Separation Regions and Processes of Zeotropic and Azeotropic Ternary Distillation

Johann G. Stichlmair and Juan-Ramon Herguijuela
University of Essen, Universitaetsstrasse 15, 4300 Essen 1, Germany

The rigorous calculation of top and bottom fractions of a multicomponent distillation is very time consuming and involved as it can only be done iteratively, and convergence problems are often encountered, especially in azeotropic systems. This article presents a method for the easy determination of possible top and bottom fractions of a ternary distillation. This method, which works for zeotropic as well as for azeotropic mixtures, is especially useful in the first steps of process synthesis and design since impossible separations can be determined and thus excluded from further analysis so that work can be concentrated on feasible processes. A very important application of the method developed in this article is to the design and analysis of processes for complete separation of binary azeotropic mixtures by use of an entrainer (for example, Azeotropic Distillation and Extractive Distillation). Knowledge of the separation regions in the distillation diagram allows for the development of a generalized process and the formulation of criteria for entrainer selection. The effectiveness of the method is demonstrated on a number of industrial important processes.

Separation Regions of Ternary Distillation

The top and bottom fractions of a distillation column have to meet two conditions. The first condition requires the material balance around the column to be fulfilled:

$$F=D+B$$

$$F\cdot x_{Fi}=D\cdot x_{Di}+B\cdot x_{Bi} \qquad (1)$$

This system of linear equations is represented in Figure 1 by a straight line on which the feed F, the top fraction D and the bottom fraction B have to lie. The second condition requires that the concentrations x_{Di} (of the top fraction) and x_{Bi} (of the bottom fraction) are the end points of the concentration profile developed within the column during operation. Generally, the internal concentration profile is a very complex function:

$$x_{i,n}=f(x_{Fi},p_i^o,\gamma_i,T,p,n_1,n_2,R,D/F,\dots) \qquad (2)$$

This relationship is represented by two sections of a curve in Figure 1. In general, there exists a concentration jump at the feed point. The numerical evaluation of Eqs. 1 and 2 is very difficult and cumbersome. It can be performed with the aid of complex computer programs and only by iteration during

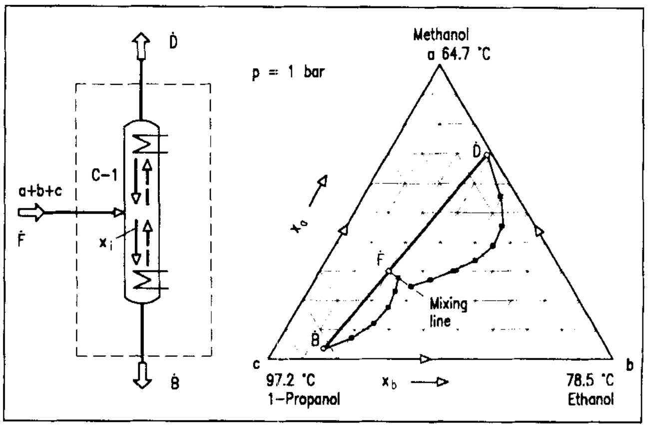

Figure 1. Representation of ternary distillation in a triangular composition diagram.

In general, there exists a concentration jump at the feed point. ——Material balance around the column, —o—o— Internal concentration profile.

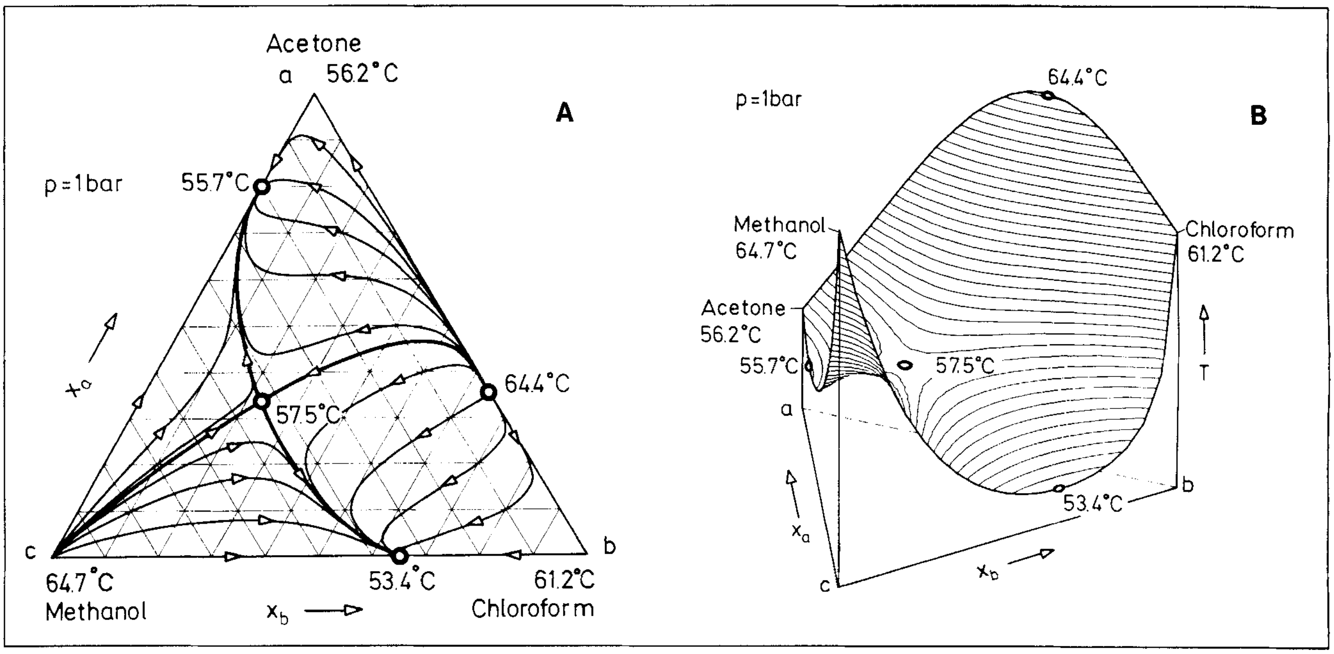

Figure 2. Distillation lines (A) and boiling point surface (B) of the ternary mixture acetone-chloroform-methanol.

The formation of a ridge and a valley in the boiling point surface leads to border distillation lines.

which convergence problems are very often encountered. Therefore, it is not advisable to perform rigorous column calculations for all process alternatives to be checked in the first steps of process design. The following method allows the engineer to determine all possible top and bottom fractions of a ternary distillation without having to go through a rigorous column calculation.

Separation regions at total reflux

If the reflux R in a column is very high ($R \rightarrow \infty$), the internal concentration profile becomes identical with a section of a distillation line (Stichlmair, 1988; Stichlmair et al., 1989). Distillation lines represent a sequence of equilibrium states which can be easily calculated by the following recursion formula:

$$\overset{*}{y}_{i,n} = f(x_{i,n}, \gamma_i, p_i^o, \dots) \tag{3}$$

$$x_{i,n+1} = \overset{*}{y}_{i,n}$$

By using vapor liquid equilibrium data obtained experimentally or from well known correlations, the composition $\overset{*}{y}_{i,n}$ of a vapor in equilibrium with a starting liquid mixture $x_{i,n}$ is established. It is then assumed that the vapor is totally condensed to form an enriched liquid with the composition $x_{i,n+1}$ different from that of the starting mixture. The composition of this condensate is then plotted in the triangular diagram of Figure 2A. The process is repeated, each time starting with the new enriched composition. The result of connecting these points is a distillation line. Different distillation lines result from different starting compositions. Arrows on these lines point in the direction of increasing content of the more volatile component and of decreasing boiling temperatures.

Figure 2A shows the course of distillation lines of the system acetone-chloroform-methanol calculated by using the Wilson equation for free excess enthalpy (Gmehling et al., 1979). This method has been used in most systems of this article. As a first approximation, distillation lines follow the direction of steepest descent on the boiling point surface shown in Figure 2B. (This comparison is oversimplified. Distillation lines are a special form of phase equilibrium presentation. Phase equilibria cannot be described by the state of the liquid phase alone.) Thus, distillation lines always originate at a peak and terminate at a hollow of the boiling point surface.

In Figure 3A three possible top and bottom fractions from the distillation of a ternary zeotropic mixture are shown. The top and bottom fractions have to be both on the same distillation line (due to the assumption of near-total reflux) and also lie on a straight line that passes through F to satisfy the material balance. The straight line represented by Eq. 1 forms a chord to the distillation line represented by Eq. 3. Obviously, there exists a large number of different chords that pass through F. At the extreme positions they go through the origin or terminus of the distillation lines. Top and bottom fractions can both lie on various distillation lines, too. It should be noted that the sides of the triangle are themselves distillation lines. The family of all possible top and bottom fractions form the separation regions shaded in Figure 3B. These separation regions are limited by the distillation line through the feed F and by a section of the straight lines through F and the origin and terminus of the distillation lines.

