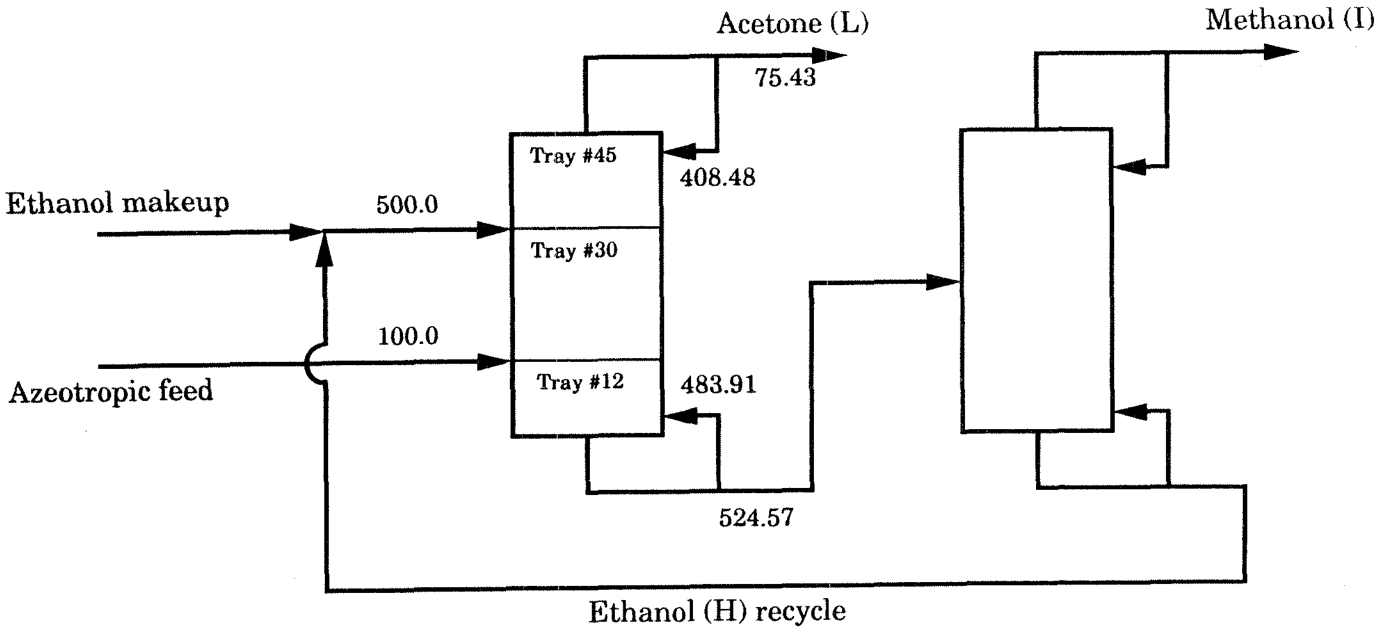


Fig. A.16: The acetone - methanol - ethanol separation sequence

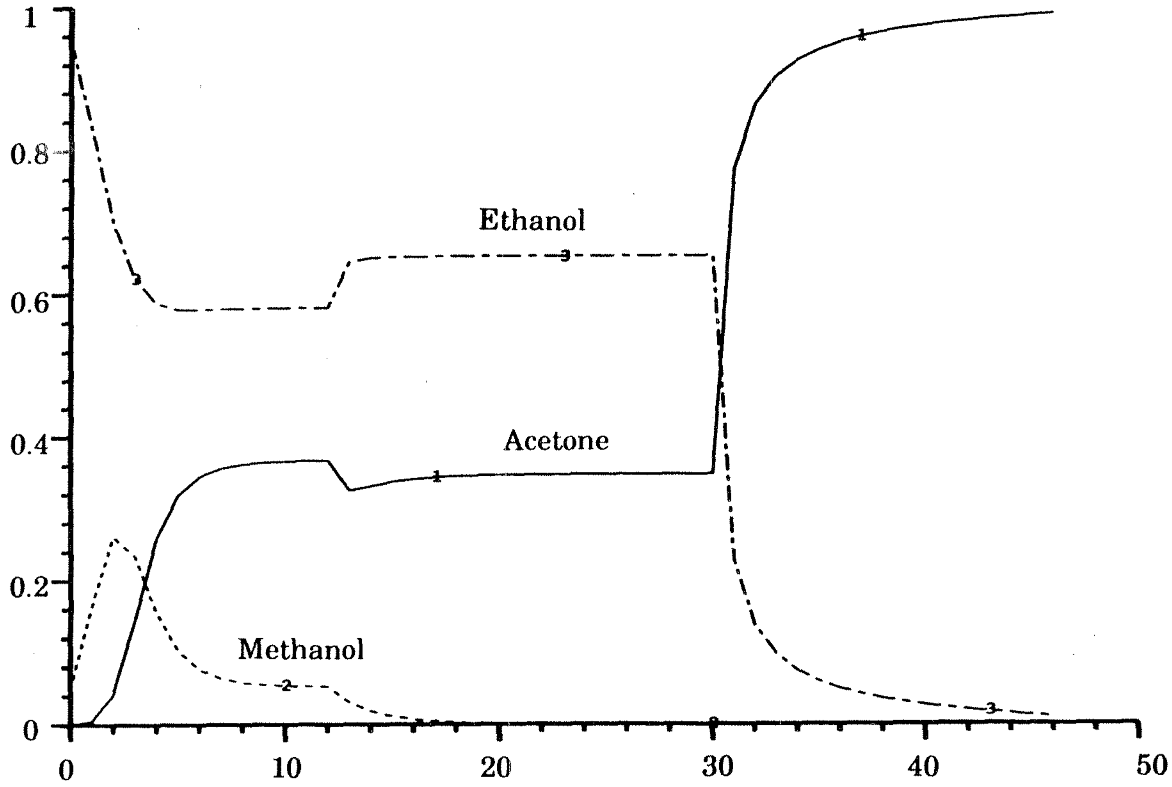
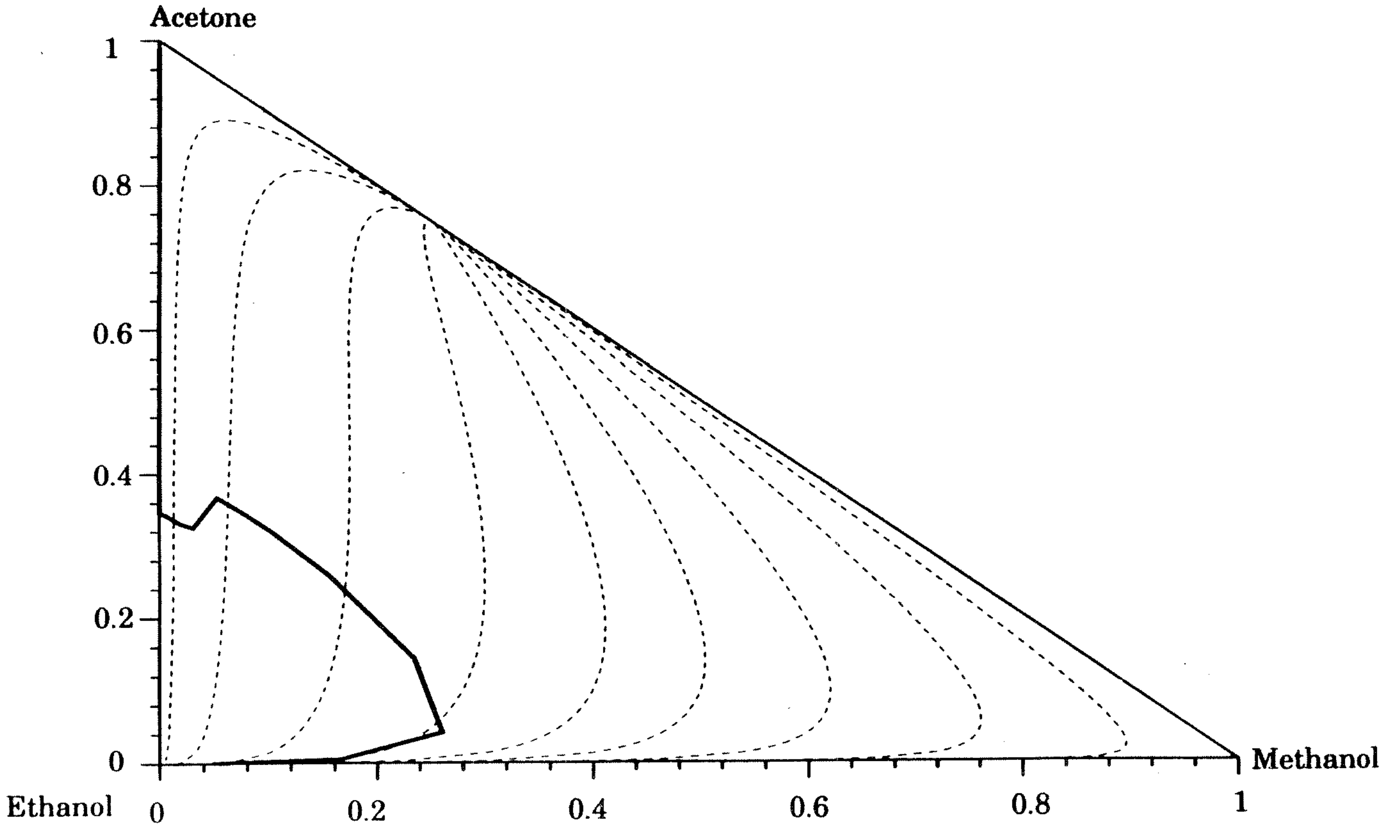


Fig. A.17: Acetone (1) - methanol (2) - ethanol (3)
extractive column composition profile

Fig. A.18: Acetone - methanol - ethanol residue curve diagram and extractive column composition profile



Concentration	Entrainer feed	Azeotropic feed	Distillate	Bottoms
Acetone (L)	0.0	0.7480	0.99	0.00100
Methanol (I)	0.0	0.2520	0.0093	0.19666
Isopropanol (H)	1.0	0.0	0.0007	0.80234

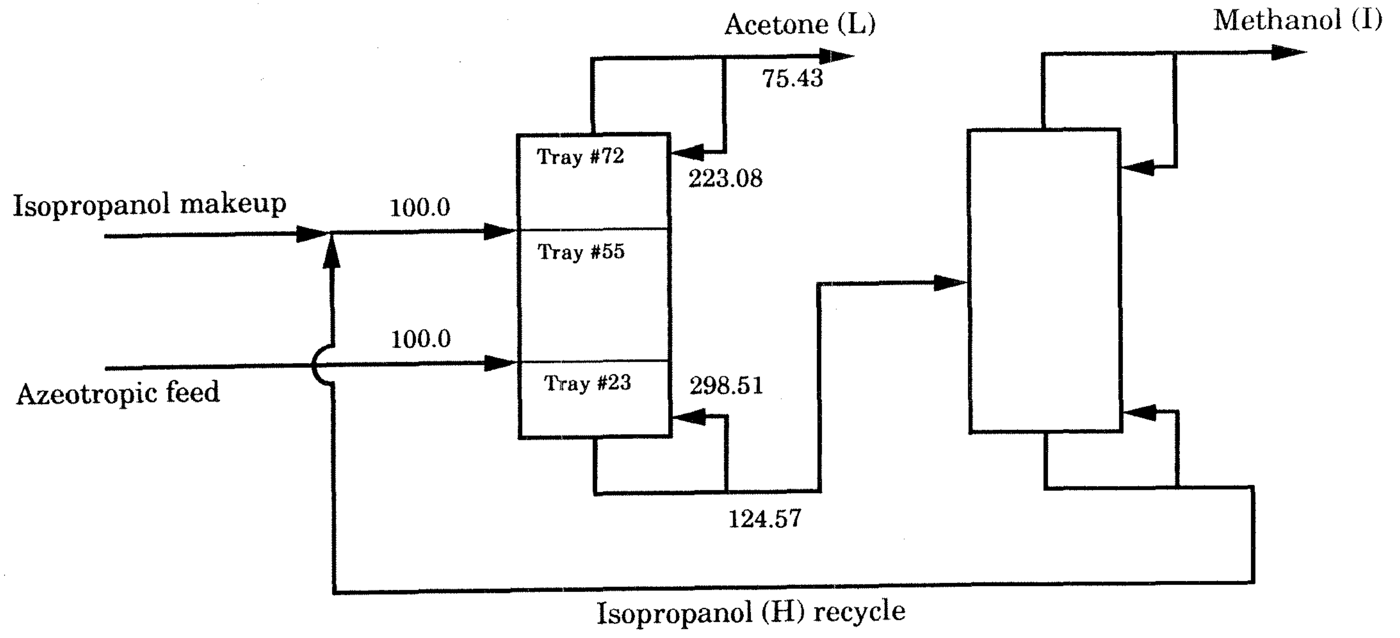
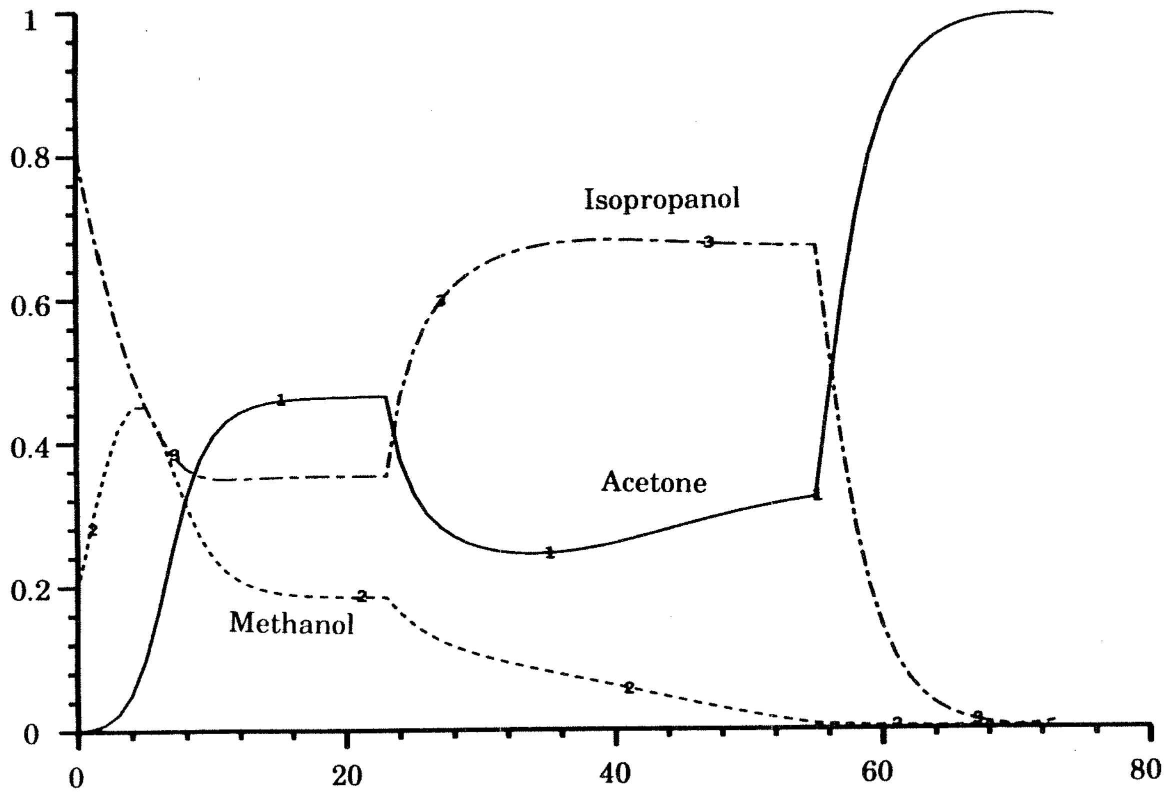


Fig. A.19: The acetone - methanol - isopropanol separation sequence

Fig. A.20: Acetone (1) - methanol (2) - isopropanol (3) extractive column composition profile



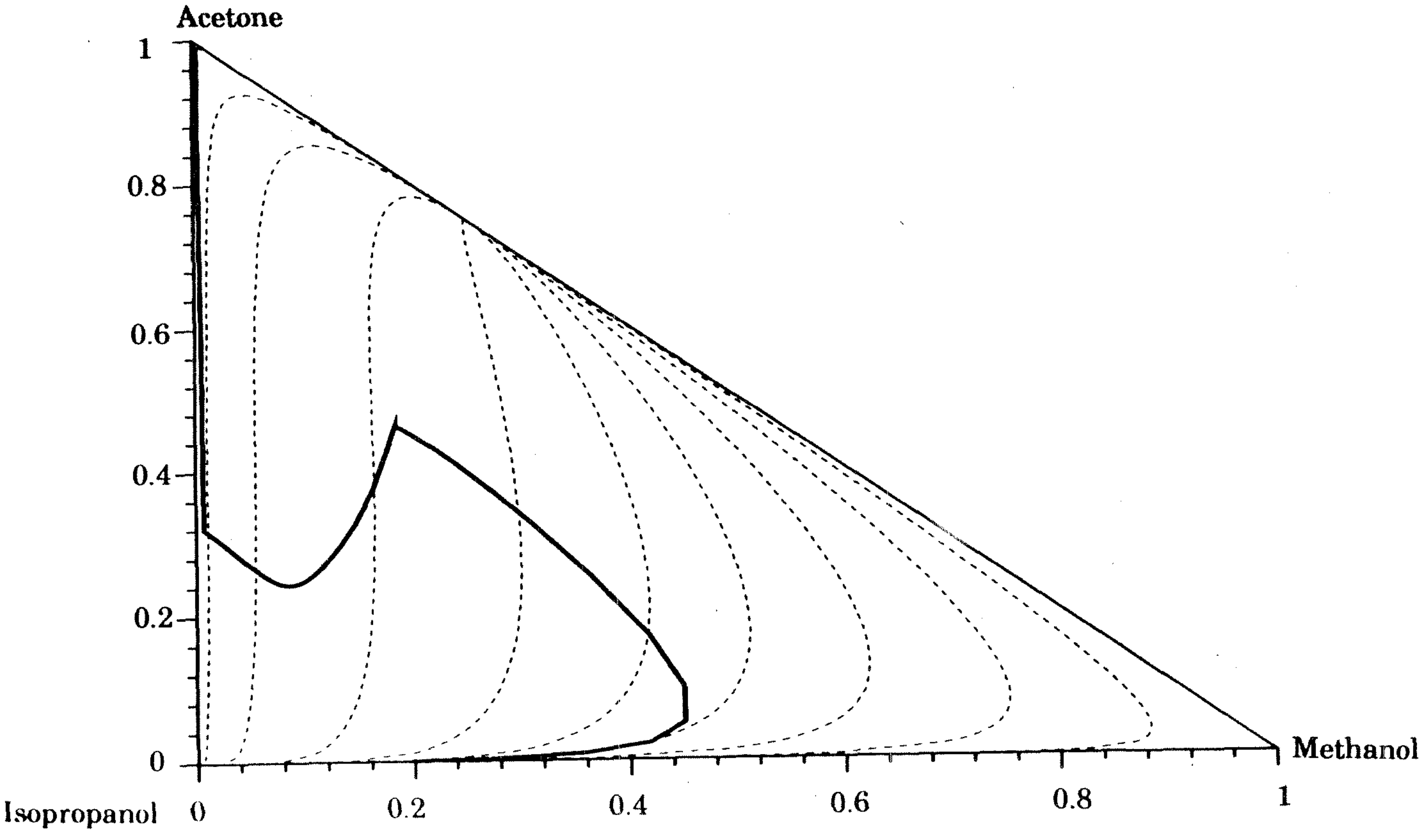


Fig. A.21: Acetone - methanol - isopropanol residue curve diagram and extractive column composition profile

