Multiple Steady States in Heterogeneous Azeotropic Distillation

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Abstract

In this article we study multiple steady states in ternary heterogeneous azeotropic distillation. We show that in the case of infinite reflux and an infinite number of trays one can construct bifurcation diagrams on physical grounds with the distillate flow as the bifurcation parameter. Multiple steady states exist when the distillate flow varies non-monotonically along the continuation path of the bifurcation diagram. We show how the distillate and bottom product paths can be located for tray or packed columns, with or without decanter and with different types of condenser and reboiler. We derive a necessary and sufficient condition for the existence of these multiple steady states based on the geometry of the product paths. We also locate in the composition triangle the feed compositions that lead to these multiple steady states. We show that the prediction of the existence of multiple steady states in the case of infinite reflux and an infinite number of trays has relevant implications for columns operating at finite reflux and with a finite number of trays.

KEYWORDS: distillation, azeotropic distillation, multiplicity, multiple steady states, distillation design.

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1 Introduction

Azeotropic distillation is one of the most widely used and most important separation operations in the chemical and the specialty chemical industry. Among their surprising features, it has been discovered that such columns can exhibit multiple steady states i.e. two or more different steady states for the same set of operating parameters. In this article, by multiple steady states we mean what is generally referred as *output multiplicities* i.e. columns with the same inputs (the same feed, distillate, bottoms, reflux and boilup molar flows, the same feed composition, number of stages and feed location) but different outputs (product compositions) and hence different composition profiles. We are mainly investigating this type of multiplicities although we also discuss some aspects of *state multiplicities* i.e. columns with the same inputs and outputs but with different composition profiles (states).

The study of multiplicities in distillation has a long history. A thorough review of the literature on multiplicities in distillation has been presented by Bekiaris et al. (1993). Here we focus on the articles on multiplicities in heterogeneous mixtures. Magnussen et al. (1979) first presented simulation results that show the existence of three steady states (two stable and one unstable) for the heterogeneous mixture of ethanol - water - benzene. In these calculations (1) constant molar overflow is assumed and (2) the phase splitter is removed; instead, a second feed at the top of the column is considered (this second feed is the same for all three steady states). The multiplicities were observed with the UNIQUAC and NRTL activity coefficient models but a unique steady state was found with the Wilson equation model. On all the stages in all three profiles there is only one liquid phase. A similar multiplicity was observed for the system ethanol - water - pentane.

The results of Magnussen et al. (1979) triggered great interest in multiple steady states in distillation. The belief that heterogeneity is a possible cause for such multiple steady states directed the attention towards heterogeneous azeotropic distillation. Consequently, several articles were published where the mixture ethanol - water -benzene and especially the results of Magnussen et al. (1979) were studied extensively and where multiplicities for other heterogeneous systems were reported.

More specifically, Prokopakis et al. (1981) using a column without decanter (fixed second feed composition), the NRTL thermodynamic model and including enthalpy balances verified the three "regimes" found by Magnussen et al. (1979) but not multiplicity. For the mixture isopropanol - water - cyclohexane they report two steady states for the same specifications. In these steady states, however, the entrainer flowrate in the boilup and the reflux flowrate and composition are held constant while the product flowrates are different. Hence these do not constitute an output multiplicity as defined above. For both mixtures they find that one of the steady states is "infeasible" in the sense that its overhead vapor composition lies outside the binodal curve and hence this profile cannot describe the profile of the column with the decanter. Again, there is no phase separation on the stages.

Prokopakis and Seider (1983a,b) using a column with decanter, the UNIQUAC thermodynamic model with binary parameters different from the ones used by Magnussen et al. (1979) and including enthalpy balances, again verified the three operating regimes, conjectured that one of them is unstable but no multiplicities were found.

Kovach and Seider (1987a,b) present simulation (homotopy-continuation) and experimental results of the mixture secondary butanol - water - disecondary butyl ether (together with butylenes and methyl ethyl ketone impurities). Although no multiplicity is found, they locate two steady states (one with a single liquid phase on all trays and the other with two liquid phases on 70% of the trays) over a narrow range of the reflux ratios and conclude that this is consistent with the experimentally observed erratic behavior of the column. Using homotopy-continuation for the mixture ethanol - water - benzene they locate five steady states for the same specifications (output multiplicity). There is some concern whether the overhead vapor composition lies outside the binodal curve for three of the five profiles. Note that in all these calculations the condenser and the decanter are not included in the model. When they are included in the model three steady states are calculated.

Venkataraman and Lucia (1988) perform continuation studies for the ethanol - water - benzene column studied by Prokopakis and Seider (1983a) with the bottoms flow as the continuation parameter. They find three steady states over a narrow range of bottoms flow. Kingsley and Lucia (1988) show that there is a minimum tray efficiency for which these multiplicities exist. For columns with tray efficiency less than this minimum, a unique steady state exists for the whole range of bottoms flow. It is important, however, to note that the three steady states are calculated without taking into account the presence or absence of two liquid phases on a tray (ignoring the liquid split) and hence they do not correspond to any realistic column (they can be used as the starting point of a heterogeneous distillation calculation). Kingsley and Lucia (1988) show that all these three profiles "ultimately lead to the same heterogeneous solution." The authors were unable to produce heterogeneous multiplicities.

Widagdo et al. (1989) perform parameterization with respect to the aqueous reflux ratio for the mixture secondary butanol - water - disecondary butyl ether (also Kovach and Seider, 1987a,b). They find three steady states over a narrow range of the aqueous reflux ratio. This multiplicity occurs when a second liquid phase appears on the top tray. A single-stage bifurcation analysis shows a unique solution and the authors suggest that other effects, such as the recycle, may be responsible.

Rovaglio and Doherty (1990) study the mixture ethanol - water - benzene using a column with decanter and different sets of parameters for the UNIQUAC model. They find three steady states for all parameter sets (including those used by Magnussen et al., 1979 and Prokopakis and Seider, 1983a,b) through dynamic simulations. For some sets two liquid phases exist on some trays, for others a single liquid phase exists on all trays. Their dynamic simulation results are consistent with the five steady states reported by Kovach and Seider (1987b).

Cairns and Furzer (1990) study the multiplicities by Magnussen et al. (1979) using the UNIFAC(VLE) model. Two of the steady states were obtained only by ignoring the phase splitting and hence they conclude that these profiles are fictitious. They also report two steady states (one again obtained by ignoring the liquid split) for the mixture ethanol - water - isooctane.

Bossen et al. (1993) study the mixture ethanol - water -benzene for a column with decanter using UNIFAC and UNIFAC(VLE). They find four steady states. In one of them, the whole profile as well as the decanter lies in the homogeneous region. The products of the other three profiles have exactly the same compositions and flowrates. The only difference between these three profiles is the location of the front of sharp ethanol and benzene composition changes. These three profiles are in good agreement with the results of Rovaglio and Doherty (1990).

Rovaglio et al. (1993) study the multiplicities found by Rovaglio and Doherty (1990) through dynamic simulations as well as many of the previously reported multiplicities for the mixture ethanol - water - benzene. They demonstrate that although these steady states satisfy the convergence criteria "there may be small differences in the necessary make-up flowrates needed to keep these states constant and stable." They conclude that "the problem of multiple steady states seems to be associated with the numerical aspects related to the relative small amount of feed make-up."

The study presented here is the continuation of our previous work (Bekiaris et al., 1993) on homogeneous azeotropic distillation. A summary of this previous work will be presented in the following.

2 Preliminaries

The term *heterogeneous azeotropic distillation* covers the general notion of distillation of azeotrope forming mixtures where two liquid phases exist in some region of the composition space. Usually, heterogeneous azeotropic distillation units perform the separation of a binary azeotrope into two pure components through the addition of an entrainer which alters the relative volatility of the two azeotropic constituents and enables separation by inducing liquid - liquid phase separation.

Unless stated otherwise, we use the following convention to refer to a given mixture: L (I, H respectively) corresponds to the component which has the lowest (intermediate, highest resp.) boiling point; we also denote the entrainer by E. We use the same notation in italics (L, I, H, E) to denote the corresponding flow rates of the components in the feed. The locations of the feed, distillate, bottoms, reflux and overhead vapor in the composition triangle are denoted by F, D, B, R and V respectively. Again, the corresponding flowrates are denoted by the same letters in italics (F, D, B, R and V).

Two widely used tools for the description of azeotropic distillation are the simple distillation residue curves (hereafter called residue curves) and the distillation lines. The *simple distillation process* involves charging a still with a liquid of composition $\underline{x}$ and gradual heating. The vapor formed, $\underline{\mathrm{y}}(\underline{\mathrm{x}})$, is in equilibrium with the liquid left in the still; the vapor is continuously removed from the still.

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

$$\frac{d\underline{x}}{d\xi} = \underline{x} - \underline{y}(\underline{x}) \qquad (1)$$

where $\underline{\mathrm{x}}$ and $\underline{\mathrm{y}}(\underline{\mathrm{x}})$ are the molar compositions of the liquid and vapor phase respectively, and ξ is the dimensionless warped time.

In this article, a *distillation region* is defined as a subset of the composition simplex in which all residue curves originate from the same locally lowest-boiling pure component or azeotrope and end at the same locally highest-boiling one. The curves which separate different distillation regions are called residue curve boundaries. In this article, the term distillation region boundary (or just boundary) is used for both residue curve boundaries (interior boundaries) and the edges of the composition simplex.

The definition of *distillation lines* (Zharov and Serafimov, 1975; Stichlmair et al., 1989; Stichlmair and Herguijuela, 1992), on the other hand, originates directly from the description of tray columns operating at infinite reflux. In these columns, the liquid composition of tray n+1 equals the composition of the vapor in equilibrium with the liquid of tray n (the tray below):

$$\underline{x}_{n+1} = \underline{y}(\underline{x}_n) = \underline{y}_n \qquad (2)$$

Zharov and Serafimov (1975) define the distillation line as the set of points $\underline{\mathrm{x}}$ whose $\underline{\mathrm{y}}(\underline{\mathrm{x}})$, i.e. the vapor composition in equilibrium with $\underline{\mathrm{x}}$, also lies on the same distillation line. Using the recursion formula (2) forward ($\underline{x}_n \rightarrow \underline{x}_{n+1}$) and backwards ($\underline{x}_{n+1} \rightarrow \underline{x}_n$), a sequence of points in the composition space can be calculated. By definition, all the points of this sequence lie on the same distillation line. Although it is very easy to calculate a sequence of points, the calculation of the whole distillation line is not trivial because there does not exist an explicit expression to exactly calculate the points of a distillation line between two points of a sequence. It is very common, hence, to just connect these points by straight lines and use this as the approximate distillation line. Note that these approximate distillation lines may cross each other which is not generally true for the exact ones (Figure 1a); as we show later, the exact distillation lines may only coincide in the two-liquid phase region. In illustrations of distillation line diagrams we use the smooth exact distillation lines, while in computations the line that connects the points of a sequence is used.

Zharov and Serafimov (1975) further showed that distillation lines (1) have the same singular points with residue curves and (2) behave similarly to residue curves close to singular points. Nevertheless, distillation lines do not generally coincide with residue curves. Usually, the direction opposite to that of residue curves is used for the distillation lines. In this article, in order to avoid the confusion of referring to the same singular point as a stable node in residue curve diagrams and as an unstable node in distillation line diagrams, we use the direction of residue curves for distillation lines too. Figure 1b illustrates the residue curve, the distillation line and the approximate distillation line that go through a point $\underline{\mathrm{x}}$ in the composition triangle. The residue curve crosses the (exact) distillation line and is tangent to the line segment of the approximate distillation line connecting $\underline{\mathrm{x}}$ and $\underline{\mathrm{y}}(\underline{\mathrm{x}})$.

Similarly to residue curves, in the distillation line diagram there may exist distillation regions and boundaries which can be different from the regions and boundaries in the residue curve diagram. The calculation of distillation line boundaries is easier than the calculation of any other distillation line. The reason is that using equation (2) we can determine arbitrarily large sets of points that belong in one or the other of the two regions the boundary separates. The distillation line boundary lies between the two sets and hence a much better approximation (compared to just connecting the points of a single sequence) can be obtained.

As an illustrative example throughout this article we use the mixture ethanol (L) - water (H) - benzene (I-E). Ethanol and water form an azeotrope which can be separated using benzene as the entrainer. Figure 2a shows the residue curve diagram of this type of ternary mixture at 1 atm. In this diagram, there are two binary homogeneous azeotropes (X and Y), one binary heterogeneous azeotrope (Z) and one ternary heterogeneous azeotrope (T). The ternary azeotrope is an unstable node, the pure components are stable nodes and the binary azeotropes are saddles. All residue curves start from the ternary azeotrope (globally lowest-boiling point) and end at one of the three pure component corners (locally highest-boiling points). There are three interior distillation boundaries in this diagram running from the ternary azeotrope to the three binary azeotropes. The boundaries separate the composition space in three distillation regions.