Of special interest are the pure substances that can be separated from a ternary mixture. In Figure 3B only the low boiler a and the high boiler c can be separated by a single distillation step from the ternary mixture.

This is intuitively correct in the case of a simple zeotropic ternary distillation. But the possible products of a distillation involving an azeotrope and entrainer may not be that obvious.

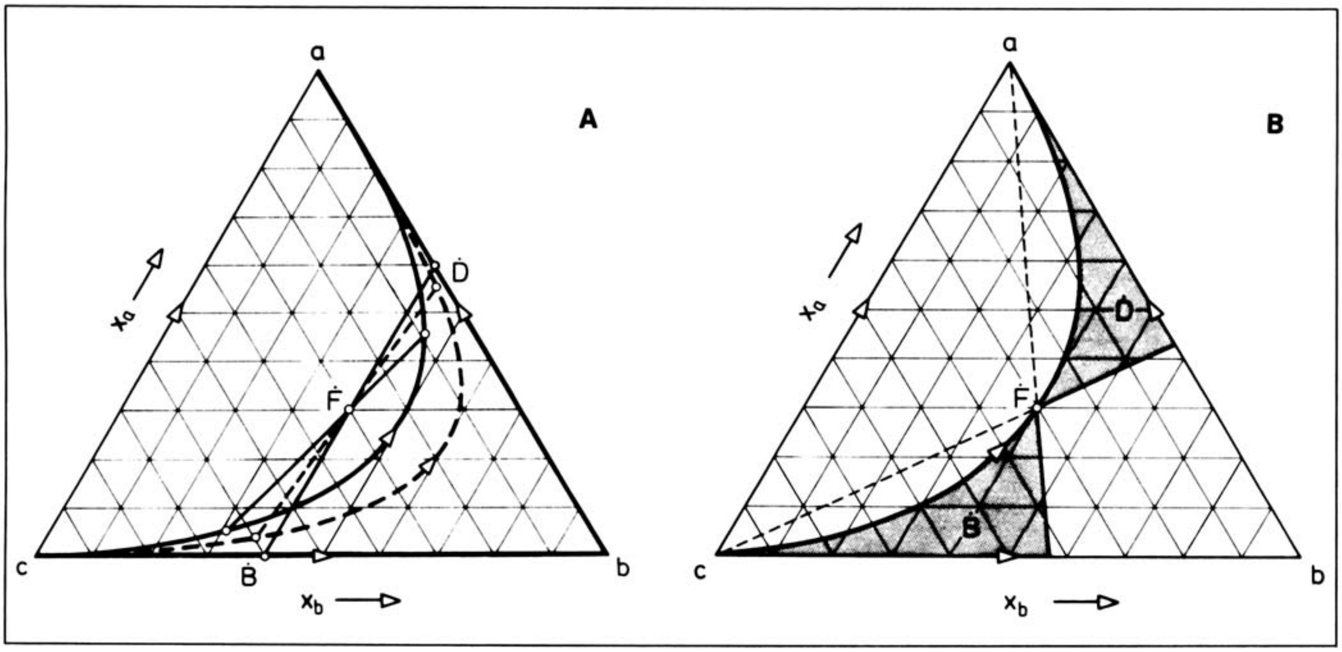

Figure 3. Separation region of a ternary zeotropic mixture: (A) determination of possible top and bottom fractions; (B) separation region.

The procedure outlined above can be applied to any ternary distillation to determine possible top and bottom products achievable by distillation.

This method for the determination of the separation regions is applied to a system with an *b-c* minimum azeotrope in Figure 4. This mixture exhibits two different origins of distillation lines (local maxima of boiling point surface). Consequently, there has to exist a valley between these two peaks. The position of the valley is approximately marked by the course of the border distillation line that runs from the minimum azeotrope to the low boiler *a*. Since the straight line through *F* is always a chord of a distillation line, the top and bottom fractions (*D* and *B*, respectively) can lie only on the same side of the border distillation line as the feed *F*. The border distillation line forms then a barrier that cannot be crossed by distillation, much like a binary azeotrope. As can be seen in Figure 4B, the border

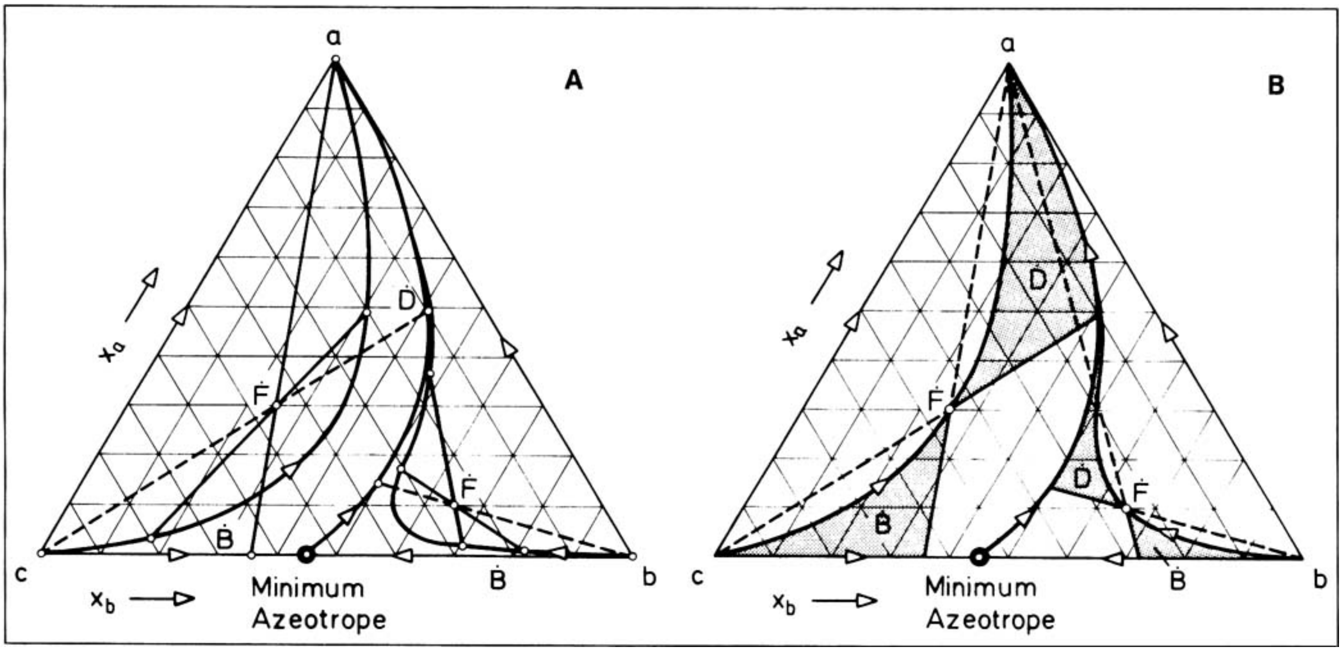

Figure 4. Separation region of a ternary mixture with a *b-c* minimum azeotrope.

The border-distillation line forms a barrier that cannot be crossed by distillation: (A) determination of possible top and bottom fractions; (B) separation region.

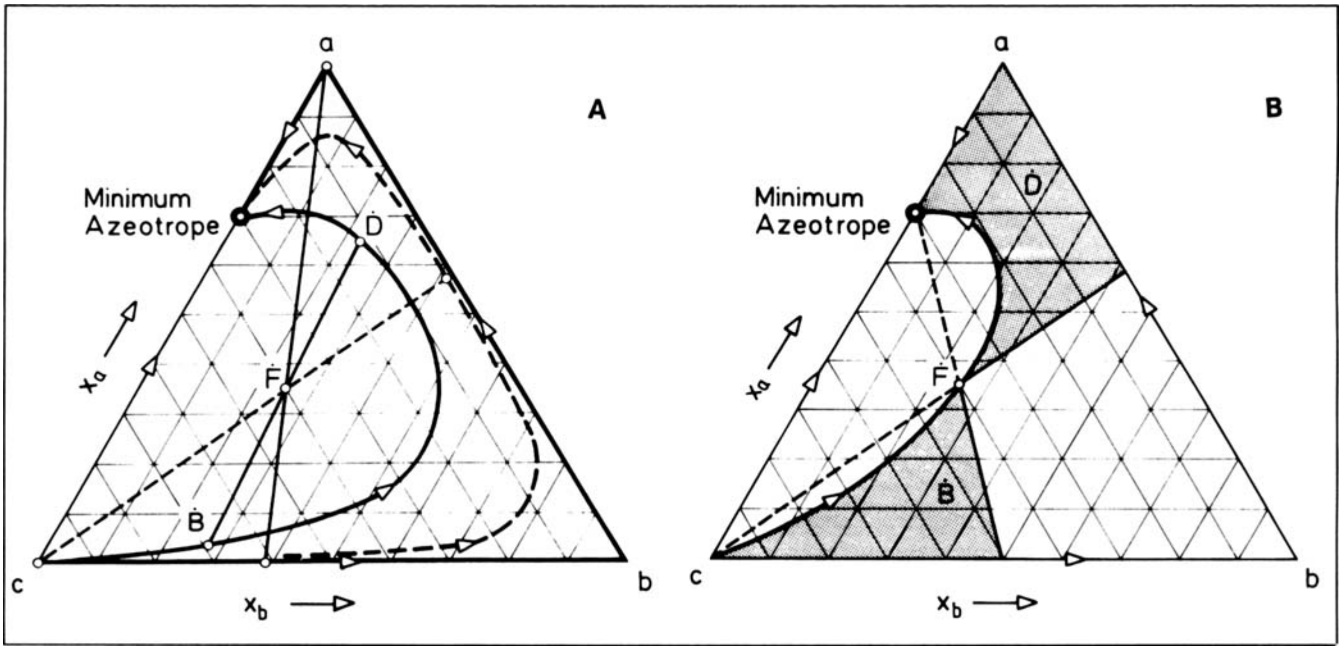

Figure 5. Separation region of a ternary mixture with an *a-c* minimum azeotrope.