Concentration	**Entrainer feed**	**Azeotropic feed**	**D1**	**B1**	**D2**	**B2**
Isopropanol (I)	0.0	0.848	0.021	0.01	0.0	0.99
Toluene (H)	0.121	0.152	0.118	0.99	0.121	0.007
Methanol (L)	0.879	0.0	0.861	0.0	0.879	0.003

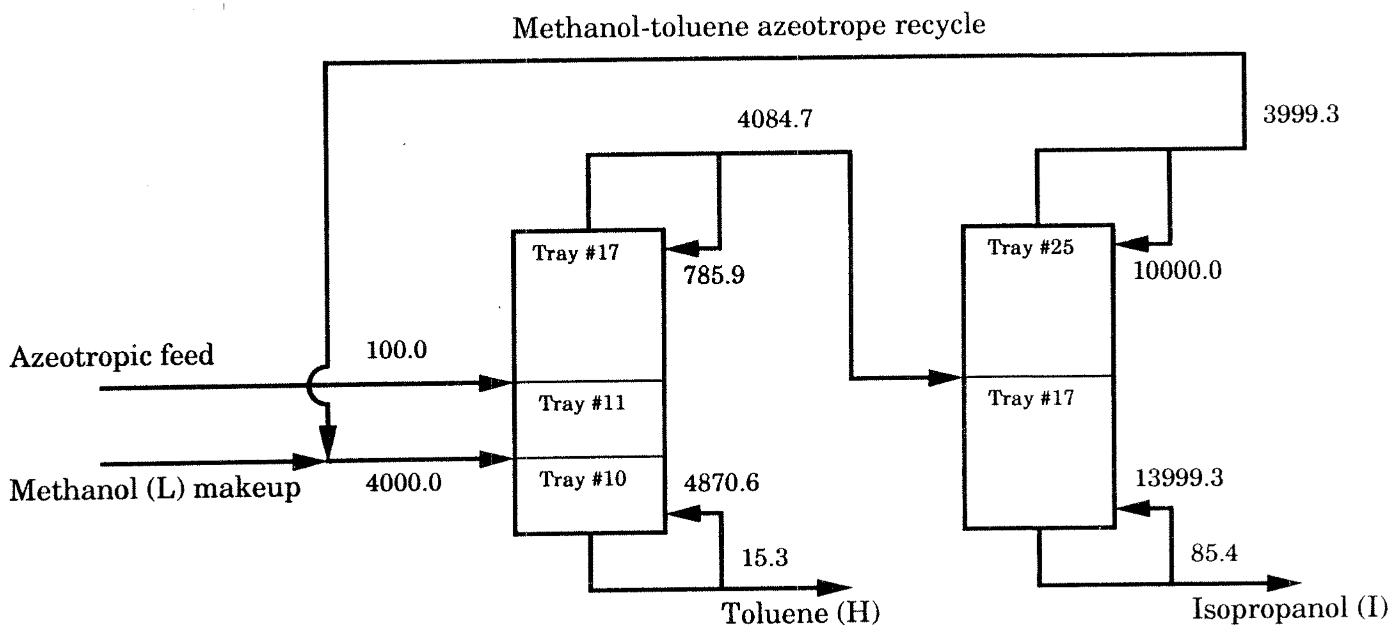


Fig. A.22: The isopropanol - toluene - methanol separation sequence

Fig. A.23: Isopropanol (1) - toluene (2) - methanol (3) extractive column composition profile

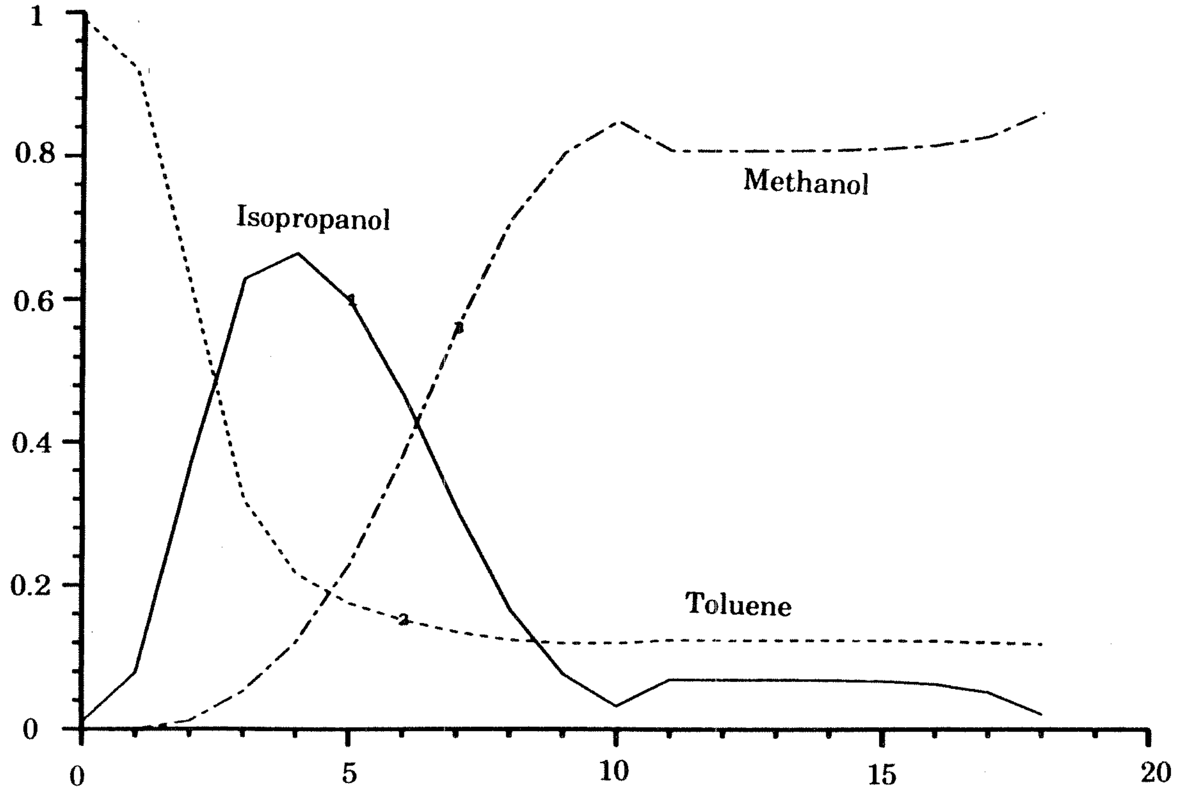


Fig. A.24: Isopropanol (1) - toluene (2) - methanol (3) entrainer recovery column composition profile

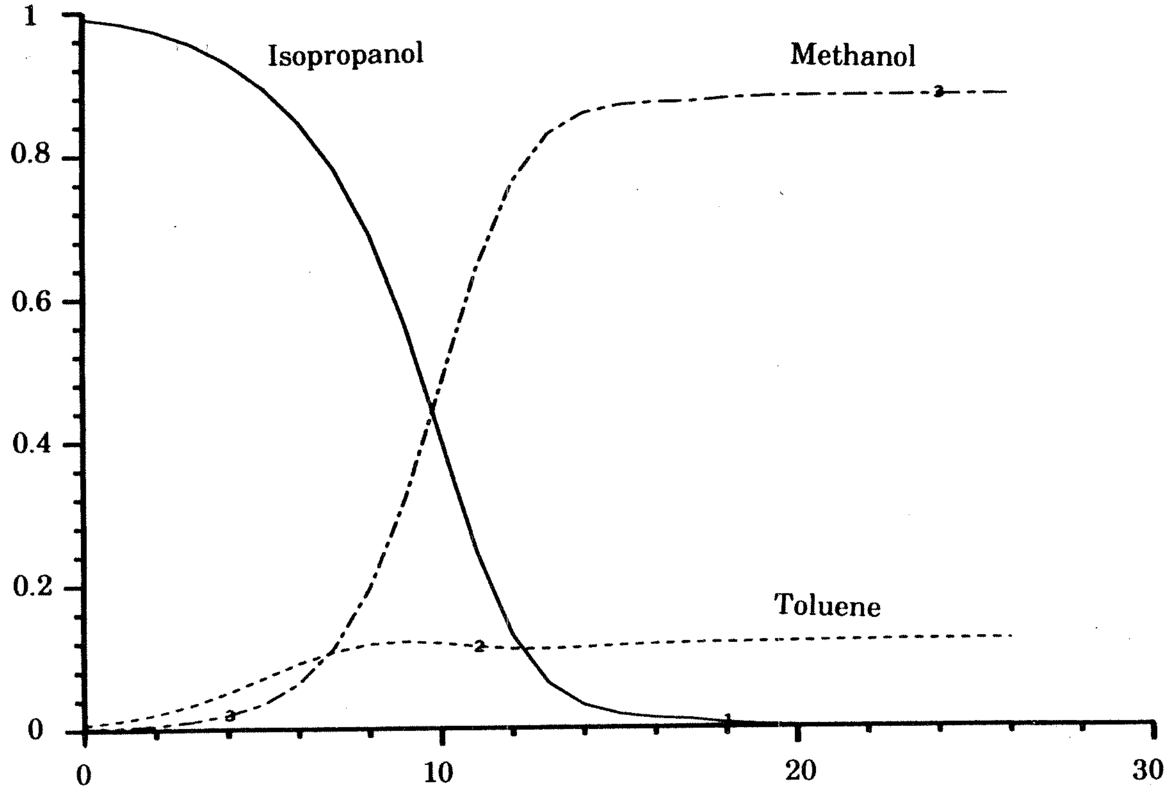
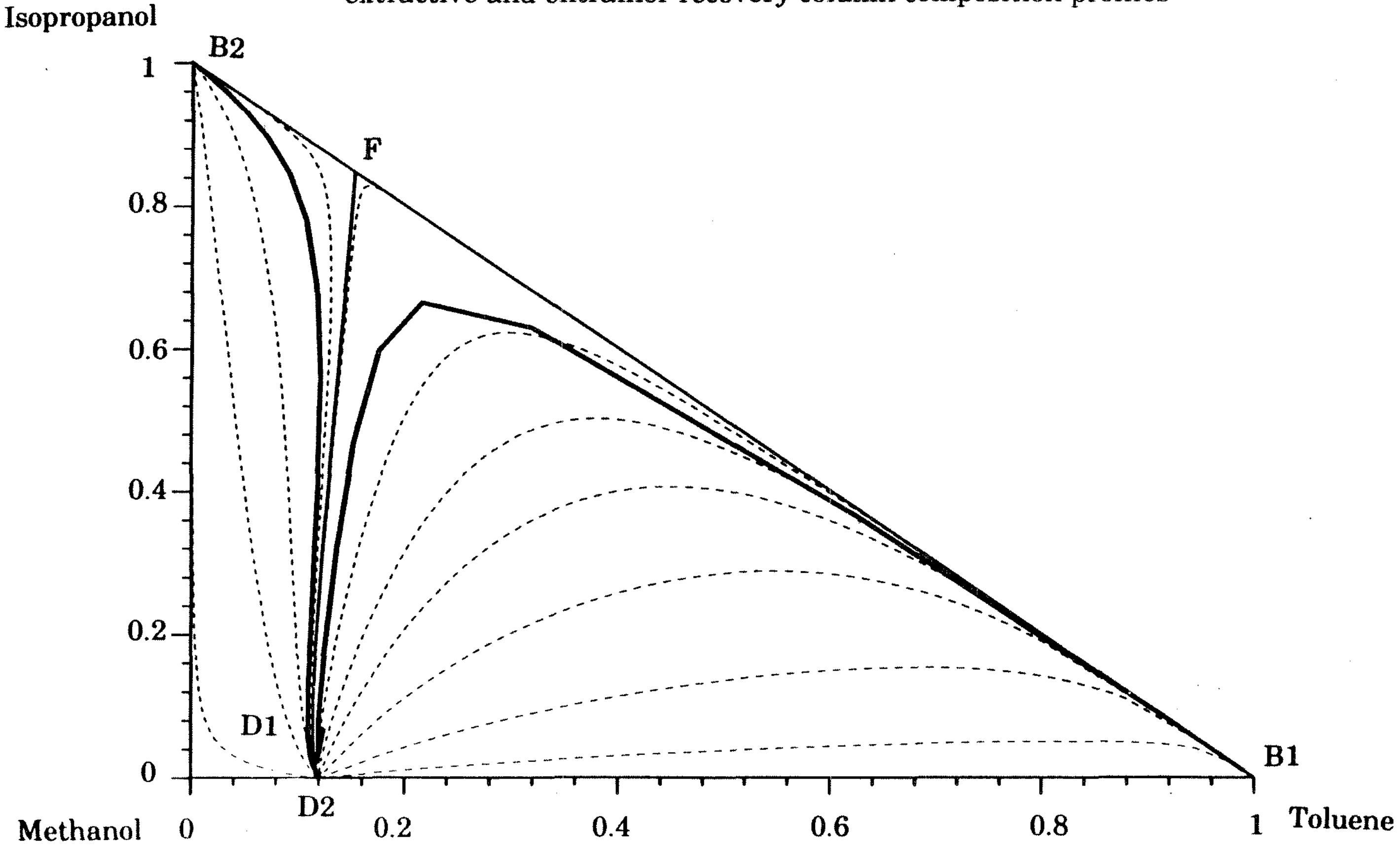


Fig. A.25: Isopropanol - toluene - methanol residue curve diagram and the extractive and entrainer recovery column composition profiles



Concentration	Entrainer feed	Azeotropic feed	D1	B1	D2	B2
Isopropanol (I)	0.0	0.848	0.175	0.01	0.0	0.99
Toluene (H)	0.198	0.152	0.163	0.99	0.197	0.002
Ethanol (L)	0.802	0.0	0.662	0.0	0.813	0.008

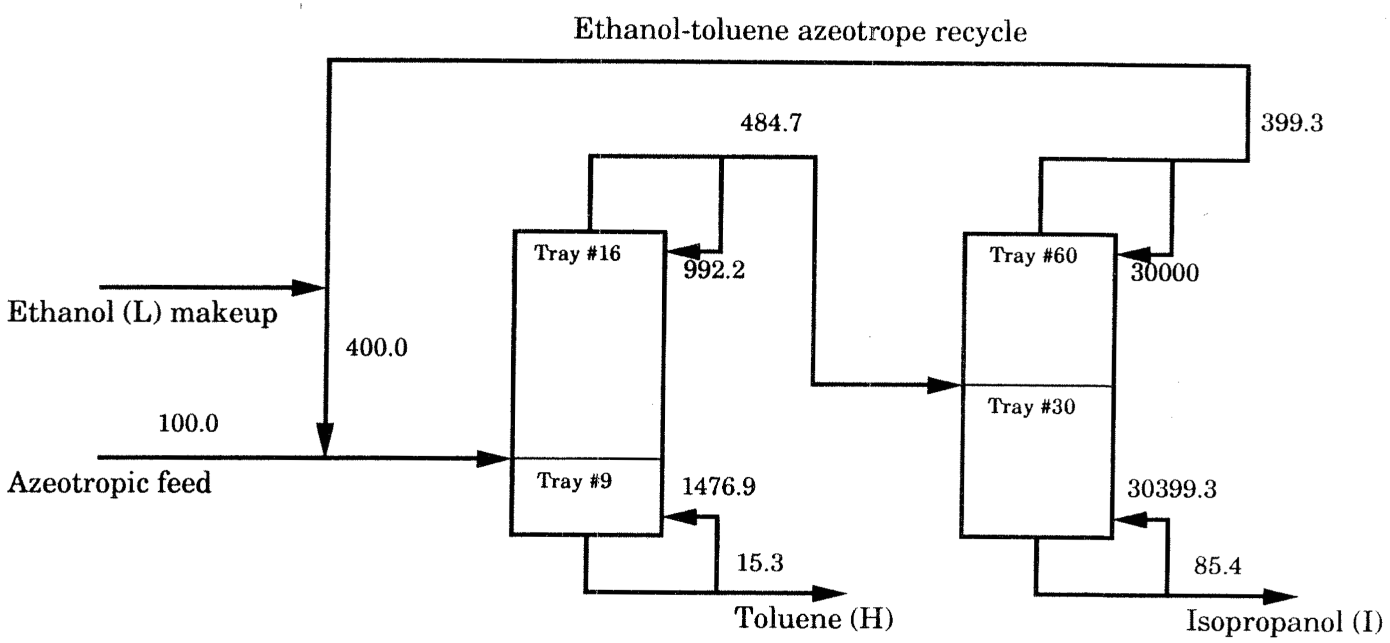


Fig. A.26: The isopropanol - toluene - ethanol separation sequence

Fig. A.27: Isopropanol (1) - toluene (2) - ethanol (3)
extractive column composition profile