Figure 2a also shows the heterogeneous liquid boiling envelope (line UCW) of this mixture at 1 atm. Liquid compositions located inside the heterogeneous liquid boiling envelope will split in two liquid phases whose compositions will lie on the envelope. Point C is the critical point. We refer to the water-rich phase (line UC) as phase 1 and to the entrainer-rich phase (line CW) as phase 2. The straight lines connecting two liquid phases in equilibrium are the tie lines. The vapor in equilibrium with any liquid in the two-phase region lies on the vapor line ZTQ. Point Q is the vapor in equilibrium with a liquid located at the critical point. Note that heterogeneity causes a singularity of the VLLE: the liquid composition in equilibrium with a vapor composition on the vapor line is not unique since it can be any point on some tie line.

Figure 2b illustrates the distillation line diagram for the same mixture at 1 atm. Qualitatively, the distillation line diagram is similar to the residue curve diagram of Figure 2a. The location of the boundaries and the distillation regions, however, are somewhat different. In the heterogeneous region, some part of the boundaries has to coincide with the vapor line and hence the boundaries TX and TY and the vapor line coincide close to the ternary azeotrope. The point of deviation from the vapor line for each boundary is the composition of the vapor in equilibrium with the liquid at the intersection of the heterogeneous liquid boiling envelope and the boundary. The boundary TZ lies on the vapor line while the other two boundaries deviate from the vapor line at some point and therefore they do not contain point Q. This is because the boundaries do not contain the critical point C.

With this information (residue curve and distillation line diagrams and VLLE) we are able to thoroughly analyze the case of infinite reflux and infinite number of trays (or infinitely long columns), which we hereafter denote as the ∞/∞ case. In the following we present a general method for the study of multiplicities in the ∞/∞ case. We discuss both tray and packed columns for completeness. We illustrate this method using the mixture ethanol - water - benzene as the illustrative example. In this example, the column operates under constant atmospheric pressure, there is no pressure drop in the column, a tray efficiency of 1 is assumed and the condenser is total. We discuss the issues of tray efficiency and other condenser and reboiler types in the special topics section. It is assumed that Figures 2a and 2b, describe the thermodynamic equilibrium of the mixture at 1 atm. These figures could be obtained from experimental data or using any thermodynamic model. In fact, the specific figures are drawn so that they illustrate the qualitative characteristics of the following thermodynamic model: (1) Ideal vapor (2) Vapor pressures are calculated using the Antoine equation with parameters from Gmehling and Onken (1977) (3) liquid activity coefficients are calculated using the UNIQUAC equation with pure component parameters from Gmehling and Onken (1977) and binary parameters estimated from UNIFAC using Aspen Plus. The appendix contains more information on the thermodynamic model as well as the Antoine and UNIQUAC parameters. Note that Figures 2a and 2b have been exaggerated for illustrative purposes. Figures 3a and 3b show the exact residue curve and distillation line diagrams, respectively, using the above thermodynamic model.

In the following we summarize the results obtained in the ∞/∞ case for homogeneous mixtures (Bekiaris et al., 1993). Although these results were derived for packed columns using residue curve diagrams, we show that similar results hold for tray columns using distillation line diagrams.

2.1 Composition Profiles in the ∞/∞ Case

At infinite reflux, the differential equations which describe packed columns become identical to the residue curve equations. Thus residue curves coincide exactly with the liquid composition profiles of packed columns operated at total reflux. In the special case of infinitely long packed columns there is one additional requirement: The column profile should contain at least one pinch point. Pinch points at infinite reflux can only be the singular points of the residue curve diagram i.e. the pure components and the azeotropes. Therefore, the packed column liquid composition profiles in the ∞/∞ case should follow residue curves and contain at least one pure component or azeotrope. Hence the only acceptable columns belong to one of the following types:

I. Columns whose top liquid composition[1] is that of an unstable node. In this case, the column liquid composition profile starts from the unstable node (top liquid composition), follows a residue curve and ends at an arbitrary point on the same residue curve (bottom liquid composition).

II. Columns whose bottom liquid composition is that of a stable node. In this case, the column liquid composition profile starts from an arbitrary point in the composition triangle, follows the residue curve that passes through this starting point and ends at the stable node (bottom liquid composition).

III. Columns whose liquid composition profiles run along the boundaries (edges of the triangle and/or interior boundaries) and contain at least one of the saddles. In this case, the top and bottom liquid compositions lie on the boundaries.

Figure 4 illustrates the three acceptable types of liquid composition profiles of packed columns for the mixture shown in Figure 2a. The type I and II profiles contain a node singular point at one of the two ends (at the top and at the bottom resp.). The type III profiles contain an interior pinch point which can only be a saddle. Note that at any point in the column, the liquid and vapor compositions are identical (by the material balances) and hence the liquid and vapor profiles coincide.

Similarly, composition profiles of tray columns in the ∞/∞ case should follow distillation lines and contain at least one pinch point i.e. pure component or azeotrope. Again there are three acceptable types of profiles similar to the ones described above; simply replace residue curves and boundaries with distillation lines and distillation line boundaries in the above. Although residue curves and distillation lines do not coincide, it is very common

[1] The top (bottom) liquid composition refers to the upper (lower) end liquid composition of the column profile without the reboiler and condenser. Therefore, the top (bottom) liquid composition does not generally coincide with the top (bottom) product composition. We discuss the effect of the reboiler and condenser on the product compositions in the special topics section.

to consider that residue curves give a good approximation of composition profiles of tray columns at infinite reflux. In our previous article on homogeneous azeotropic distillation, this assumption was made. We will show later that this approximation may not be appropriate when the residue curve boundaries and the distillation line boundaries significantly deviate from each other. The effect of heterogeneity on this approximation will also be discussed later.

2.2 Existence of Multiple Steady States

In the previous section we demonstrated how the column composition profiles should look in the ∞/∞ case. Using the information above and the overall material balances, we can locate the feasible distillate and bottom product compositions for any given feed. In the ∞/∞ case of a homogeneous column, given a feed composition and a feed flowrate F, the only unspecified parameter is one product flow, e.g. the distillate flow rate D (the other flow rate is specified by the overall material balance). In order to find whether multiple steady states can occur (i.e. whether different column profiles correspond to the same value of D) we find all possible composition profiles by tracking the distillate and bottoms in the composition triangle, starting from the column profile with $D = 0$ and ending with the column profile with $D = F$. That is, we perform a bifurcation study (continuation of solutions) using the distillate flow as the bifurcation parameter. This task can be achieved because in the ∞/∞ case a continuation of solutions can be obtained based on physical arguments only. Multiple steady states exist when the distillate flow varies non-monotonically along the continuation path of the bifurcation diagram and more specifically, for our continuation path choice, when the distillate flow decreases in a segment along this path. Therefore, in order to find rules for the existence of multiple steady states, we have to first find out when D decreases along the continuation path.

Some important results of our thorough analysis (Bekiaris et al., 1993) are the following: Along the continuation path, D increases monotonically as we track all type I and type II column profiles. Therefore, a decrease in D can only occur as we track the type III column profiles i.e. columns whose composition profiles run along distillation region boundaries and contain at least one of the saddle singular points. We further show that the existence of multiplicities depends on the relative position (geometry) of the distillation region boundaries, and hence the location of the distillation boundaries is the only information required to conclude on the existence of multiplicities.

Using the results of this analysis we derive the necessary and sufficient geometrical condition for the existence of multiple steady states which is summarized in the following:

Geometrical, necessary and sufficient multiplicity condition: The continuation path is defined as the path generating all possible column profiles starting from the profile with D=0 and ending at the profile with D=F. Multiple steady states occur when D decreases somewhere along this path. This can be checked by the following procedure: Pick a distillate D and a bottom product B, both located on some distillation region boundaries and such that the column profile that runs from D to B along the distillation region boundaries contains at least one saddle singular point (type III column profile). Now pick D′ and B′ sufficiently close to D and B respectively and such that the column profile from D′ to B′ is a "later" profile along the continuation path. For the existence of multiple steady states it is required that: As we move along the continuation path from D to D′ and accordingly from B to B′, the line that passes from D and is parallel to BB′ crosses the D′B′ line segment (Figure 5a).

We further show that the existence of multiplicities depends on the feed composition and we locate the feed composition region that leads to multiple steady states. The condition for the appropriate feed region is summarized in the following:

Appropriate feed region condition: Pick a distillate D. Find the set of all bottom products such that the geometrical condition is satisfied for the picked D. Name this set S_B(D). Note that S_B(D) is always part of a distillation region boundary and that in some rare cases, S_B(D) may contain an inflexion point and/or it may consist of more than one non-connected boundary segments. Draw the straight line segments connecting D with the end points of each boundary segment that belongs to S_B(D). For the chosen D, the appropriate feed composition is the union of the areas enclosed by each boundary segment that belongs to S_B(D) and the corresponding straight line segments connecting D with the end points of the boundary segment of S_B(D). Pick another distillate D and repeat. In general, for each distillate D there exists a different set of bottoms compositions, S_B(D), that satisfies the geometrical condition. Therefore, for any given mixture, the feed compositions that lead to multiplicities lie in the union of all the areas enclosed by each boundary segment that belongs to *some* S_B(D) and the corresponding straight line segments connecting the distillate D associated to S_B(D) with the end points of the boundary segment of S_B(D).

Figure 5b illustrates the appropriate feed region condition. The geometrical condition is satisfied for distillate compositions D on the boundary segment ad. For any D on the boundary segment ad, the set S_B(D) is the straight line segment Ic. Hence, for any D on the boundary segment ad, the appropriate feed region is the triangle DIc. Therefore, the appropriate feed region for this mixture is the union of all these triangles, i.e. the shaded area adIc. Note that, for the mixture shown in Figure 5b, the set S_B(D) (1) consists of just one, straight line boundary segment and (2) is the same for all distillate compositions D that satisfy the multiplicity condition. The appropriate feed region condition described above covers the general case of S_B(D) consisting of more than one, curved boundary segments and being different for each D.

The above results have been originally derived for residue curve diagrams. It is obvious that similar results hold for distillation line diagrams by simply substituting residue curve boundaries with distillation line boundaries. Using the above results, we are able to study the existence of multiple steady states in the ∞/∞ case for mixtures that exhibit two liquid phases. We will perform this task in two steps: First for packed and tray columns without decanter and then for columns with decanter.

3 Columns without decanter

In the homogeneous case, the composition of the distillate is that of the stream drawn from the top of the column. This is also the case when no decanter is used in heterogeneous azeotropic distillation. Hence the techniques developed for homogeneous azeotropic distillation can be directly applied in this case. In particular, the case of heterogeneous mixtures using *packed* columns without decanter is identical to the one studied in our previous article on homogeneous azeotropic distillation (Bekiaris et al., 1993). We study packed columns first.

The only information required in this case is the residue curve boundaries as shown in Figure 6a. No information about the VLLE is required and hence the mixture depicted in Figure 6a can be treated as if it was a homogeneous mixture belonging to the 222-m class according to the classification by Matsuyama and Nishimura (1977).

In each of the three regions, there are two routes which go from the unstable node to the stable node along the region boundaries (a total of six routes, namely T→X→L, T→X→H, T→Y→L, T→Y→I, T→Z→I, T→Z→H). Note that the distillate and bottoms compositions should lie on the same route and therefore we only have to check the geometrical condition along the six routes mentioned above. All routes contain only one saddle singular point. Since the type III profile of an infinitely long column should contain at least one saddle, it is apparent that for any route the distillate may only lie on the interior boundary while the bottoms may only lie on the edge of the triangle.

It is only for these locations of D and B that the geometrical condition needs to be checked. The condition is even further simplified since the line BB′ (see the geometrical condition above) may only lie on some edge of the triangle. Moreover, for this type of residue curve diagram, the distillate of type III profiles along the continuation path will move along one of the interior boundaries *monotonically* in the direction from T towards the other end of the boundary. The geometrical condition for this particular type of residue curve diagram can be then simplified to the following: For the existence of multiple steady states it is required that (1) some line parallel to the LH edge intersects the interior boundary TX more than once, or (2) some line parallel to LI intersects TY more than once, or (3) some line parallel to IH intersects TZ more than once.

In applying the geometrical condition, caution should be taken close to the boundary end points (singular points) because the curvature of the boundary may change dramatically in the neighborhood of a singular point and hence there might exist a small boundary segment that enables the existence of multiple steady states. For mixtures belonging to the 222-m class the geometrical condition cannot be satisfied close to any binary azeotrope no matter what is the orientation of the boundary. Close to T, on the other hand, the interior boundaries (as well as the vapor line) are tangent to the direction of the eigenvector associated with the smallest absolute eigenvalue of the linearized equation (1) at point T (principal eigendirection). Depending on the orientation of the principal eigendirection and on the side from which each boundary approaches T, the geometrical condition may or may not be satisfied. In Figure 6a, the geometrical condition is not satisfied for any interior boundary and therefore no multiplicities exist for packed columns.