Pure *a* can be recovered even though it is not the endpoint of distillation lines: (A) determination of possible top and bottom fractions; (B) separation region.

distillation line divides the ternary mixtures into two regions (distillation fields). Separation by distillation is possible only within one field.

As a rule only those constituents where distillation lines begin or end can be recovered in pure form from a ternary mixture. In systems with more than one origin or terminus there always exists at least one borderline that cannot be crossed by distillation.

There are a few exceptions from this rule. One of these exceptions is illustrated in Figure 5. Here, the origin and terminus of the distillation lines are both on the same side of the triangle and the outer distillation lines pass through two corners of the triangular diagram. In this case there exists a straight line through F that intersects the distillation lines on the sides of a corner (here the component a-corner). Under these special conditions pure substance a can be separated from a ternary mixture even though it does not represent an origin or terminus of distillation lines.

A second exception is dealt with in Figure 6. If the feed F lies in the concave region of the border distillation line, then the straight line through F can also form a chord to distillation lines on the other side of the border. Under these special conditions the border distillation line does not form a barrier for distillation. This exception is very important and is frequently used in distillation processes.

Separation regions at finite reflux

Under finite reflux the top and bottom fractions, D and B, respectively, do not necessarily lie on the same distillation line. Thus, the border distillation line is not a barrier for distillation at finite reflux. Several authors report that at low reflux ratio the border distillation line can be crossed to a certain extent (Doherty and Calderola, 1985; Morari, 1991; Wahnschaft et al., 1992). The effective distillation border depends on reflux ratio as well as on concentrations of feed and products. Generally, the border at finite reflux can be determined only by tiresome iteration of rigorous column calculations.

A special case with a nonvolatile third component is dealt with in Figure 7. In the system HCl-H_2O-H_2SO_4 the vapor does not contain any H_2SO_4. Thus, concentration profiles may be determined in the McCabe-Thiele diagram like for a binary system.

It is assumed that hydrochloric acid with 18 mol % HCl (31 wt. %) has to be recovered as overheads by a stripping column. The sulfuric acid concentration, $x_{H_2SO_4}$, is approximately constant within the column. However, a sharp change of sulfuric acid concentration is caused by evaporating part of the liquid in the reboiler. The sulfuric acid concentration is higher in the bottoms than within the column. A material balance yields:

$$x_{BH_2SO_4} = \frac{L/G}{L/G-1}\, x_{H_2SO_4} \tag{4}$$

Here, L/G is the slope of the operating line in the McCabe-Thiele diagram. At minimum reboil ratio the slope is determined by extending the tangent to the equilibrium line at $y_{HCl} = 18$ mol%. The intersection of the tangent with the diagonal gives the HCl concentration, x_{BHCl}, in the bottoms. The effective borderline in the triangular diagram is found by plotting pairs of x_{BHCl} and $x_{BH_2SO_4}$ for several internal sulfuric acid concentrations.

The border distillation line is represented in this system by points of intersection of the straight line $y_{HCl} = (y_{HCl})_{azeo}$ with the equilibrium lines in the McCabe-Thiele diagram of Figure 7A. The border distillation line and the effective border line lie very close together in the triangular diagram. The maximum

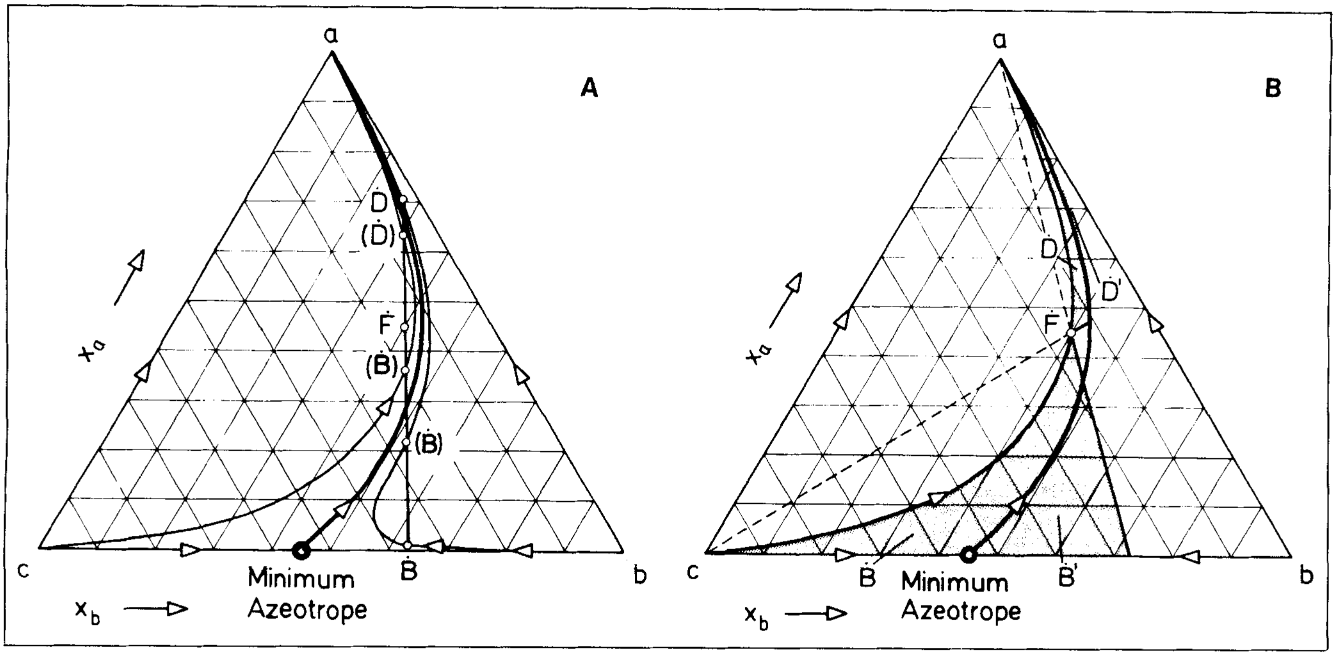

Figure 6. Separation region of a ternary mixture with a *b-c* minimum azeotrope when the feed is lying in the concave section of the border distillation line: (A) determination of possible top and bottom fractions; (B) separation region.

deviation is far less than 1 mol-% HCl. However, it is very important that the effective borderline reaches $x_{HCl} = 0$ at a sulfuric acid concentration of 15.8 mol % (50 wt. %), whereas the border distillation line approaches $x_{HCl} = 0$ asymptotically.

According to the present state of the art the border distillation line is a good and easy way to find approximation of the effective distillation border. Thus, in the first step of process design only operating regions determined under the assumption of total reflux may be considered. However, one should be aware that the effective separation region might be slightly different. During detailed engineering the possiblity of crossing the border can be checked and an evaluation whether or not different column operation strategies will simplify the process can be made.