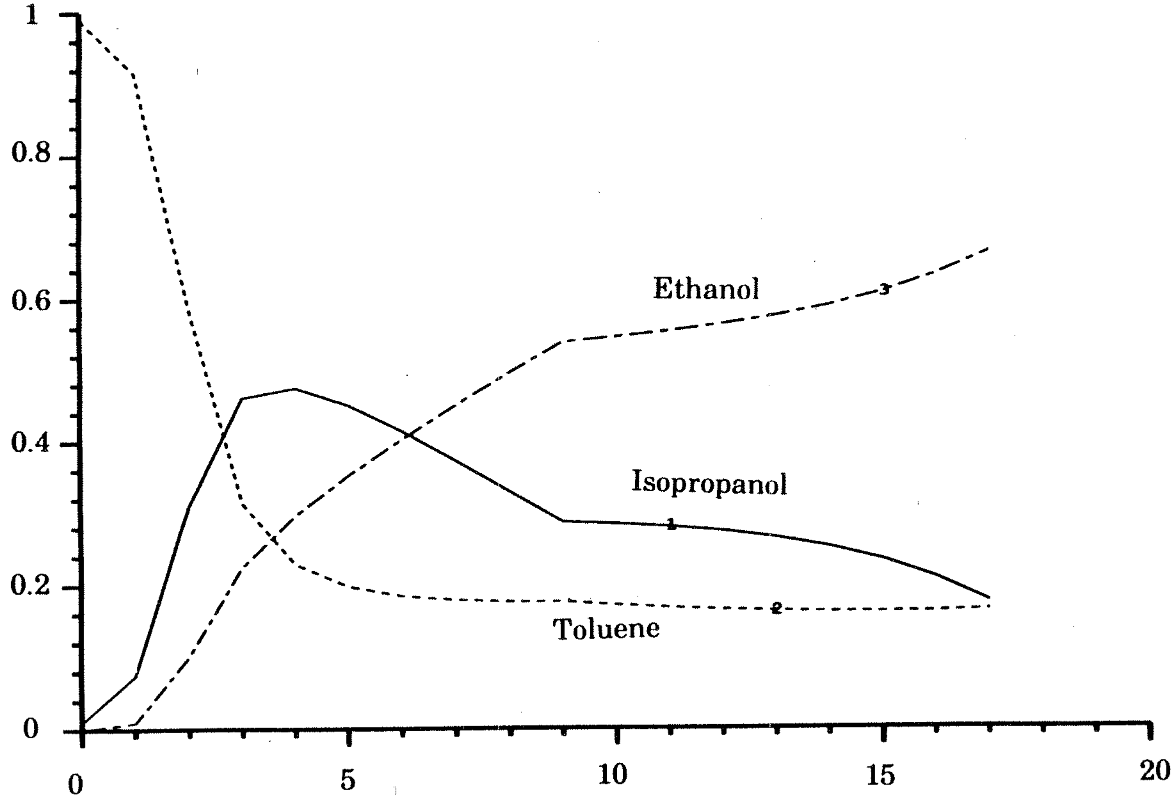


Fig. A.28: Isopropanol (1) - toluene (2) - ethanol (3) entrainer recovery column composition profile

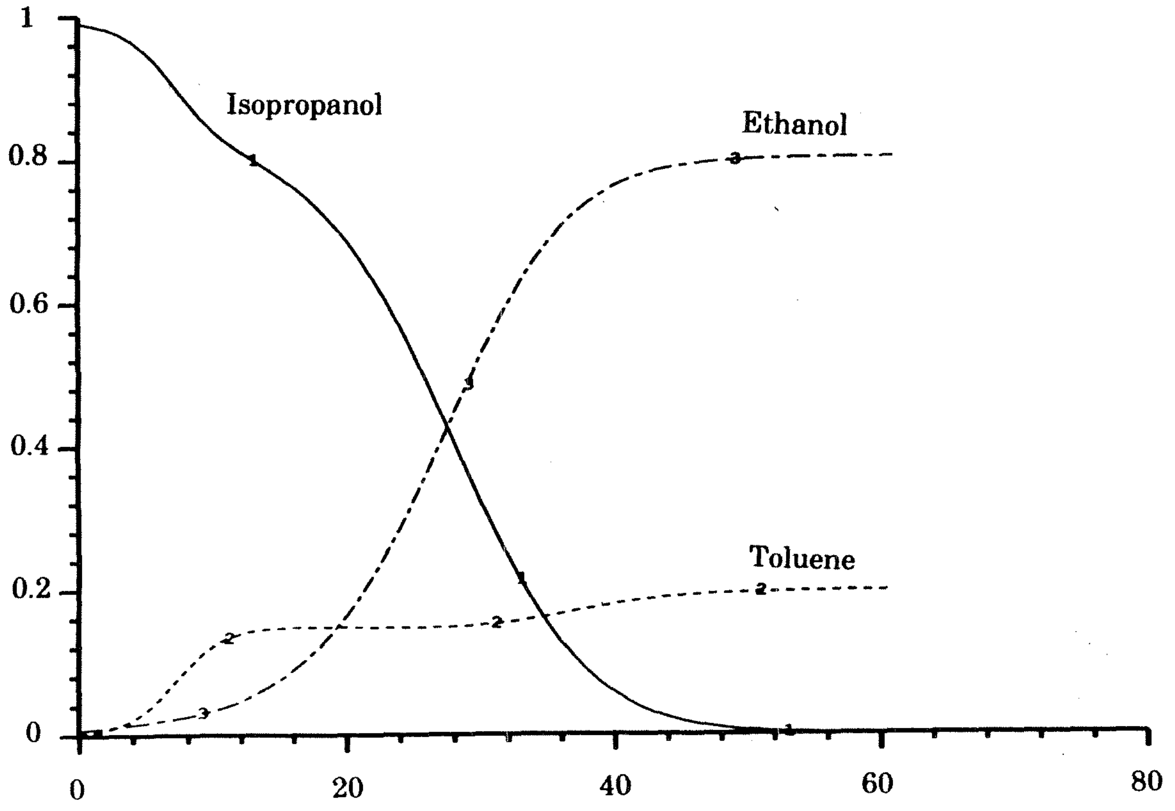
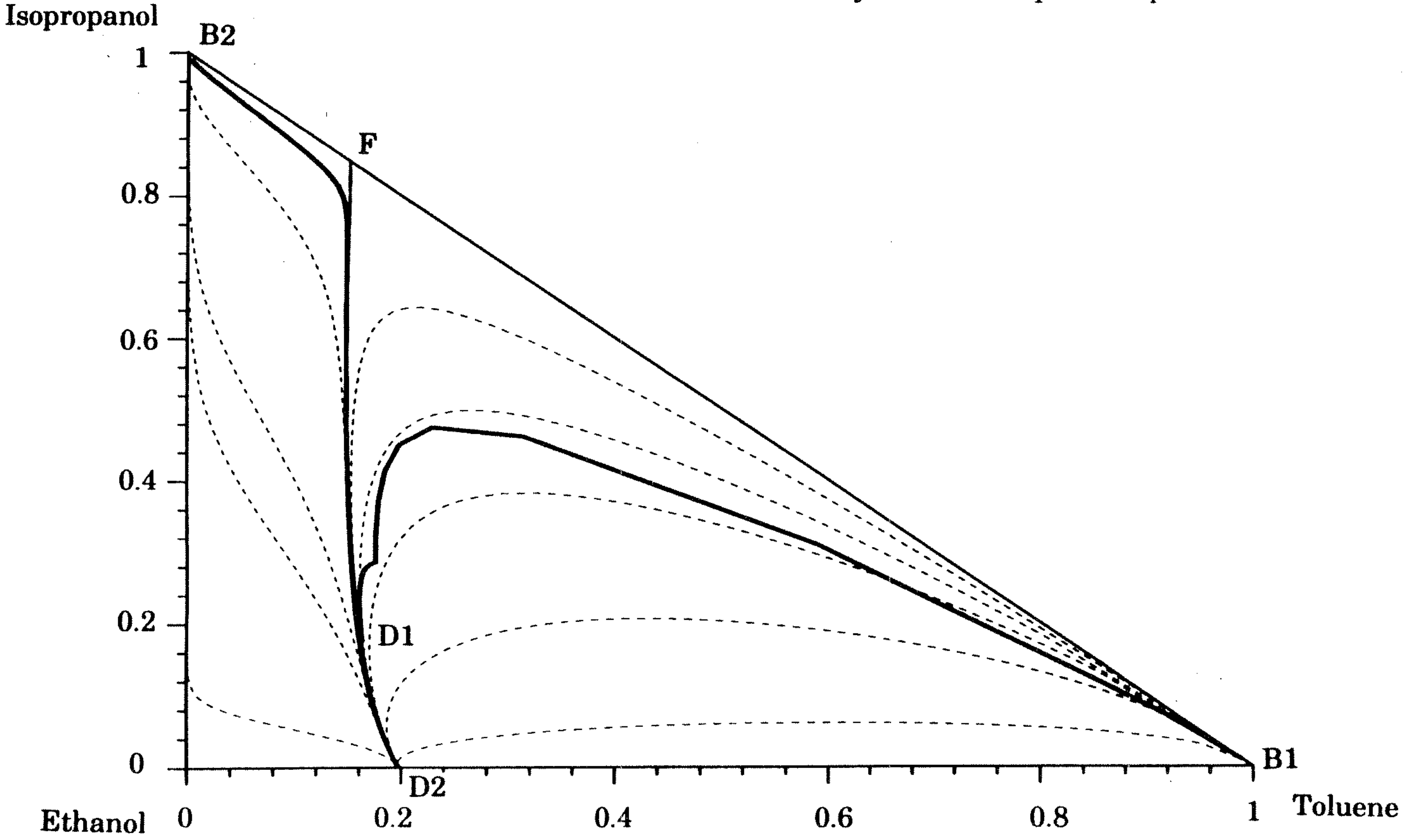


Fig. A.29: Isopropanol - toluene - ethanol residue curve diagram and the extractive and entrainer recovery column composition profiles



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 (H)	0.7325	0.0	0.67511	0.0

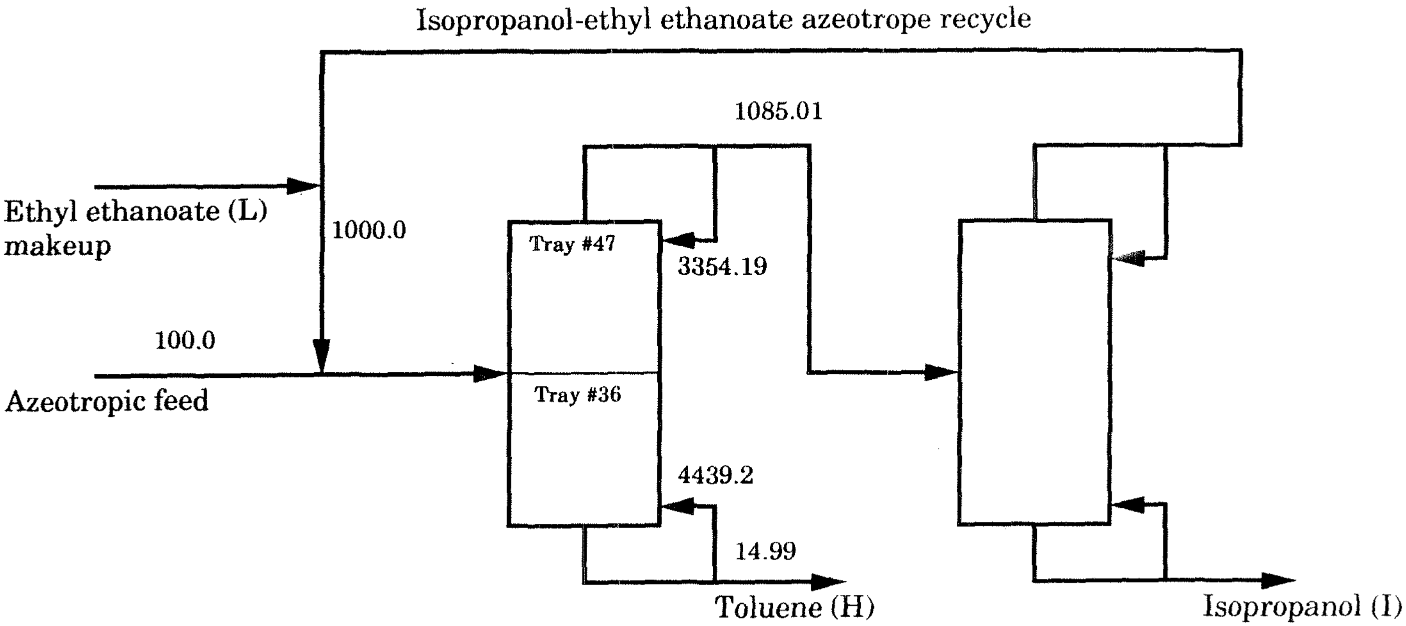


Fig. A.30: The isopropanol - toluene - ethyl ethanoate separation sequence

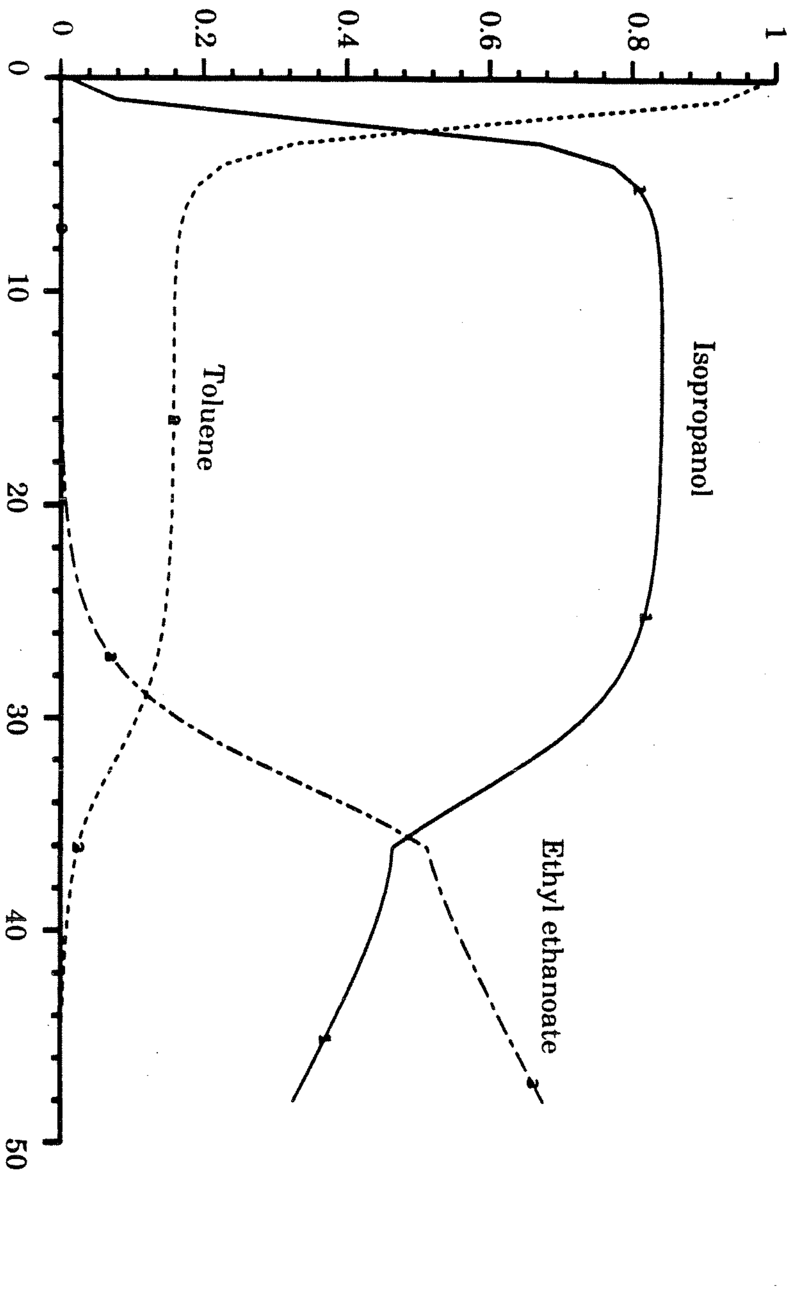
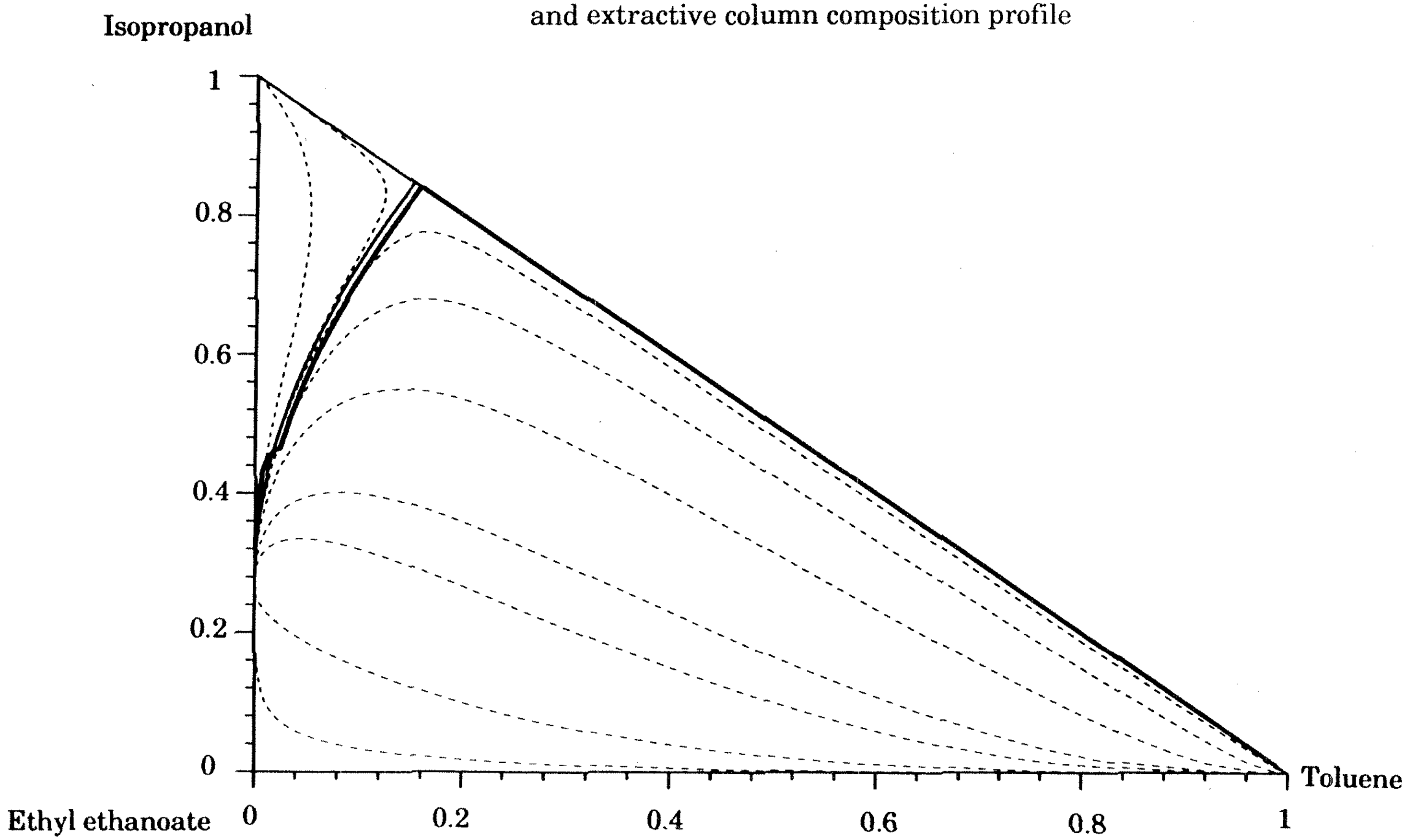