Similarly, for tray columns, we only have to check the aforementioned simplified geometrical condition for the interior distillation line boundaries which are shown in Figure 6b. Points a and b in Figure 7 are defined as the points of TX where the tangent to the boundary is parallel to the LH edge. The condition is not satisfied for the boundaries TY and TZ, it is satisfied, however, for the boundary TX. By applying the geometrical condition in its original form, it is easy to show that the distillate flowrate decreases along the continuation path for distillate compositions located on the ab segment of the boundary TX and bottoms located at any point on the LH edge. Therefore, the set $S_B(\mathrm{D})$ is the edge LH for any D on ab. Hence, the shaded region in Figure 6b depicts the feed composition region that leads to multiple steady states.

We will next track the whole continuation path (as described above) for a tray column with the feed composition F shown in Figure 7. The feed is homogeneous and lies in the lower left distillation region where T is the unstable node and H the stable node. The light component mole fraction in the bottoms x_{BL} is recorded along the continuation path. Figure 7 also depicts the feasible distillate and bottoms compositions (D and B) in the composition triangle and Table I shows the location of D and B, the distillate flowrate D changes, the light component mole fraction in the bottoms x_{BL} and the type of the column profile along the continuation path. In summary, the continuation path goes as follows:

We start with the type I profile with the distillate D at the ternary azeotrope T and the bottoms B at the feed F. Hence, $D = 0$ and $x_{BL} = x_{FL}$. Then, we track all type I profiles. The distillate D for all profiles lies on T while the bottoms B lies on the straight line Fd by the material balance. Along this part of the continuation path both D and x_{BL} increase.

Next, we track all type III profiles with the distillate D for all profiles on the vapor boundary TX and the bottoms B on the LH triangle edge. As D moves from T to a, B moves from d to e and hence x_{BL} decreases while D increases. It is very simple to show using the lever material balance rule that D decreases as D moves from a to b. At this part of the continuation path, B moves from e to f and hence x_{BL} decreases. Then, as D moves from b to c, B moves from f to H and hence x_{BL} decreases while D increases. Note, that beyond some point along this last part of the continuation path, the column profile becomes totally homogeneous (some part of the profile was in the heterogeneous region before).

Finally, we track all type II profiles. The bottoms B for all profiles lies on H while the distillate D lies on the straight line cF by the material balance. Along this part of the continuation path D increases (reaching F at the end point) while x_{BL} remains constant $x_{BL} = 0$. Figure 8 shows a sketch of the bifurcation diagram of x_{BL} vs. the bifurcation parameter D. It is apparent that for some distillate flowrate range, three steady states exist. Hence, for the mixture under consideration, there exists a qualitative difference between packed and tray columns.

3.1 Tray vs. packed columns

If the residue curve boundaries are straight lines then the corresponding distillation line boundaries are also straight lines and they coincide with the residue curve boundaries. In this case, the study of multiplicities gives identical results for both packed and tray columns. This was the case with the homogeneous mixture acetone - heptane - benzene studied in Bekiaris et al. (1993) where the edges of the composition triangle were the only boundaries.

In the case of curved boundaries, however, some discrepancy between the residue curve and distillation line boundaries is expected. At a first level, this discrepancy results in some *quantitative* differences between packed and tray columns i.e. differences in the appropriate feed region, the range of distillate flow where multiplicities exist etc. Because residue curve diagrams are much easier to calculate, it is commonly assumed that they provide a good approximation of tray columns as well. In our previous article on homogeneous azeotropic distillation, we used only residue curve diagrams for the theoretical study of multiplicities while the simulations were conducted for columns with trays. A very good agreement between the theory and the simulations was obtained even for residue curve diagrams with highly curved boundaries where tray column profiles may significantly deviate from residue curves.

The study of the mixture ethanol - water - benzene, however, showed that *qualitative* differences are also possible. Note that qualitatively different results may also be obtained for homogeneous mixtures. Also note that the curvature of a boundary is not the only measure of the discrepancy between residue curve and distillation line boundaries. The local "difficulty" of a separation, the "distance" between a liquid and a vapor composition in equilibrium plays a role, too. The more "difficult" a separation is i.e. the smaller is the distance between $\underline{x}$ and $\underline{y}(\underline{x})$, the smaller is the difference between the residue curve and distillation line boundaries. It is not easy, however, to identify the mixtures where qualitative differences occur between the predictions using the residue curve boundaries and the behavior of tray columns. This is particularly true for homogeneous mixtures although we are not aware of any mixture exhibiting such qualitative differences.

Next we show (1) why the difference between the residue curve and distillation line boundaries can be much more profound for heterogeneous mixtures and (2) how the VLLE, in particular the vapor line, can give us an indication when to expect qualitative differences between packed and tray columns. Note that the above statement is not in conflict with the fact that heterogeneous columns without decanter and homogeneous columns are treated identically regarding multiplicities.

It was mentioned above that the residue curve diagram of the heterogeneous mixture depicted in Figure 6a could also be the residue curve diagram of a homogeneous mixture belonging to the 222-m class. This is not true, however, for the distillation line diagram of the same mixture i.e. Figure 6b cannot be the distillation line diagram of any homogeneous mixture. In Figure 6b both distillation line boundaries TX and TY lie on the vapor line close to T and they share a common part. Boundaries for homogeneous mixtures cannot coincide at some segment and then divert. This can only happen for mixtures exhibiting two liquid phases and it is due to the singularity of the VLLE: the vapor compositions in equilibrium with the liquid compositions of the *two-dimensional* two-liquid phase region lie on the *one-dimensional* vapor line.

Hence, distillation line boundaries inside the heterogeneous region eventually have to lie on the vapor line. This can be easily shown using equation (2): consider a tray with liquid composition in the heterogeneous region; then by (2) the liquid composition of the tray above, as well as of all the trays on top of that, will lie on the vapor line. Therefore, for heterogeneous mixtures distillation line boundaries may significantly deviate from the corresponding residue curve boundaries because they have to follow part of the vapor line. Hence, the vapor line gives an indication of the geometry of some part of the distillation line boundaries which can be useful for the prediction of multiplicities of tray columns.

For heterogeneous mixtures similar to ethanol - water - benzene, in particular, it is very probable that some distillation line boundary will significantly deviate from the corresponding residue curve boundary because there are 3 residue curve boundaries running from T to each binary azeotrope and only 2 directions to approach T along the vapor line. The vapor line in Figure 2a lies close to the residue curve boundaries TY and TZ, but far from the third residue curve boundary TX. Note however that this is not the key feature that leads to multiplicities for tray columns; it is the geometry of the vapor line and in particular the turn from the left to the right of the top end of the vapor line. Figure 9 shows the same mixture (Figure 2a) with a slightly different vapor line that runs close to TZ and TX. From

Z to Q, the vapor line runs continuously from the right to the left. In this case, it is highly probable that, similarly to packed columns, no multiplicities exist for tray columns (since parts of the vapor line coincide with parts only of the distillation line boundaries we cannot be absolutely sure).

3.2 Summary

In this section we studied the ∞/∞ case of packed and tray columns without decanter for mixtures that may exhibit two liquid phases. We presented the accurate geometrical condition for the existence of multiplicities for the aforementioned cases as well as for packed and tray homogeneous columns. We discussed the differences between packed and tray columns, between residue curve and distillation line boundaries and the role of the vapor line for heterogeneous mixtures. Since residue curve boundaries are easier to calculate than distillation line boundaries, we derived guidelines on when it is justified to use residue curve boundaries for the study of multiplicities of tray columns.

These guidelines are: (1) For homogeneous mixtures: residue curve boundaries provide a good approximation except when the boundaries are highly curved (although we are not aware of any mixture where the approximation fails). (2) For heterogeneous mixtures: on one hand, residue curve boundaries inside the two-liquid phase region may provide a very poor approximation of distillation line boundaries. On the other hand, the vapor line gives an indication of the geometry of the distillation line boundaries in the two phase region. Hence, the combination of residue curve boundaries and the vapor line can be used for the qualitative prediction of multiplicities of tray columns (Figures 2a and 9). If this prediction is different from the one for packed columns, then it is suggested that the distillation line boundaries should be used for detailed results on multiplicities of tray columns.

A final note on the significance of this section. Although a column *with decanter* is required for the separation of the mixture ethanol - water - benzene (illustrative example), there exist other heterogeneous mixtures where a column without decanter is needed to achieve separation e.g. ethanol - water - ethyl ether. More importantly, however, this section's analysis provides necessary information for the study of the far more common case of heterogeneous columns with decanter: the location of the feasible compositions of the stream drawn from the top of the column and consequently the overall composition of the liquid that settles in the decanter.

4 Columns with decanter

The existence of two liquid phases in the decanter at the top of a heterogeneous azeotropic distillation column in the ∞/∞ case adds another parameter to the problem. The column with the decanter is depicted in Figure 10. The overhead vapor V is fed to a total condenser and the resulting liquid settles in the decanter. The overall distillate flow is composed of two liquid streams with compositions those of the two liquid phases in equilibrium. The two stream flows, D_1 and D_2, are the independent parameters in this case and $D = D_1 + D_2$. In general, $\underline{x}_D \neq \underline{x}_V$ and $\underline{x}_D \neq \underline{x}_R$. Since the column operates at infinite reflux ($R/D \to \infty$ and $V/D \to \infty$) the compositions of R and V are the same ($\underline{x}_R = \underline{x}_V$) and hence the residue curve and distillation line models accurately describe the column profiles of packed and tray columns with decanter respectively. For specific choices of D_1 and D_2 it is possible to have $\underline{x}_D = \underline{x}_R = \underline{x}_V$ and hence columns without decanter are a special case of columns with decanter. When $\underline{x}_V$ lies outside the heterogeneous liquid region there is no phase separation in the decanter and hence the column becomes identical to the column without decanter.

In this framework, the first step will be to locate the feasible overhead vapor V, distillate D and bottoms B regions for the column with decanter shown in Figure 10. In the case of columns without decanter a feasible column (1) has to belong to one of the three acceptable column profile types (restriction on the location of B and D) and (2) D, F and B have to lie in this order on a straight line (material balance). The situation is slightly different for columns with decanter. The material balance condition is obviously the same, but the condition imposed by the acceptable profile types restricts the location of B and V, not D. We proceed then as follows: for each profile type (1) we locate the acceptable V and B (this is just from the definition of the profile types and hence the feed location is not considered at this stage), (2) for the acceptable V found, we locate the possible D that can be drawn from the decanter (3) the feasible D and B, then, are the pairs of the previously located sets that satisfy the material balance and finally (4) from the feasible D we can locate the corresponding feasible V region. We apply the above procedure for the feed F shown in Figure 11a for a packed column. The feed composition is again located at the lower left distillation region.

We start with the type I profiles. In these profiles, V may only lie at the ternary azeotrope T while B can be any point in the composition triangle. Since V lies in the heterogeneous region, the distillate D can be any point on the tie line ab that goes through T. From the material balance, we find that the feasible B region is the quadrangle FcLd and the feasible D lies on ab (aFc and bFd are straight lines). The feasible regions are shown in Figure 11a.

Next, the type III profiles. For columns without decanter, it was shown that the distillate may only lie on an interior boundary (e.g. TX) while the bottoms may only lie on the corresponding edge of the triangle (e.g. LH). Similarly, for columns with decanter, V may lie on an interior boundary while B may only lie on the corresponding edge of the triangle. If V lies on TZ, then B has to lie on IH and the material balance cannot be satisfied. If V lies on TY (Figure 11b) then B has to lie on LI and hence for the material balance to be satisfied the distillate D has to lie somewhere on the left of the straight line LF. Let f and e be the points where the LF straight line intersects the heterogeneous liquid boiling envelope and the aTb tie line respectively. Let g be the point where the tie line from f intersects the boundary TY. Then, the feasible D lies in the $afea$ part of the heterogeneous region, the feasible B on the Lc line segment and the feasible V on the gT part of the boundary TY.

If V lies on TX (Figure 11c) then B has to lie on LH and hence for the material balance to be satisfied the distillate D has to lie somewhere on the right of the straight lines LF and HF. Let h and j be the points where the TX boundary intersects the heterogeneous envelope and the HF straight line respectively. Let hi be the tie line from h. If V lies on jh then the feasible D also lies on jh and the feasible B on Hk (hFk is a straight line). If V lies on hT then the feasible D lies in the $efhibe$ part of the heterogeneous region that is shown shaded in Figure 11c and the feasible B lies on Lk.

Finally, in the type II profiles (Figure 11d), the bottoms B always lies on H. Then D can only be a point on the straight line Fj by the material balance. Since D lies in the homogeneous region V also lies on Fj.