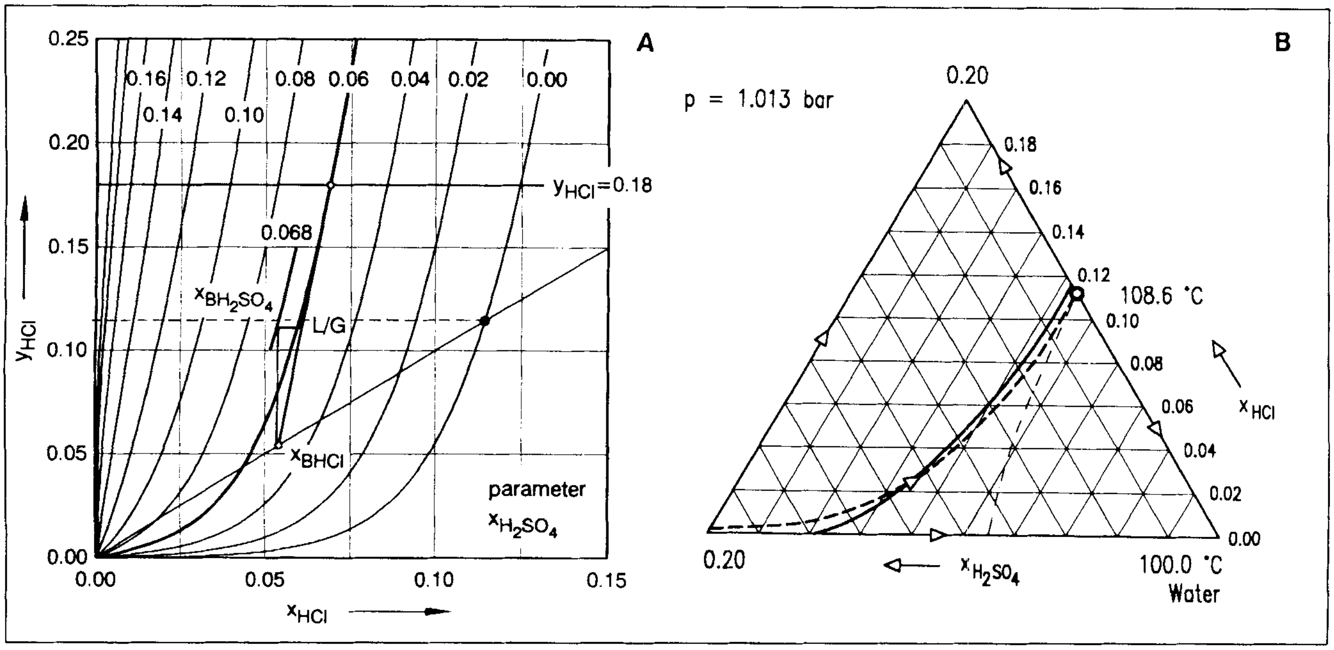

Figure 7. Determination of the effective distillation border for the system $HCl—H_2O—H_2SO_4$ by recovering hydrochloric acid with 18 mol-% HCl as overhead fraction of a stripping column: (A) equilibrium lines; (B) distillation borders: —effective distillation border. - - - border distillation line. ····· line of pseudo azeotropes.

Table 1. Criteria for Entrainer Selection for Processes Without Distillation Border Crossing (Figure 8)

Entrainer for the Separation of a Mixture with a Minimum Azeotrope
- Medium boiler.
- Low boiler, which forms a medium boiling maximum azeotrope with constituent *a*.

Entrainer for the Separation of a Mixture with a Maximum Azeotrope
- Medium boiler.
- High boiler, which forms a medium boiling minimum azeotrope with constituent *b*.

Processes of Azeotropic Distillation

Knowledge of separation regions can be used in process design for zeotropic and azeotropic mixtures. The separation of azeotropic binary mixtures by use of an entrainer is of special importance (Azeotropic Distillation, Extractive Distillation). In these processes only the two constituents *a* (low boiler) and *b* (high boiler) have to be separated in pure form from the ternary mixture. The entrainer *e* doesn't need in most cases to be recovered in pure form, because it can be recycled within the process as an entrainer-rich fraction.

There are two different approaches to solve this problem. In the first approach the entrainer is selected so that no distillation border ends or begins at the *a-b* azeotrope to be crossed (processes without border crossing). In the second approach the entrainer is selected so that the constituents *a* and *b* of the starting mixture are origins or termini of distillation lines. In such ternary systems the *a-b* azeotrope is always an origin or terminus of a distillation border (processes with border crossing).

Only the columns indispensable to perform the separation are considered in the following. Sometimes additional separation steps might be advantageous for economic reasons (for example, preconcentration of a dilute mixture).

Processes without border crossing

Processes without border crossing have been studied in detail by Doherty (Doherty and Caldarola, 1985). The entrainer has to be selected so that the constituents *a* and *b* are in the same distillation field. The *a-b* azeotrope must be neither an origin nor a terminus of distillation lines. Table 1 gives the criteria for entrainer selection resulting from these requirements. These criteria are minimum requirements. There may exist additional azeotropes in the system. Another possibility for a process without border crossing is the use of a high boiling entrainer for a minimum azeotrope (see the section on Hybrid Processes).

Figure 8 presents the triangular composition diagram and the flow sheet for the separation of a system with an *a-b* minimum azeotrope with a medium boiling entrainer. All distillation lines originate at the high boiler *b* and terminate at the azeotrope because it has the lowest boiling point of the mixture. The feed *F* is mixed with the entrainer *e* to form *M* from which the high boiler *b* is separated in column C-1 as bottom fraction B1. The top fraction D1 is (vaporously) fed to column C-2 that yields the low boiler *a* as top and the entrainer *e* as bottom fraction. The entrainer is recycled to

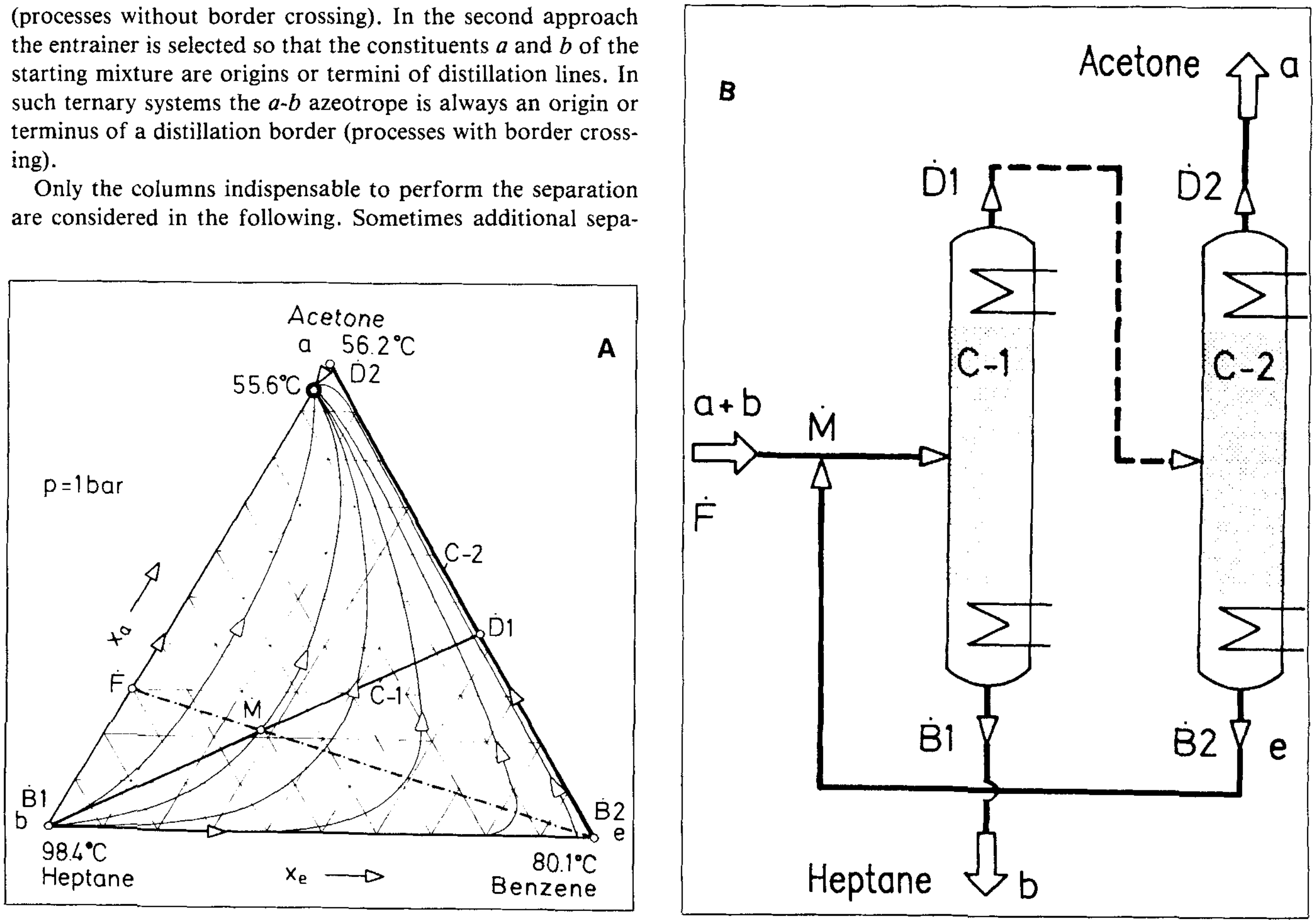

Figure 8. Process for separation of a mixture with a minimum azeotrope by an intermediate boiling entrainer.

The same process works for a maximum azeotrope: (A) triangular diagram; (B) flow sheet.

Table 2. Criteria for Entrainer Selection for the Generalized Process*

Entrainer for the Separation of a Mixture with a Minimum Azeotrope
- Low boiler (lower than the minimum azeotrope).
- Medium boiler, which forms a new minimum azeotrope with the low boiling constituent of the given mixture.
- High boiler, which forms new minimum azeotropes with both constituents of the given mixture. At least one of them has to boil lower than the azeotrope of the given mixture.