Fig. A.31: Isopropanol (1) - toluene (2) - ethyl ethanoate (3) extractive column composition profile

Fig. A.32: Isopropanol - toluene - ethyl ethanoate residue curve diagram and extractive 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

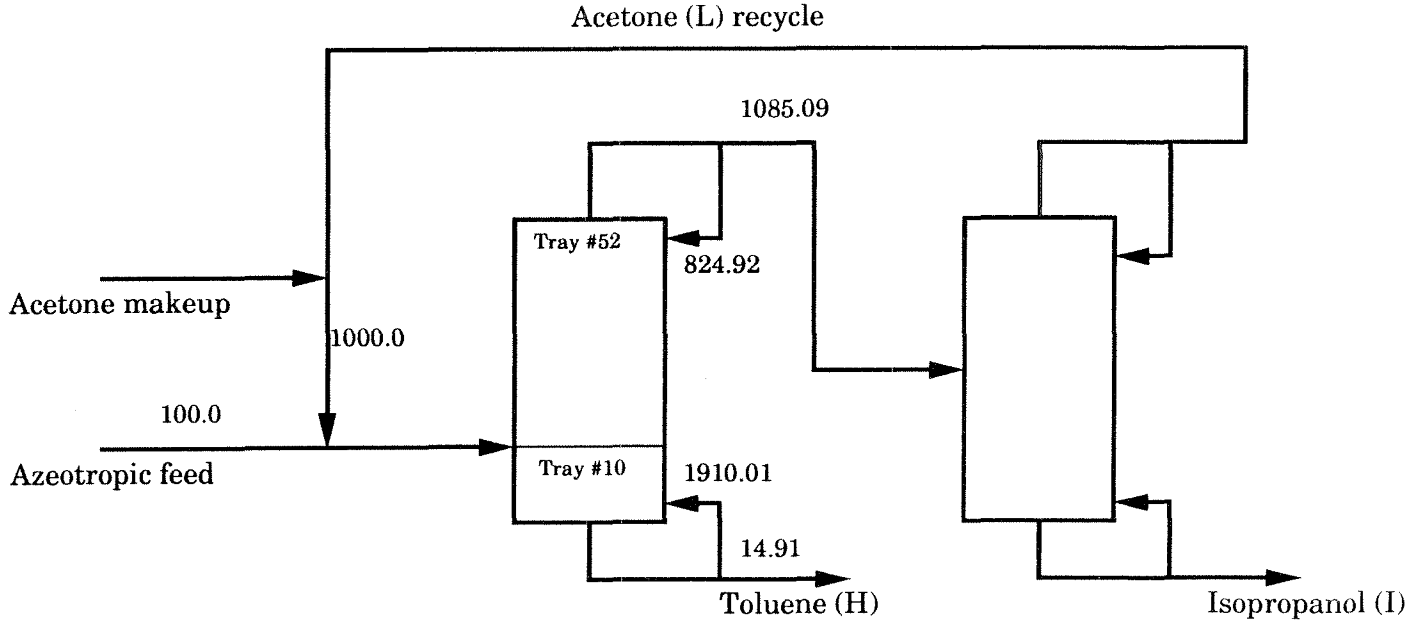


Fig. A.33: The isopropanol - toluene - acetone separation sequence

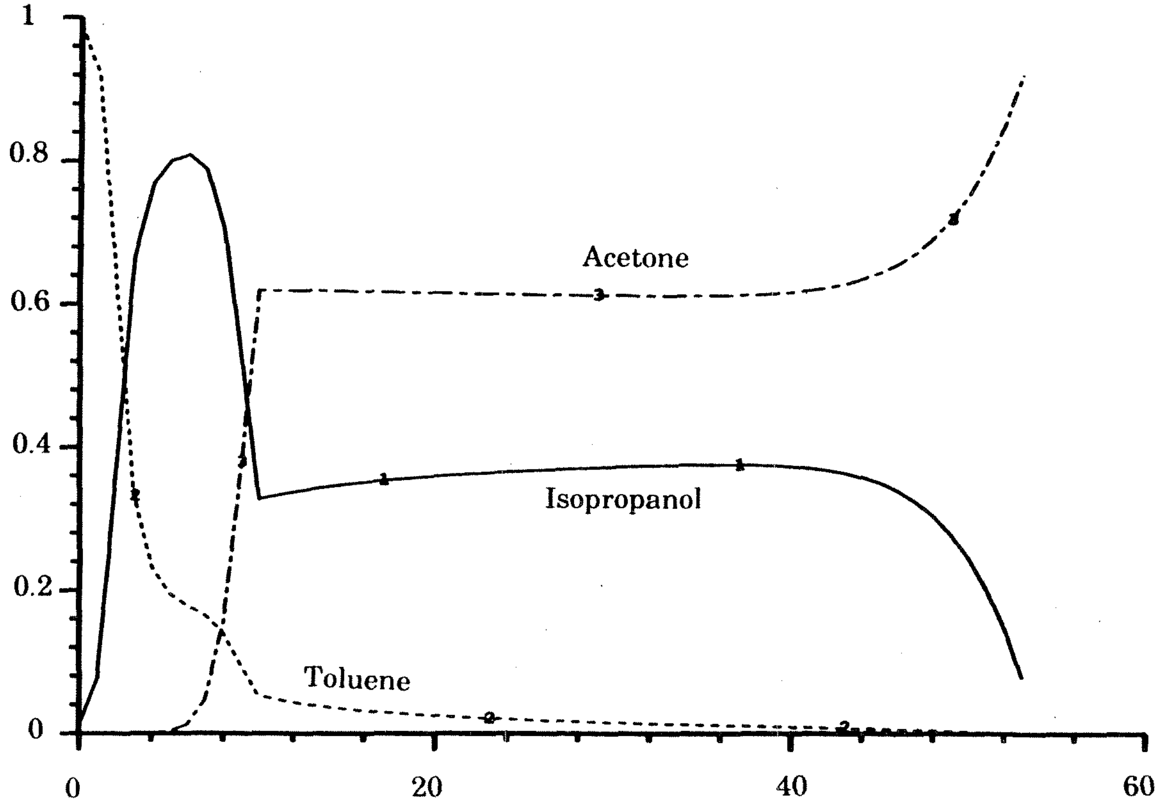
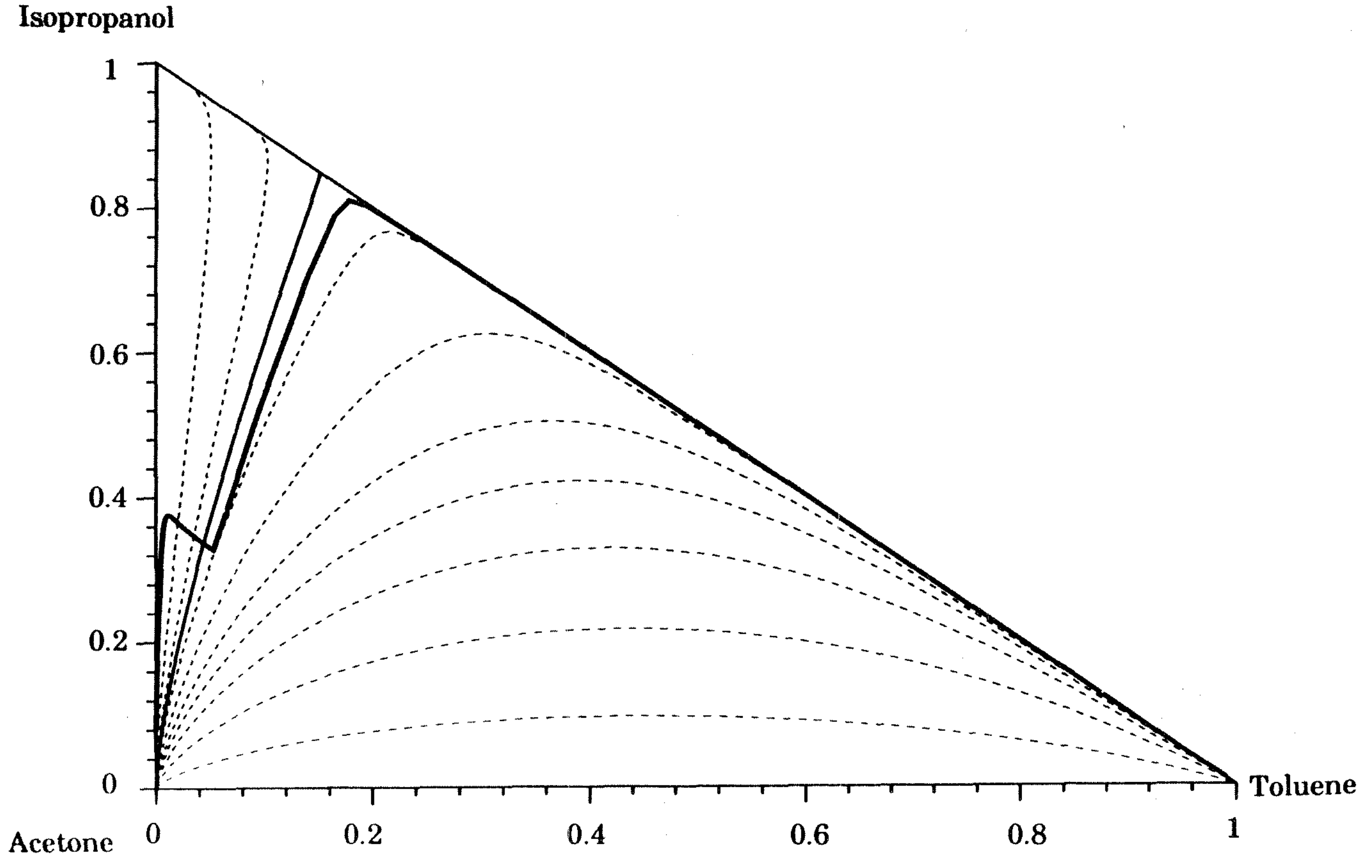


Fig. A.34: Isopropanol (1) - toluene (2) - acetone (3) extractive column composition profile

Fig. A.35: Isopropanol - toluene - acetone residue curve diagram and extractive column composition profile



Appendix B

Residue Curves and Differential Equations

Acrivos & Amundson (1955) describe the composition profiles of packed column rectifying sections by the following equations:

$$\begin{aligned} \frac{d\underline{y}}{dn}(n) &= \underline{y}'(n) - \underline{y}(n) && \text{(B.1)} \\ \underline{y}(n) &= (\frac{r}{r+1})\underline{x}(n) + \frac{\underline{x}_D}{r+1} && \text{(B.2)} \end{aligned}$$

where:

- n is a continuous variable that represents a dimensionless height of packing; n increases upwards.
- $\underline{x}(n)$ is the liquid composition at height n.
- $\underline{y}(n)$ is the vapor composition at height n.
- $\underline{y}'(n)$ is the composition of the vapor in equilibrium with $\underline{x}(n)$.
- $\underline{x}_D$ is the distillate composition.
- r is the reflux ratio.

By differentiating equation (2), we obtain:

$$\frac{d\underline{y}}{dn}(n) = (\frac{r}{r+1})\frac{d\underline{x}}{dn}(n) \qquad \text{(B.3)}$$

Substitution in equation (1) yields:

$$\frac{d\underline{x}}{dn}(n) = (\frac{r+1}{r})\underline{y}'(n) - \underline{x}(n) - \frac{\underline{x}_D}{r} \qquad \text{(B.4)}$$

Equation (4) is the same as equation (15) of Van Dongen & Doherty (1985); note that n is oriented upwards here while their height variable h' is oriented downwards.

At infinite reflux, the differential equation that describes packed column profiles becomes:

$$\frac{d\underline{x}}{dn}(n) = \underline{y}'(n) - \underline{x}(n) \qquad \text{(B.5)}$$

This equation is identical to the residue curve equation.

Physically, packed columns are made of an infinite number of differential trays; a differential amount of separation is performed on each of these differential trays. A continuous description is therefore natural for such a system. Nevertheless, chemical engineers have for many years described packed columns with plate-to-plate difference equations by using the concept of "height of packing equivalent to a tray" (Henley & Seader 1981). The success of this approach confirms Van Dongen & Doherty's conclusion, *i.e.* that the composition profiles of packed columns (obtained from differential equations) and tray columns (obtained from difference equations) do not differ significantly.

Appendix C

Entrainer Comparison Results

In this appendix, we compare the predictions we can make from the equivolatility curve diagrams azeotropic component #1 - azeotropic component #2 - entrainer with the corresponding minimum trade-off curves for several mixtures:

- **Pentane - acetone**: Benzene and toluene can both be used as heavy entrainers for the pentane (L) - acetone (I) azeotrope. Figure C.1 shows the isovolatility curves of pentane and acetone in the presence of benzene and of toluene. We see that x_E is equal to 0.44 in the case of benzene, while it is equal to 0.52 in the case of toluene. Therefore, benzene should give a lower optimum feed ratio.

  A comparison of the equivolatility curve diagrams obtained with benzene and toluene (figure C.2 and figure C.3) shows that benzene yields higher relative volatilities between pentane and acetone than toluene. Indeed, close to the pentane - entrainer edge, the relative volatility of pentane and acetone reaches as high as 2.0 with benzene, while it is limited to 1.5 with toluene. Benzene should yield a lower optimum minimum reflux ratio than toluene.

  Figure C.4 confirms these predictions. We see that the optimum feed ratio and the optimum minimum reflux ratio are both lower with benzene than with toluene.

- **Ethanol - methyl ethyl ketone**: Sec-butanol and normal butanol can both be used as heavy entrainers for the ethanol (L) - methyl ethyl ketone (I) azeotrope.

Fig. C.1: The isovolatility curves of pentane and acetone using benzene (1) and toluene (2) as entrainers

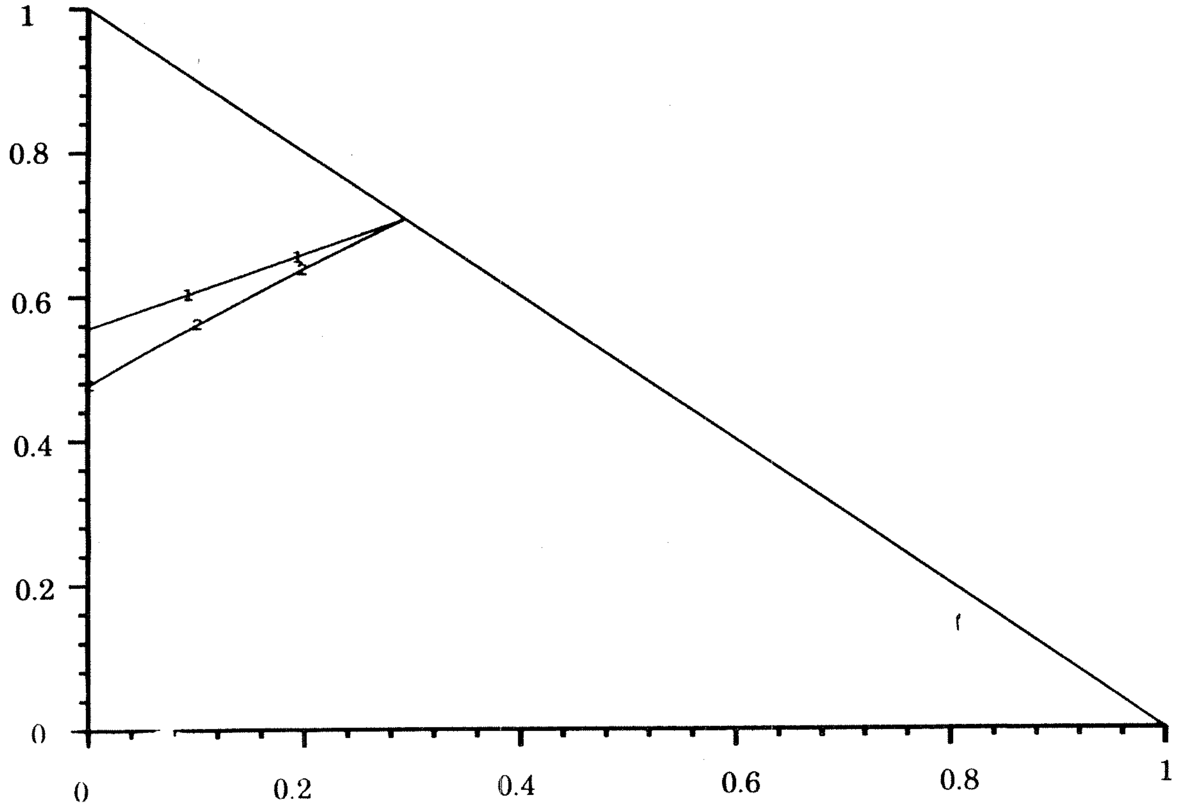


Fig. C.2: The pentane (L) - acetone (I) - benzene (H)
equivolatility curve diagram