Now we put all these pieces together (Figure 12): (1) the feasible V region is the boundary segments Tg and Tj and the straight line jF, (2) the feasible D region consists of the straight line jF, the boundary segment jh and the $abiha$ part of the heterogeneous region (shaded in Figure 12), (3) the feasible B region consists of the LH edge, the Lc line and the FdLc quadrangle. Qualitatively similar results are obtained for tray columns using the distillation line boundaries. Some quantitative differences are expected because of the different boundary locations while the shape of the vapor line does not affect the location of the feasible distillate D.

So far we considered both D_1 and D_2 as the system parameters. One can reduce the system parameters to one by imposing a "policy" on the distillate, for example, keeping the ratio D_1/D_2 constant. The most common policy used in heterogeneous azeotropic distillation for columns like the one used for the separation of the mixture ethanol - water - benzene, is to recover as distillate a portion of the entrainer-poor phase only (i.e. D_2=0) and recycle a mixture of the two liquid phases. Next, this policy is studied in detail.

Since D_2=0, then $D = D_1$ and hence when V lies in the heterogeneous region, the distillate may only lie on the part of the heterogeneous liquid boiling envelope on the left of the critical point. Figure 13 shows the distillate and bottoms composition continuation path in the composition triangle when D_2=0. The distillate D follows the line $afhj$F and the bottoms B the line FcLkH. The light component mole fraction in the bottoms x_{BL} is recorded along the continuation path. Table II shows the location of D and B, the distillate flowrate D changes, the light component mole fraction in the bottoms x_{BL} and the type of the column profile along the continuation path. It is very simple to show using the lever material balance rule that D decreases as D moves from f to h and accordingly B moves from L to k. Figure 14 shows a sketch of the bifurcation diagram of x_{BL} vs. the bifurcation parameter D. It is apparent that for some distillate flowrate range, three steady states exist. Figure 15 illustrates three steady state profiles with the same D.

4.1 Geometrical Condition and Feed Region

So far, we demonstrated how to locate the feasible product regions for a given feed when both D_1 and D_2 are used as parameters. We also showed how to locate the products continuation path in the triangle and how to construct the corresponding bifurcation diagram using the distillate flow as parameter for a given feed and a given distillate policy, D_2=0. Here, we answer the following questions: Given a residue curve (or distillation line) diagram and a distillate policy for columns with decanter, find if multiple steady states exist for some feed compositions and for some distillate flowrates. Locate the feed compositions that lead to multiplicities. We demonstrate these, using the ethanol - water - benzene mixture for a packed column with decanter and distillate policy D_2=0.

From the discussion above, it is apparent that the key difference between columns with and without decanter is the location of the distillate continuation path. Once this path is located, the geometrical condition for the existence of multiplicities can be directly applied because it only checks if the distillate flowrate decreases along the continuation path. The information required in this case is the residue curve boundaries and the VLLE, heterogeneous envelope and tie lines, as shown in Figure 16. In the section of columns without decanter we located the distillate and bottoms compositions for which the multiplicity condition should be checked based solely on the knowledge of how column profiles look like in the ∞/∞ case. Therefore, these are also the locations of V (the overhead vapor stream) and B for columns with decanter. Hence, we only have to check the geometrical condition for V lying on an interior boundary and B lying on the corresponding binary edge of the triangle.

Next, we locate the distillate D when V lies on the interior boundaries under the distillate policy D_2=0. If V lies on TZ then D lies on aU. Let h and l be the points where the heterogeneous envelope intersects the boundaries TX and TY respectively. If V lies on TX then D lies on ahX while if V lies on TY, D lies on ahlY (Figure 16). Now the geometrical condition can be applied for the following distillate - bottoms locations: ahX - LH, ahlY - LI, aU - HI. Since the bottoms in all pairs lies on a triangle edge (similarly to columns without decanter), the geometrical condition can be simplified to the following : For the existence of multiple steady states it is required that (1) some line parallel to the LH edge intersects the distillate route ahX more than once, or (2) some line parallel to LI intersects ahlY more than once, or (3) some line parallel to HI intersects aU more than once.

The conditions (2) and (3) are not satisfied. Condition (1) is satisfied, however, between a and h. By applying the geometrical condition in its original form, it is easy to show that the distillate flowrate decreases along the continuation path for distillate compositions located on the ah segment of the distillate route and bottoms located at any point on the LH edge. Therefore, the set S_B(D) is the edge LH for any D on ah. Hence, the shaded region in Figure 16 depicts the feed composition region that leads to multiple steady states.

5 Special Topics

5.0.1 Reboiler and other condenser types

In the previous analysis, we assumed that the bottom product composition is equal to the composition of the lower end of the column profile. This is exactly correct if a total[1] or a thermosyphon[2] reboiler is used. In this case, the reboiler does not provide any additional enrichment. However, the typical reboiler type used in practice, i.e. the partial reboiler shown in Figure 17, is equivalent to an additional equilibrium stage. This does not affect at all the description of tray columns since the reboiler composition is just another point on the distillation line the column profile follows (Figure 17). It is not exactly correct, however, in the general case of packed columns since the composition of the reboiler may not lie on the residue curve that the profile follows (Figure 17). Instead, the reboiler composition is that of the liquid in equilibrium with the vapor with composition that of the lower end of the packed column profile. The effect of the use of a partial reboiler (instead of a total reboiler) on the study of multiplicities of packed columns is summarized in the following.

The use of partial or total reboiler has no impact on type II column profiles. In both

[1]By total reboiler we mean the equivalent of the total condenser i.e. a unit that boils the whole amount of liquid exiting the lower end of the column; the bottoms product is some portion of the vapor formed in the reboiler.

[2]The bottoms product of the thermosyphon reboiler is some portion of the liquid exiting the lower end of the column. The remaining amount of liquid exiting the lower end of the column is boiled and returned to the column as boilup. The thermosyphon reboiler is identical to the total reboiler in terms of input-output stream compositions.

cases, the bottom product composition is that of a stable node and both column profiles are identical, i.e. they follow the same residue curve, for the same distillate flowrate. In type I column profiles, the feasible bottom product compositions lie on the straight line that goes through the feed F and the unstable node (Figure 18a) independent of the reboiler type. Hence, the reboiler type does not affect the part of the product continuation path that corresponds to type I profiles. The profiles, however, of columns with the same B but different reboilers are different, i.e. they follow different residue curves, as it is shown in Figure 18a.

The use of a partial reboiler may have a significant effect on the feasible products only for type III column profiles. This effect is illustrated in Figure 18b. In this figure, the top profile end lies on LX and the lower profile end lies on the residue curve boundary XH (plain line). The dashed XH line is the location of the liquid compositions whose vapor in equilibrium lies on the residue curve boundary XH. If a total reboiler is used then the bottoms product composition is equal to the profile lower end composition and therefore B lies on the residue curve boundary XH. This is the case we studied in the analysis of multiplicities in the previous sections. If a partial reboiler is used, however, B will lie on the dashed XH line. This is the case when the use of a partial reboiler affects quantitatively and possibly qualitatively the existence of multiplicities.

Note, however, that in the special case of type III column profiles with the profile lower end lying on a straight line residue curve boundary (or a binary edge), B lies on the boundary (or edge) regardless of the reboiler type. In this case, the plain and dashed lines of Figure 18b are identical. This is the case with the mixture ethanol - water - benzene. For this mixture, we have shown above that the type III profile lower ends (or equivalently the bottoms product B for columns with total reboiler) cannot lie on an interior residue curve boundary; they can only lie on a binary triangle edge. Therefore, for the ethanol - water - benzene mixture type, the use of the partial reboiler does not affect at all the multiplicity results derived above for columns with a total reboiler.

In addition, all our analysis was made for columns with a total condenser. We can study other condenser types in a way similar to the above study of columns with different reboiler types. For example one can consider using a partial condenser and recovering as distillate only the vapor from the partial condenser. This situation is equivalent to the previous case of the partial reboiler. No difference for tray columns is expected since the partial condenser vapor composition lies on the distillation line. One has to calculate the lines of vapor compositions in equilibrium with the residue curve boundaries for accurately describing packed columns. These lines are depicted dashed in Figure 18c for the mixture ethanol - water - benzene. This is where D may lie and this time it affects the results for packed columns.

Note that these dashed lines lie between the residue curve boundary and the corresponding distillation line boundary and that similarly to the distillation line boundaries, the dashed lines in Figure 18c coincide with some part of the vapor line in the heterogeneous region. This is why the dashed lines look similar to the distillation line boundaries although they do not generally coincide with them (unless the whole boundary lies in the heterogeneous region). By applying the multiplicity condition when D lies on the dashed lines (packed columns using a partial condenser and recovering as distillate only the vapor from the partial condenser) we conclude that multiplicities do exist. In the previous sections a unique steady state was found for packed columns with a total condenser. Therefore, for the mixture ethanol - water - benzene and for packed columns without decanter we conclude that the existence of multiplicities critically depends on the condenser type.

Recovering portions of both the liquid and the vapor phase as distillate, makes the situation similar to the previous study of columns with decanter since it adds another parameter to the problem (the liquid to vapor flow ratio recovered as distillate). For tray columns, D will lie on the approximate distillation line while for packed columns, D will lie between the residue curve boundary and the corresponding curve (dashed line in Figure 18c) of vapor compositions in equilibrium with liquid compositions on the residue curve boundary. For columns with decanter, the combination of a partial condenser and a decanter can also be studied in a similar way.

Another situation very commonly encountered in practice is the use of a subcooled condenser in columns with decanter. In the ∞/∞ case, using a subcooled condenser does not affect the column profile. The only difference would be the use of the binodal curve at the temperature and pressure of the subcooled condenser (instead of the heterogeneous liquid boiling envelope used for the total condenser) to locate the distillate composition.

The examples above show that one can easily study the existence of multiplicities for many combinations of reboiler and condenser types with or without decanter; it only requires to locate the feasible product curves or regions for the various alternatives based on the ideas described above.

5.0.2 Tray efficiency

So far, we considered tray columns with a tray efficiency of 1. We also considered packed columns which can be regarded as tray columns with an infinitesimal tray efficiency ϵ ($\epsilon \to 0$). It is apparent that columns with tray efficiency $0 < \eta < 1$, would "lie" somewhere in between. In fact, the corresponding distillation region boundaries would really lie between the residue curve and distillation line boundaries. Note that the fact that distillation lines coincide with the vapor line close to T is true only if $\eta = 1$. For the illustrative example studied for columns without decanter, there exists a tray efficiency value η^* such that multiplicities exist only if $\eta > \eta^*$. For columns with decanter, however, only quantitative differences are expected.

5.0.3 A degenerate multiplicity

Bekiaris et al. (1993) showed that in homogeneous azeotropic distillation a different, degenerate, type of multiplicity (infinite number of profiles with the same product compositions for a specific distillate flowrate) occurs for feeds located on the straight line connecting the unstable node with the stable node of a distillation region and for the specific distillate flowrate that places the distillate at the unstable node and the bottoms at the stable node. This is because there is an infinite number of residue curves running from the unstable node to the stable node. More specifically, for a mixture belonging in the 222-m class, this type of multiplicity occurs when D is located at the ternary azeotrope T and B at a pure component corner. The column type, packed or tray, is irrelevant for homogeneous mixtures.

The case of heterogeneous mixtures and packed columns without decanter is identical with the homogeneous case, i.e. the degenerate type of multiplicities occurs for feeds located on the straight line segments TL, TI and TH. For tray columns without decanter, however, there is a difference because a part of every distillation line (sufficiently close to T) coincides with some part of the vapor line (Figure 2b). Hence, there is an infinite number of distillation lines that connect a point on the vapor line with a pure component corner (Figure 19). Note that the above does not affect the characteristics of this degenerate multiplicity; it only affects the feed region for which this degenerate type of multiplicities occurs. For tray columns, the feed region, instead of being three one-dimensional lines, is the union of the three areas enclosed by the part of the vapor line in each distillation region and the corresponding pure component vertex i.e. it is a two-dimensional region (shaded region in Figure 19). Note however that this two-dimensional feed region is not generic because the distillation lines do not coincide with the vapor line for columns with tray efficiency $\eta < 1$. For these columns the degenerate multiplicities occur for the feeds described above for packed columns.

The situation is different for columns with decanter and distillate policy D_2=0. If the bottoms is located at a stable node and the distillate D on the left part UC of the heterogeneous envelope ($D = D_1$), then there exists an infinite number of profiles whose bottoms is the stable node and their other end, V, is located on the tie line from D. This is true for both tray and packed columns. Figure 20 illustrates the degenerate type of multiplicity by depicting five different tray column profiles with identical B and D. The overhead vapor V lies on the tie line from D. The composition of the liquid at the top tray is different for all five profiles. The overhead vapor V, however, is the same for the three profiles on the right because the corresponding top tray liquid compositions lie on the tie line in equilibrium with the vapor with composition the point where the tie line from D and the vapor line intersect. Note, however, that the latter phenomenon, infinite number of different column profiles with the same D, B *and* V, occurs only for tray columns with tray efficiency equal 1.