Entrainer for the Separation of a Mixture with a Maximum Azeotrope
- High boiler (higher than the maximum azeotrope).
- Medium boiler, which forms a new maximum azeotrope with the high boiling constituent of the given mixture.
- Low boiler, which forms new maximum azeotropes with both constituents of the given mixture. At least one of them has to boil higher than the azeotrope of the given mixture.

* In all cases, the border distillation line has to be curved

column C-1. This separation sequence is similar to the well-known separation of a zeotropic ternary mixture.

According to Figure 5 the low boiler *a* can also be separated first from the ternary mixture. In such a process the column C-2 splits the fraction B1 in top fraction D2 with the entrainer and bottom fraction B2 which consists of pure high boiler *b*. However, this variant of the process is in most cases less advantageous.

The processes without border crossing consist of two columns and one recycle. The problem of all these processes lies in the existence of an appropriate entrainer. As it is well-known, the probability of azeotrope formation increases with decreasing boiling point differences of the constituents *a* and *b*. Consequently, most azeotropic mixtures to be separated by distillation are close boiling ones. In many cases it will be impossible to find a substance that boils between or that forms an intermediate boiling azeotrope. But even if such an entrainer exists the process might be uneconomical because of the small boiling point differences in the system. The full process has to be performed in the boiling point range of the *a-b* mixture.

Processes with border crossing

Processes with border crossing have been studied in Stichlmair (1988) and Stichlmair et al. (1989). The entrainer has to be selected so that the constituents *a* and *b* of the azeotropic mixture to be separated are both either origins or termini of distillation lines. There exist at least two distillation fields divided by a border that ends at the *a-b* azeotrope. Table 2 gives the criteria for entrainer selection resulting from this requirement. Table 2 gives the minimum requirements. There may exist additional azeotropes, but they all have to be of the same type.

Figure 9 presents the generalized process for an *a-b* minimum azeotrope with an entrainer that boils lower than the minimum azeotrope. Distillation lines start at pure substance *a* as well as at pure substance *b* and end at the entrainer. Therefore, the constituents *a* and *b* of the given system can be recovered as bottom fractions of different distillation steps.

First, it is assumed that the feed *F* lies in that region where the low boiler *a* can be separated as bottoms of column C-1. The top fraction D1 is close to the azeotrope. By admixing the entrainer the distillation border is crossed and M2 lies on the other side of the border where substance *b* can be separated as bottoms of column C-2. The top fraction D2 lies close to the distillation border. Assuming that both the distillation line

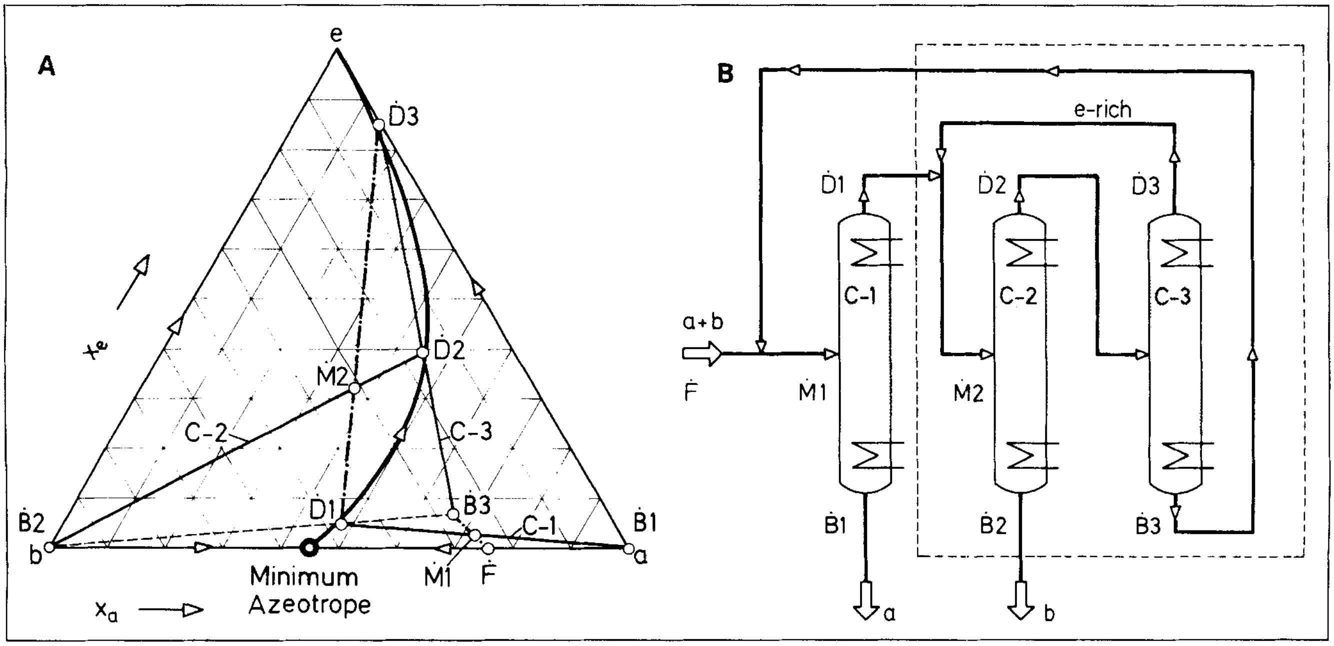

Figure 9. Generalized process for the separation of a binary mixture with a minimum azeotrope by a low boiling entrainer.

The feed is rich in a. An upside down version of the process works for a maximum azeotrope when a high boiling entrainer is used: (A) triangular diagram; (B) flow sheet.

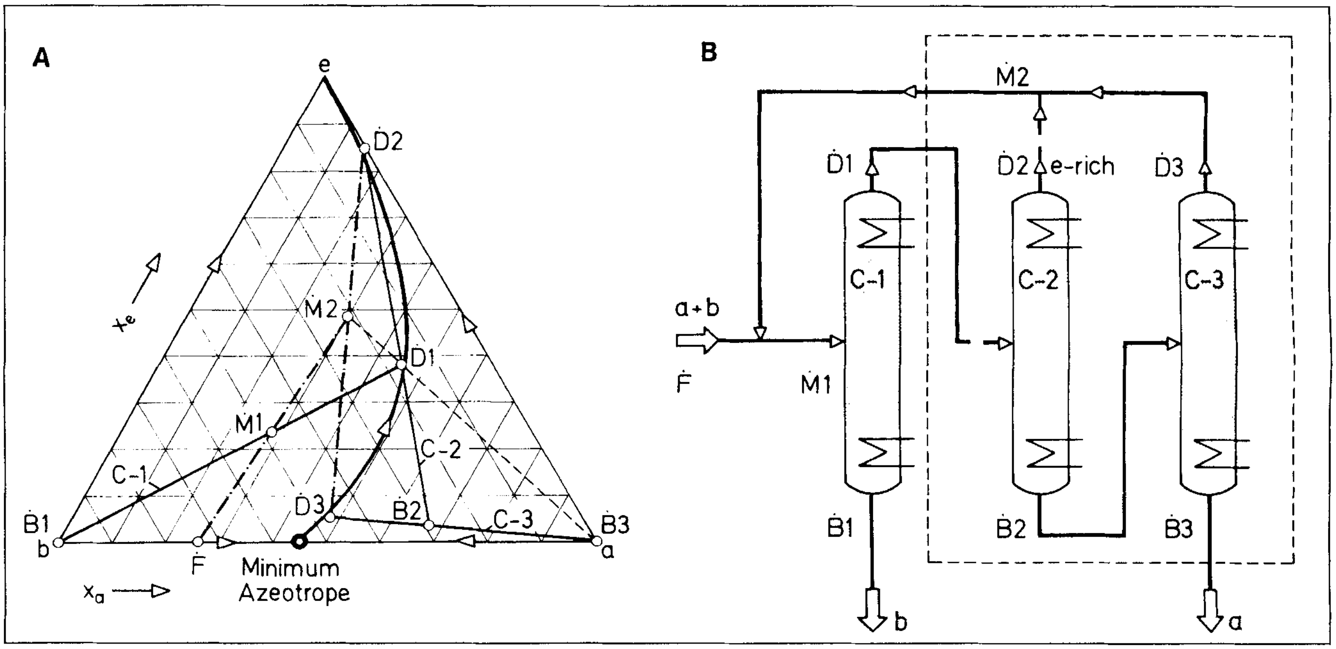

Figure 10. Generalized process for the separation of a binary mixture with a minimum azeotrope by a low boiling entrainer.

The feed is rich in b: (A) triangular diagram; (B) flow sheet.

is curved and D2 lies on its concave side, the fraction D2 can be split by column C-3 in a top fraction D3 and a bottom fraction B3 both lying on the other side of the borderline (Figure 6). The top fraction D3 is recycled as entrainer. The bottom fraction is mixed with the feed and recycled to column C-1. Depending on composition the fraction B3 can be fed into column C-1 either directly or after mixing with the feed *F*.