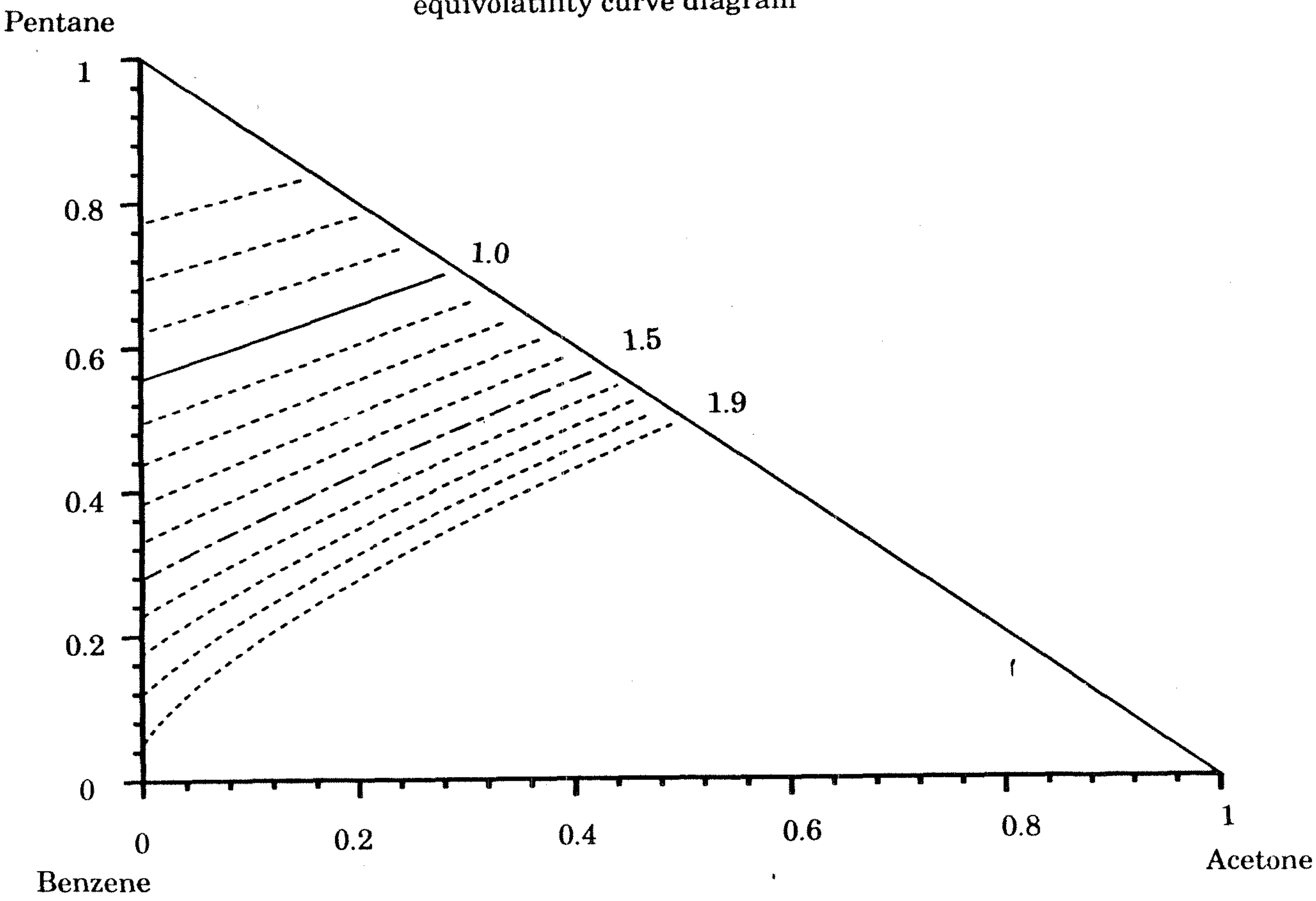


Fig. C.3: The pentane (L) - acetone (I) - toluene (H) equivolatility curve diagram

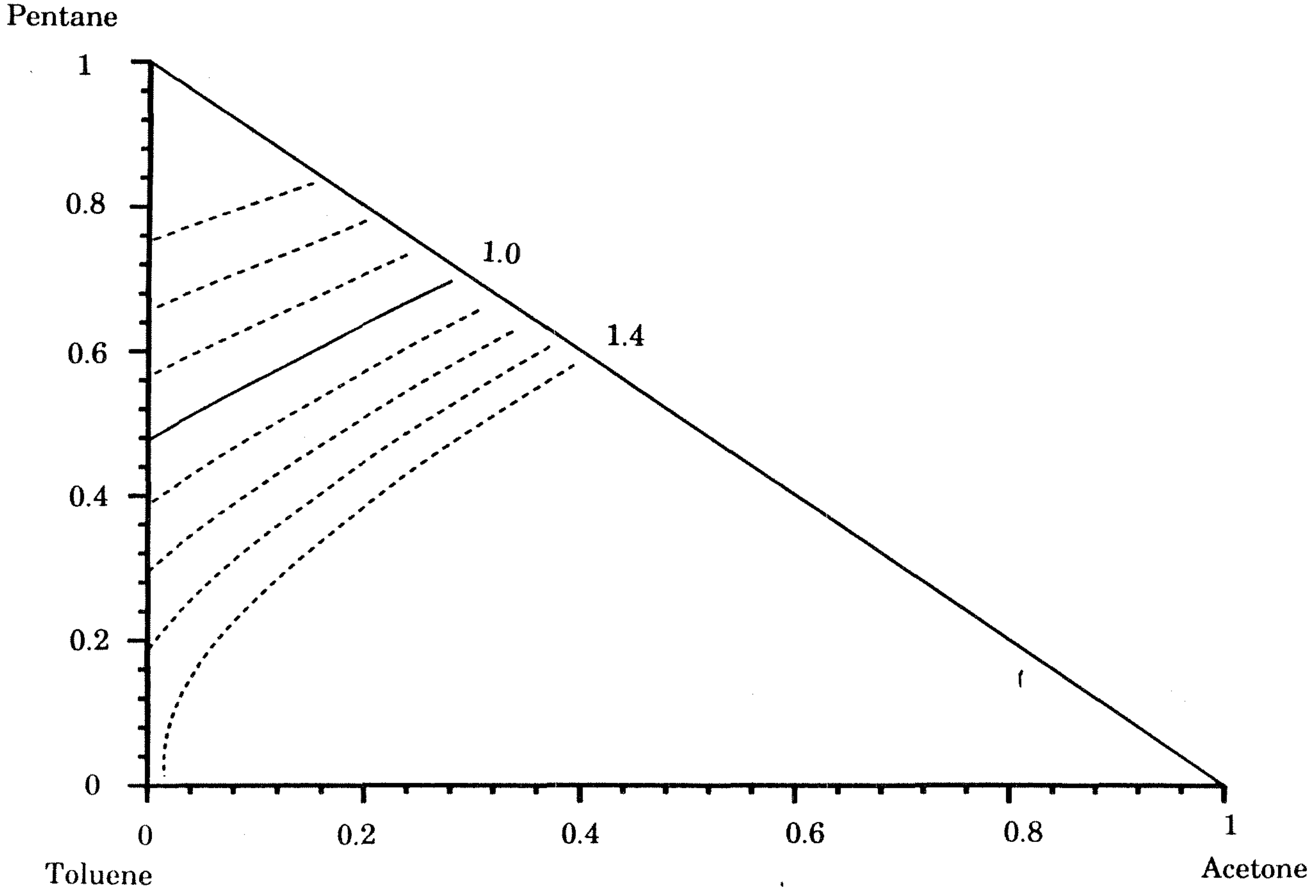


Fig. C.4: The minimum trade-off curves of pentane and acetone using benzene (1) and toluene (2) as entrainers

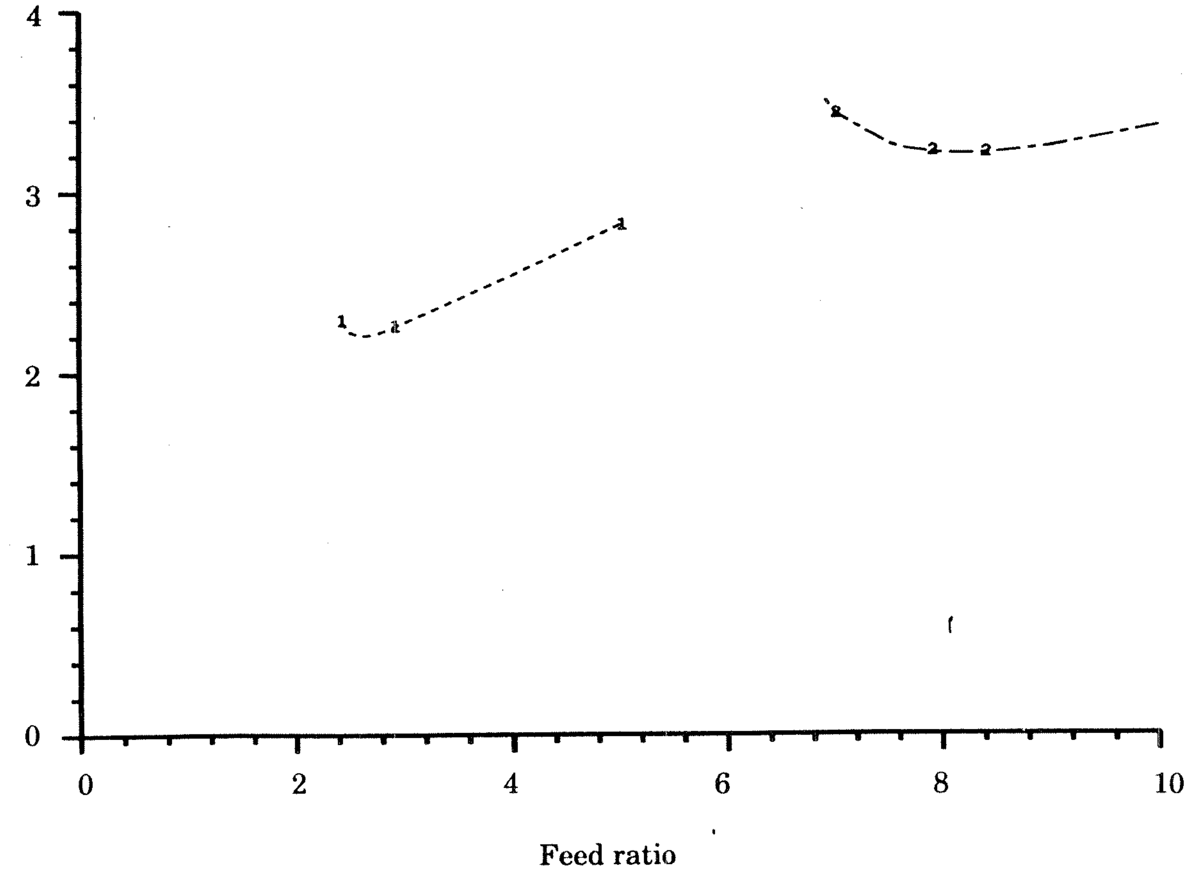


Figure C.5 shows the isovolatility curves of ethanol and methyl ethyl ketone in the presence of both butanols. We see that x_E is equal to 0.81 in the case of sec-butanol, while it is equal to 0.60 in the case of n-butanol. Therefore, n-butanol should give a lower optimum feed ratio. Here, we expect separation to be difficult with sec-butanol because of the high value of x_E. Large feed ratios should be necessary.

A comparison of the equivolatility curve diagrams obtained with sec-butanol and n-butanol (figure C.6 and figure C.7) shows that n-butanol yields higher relative volatilities between ethanol and methyl ethyl ketone than sec-butanol. Indeed, close to the methyl ethyl ketone - butanol edge, the relative volatility of ethanol and methyl ethyl ketone goes up to 1.7 with n-butanol, while it is limited to 1.2 with sec-butanol. N-butanol should yield a lower optimum minimum reflux ratio than sec-butanol.

Figure C.8 confirms these predictions. We see that the optimum feed ratio and the optimum minimum reflux ratio are both lower with n-butanol than with sec-butanol. Note that separation does require large feed ratios with sec-butanol.

- **Butanal - ethanol**: Isobutanol and normal butanol can both be used as heavy entrainers for the butanal (L) - ethanol (I) azeotrope. Figure C.9 displays the isovolatility curves of butanal and ethanol in the presence of both butanols. We see that x_E is equal to 0.39 in the case of isobutanol, while it is equal to 0.08 in the case of n-butanol. Therefore, n-butanol should give a lower optimum feed ratio than isobutanol.

  A comparison of the equivolatility curve diagrams obtained with isobutanol and n-butanol (figure C.10 and figure C.11) shows that isobutanol yields higher relative volatilities between butanal and ethanol than n-butanol. Indeed, close

Fig. C.5: The isovolatility curves of ethanol and methyl ethyl ketone using sec-butanol (1) and n-butanol (2) as entrainers

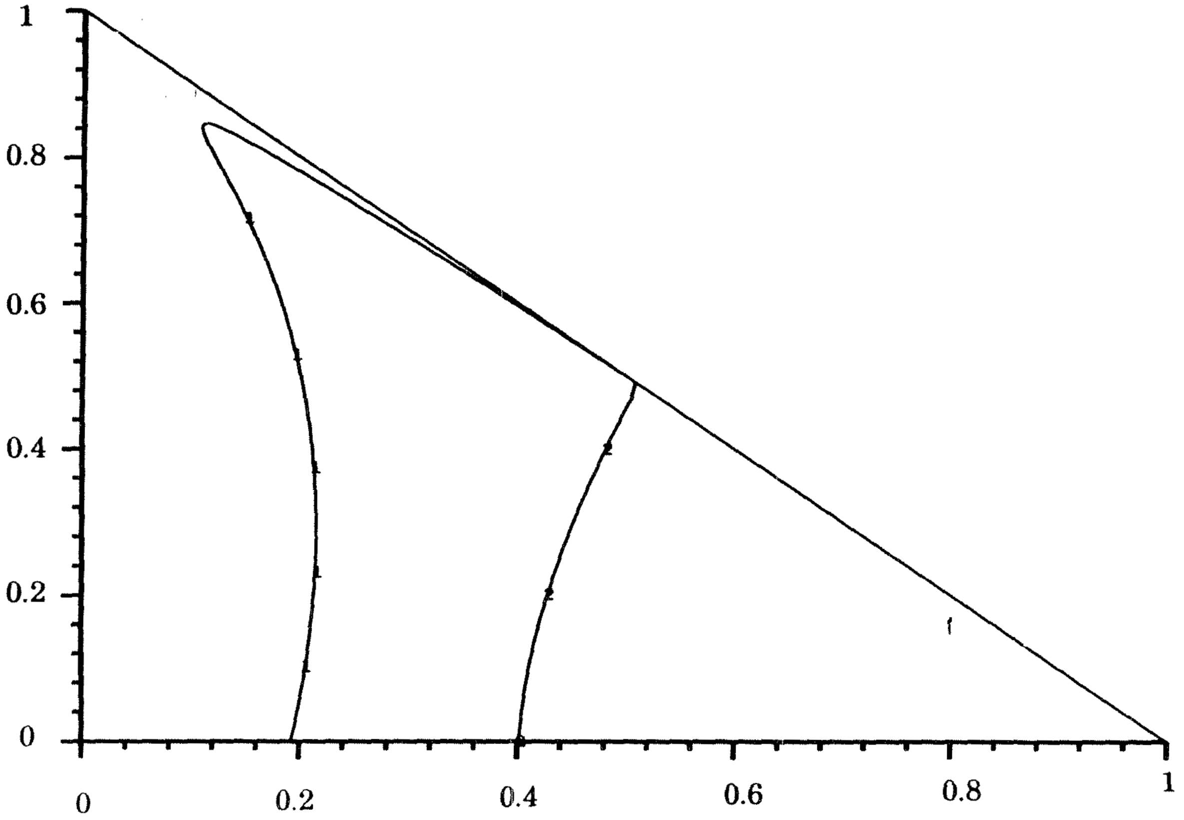


Fig. C.6: The ethanol (L) - methyl ethyl ketone (I) - sec-butanol (H) equivolatility curve diagram

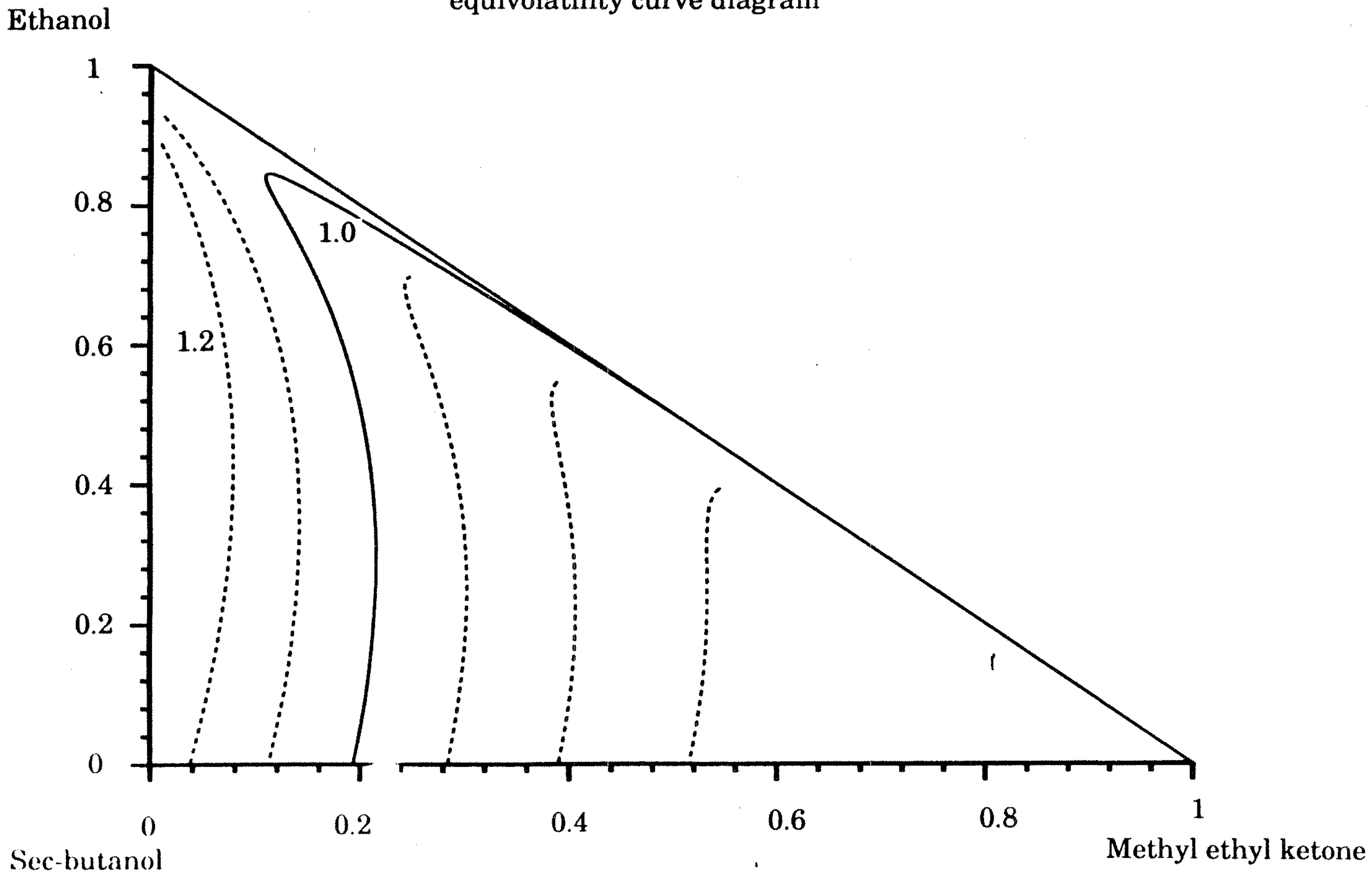


Fig. C.7: The ethanol (L) - methyl ethyl ketone (I) - n-butanol (H) equivolatility curve diagram