Hence, the degenerate type of multiplicities for columns with decanter occurs for feeds located in the union of the three areas enclosed by each one of the three pure component vertices and the corresponding part of UC that D may lie on (L-al, I-UC, H-Uh). This region is shown shaded in Figure 21. In this case, contrary to the case of tray columns without decanter, the existence of the two-dimensional feed region is generic and more specifically, independent of the tray efficiency η. This difference may help the study of the degenerate multiplicities since in the previous cases the feed had to exactly lie on a straight line that cannot be very accurately located. Another slight difference with the case of columns without decanter is that although the product compositions are the same for all the infinite number of profiles, the location of V maybe different. As it was shown before, V is the same only in some profiles of tray columns with tray efficiency equal 1.

Another important point for some future investigation of this degenerate type of multiplicities is that for the feed shown in Figure 13 the continuation of profiles should go through this infinity of profiles. The reason is very simple. In Figure 13 if B is located close to L on Lc, then the profile runs along the TYL boundary like profile 1 does in Figure 15. If B is located close to L on Lk, the profile runs along the TXL boundary (similarly to profile 2 in Figure 15). Therefore, when B is located at L and D at f (Figure 13) the profile should move from the TYL boundary to the TXL boundary, i.e. it will scan the infinite number of profiles of the degenerate type of multiplicity. This phenomenon occurs for packed as well as tray columns with decanter and arbitrary tray efficiency.

This type of multiplicities (infinite number of profiles with the same product compositions for a specific distillate flowrate) may be similar to those reported by Kienle and Marquardt (1991) and Helfferich (1993)[1]. The practical implications of the degenerate type of multiplicities reported here are unclear i.e. we don't know whether (1) these multiplicities are an artifact of the ∞/∞ case and therefore do not exist for finite columns at finite reflux or (2) some finite number of multiple steady states still exist for finite columns at finite reflux. Hence, a more thorough investigation of this topic is needed.

5.0.4 Distillate policies - Discontinuity

In our study of columns with decanter we discussed the commonly used distillate policy D_2=0. One can define another policy by tracing an arbitrary path of D in the heterogeneous shaded region in Figure 12. For example, the column without decanter defines another path. It is apparent that since the paths are defined arbitrarily, one can easily draw paths that would exhibit an arbitrary number of steady states. For example, in Figure 12, a continuous-S-shaped path along a vertical line will exhibit a number of steady states proportional to the number of the path S's.

We have shown that in the ∞/∞ case of columns with decanter there exist two parameters yet to be specified: D_1 and D_2 or equivalently the distillate flowrate D and the ratio D_1/D. For the feed shown in Figure 12, we now want to draw the 3-D surface which depicts the light component mole fraction in the bottoms x_{BL} as a function of both the distillate flowrate D and the ratio D_1/D (bifurcation diagram with two bifurcation parameters). We derive this 3-D diagram by sketching the "cuts" of the surface for several distillate policies with constant ratio D_1/D i.e. we draw the bifurcation diagrams with the distillate flowrate D as the only bifurcation parameter while the ratio D_1/D is fixed. We focus on the part of the bifurcation diagrams which corresponds to heterogeneous profiles.

If D_1/D=1 (i.e. D_2=0) we obtain the bifurcation diagram of Figure 14 which we place in Figure 22 at the D_1/D=1 plane. The line abc (Figure 22) corresponds to heterogeneous profiles. Along ab, x_{BL} and D monotonically increase and along bc, they both decrease. Point b marks the point of the highest x_{BL} achieved and point c denotes the end of the heterogeneous part of the bifurcation diagram. The points b' and c' are the projections of b and c on the plane $x_{BL} = 0$. Two heterogeneous steady states exist for distillate flowrates between c' and b'.

If D_1/D=0, it is easy to show that D will move on the bi part of the heterogeneous envelope (Figure 12). The line def of Figure 22 sketches the heterogeneous part of the bifurcation diagram of columns with distillate policy D_1/D=0. Along de, x_{BL} and D increase and along ef, x_{BL} decreases while D still increases. The distillate flowrate D is monotonically increasing along def and therefore, a unique heterogeneous steady state exists for columns with distillate policy D_1/D=0.

Using similar arguments we sketch the other two "cuts" in Figure 22 which show bifurcation diagrams for constant D_1/D. Now it is easy to draw the whole surface which is shown in Figure 22. The line be is the set of points of the highest x_{BL} achieved for every fixed

[1]Kienle and Marquardt (1991) and Helfferich (1993) investigated multiplicities in single column sections. Helfferich (1993) argues that these types of multiplicities disappear in practice (finite length column sections with finite mass-transfer rates). The implications of those multiplicities for complete distillation columns are unclear.

D_1/D. The line cf is the end of the heterogeneous part of the bifurcation diagram for every fixed D_1/D. The lines $b'e'$ and $c'f'$ are the projections of be and cf on the plane $x_{BL} = 0$.

We can distinguish two parts of the surface shown in Figure 22. The surface $abeda$ is formed by the part of the "cuts" with constant D_1/D where x_{BL} and D monotonically increase until x_{BL} reaches its highest value. The second part of the surface, $bcfeb$, is formed by the part of the "cuts" of constant D_1/D where x_{BL} monotonically decreases beyond the point of the highest x_{BL} value. The dark-shaded (light-shaded resp.) portion of $bcfeb$ depicts the part of the "cuts" of constant D_1/D where the distillate flowrate D decreases (increases resp.). For simplicity, one may consider the dark-shaded part of the surface $bcfeb$ as the portion of $bcfeb$ that lies under the surface $abeda$, although this is not exactly correct.

It is apparent that the projection of the dark-shaded portion of the surface $bcfeb$ on the plane $x_{BL} = 0$ marks the parameter space region where two heterogeneous steady states exist. The region $c'b'gc'$ in Figure 22 depicts the approximate parameter space region of two heterogeneous steady states. Figure 22 also shows that if D_1/D is less than some value r, a unique heterogeneous steady state exists. Any arbitrary path of D in Figure 12 will correspond to a different "cut" of the surface in Figure 22 and depending on the shape of the "cut," to a different number of multiple steady states.

Also note that the kF part of the bifurcation diagram of Figure 14 that corresponds to homogeneous profiles is placed at the D_1/D=1 plane in Figure 22 (ch line). This is obviously its "natural" location by continuity (point h of Figure 12 belongs to the phase 1 part of the heterogeneous boiling envelope). Any other constant D_1/D distillate policy exhibits a discontinuity at the point where the profile along the continuation path becomes homogeneous. For example, if D_1/D=0 the bifurcation diagram consists of the lines def (heterogeneous part) and ch (homogeneous part) of Figure 22 and apparently it exhibits a discontinuity (jump from f to c). A very important factor for the presence or absence of discontinuities in the bifurcation diagrams is the location of the critical point C. If C was located on the left of point h in Figure 13 (D_2=0), a discontinuity would occur between points C and h i.e. the distillate would not be allowed to lie on Ch under the distillate policy D_2=0 since Ch would correspond to phase 2. In addition, the changed orientation of the tie lines would give different feasible product regions in Figure 12.

In the case of columns without decanter, similarly to the homogeneous case, there is no discontinuity along the continuation path and therefore, multiple steady states exist if and only if the distillate flowrate decreases along some part of the continuation path. In the case of columns with decanter and a given distillate policy, however, we just showed that discontinuity is possible at the transition from heterogeneous to homogeneous profiles. Therefore, in this case, in addition to the aforementioned multiplicity condition, one has to check the distillate flowrate ranges of the heterogeneous and homogeneous branches of the continuation path for possible distillate flowrate overlap and consequently multiplicity.

6 Finite Reflux and Finite Number of Trays

The ∞/∞ case is the limiting case of high reflux and a large number of trays. Therefore, if the geometrical condition is satisfied for a given mixture then multiplicities will exist for some sufficiently large finite reflux and finite number of trays. However, the inverse is not true. The geometrical condition is only a sufficient condition for the existence of multiplicities when the reflux and the number of trays are finite. At infinite reflux, the column profiles coincide with residue curves or distillation lines. This is not true at finite reflux. Moreover, column profiles at finite reflux depend on the location and the number of the feed streams. Therefore, the residue curve and distillation line diagrams do not provide an accurate description of columns at finite reflux and with a finite number of trays.

In this section, we present steady state bifurcation results for the mixture ethanol (L) - water (H) - benzene (I-E) with the distillate flow D as the bifurcation parameter. These bifurcation results show (1) that the predictions for the existence of multiple steady states in the ∞/∞ case carry over to columns operating at finite reflux and with a finite number of trays and (2) that, although the predictions were made in the ∞/∞ case, it does not mean that multiple steady states do not exist for realistic operating conditions (low reflux and number of trays).

In all simulations presented here, we use a tray column with a total condenser while the reboiler constitutes an additional equilibrium stage (partial reboiler). Constant molar overflow and a tray efficiency of 1 are assumed. Finally, the column operates under atmospheric pressure and there is no pressure drop in the column. The thermodynamic model described in the preliminaries of this article is used for the VLLE calculations. The tray counting starts from the reboiler (number 1) and ends at the top. The bifurcation calculations were conducted with AUTO, a software package developed by Doedel (1986). In the following, we present steady state bifurcation results for two columns, one without decanter and one with decanter.

Column without decanter:

The column characteristics are depicted in Figure 23 and they are similar to the column studied by Magnussen et al. (1979). The column has 27 ideal stages (including the reboiler). The reflux flow is fixed at R=345.157. A mixture of 89% ethanol and 11% water, is fed at stage 23 (F_1). It is assumed that the distillate D of the column in Figure 23 is fed to a decanter (not included in the model); the benzene-rich phase from the decanter is returned to the column. Since the decanter is not included in the model, a second stream (F_2) is fed at the top of the column (Figure 23) to compensate for the returned benzene-rich phase from the decanter and the benzene make-up stream. The flowrate and composition of the second feed F_2 are the same as the one Magnussen et al. (1979) specified "according to experimentally observed liquid-liquid equilibria." The location of the overall feed ($F=F_1+F_2$) composition in the composition triangle is similar to the one illustrated in Figure 7. Therefore, Figure 8 illustrates the predicted ∞/∞ case bifurcation diagram for the column in Figure 23.

Figure 24 shows the computed bifurcation diagram with the distillate flow as the bifurcation parameter. A unique stable steady state exists for low D. D increases until the continuation algorithm reaches the first limit point. Beyond that point an unstable steady state is calculated (dashed curve). Along this part of the continuation path x_{BL} decreases while D decreases until the second limit point is encountered. Beyond the second limit point, D increases again and a second stable steady state is calculated. Hence, two stable and one unstable steady states exist for distillate flows between the two limit points (multiplicity region); a unique stable steady state exists otherwise. Note the similarity of this continuation path with the continuation path we tracked in the ∞/∞ case (Figure 8). Some discrepancy from the ∞/∞ case prediction is expected. Finally, note that, although those multiple steady states were predicted at infinite reflux, they still exist at low reflux values (R/F =2.4).

Column with decanter:

The column characteristics are depicted in Figure 25. The column has 27 ideal stages (including the reboiler). The reflux flow is fixed at R=508.369. A mixture of 89% ethanol and 11% water, is fed at stage 23 (F_1). In this case, the second feed (F_2) at the top of the column is the benzene make-up stream. The location of the overall feed ($F=F_1+F_2$) composition in the composition triangle is similar to the one illustrated in Figure 13 and hence, Figure 14 illustrates the predicted ∞/∞ case bifurcation diagram for the column in Figure 25 with the exception that the mole fraction of ethanol at point k of Figure 14 is larger than x_{FL}.

Figure 26 shows the computed bifurcation diagram with the distillate flow as the bifurcation parameter. A unique stable heterogeneous steady state exists for low D. D increases until the continuation algorithm reaches the first limit point. Beyond that point an unstable heterogeneous steady state is calculated (dashed curve). The distillate flow D decreases along the unstable part of the continuation path until the second limit point is encountered. Note that it is purely coincidental that the second limit point appears to be on the heterogeneous stable part of the continuation path (it does not because the other component mole fractions are different). Beyond the second limit point, D increases again and a second stable, but homogeneous, steady state is calculated. Hence, two stable (one heterogeneous and one homogeneous) and one unstable (heterogeneous) steady states exist for distillate flows between the two limit points; a unique stable steady state exists otherwise. Again, note the similarity of this continuation path with the continuation path we tracked in the ∞/∞ case (Figure 14) although some discrepancy from the ∞/∞ case prediction is expected.

7 Conclusions

In this article we examine in detail the existence of multiple steady states in the ∞/∞ case of a ternary mixture. More specifically, we answer the following questions: Given a ternary (homogeneous or heterogeneous) mixture and its VL(L)E diagram (residue curve diagram for packed columns, distillation line diagram for tray columns),

(1) find whether multiple steady states exist for some feed composition and

(2) locate the feed composition region that leads to these multiple steady states.