The generalized process of Figure 9 consists of three separation steps and two recycles. A material balance around column C-2 and C-3 requires that fraction D1, B2 and B3 all lie on a straight line (dotted line in Figure 9A).

From an economical point of view it is essential that the amount of the entrainer to be recycled is as small as possible. A detailed study reveals that the amount of D2 has to be as small as possible because both fractions out of D2 are recycled. Decisive for the amount of D2 is the split of M2 in D2 and B2. Since the bottom fraction B2 contains all of substance *b* in the feed the following holds:

$$B2 = F \cdot x_{Fb} \tag{5}$$

The lever arm rule gives:

$$D2 = F \cdot x_{Fb} \cdot \overline{B2M2} / \overline{D2M2} \tag{6}$$

The recycles D3 and B3 are small when the length $\overline{D2M2}$ is large with respect to the length $\overline{B2M2}$. This requires a heavily curved borderline and an optimal position of *M2*.

Figure 10 presents the generalized process when the feed lies in that region, where the high boiler *b* can be separated. In this case just the sequence of the separations is different from the process in Figure 9. Both modifications of the generalized process are characterized by two separations performed at the convex and one separation performed at the concave side of the borderline.

According to the criteria for entrainer selection in Table 2 a minimum azeotrope can be separated by an intermediate or high boiling entrainer instead of a low boiler if additional azeotropes are formed. A detailed study reveals that one of the azeotropes formed by the entrainer *e* acts as pseudo entrainer. Other than that, the process is the same as in Figures 9 and 10.

In principle, the generalized process works also for mixtures with a maximum azeotrope. But the constituents *a* and *b* are required as overhead fractions in this case.

The generalized process presented here allows the separation of two pure constituents from a ternary mixture if the borderline is curved. This requirement is more or less met by real systems. However, the process is the more economical the more curved the distillation border is. The temperature range of the process lies between the boiling points of the entrainer *e* and the high boiler *b* (in case of a minimum azeotrope). The temperature range is much higher in processes with border crossing than in processes without border crossing. Therefore, the separations can be more easily performed.

Simplifications of the Processes with Border Crossing

The generalized process with three distillation columns and two recycles is expensive with respect to investment and operating costs. However, there exists some possibilities for process simplification. A few examples are presented in the following sections.

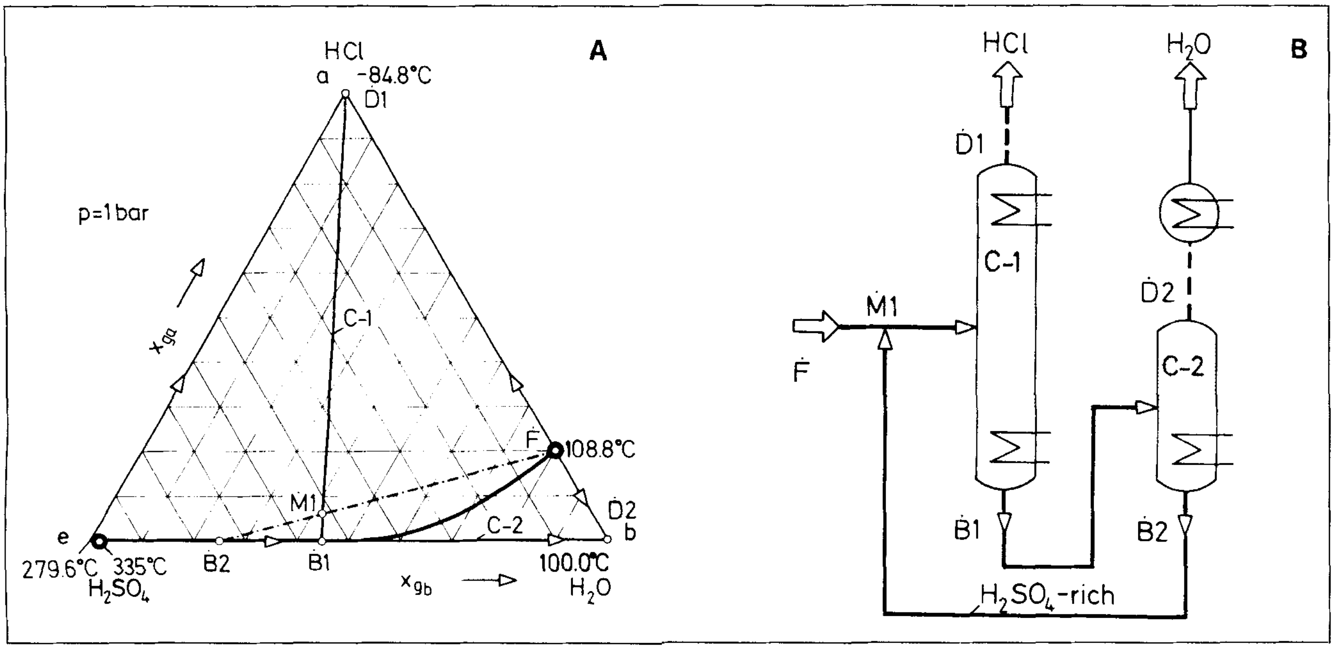

Figure 11. Two column process for HCl-H_2O separation by sulfuric acid.

As the distillation border is partially lying on the side of the triangular diagram the third distillation step of the generalized process can be omitted: (A) triangular diagram; (B) flow sheet.

Two column process

Under special conditions one of the three separation steps of the generalized process can be discarded. This is possible when the distillation border is heavily curved and the stream M2 is lying close to the entrainer. In this case the separation performed in column C-2 (Figure 10) yields a bottom fraction B2 that contains the substance *a* in high purity. Thus, the column C-3 and the recycle D3 can be omitted. This advantageous modification of the generalized process requires a very heavily curved distillation border that lies in part on a side of the triangular diagram. Additionally, a large amount of entrainer has to be recycled within the process. This process modification is facilitated by the existence of one or two azeotropes formed by the entrainer with the constituents *a* and *b*.

Figure 11 presents the flow sheet and the triangular diagram for concentrating diluted hydrochloric acid (Grewer, 1971). The system HCl-H_2O forms a maximum azeotrope (21 wt. % HCl, 108°C). According to Table 2 the entrainer has to be the high boiler in the system. Sulfuric acid used in the process meets this requirement. The distillation borderline, a ridge in the boiling point surface, lies in part on the basis of the triangle diagram. The feed with high water content is mixed with concentrated sulfuric acid (approximately 75 wt. %). The mixture M1 lies in that distillation region, where HCl (or an HCl-rich mixture) can be separated as top fraction D1. If M1 is sufficiently close to the entrainer, then the bottom fraction B1 is nearly free of HCl. The subsequent separation step (single stage distillation) yields HCl-free water as top fraction. The process can be modified by feeding the entrainer directly at the top of column C-1 instead of mixing it with the feed (see the section on Absorption). A process similar to this one is used for concentrating diluted nitric acid (Gericke, 1973).

A novel process for the separation of ethanol and water is proposed in Figure 12. Tetrahydrofuran is used as entrainer because it forms an *e-b* minimum azeotrope that is not required by the rules in Table 2. The distillation border is sufficiently curved to use the two column process. The feed *F* is mixed with the top fraction D2 of column C-2 that acts as entrainer. In column C-1 the high boiler *b* is separated as bottoms. The top fraction D1 lies close to the concave side of the distillation border. This fraction is separated in column C-2 into pure component *a* as bottoms *a-b* azeotrope as top fraction.

A similar process with a high boiling entrainer *e* is depicted in Figure 13. A ternary minimum azeotrope not required by the entrainer selection rules is formed in this system. The distillation border running from the *a-b* azeotrope to the ternary azeotrope is so heavily curved that the separation in column C-2 yields the pure substance *a* as bottoms. While the generalized process with three separation steps can be performed even in systems with a slightly curved distillation border the two column process requires a heavily curved borderline. Thus, the two column process is a special case of the generalized process.

Hybrid processes

The generalized process might be simplified by performing one (or two) of the separation steps not by distillation but by any other separation technique, for example, decantation, absorption, extraction, adsorption or membrane permeation. Some examples will be shown in the following.