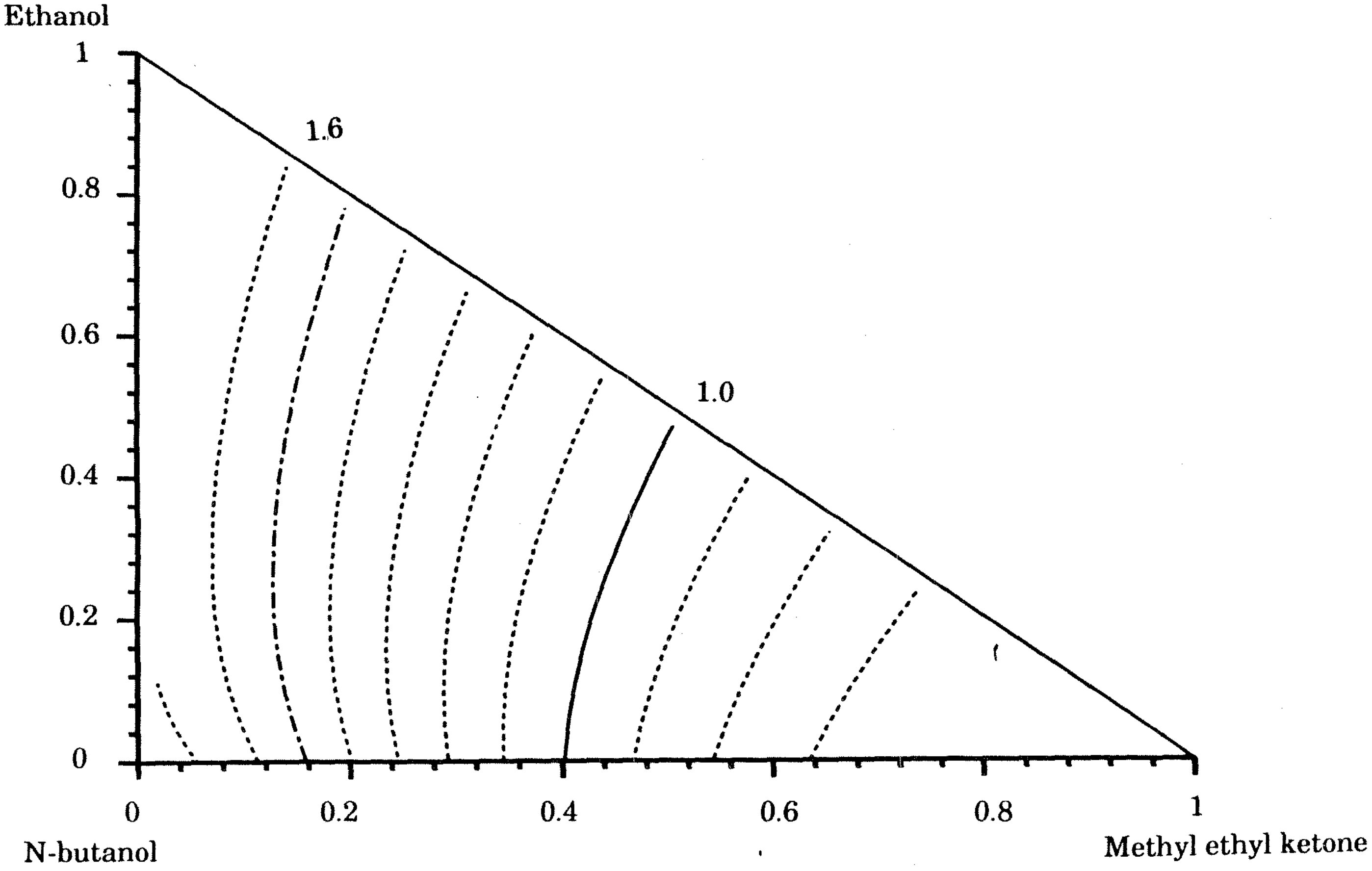
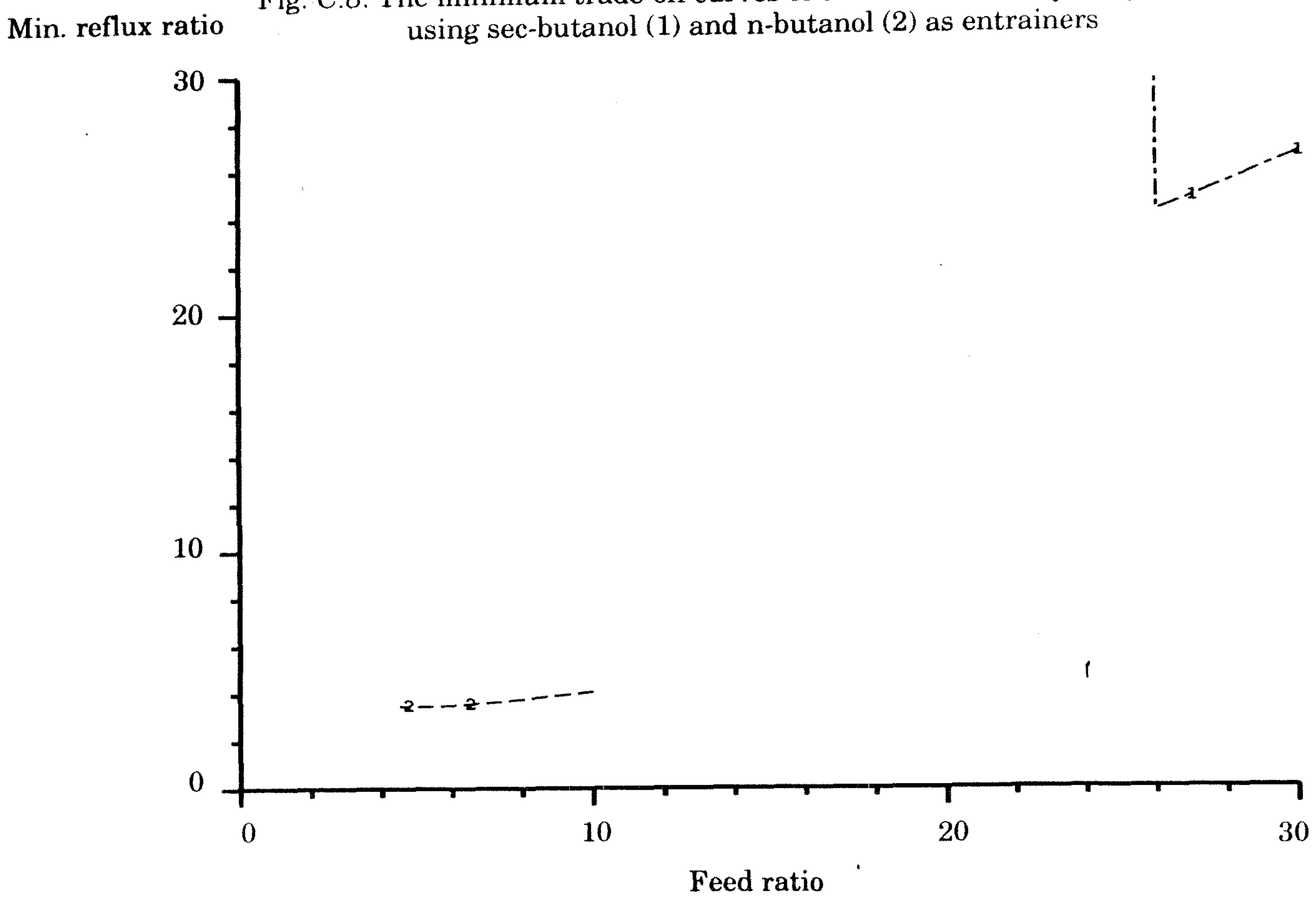


Fig. C.8: The minimum trade-off curves of ethanol and methyl ethyl ketone using sec-butanol (1) and n-butanol (2) as entrainers



to the butanal - butanol edge, the relative volatility of butanal and ethanol goes up to 2.3 with isobutanol, while it is limited to 1.3 with n-butanol. Isobutanol should yield a lower optimum minimum reflux ratio than n-butanol.

Figure C.12 confirms these predictions. The optimum feed ratio is lower with n-butanol than with isobutanol, while the optimum minimum reflux ratio is lower with isobutanol than with n-butanol.

- **Methyl ethanoate - methanol**: Ethanol and isopropanol can both be used as heavy entrainers for the methyl ethanoate (L) - methanol (I) azeotrope. Figure C.13 displays the isovolatility curves of methyl ethanoate and methanol in the presence of both alcohols. We obtain very similar values of x_E in this case, so the optimum feed ratio should be similar.

  A comparison of the equivolatility curve diagrams obtained with isopropanol and ethanol (figure C.14 and figure C.15) shows that isopropanol yields slightly higher relative volatilities between methyl ethanoate and methanol than ethanol, but the difference is quite small: 2.8 for isopropanol versus 2.6 for ethanol. So we expect comparable optimum minimum reflux ratios.

  Figure C.16 does not confirm these results. Ethanol is actually a much worse entrainer than isopropanol for the methyl ethanoate - methanol azeotrope, because the relative volatility of methyl ethanoate and ethanol is quite low close to the methyl ethanoate corner: The relative volatility of ethanol and methyl ethanoate drops below 1.1 when the mole fraction of methyl ethanoate exceeds 97.8%. In this case, the rectifying section becomes the bottleneck of the column. This problem does not arise with isopropanol.

- **Methanol - ethyl ethanoate**: Ethanoic acid, chlorobenzene and ethyl benzene can be used as heavy entrainers for the methanol (L) - ethyl ethanoate (I) azeotrope. Figure C.17 shows the isovolatility curves of methanol and ethyl

Fig. C.9: The isovolatility curves of butanal and ethanol using isobutanol (1) and n-butanol (2) as entrainers

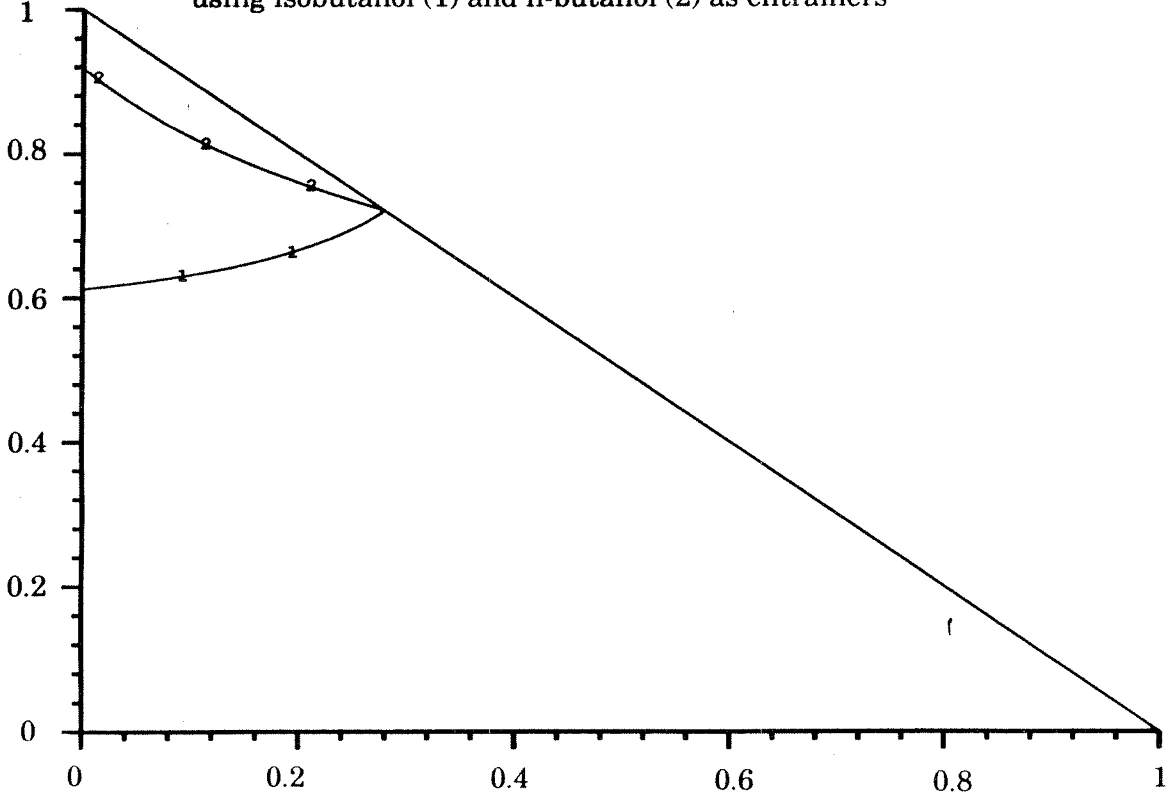
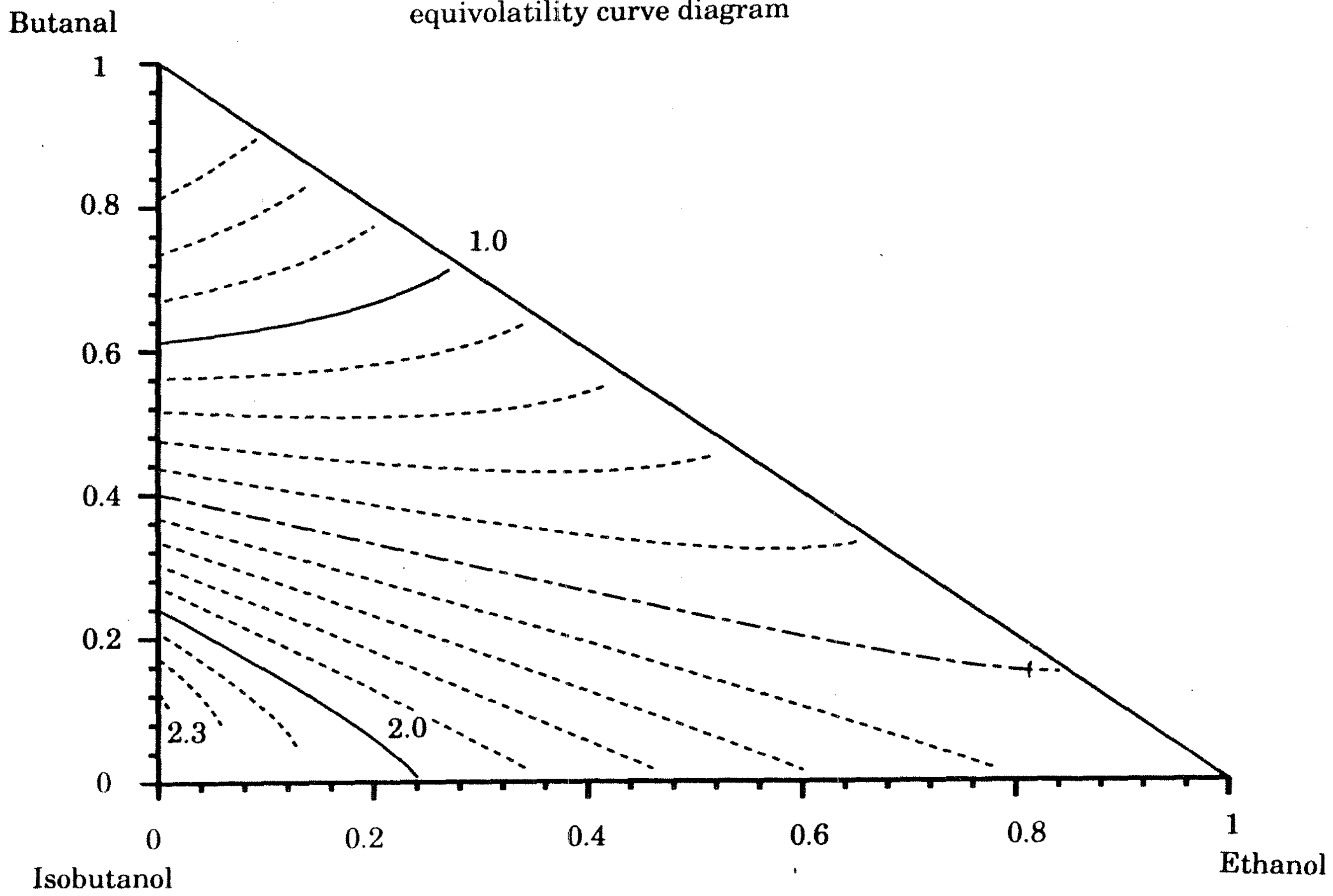


Fig. C.10: The butanal (L) - ethanol (I) - isobutanol (H) equivolatility curve diagram