The existence of multiplicities (question 1) can be checked by the procedure depicted in Figure 27 which is summarized in the following:

Locate the singular points (pure components and azeotropes) in the VL(L)E diagram. Locate the m distillation regions. In every distillation region containing k singular points, there is one unstable node, one stable node and k-2 saddles. For each region there exist two routes which go from the unstable node to the stable node along the region boundaries (a total of 2m routes).

For each route, mark the n singular points along the route as follows: point 1, the unstable node; points 2 to n-1, the saddles; point n, the stable node. The only eligible column profile lower end compositions along this route lie on the part between points 2 and n. This is the profile lower end route. Accordingly, the eligible column profile upper end (overhead vapor) lies on the part of the route between points 1 and n-1. This is the profile upper end route. These two routes define the locations of the upper and lower end column profile compositions for which the geometrical condition should be checked (type III column profiles).

Note, however, that the geometrical condition directly involves the distillate and bottom product routes which may be different from the profile upper and lower end routes depending on the type of the equipment used at the column ends (condenser, reboiler, decanter). In this article, we show how the distillate and bottoms routes (associated with a given pair of upper and lower profile end routes) can be located for any equipment combination. Tables IIIa and IIIb show how the distillate and bottom product routes are related to the profile upper and lower end routes for some equipment types and for tray and packed columns respectively.

Finally, we define the continuation path (and its direction) as the path generating all possible column profiles starting from the profile with D=0 and ending at the profile with D=F. Multiple steady states occur when D decreases along this path. This can be checked by the following condition:

Geometrical, necessary and sufficient multiplicity condition: Pick a distillate D and a bottom product B, both located on some pair of distillate and bottoms product routes and such that (1) the line segment D′B′ crosses the line segment DB (to ensure that there exists a feed composition associated with both profiles) and (2) the column profile that runs from D to B along the distillation region boundaries contains at least one saddle singular point (type III column profile). Now pick D′ and B′ sufficiently close to D and B respectively and such that the column profile from D′ to B′ is a "later" profile along the continuation path. For the existence of multiple steady states it is required that: As we move along the continuation path from D to D′ and accordingly from B to B′, the line that passes from D and is parallel to BB′ crosses the D′B′ line segment.

Finally, for columns with decanter and a given distillate policy, we show that discontinuity is possible at the transition from heterogeneous to homogeneous profiles along the continuation path. In this case, in addition to the aforementioned geometrical condition, one has to check the distillate flowrate ranges of the heterogeneous and homogeneous branches of the continuation path for possible distillate flowrate overlap and consequently multiplicity.

The condition for the appropriate feed region (question 2) is summarized in the following:

Appropriate feed region condition: Pick a distillate D. Find the set of all bottom products such that the geometrical condition is satisfied for the picked D. Name this set S_B(D). Note that S_B(D) is always part of a distillation region boundary and that in some rare cases, S_B(D) may contain an inflexion point and/or it may consist of more than one non-connected boundary segments. Draw the straight line segments connecting D with the end points of each boundary segment that belongs to S_B(D). For the chosen D, the appropriate feed composition is the union of the areas enclosed by each boundary segment that belongs to S_B(D) and the corresponding straight line segments connecting D with the end points of the boundary segment of S_B(D). Pick another distillate D and repeat. In general, for each distillate D there exists a different set of bottoms compositions, S_B(D), that satisfies the geometrical condition. Therefore, for any given mixture, the feed compositions that lead to multiplicities lie in the union of all the areas enclosed by each boundary segment that belongs to *some* S_B(D) and the corresponding straight line segments connecting the distillate

D associated to S_B(D) with the end points of the boundary segment of S_B(D).

The procedures and conditions described above constitute the fully detailed, accurate and totally general answers to the questions about the existence of multiplicities and the feed compositions that lead to these multiplicities. Given a mixture and its VL(L)E diagram, we show via an illustrative example how the specific VL(L)E diagram structural information can be used to simplify these conditions (unavoidably by reducing the degree of generality) to some very simple tests. We also discuss the differences between packed and tray columns, between residue curve and distillation line diagrams, the effect of tray efficiency as well as the role of the vapor line for heterogeneous mixtures. Since residue curve boundaries are easier to calculate than distillation line boundaries, we derive guidelines on when it is justified to use residue curve boundaries for the study of multiplicities of tray columns (at the expense of less quantitative accuracy).

As an illustrative example throughout this article we use the mixture ethanol - water - benzene. For this mixture and the specific VL(L)E model and parameters used, we derive the following conclusions regarding multiplicities in the ∞/∞ case solely based on (1) the residue curve boundaries, the heterogeneous region envelope, the distillation line boundaries and the line of vapor compositions in equilibrium with liquid compositions on the residue curve boundaries, if accurate quantitative results are needed, or (2) the residue curve boundaries, the heterogeneous region envelope and the vapor line, if somewhat less accurate quantitative results are sufficient.

Columns without decanter: In this case, we identify that the existence of multiplicities critically depends on the location of the distillate path away from the binary edges and more specifically in the heterogeneous region. We show that the location of the vapor line is very crucial in this case. We further show that the reboiler type has absolutely no effect on the existence of multiplicities for this particular mixture class.

For tray columns with tray efficiency 1, we conclude that multiplicities exist regardless of the condenser type. For packed columns, multiplicities exist if a partial condenser is used and the distillate product consists of the vapor phase only. A unique steady state exists, however, for packed columns with a total condenser. Finally, for tray columns with a total condenser, we conclude that there exists a tray efficiency value η^* such that multiple steady states exist only if $\eta > \eta^*$.

Columns with decanter: We show that the existence of multiplicities depends on the distillate policy. The most common distillate policy for this mixture, i.e. recovering as distillate a portion of the entrainer-poor phase only (D_2=0) and refluxing a mixture of the two liquid phases, is studied in detail. We conclude that under this distillate policy: (1) the existence of multiple steady states is generic for this heterogeneous mixture class and therefore the presence of multiplicities does not critically depend on some specific VL(L)E characteristic as long as the basic qualitative structural properties of the VL(L)E diagram are preserved, (2) consequently, using different reboiler, condenser and column types does not qualitatively affect the existence of multiplicities although some quantitative differences are expected.

Finally, using numerically constructed bifurcation diagrams, we show that the ∞/∞ case predictions carry over to columns operating at finite reflux and with a finite number of trays. We also discuss a different, degenerate type of multiplicity (infinite number of profiles with the same product compositions for a specific distillate flowrate) whose practical implications are unclear and therefore, a more thorough investigation of this topic is needed.

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9 Appendix

The appendix contains information on the thermodynamic model used in this article. Vapor - liquid equilibrium calculations are based on the following equation:

$$y_i P = x_i P_i^{sat}(T)\gamma_i(T, \underline{x})$$

where P=1 atm in this article.

Vapor pressures were computed by the Antoine equation:

$$ln P_i^{sat} = A_i + \frac{B_i}{T + C_i}$$

where T in ^oK and P_i^{sat} in atm. Table IV contains the Antoine coefficients given by Gmehling and Onken (1977) for the components used in this article.

Liquid activity coefficients were computed by the modified UNIQUAC model. The exact form of the modified UNIQUAC model used here is given in equations (6.11-11)-(6.11-22) and (6.15-9)-(6.15-12) in Prausnitz et al. (1986).

Table V contains the UNIQUAC parameters R, Q and Q′ for the pure components ethanol, water and benzene given by Gmehling and Onken (1977). Note that Q=Q′. Table VI contains the UNIQUAC binary parameters a_{ij} in ^oK (equation 6.11-17 in Prausnitz et al., 1986) for the mixture ethanol - water - benzene used in this article; the UNIQUAC binary parameters a_{ij} were estimated from the UNIFAC model using the Aspen Plus estimation option.

profile type	heterogeneous							homogeneous			
		I		III		III		III		II	
D	T	—	T	$\rightarrow$	*a*	$\rightarrow$	*b*	$\rightarrow$	*c*	$\rightarrow$	F
B	F	$\rightarrow$	*d*	$\rightarrow$	*e*	$\rightarrow$	*f*	$\rightarrow$	H	—	H
D	0	$\uparrow$		$\uparrow$		$\boxed{\downarrow}$		$\uparrow$		$\uparrow$	F
x_{BL}	x_{FL}	$\uparrow$		$\downarrow$		$\downarrow$		$\downarrow$	0	—	0

Table I : Information along the continuation path
for tray columns without decanter

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profile type	heterogeneous							homogeneous			
		I		III		III		III		II	
D	a	—	a	→	f	→	h	→	j	→	F
B	F	→	c	→	L	→	k	→	H	—	H
D	0	↑		↑		$\boxed{\downarrow}$		↑		↑	F
x_{BL}	x_{FL}	↑		↑	1	↓		↓	0	—	0

Table II : Information along the continuation path for packed columns with decanter and D_2 =0

Table III: The distillate and bottoms routes for various types of equipment (condenser/reboiler/decanter).
a. tray columns b. packed columns

a. Tray columns (tray efficiency=1)

<table>
<tr><td>Total Reboiler</td><td rowspan="2">B route = lower end route</td></tr>
<tr><td>Partial Reboiler
B = liquid</td></tr>
<tr><td>Total Condenser</td><td rowspan="2">D route = upper end route</td></tr>
<tr><td>Partial Condenser
D = vapor</td></tr>
<tr><td>Total (or Subcooled) Condenser
& Decanter with policy $D_2=0$</td><td>D route composed of:
- the homogeneous part of the upper end route &
- the part of the 1st phase of the heterogeneous liquid boiling envelope (or binodal curve)
that can be obtained from the phase split of the heterogeneous part of the upper end route</td></tr>
</table>

b. Packed columns (≈ tray columns w/ tray efficiency → 0)

Total Reboiler	B route = lower end route
Partial Reboiler B = liquid	B route = line of liquid compositions in equilibrium with vapor compositions on the lower end route
Total Condenser	D route = upper end route
Partial Condenser D = vapor	D route = line of vapor compositions in equilibrium with liquid compositions on the upper end route
Total (or Subcooled) Condenser & Decanter with policy $D_2=0$	D route composed of: - the homogeneous part of the upper end route & - the part of the 1st phase of the heterogeneous liquid boiling envelope (or binodal curve) that can be obtained from the phase split of the heterogeneous part of the upper end route

Table IV: Antoine coefficients for the components used in this article.

	A	B	C
Ethanol	12.0455965	-3667.705	-46.966
Benzene	9.2080465	-2755.642	-53.989
Water	11.9514465	-3984.923	-39.724

Table V: UNIQUAC pure component parameters used in this article.

	R	Q	Q'
Ethanol	2.1055	1.972	1.972
Benzene	3.1878	2.4	2.4
Water	0.92	1.4	1.4

Table VI: UNIQUAC binary parameters a_{ij} in °K for the ethanol - benzene - water mixture.

i \ j	Ethanol	Benzene	Water
Ethanol	0	-43.0334	-32.9976
Benzene	384.892	0	903.800
Water	203.843	362.300	0