Decantation

Figure 14 presents a process for ethanol-water separation by toluene. The process is identical with the generalized process but the third separation step is performed by decantation instead of distillation. This is possible because the entrainer

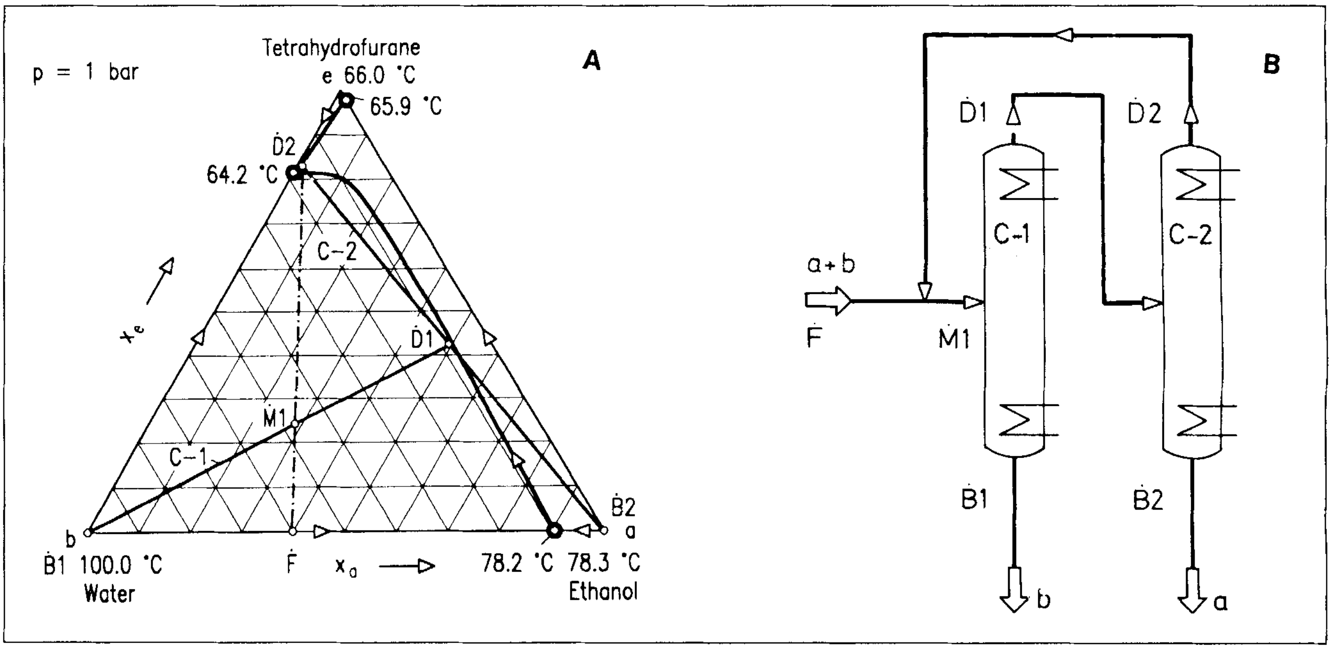

Figure 12. Two column process for the separation of ethanol and water.

The entrainer tetrahydrofuran forms an additional minimum azeotrope with the low boiler water. The distillation border is so heavily curved that the third column of the generalized process can be omitted: (A) triangular diagram; (B) flow sheet.

toluene is not completely miscible with water. By the use of a decanter instead of a third distillation column investment and operating cost are drastically reduced.

The process presented in Figure 14 is very often used. Some examples are listed in Table 3. Sometimes it is advantageous to feed the recycles S1 and S2 directly at the top of column C-1 and C-2, respectively, instead of first mixing them with *F* and D-1.

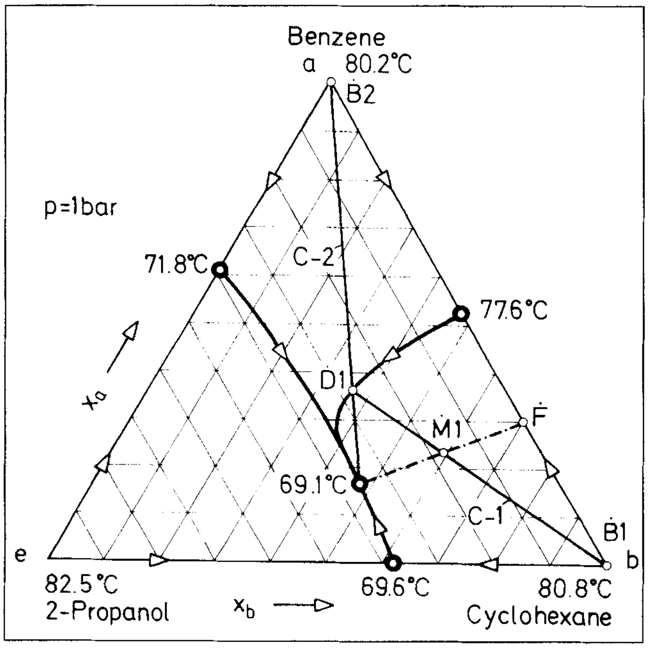

Figure 13. Two column process for the separation of a minimum azeotrope with a high boiling entrainer.

Flow sheet as in Figure 12B.

Absorption

The use of an absorption step instead of distillation is demonstrated in Figure 15. This process again can be applied to ethanol-water separation. The top fraction D1 with azeotropic composition (approximately 90 mol % ethanol) is vaporously fed into the absorber A-1 where the water is removed by an appropriate absorbent (for example, glycol, which is hygroscopic). The absorbent is regenerated in column C-3 by vacuum distillation.

The vapor at the top of the absorption column contains small amounts of the absorbent *e*. For separation the top fraction is partially condensed and recycled as reflux some stages above the absorbent feed point. Analogously, some of substance *a* is solved in the liquid in the bottom that can be separated by partial reboiling. Because of condenser and reboiler the middle column of the process depicted in Figure 15 is often misinterpreted as a distillation column. However, since the low boiling fraction D1 is fed into the bottom and the high boiling liquid B2 is (as a pure substance and below boiling point) fed into the top of the column and, additionally, both flow rates are higher than that of reflux and reboil, there is no doubt that it is an absorption process. Consequently, the amount of entrainer can be found by the methods used to determine the solvent circulation rate of an absorption process.

The azeotrope is crossed by absorption in this process. Therefore, the criteria for entrainer selection (Table 2) cannot be applied. Here, the well-known rules for absorbent selection have to be used. They require a high boiling liquid with high and selective solubility for substance *b*. In addition, some other requirements have to be met (Blass, 1989).

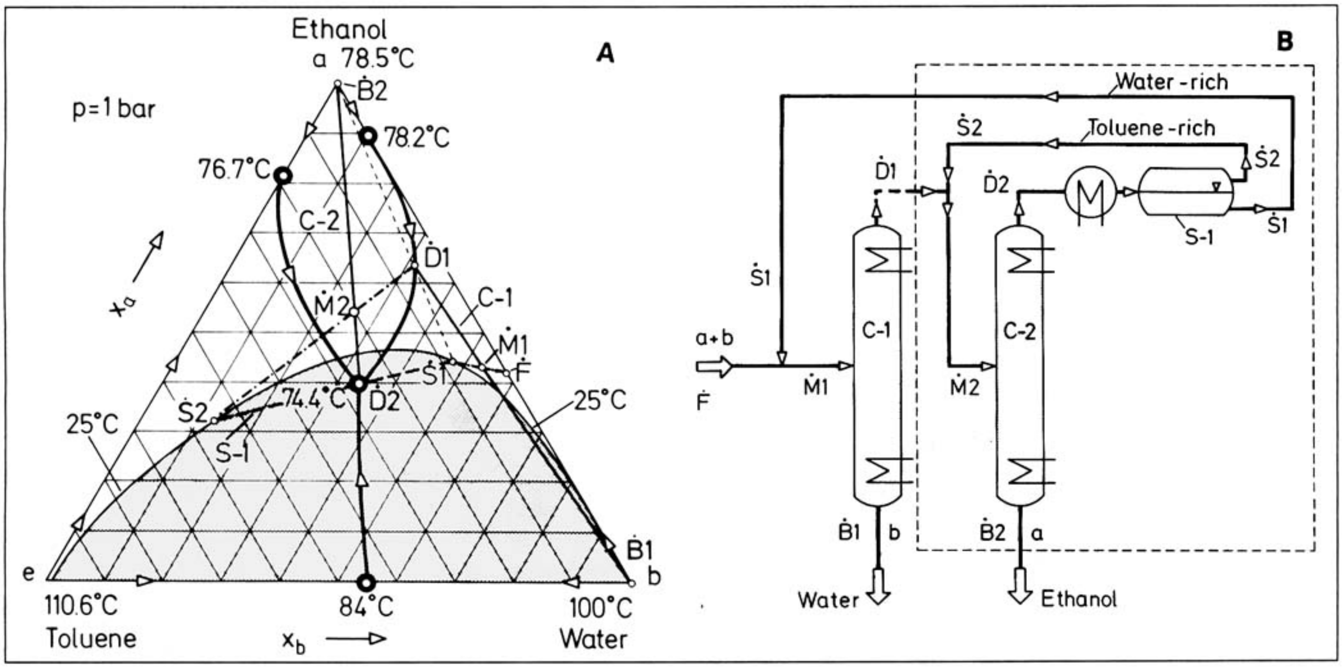

Figure 14. Combination of distillation and decantation.

The third column of the generalized process is replaced by a decanter: (A) triangular diagram; (B) flow sheet.

The process depicted in Figure 15 is widely used not only for separation of azeotropic mixtures but also for separation of close boiling mixtures. Table 4 lists some examples of industrial important processes. Depending on solubility either the light constituent *a* or the heavy constituent *b* is preferably absorbed. This process is generally known as "Extractive Distillation", even though in reality it involves an absorption step and not an extraction step.