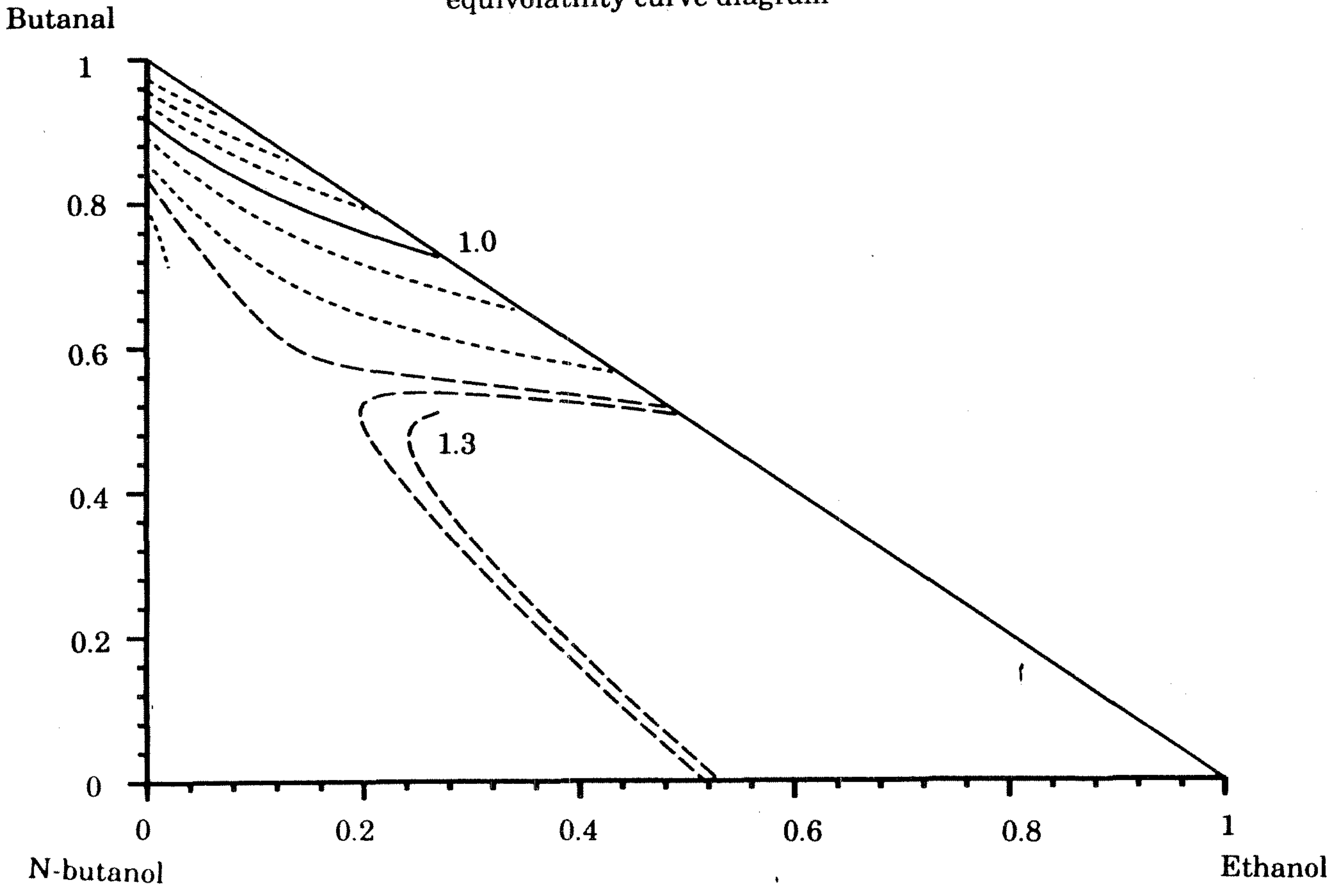


Fig. C.11: The butanal (L) - ethanol (I) - n-butanol (H) equivolatility curve diagram

Fig. C.12: The minimum trade-off curves of butanal and ethanol using isobutanol (1) and n-butanol (2) as entrainers

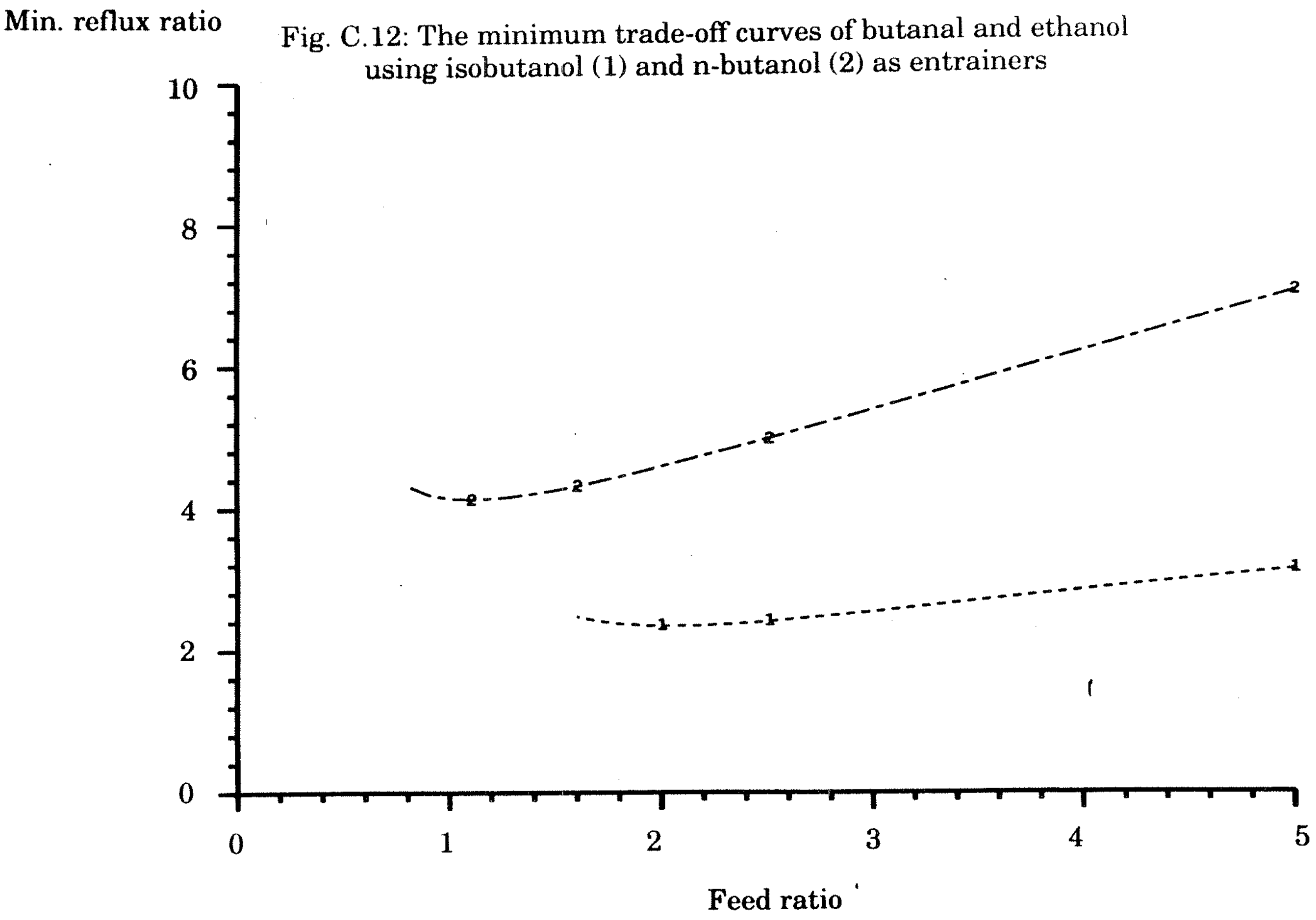


Fig. C.13: The isovolatility curves of methyl ethanoate and methanol using ethanol (1) and isopropanol (2) as entrainers

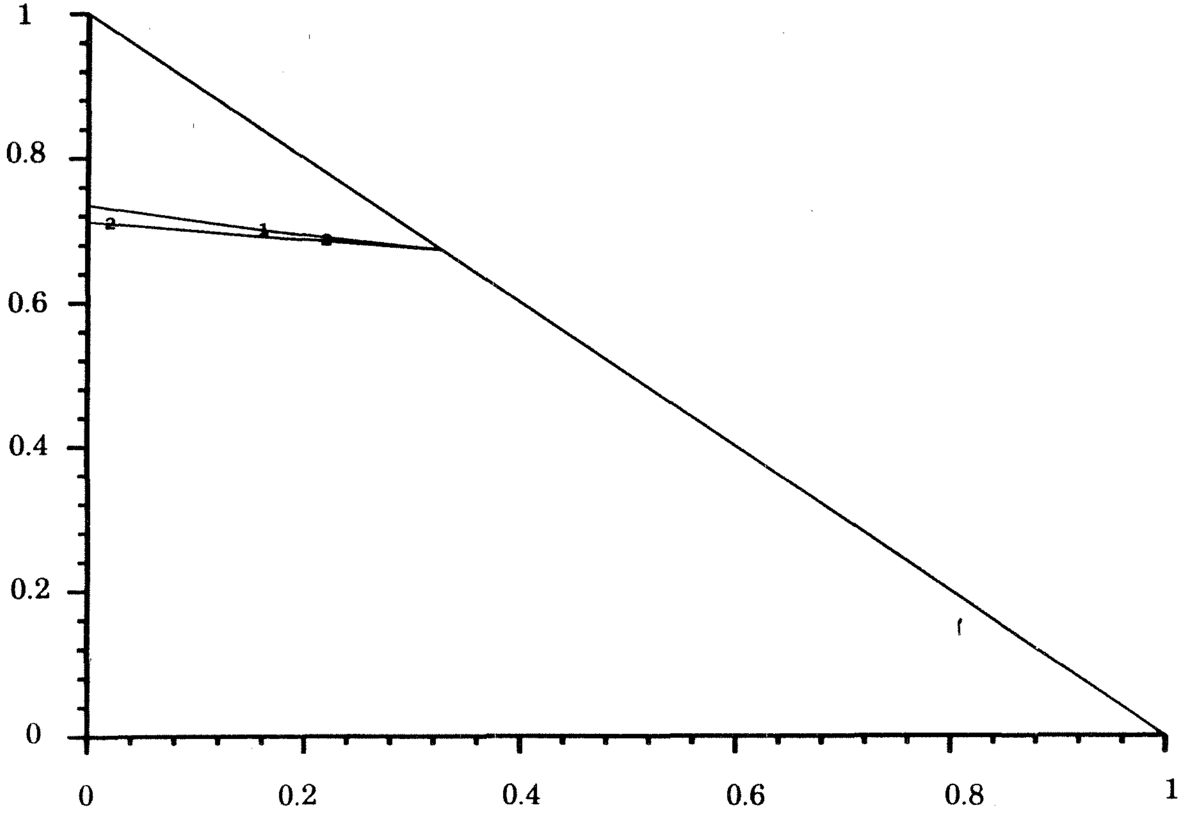


Fig. C.14: The methyl ethanoate (L) - methanol (I) - ethanol (H) equivolatility curve diagram

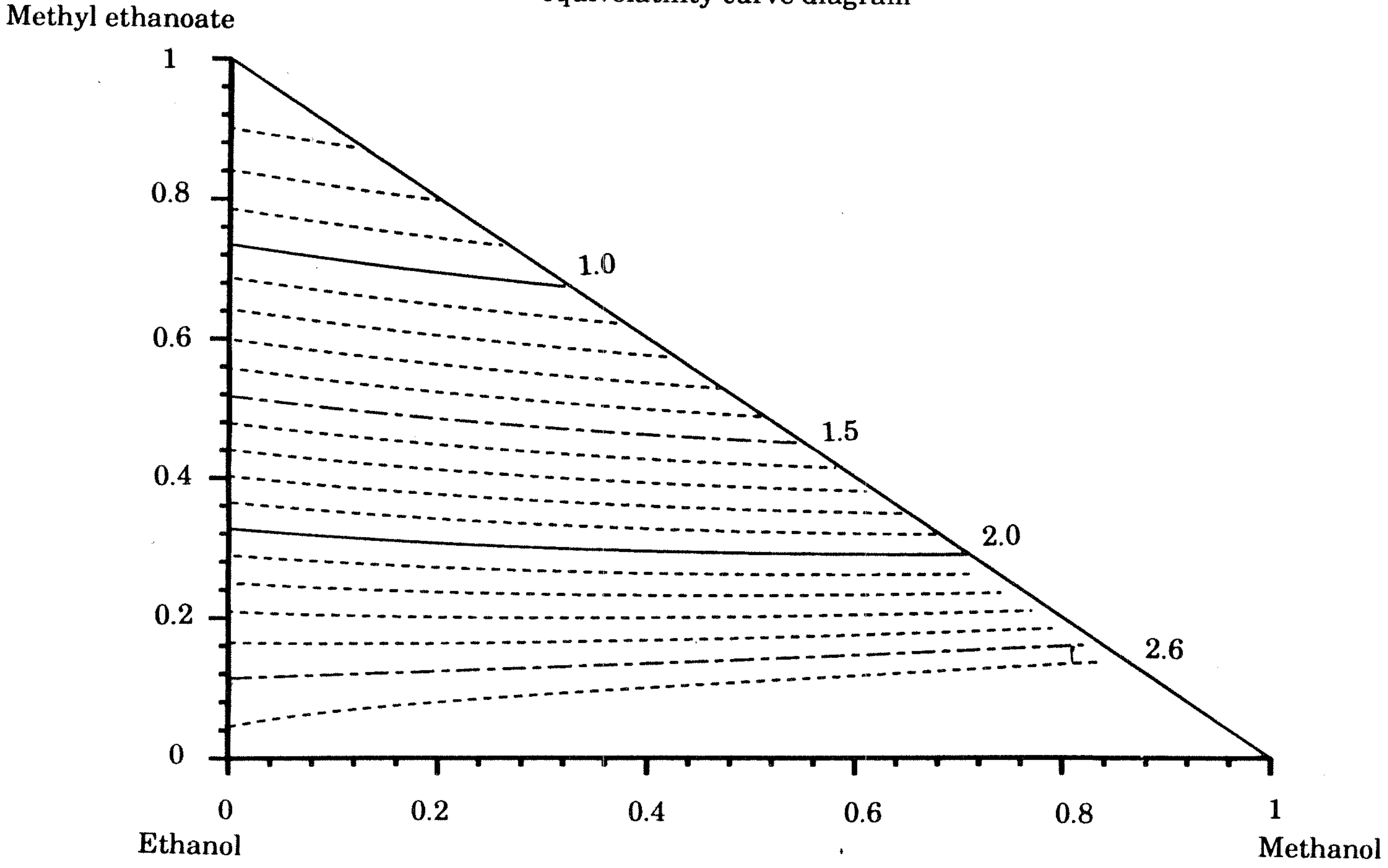


Fig. C.15: The methyl ethanoate (L) - methanol (I) - isopropanol (H) equivolatility curve diagram

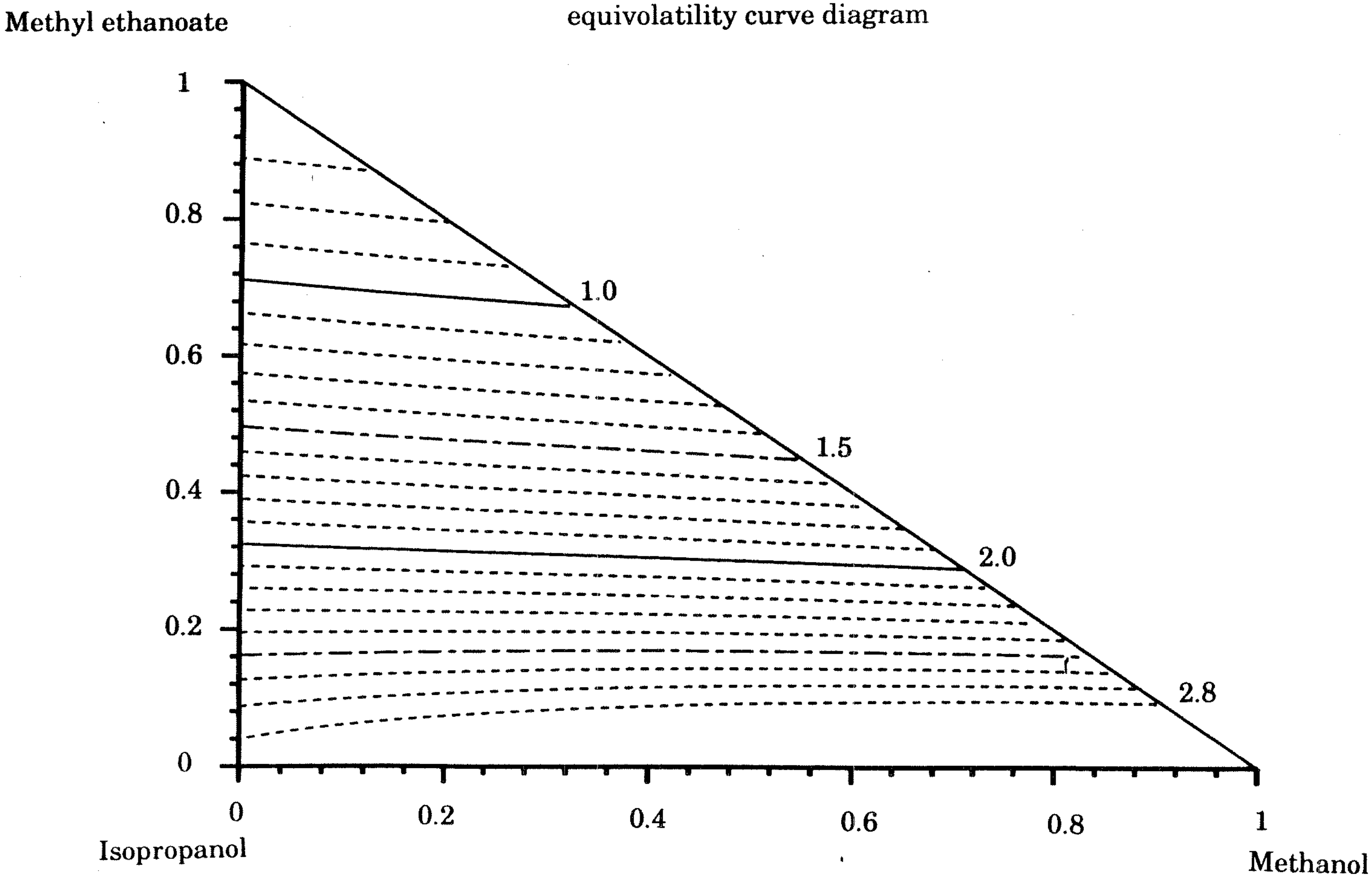
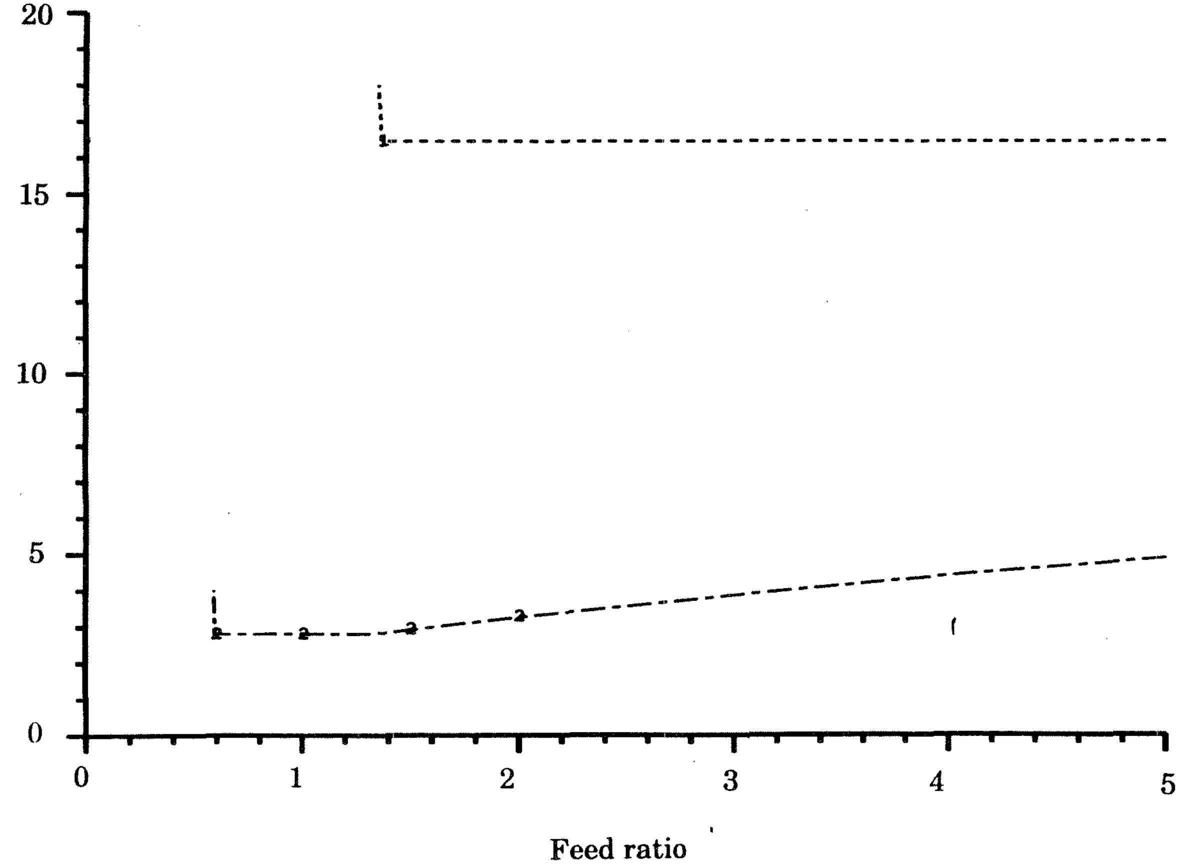


Fig. C.16: The minimum trade-off curves of methyl ethanoate and methanol using ethanol (1) and isopropanol (2) as entrainers



ethanoate in presence of these entrainers. We see that x_E is equal to 0.92 for ethanoic acid, 0.13 for chlorobenzene and 0.22 for ethyl benzene. Therefore, chlorobenzene should yield a lower optimum feed ratio than ethyl benzene, and ethyl benzene should yield a lower optimum feed ratio than ethanoic acid. We expect separation to be difficult and to require large feed ratios in the case of ethanoic acid.