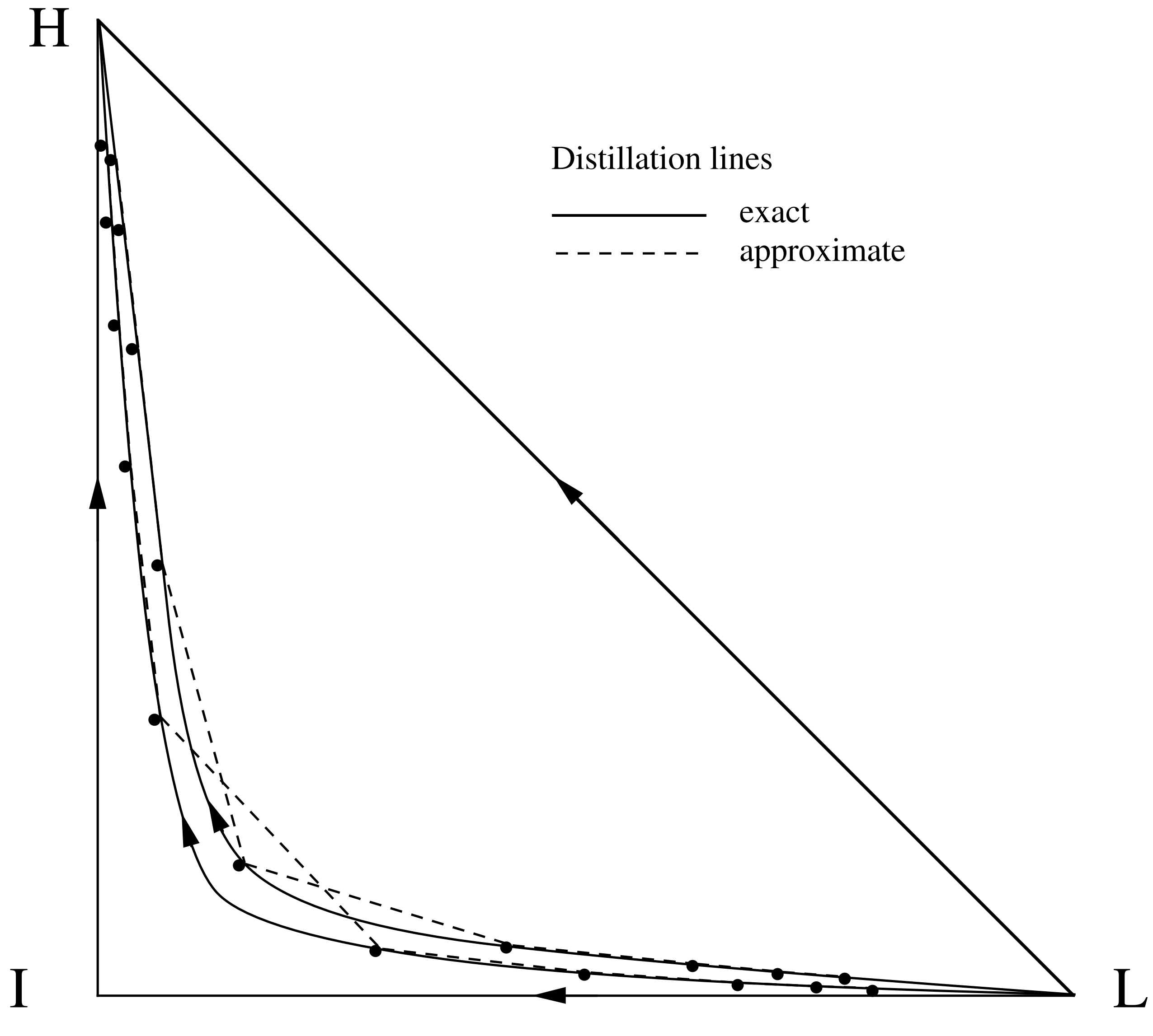

Figure 1a: Although the (exact) distillation lines do not cross, the approximate distillation lines may cross.

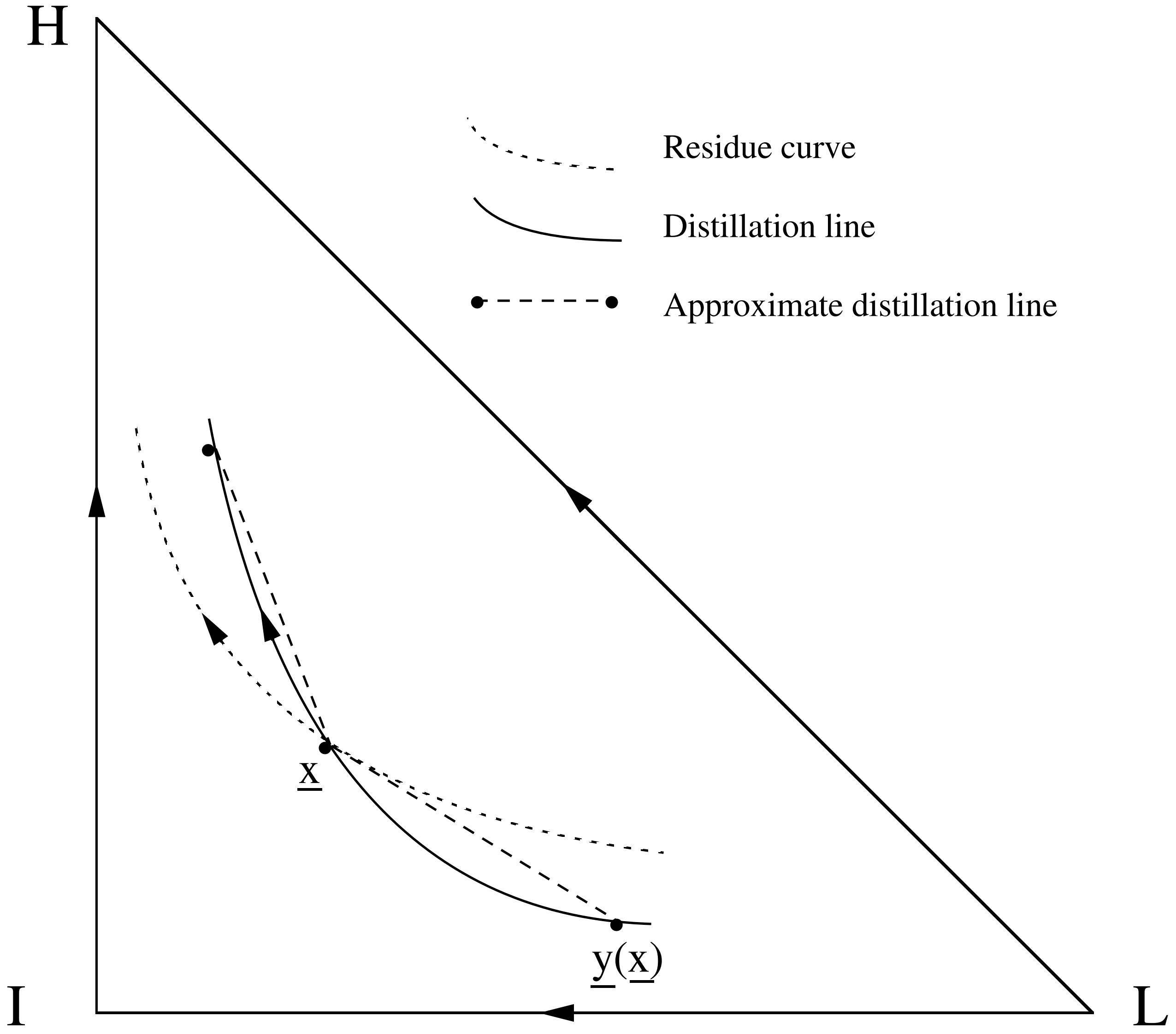

Figure 1b: The residue curve, the distillation line and the approximate distillation line that go through point $\underline{x}$.

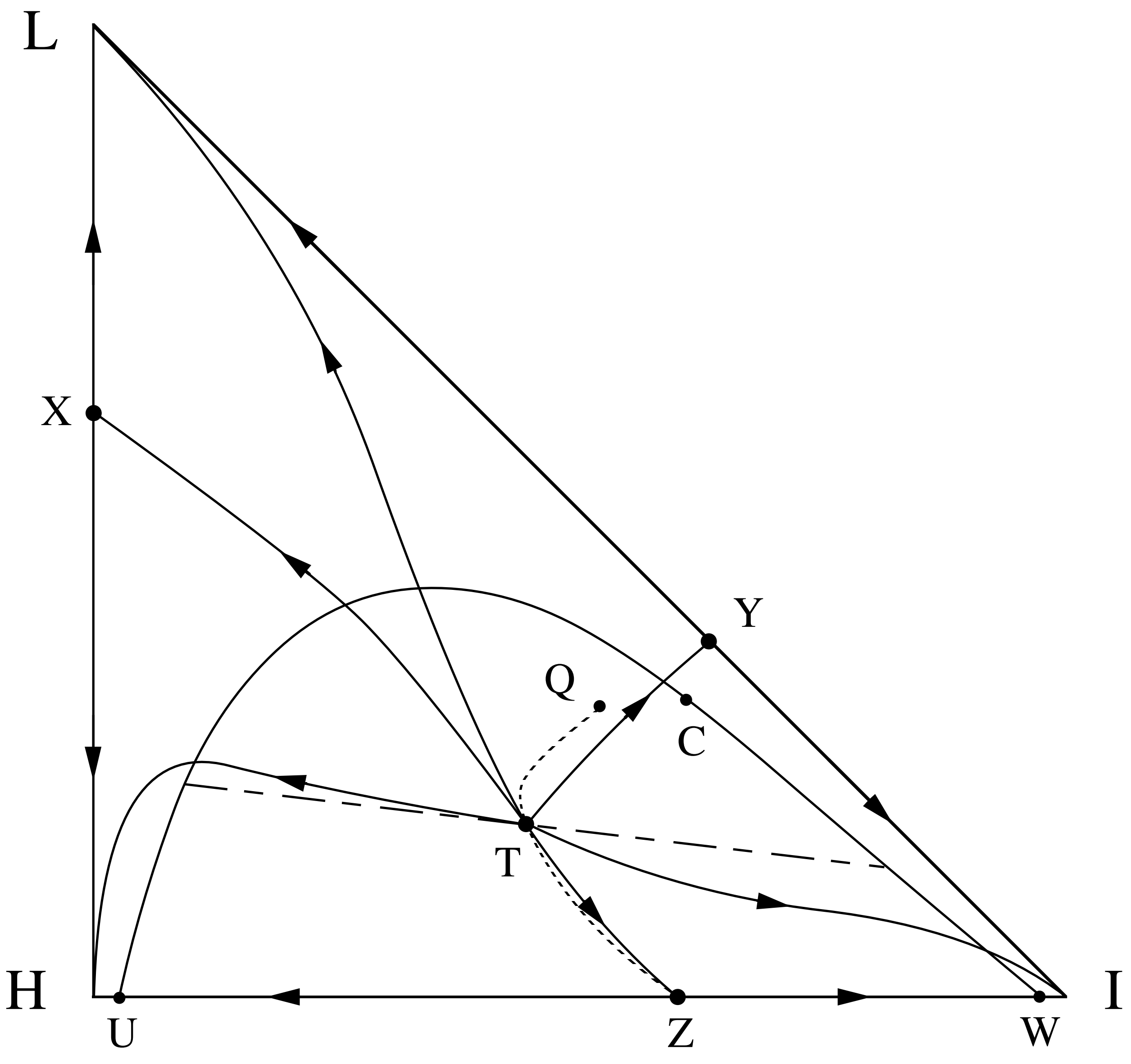

Figure 2a: Residue curve diagram and VLLE of the mixture ethanol-water-benzene.

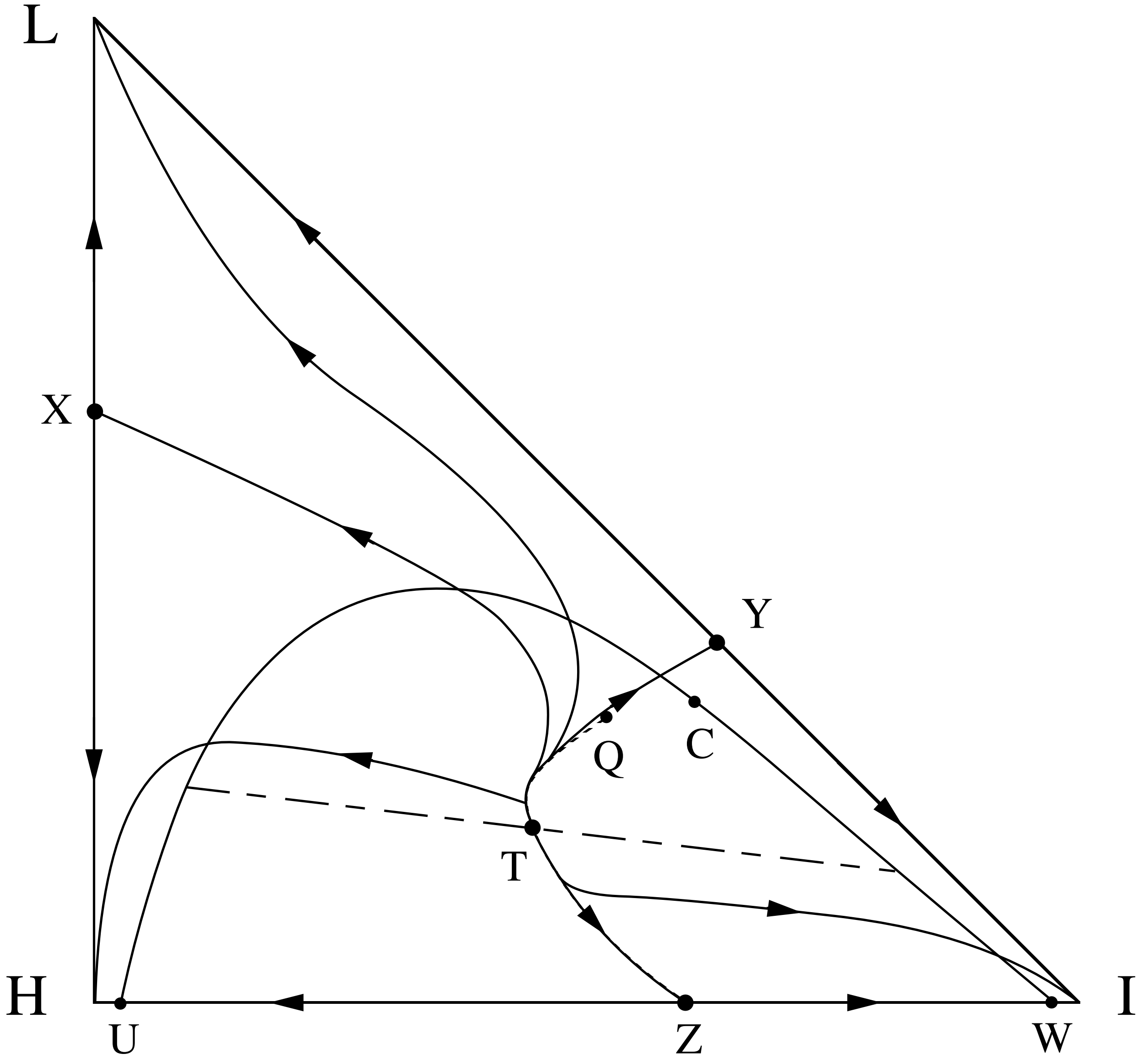

Figure 2b: Distillation line diagram and VLLE of the mixture ethanol-water-benzene.