Extraction

The separation of an azeotropic mixture by using a combination of distillation and extraction is also sometimes used in industrial processes. Figure 16 shows a process for the separation of tetrahydrofuran (THF) and water (Schoenmakers, 1984). This mixture exhibits a minimum azeotrope at about 83 mol % THF.

If the feed *F* is water-rich the water is removed as bottoms in column C-1. The distillate D1 with azeotropic concentration is fed into an extraction column E-1. Concentrated sodium hydroxide is used as solvent because it is hygroscopic. The loaded solvent is regenerated in single stage vacuum distillation. The concentrated sodium hydroxide is recycled to the extractor, the distillate containing water and some THF is fed into column C-1 either together with the feed or separate from it.

Table 3. Systems Separated by a Process with Distillation and Decantation (Figure 11)

Mixture	Entrainer	Reference
Water-ethanol	benzene	Keyes (1929)
	trichloroethylene	Fritzweiler (1938)
	pentane	Black (1980)
	toluene	Pilhofer (1983)
	cyclohexane	Herfurth (1987)
	ethylacetate	Cairns (1987)
Water-propanol	benzene	Bril (1977)
Water-pyridine	benzene	Berg (1969)
	toluene	Berg (1969)
Water-acetic acid	butylacetate	Hegner (1973)
Acetic acid-formic acid	chloroform	Hunsmann (1966)

Solvent extraction has the disadvantage that—in most cases—

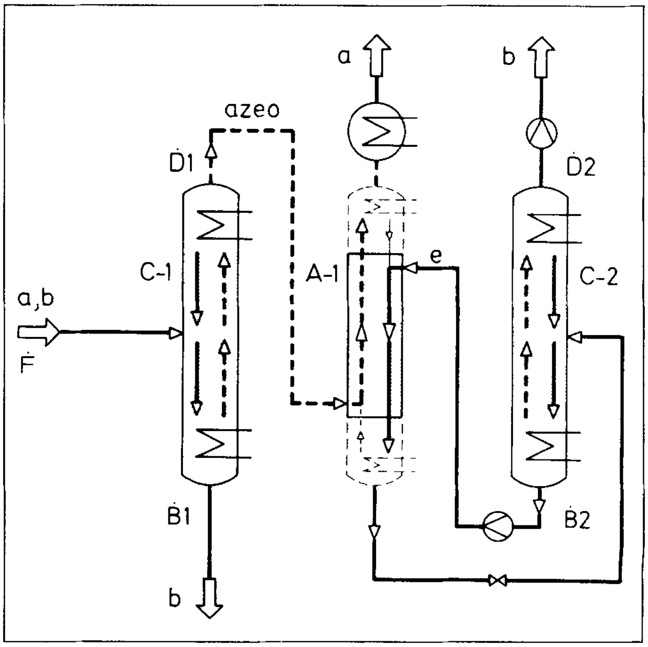

Figure 15. Combination of distillation and absorption.

This process can be applied to the system ethanol (a) and water (b). The entrainer has to be chosen according to the rules for absorbent selection.

Table 4. Processes of Extractive Distillation (Figure 15)

Mixture	Entrainer	Reference
Butane-butene-butadiene	furfural	Peters (1968)
	furfural	Happel (1958)
	acetonitril	Bittrich (1987)
	dimethyl acetamide	Coogler (1967)
	n-methylpyrrolidone	Volkamer (1981)
	dimethylformamide	Hebel (1971)
Benzene-cyclohexane	*n*-methylpyrrolidone	Mueller (1980)
	aniline	Blass (1989)
	n-formylmorpholine	Lackner (1981)
Butene-isoprene	dimethylformamide	Ushio (1972)
Ethanol-water	ethylenglycol	Black (1980)
Tetrahydrofuran-water	dimethylformamide	Drew (1979)
Acetone-methanol	water	Drew (1979)

no pure products can be obtained. According to Schoenmakers (1984) tetrahydrofuran with 99 wt.-% can be gained at best. If a higher purity is required an additional distillation step C-2 has to be used. The bottoms of C-2 is pure tetrahydrofuran, the distillate is recycled to the extractor.

Membrane permeation

Figure 17 shows a process in which the azeotrope is crossed by membrane permeation (Baker). This process can be applied to ethanol-water separation. The water-rich feed is split in water and azeotrope by distillation in column C-1. After compression up to about 3 bar the azeotropic mixture is fed into the membrane stack. A water-rich fraction permeates the membrane as a vapor that is first condensed and then pumped into column C-1. The ethanol-rich retentate is fed into column C-2, where pure ethanol is removed as bottoms. The top fraction is recycled to the membrane stack. Up to 8 membrane stacks are required. After each of them the retentate has to be heated to cover heat requirement of permeate vaporization. In this process the membrane is used just to cross the azeotrope. The pure products water and ethanol are recovered by conventional distillation.

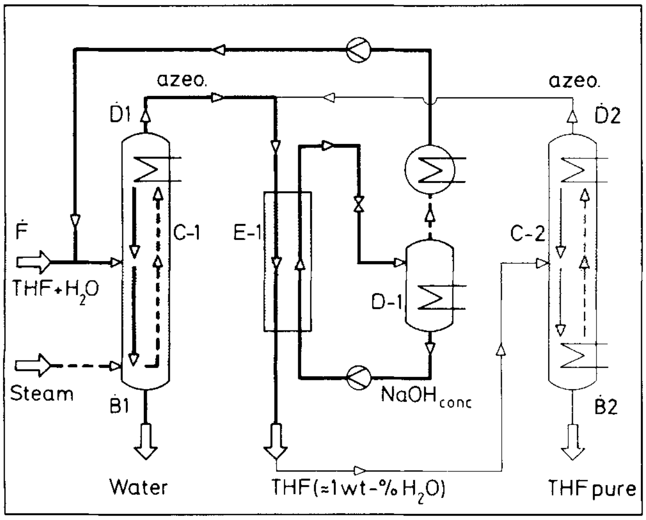

Figure 16. Combination of distillation and extraction.

The entrainer has to be chosen according to the rules for solvent selection.

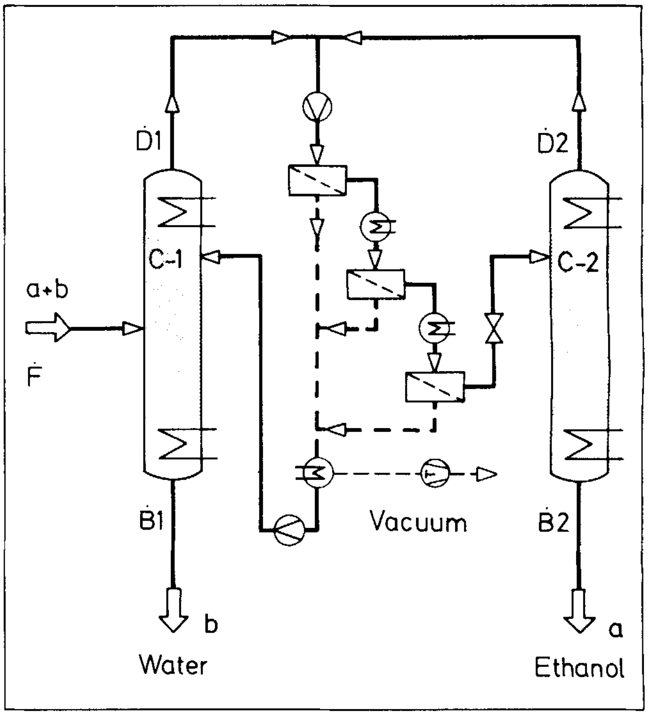

Figure 17. Combination of distillation and pervaporation.

The pervaporation step is used only to cross the azeotrope.

Summary

This article demonstrates the determination of possible top and bottom fractions of ternary distillation from knowledge of distillation lines. Distillation lines are a special form of vapor-liquid equilibrium presentation. They are easier to find than residuum lines sometimes used for the same purpose. Knowledge of separation regions allows for the design of distillation processes without rigorous column calculation. There exist two different strategies for the complete separation of ternary systems. Examples of both strategies are presented in this article. In many systems of industrial importance simplifications of the generalized process can be made either by discarding one of the distillation steps or by combining distillation with other separation techniques. This article contains a large number of examples for process simplifications.

Notation

a = low boiling component
A-1 = absorber
b = medium boiling component
B = bottom product (kmol/s)
c = high boiling component
C-1 = distillation column
D = distillate, top product (kmol/s)
e = entrainer
E-1 = extractor
F = feed (kmol/s)
G = gas flow (kmol/s)
i = component
L = liquid flow (kmol/s)
M = mixing stream (kmol/s)
n = number of equilibrium stages
p = pressure (bar, Pa)
p_i^0 = vapor pressure of substance i

R = reflux ratio
S-1 = decanter
T = temperature (K, °C)
x = mole fraction in liquid phase
x_g = weight fraction in liquid phase
y = mole fraction in vapor phase

Greek letter

γ = activity coefficient

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Manuscript received Oct. 3, 1991, and revision received May 4, 1992.