A comparison of the equivolatility curve diagrams obtained with these entrainers (figure C.18, figure C.19 and figure C.20) shows that ethyl benzene yields the highest relative volatilities in the three entrainers (up to 10), while chlorobenzene ranks second, with relative volatilities reaching up to 8.5, and ethanoic acid third, with relative volatilities which do not exceed 1.1. The optimum minimum reflux ratio should follow this classification.

Figure C.21 confirms these predictions. The optimum feed ratio is lower with chlorobenzene than with ethyl benzene, while the optimum minimum reflux ratio is lower with ethyl benzene than with chlorobenzene. We were unable to synthesize a column separating the methanol - ethyl ethanoate azeotrope using ethanoic acid as entrainer.

Fig. C.17: The isovolatility curves of methanol and ethyl ethanoate using ethanoic acid (1), chlorobenzene (2) and ethyl benzene (3) as entrainers

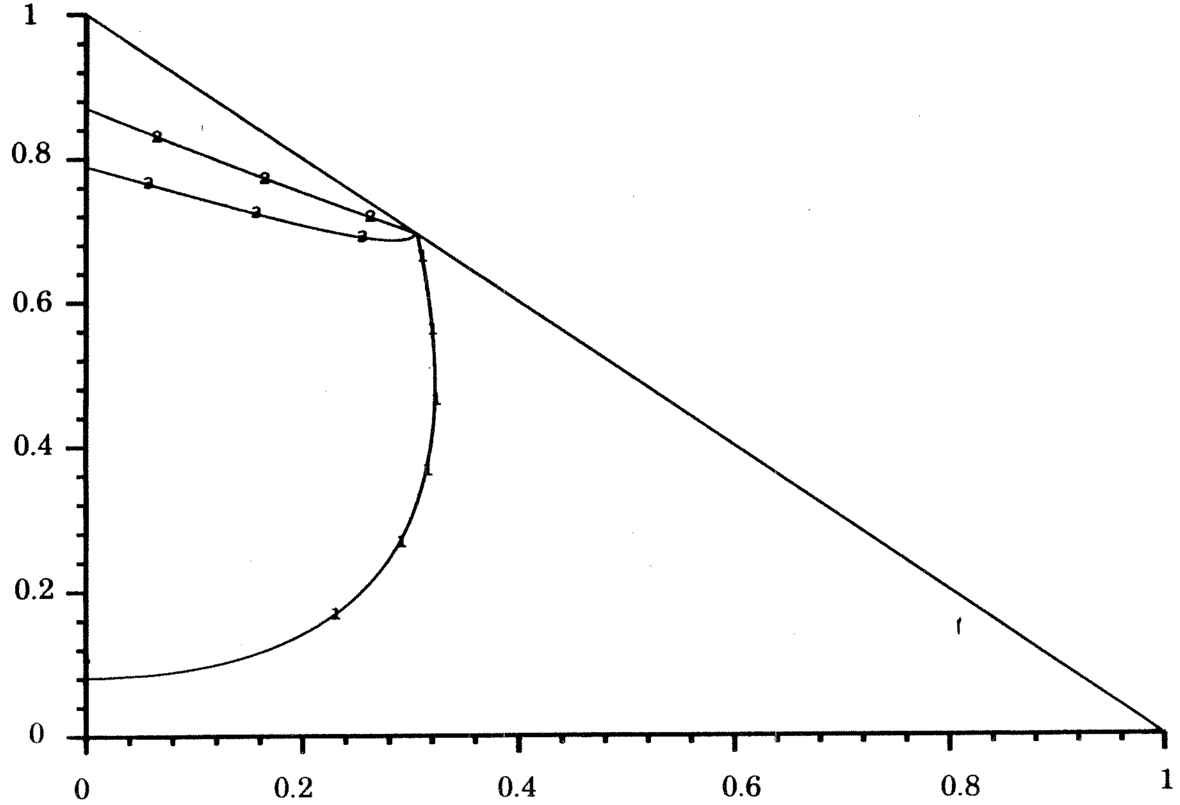


Fig. C.18: The methanol (L) - ethyl ethanoate (I) - ethanoic acid (H) equivolatility curve diagram

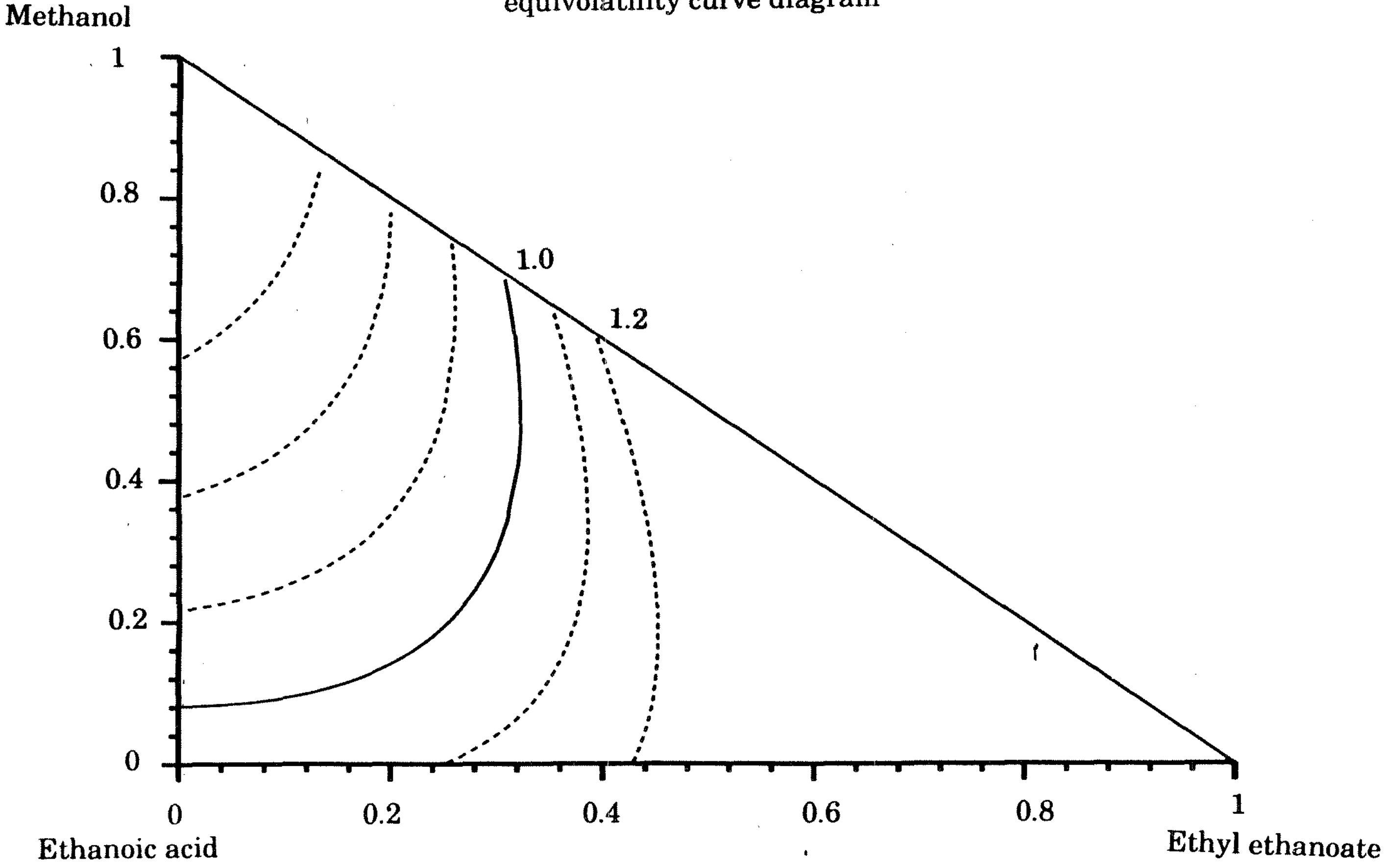


Fig. C.19: The methanol (L) - ethyl ethanoate (I) - chlorobenzene (H) equivolatility curve diagram

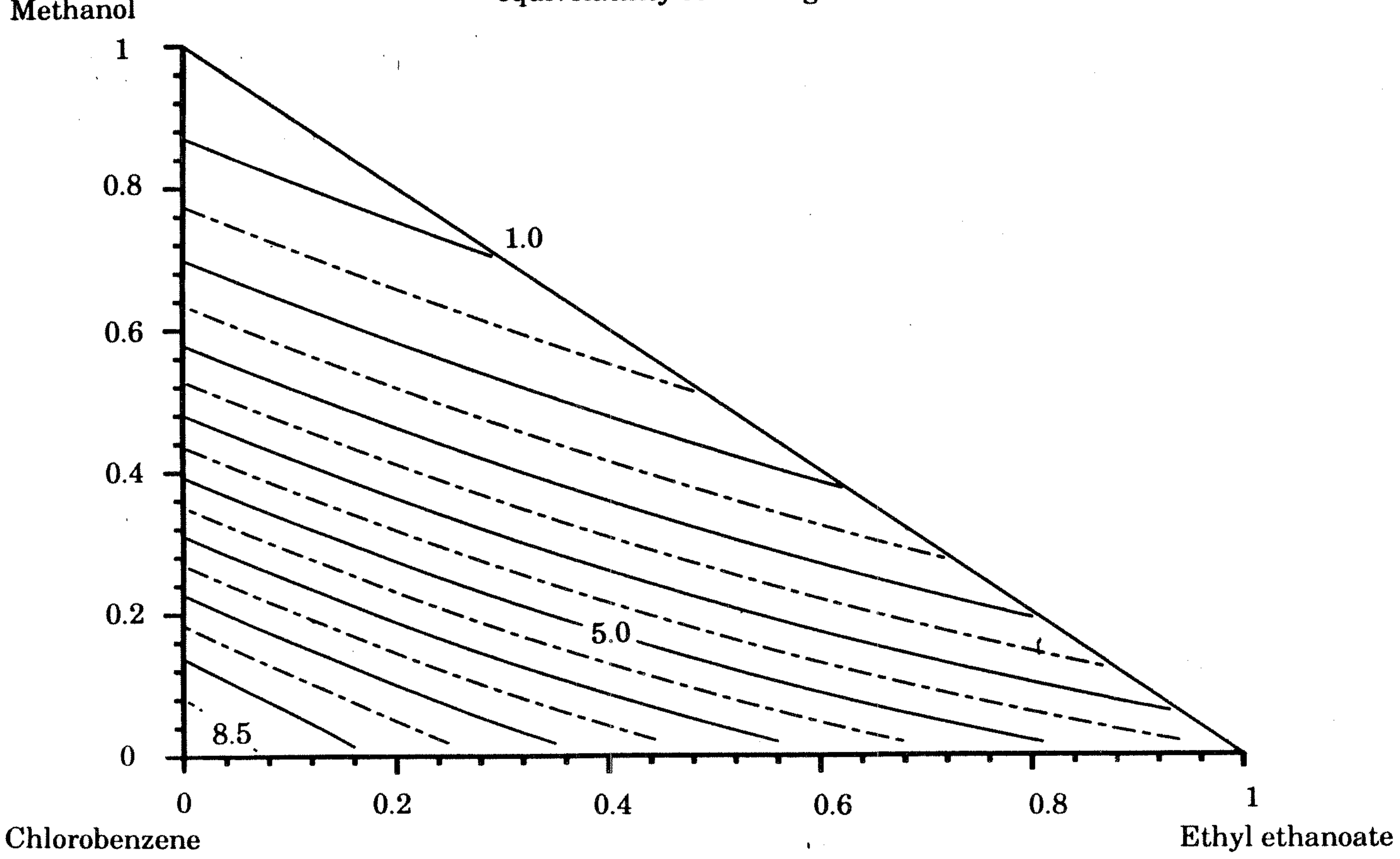


Fig. C.20: The methanol (L) - ethyl ethanoate (I) - ethyl benzene (H) equivolatility curve diagram

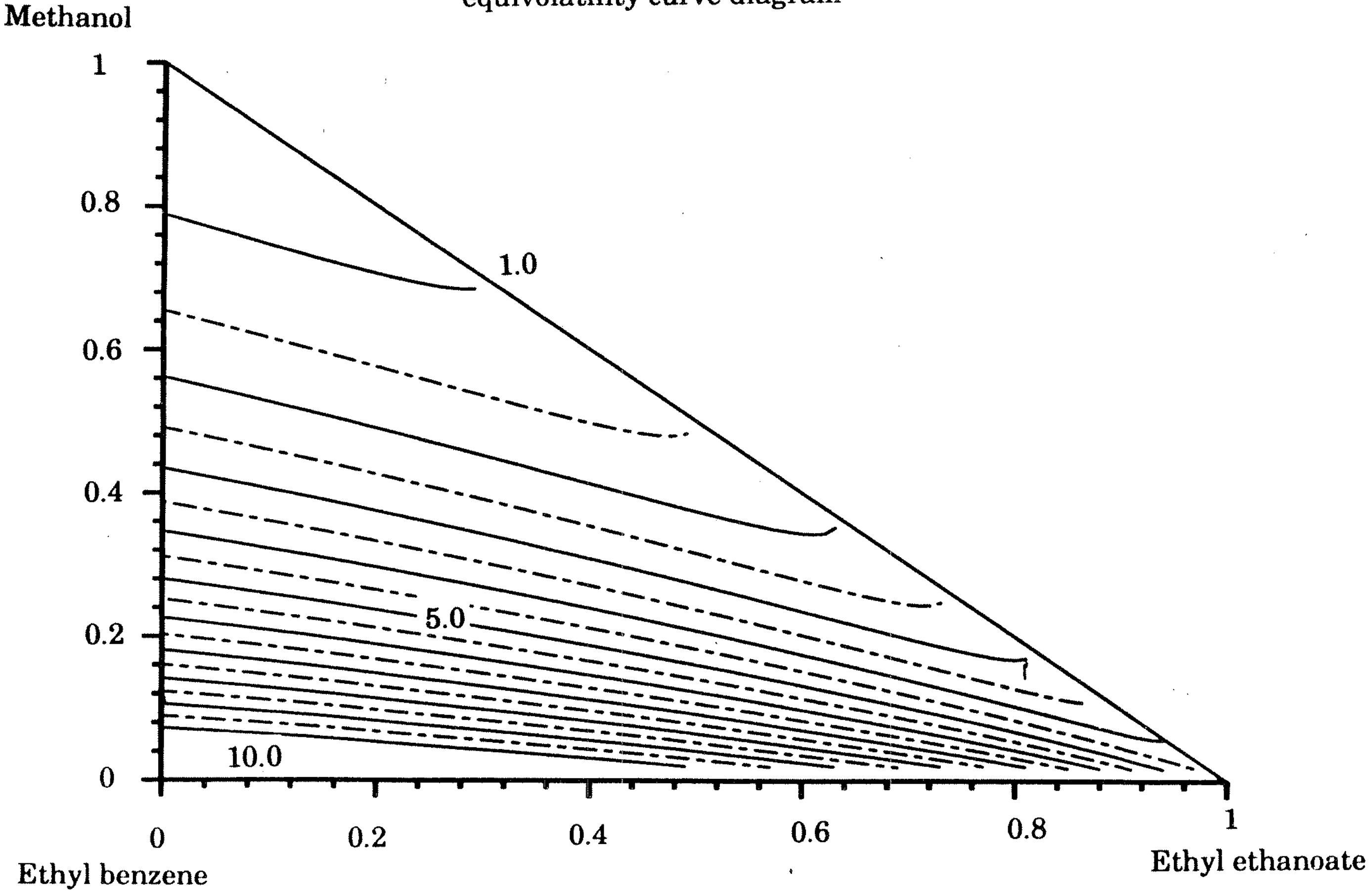


Fig. C.21: The minimum trade-off curves of methanol and ethyl ethanoate using chlorobenzene (1) and ethyl benzene (2) as entrainers