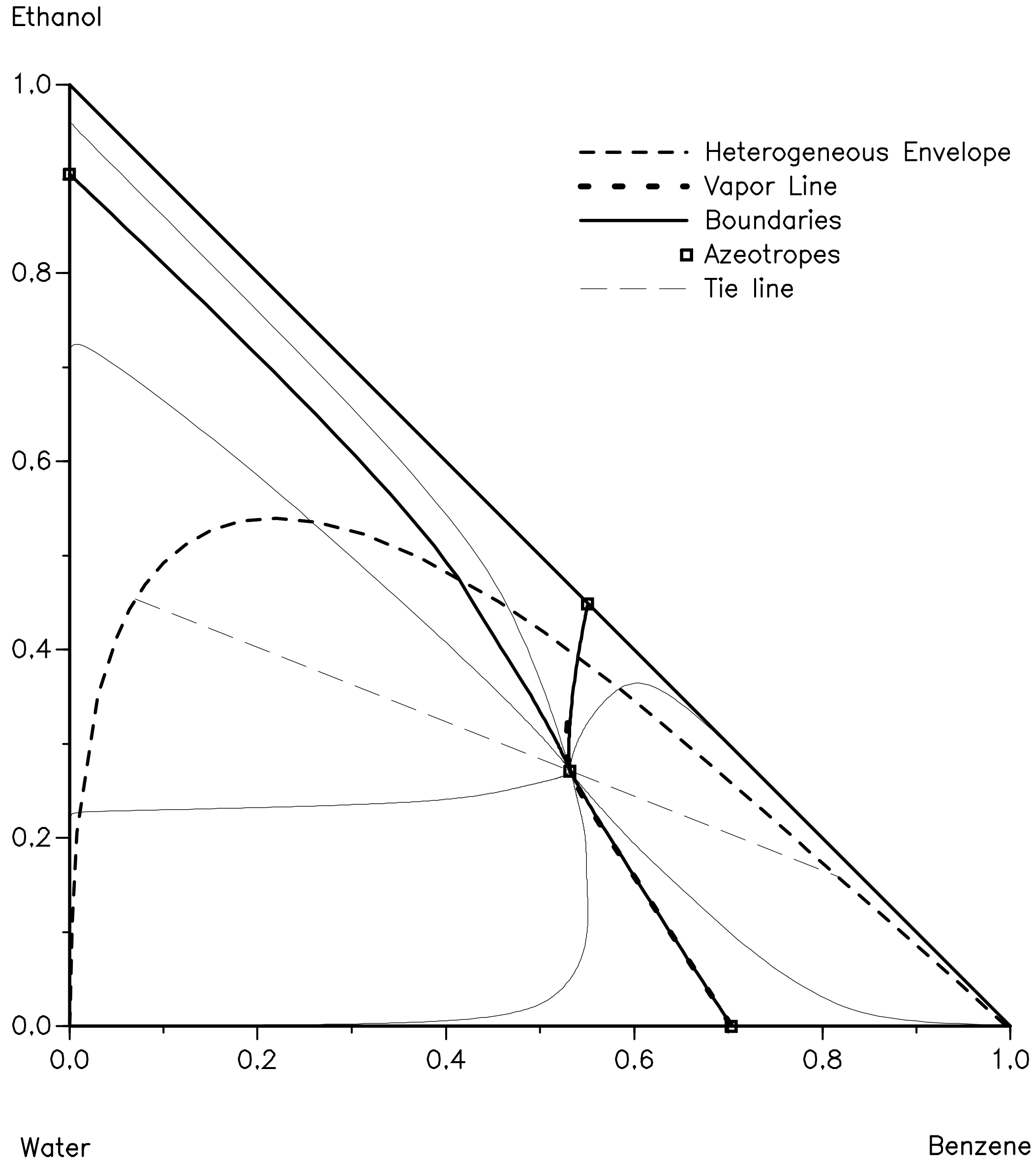

Figure 3a: The exact residue curve diagram and VLLE of the mixture ethanol – water – benzene.

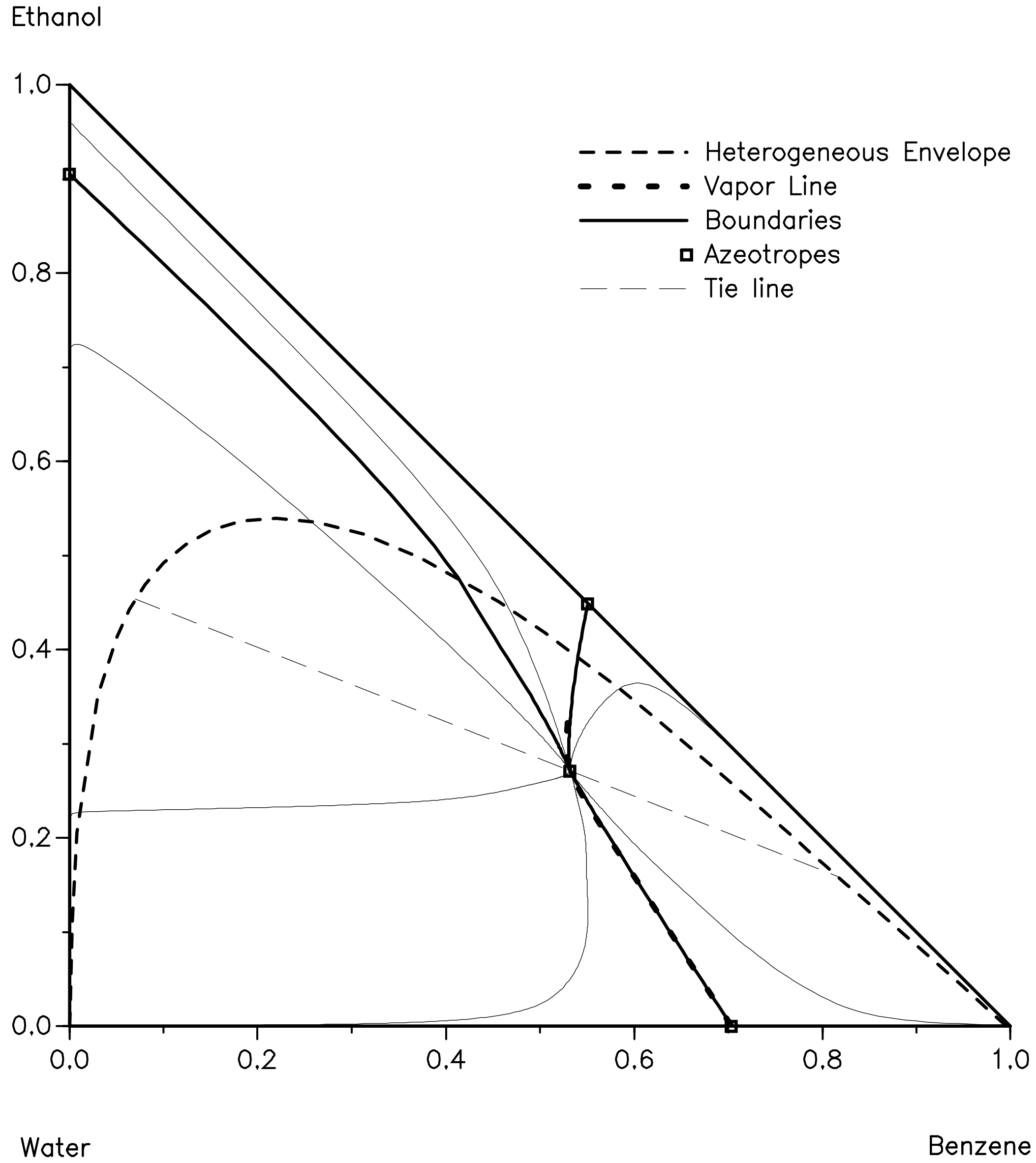

Figure 3a: The exact residue curve diagram and VLLE of the mixture ethanol – water – benzene.

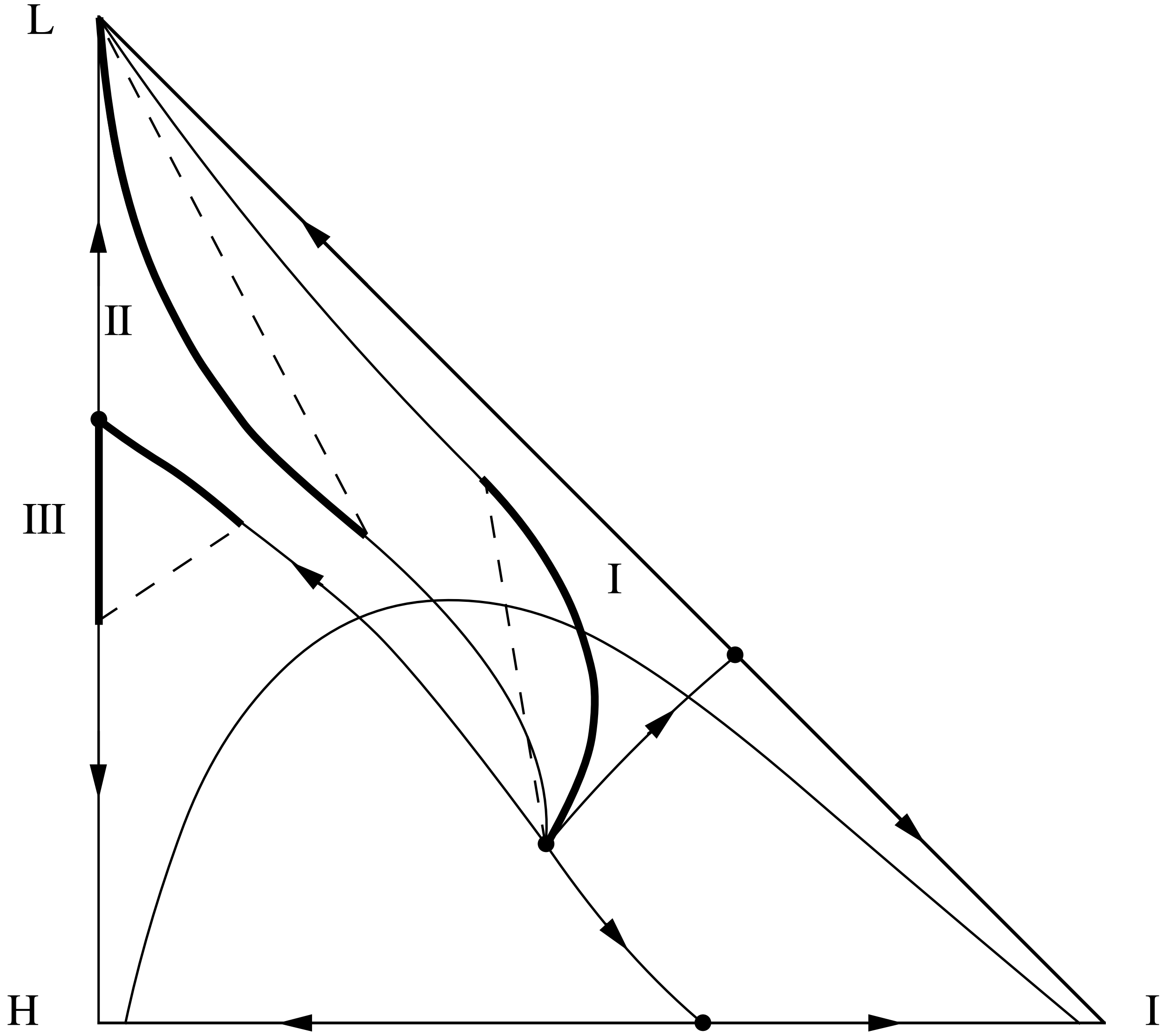

Figure 4: The three acceptable types of profiles in the ∞/∞ case

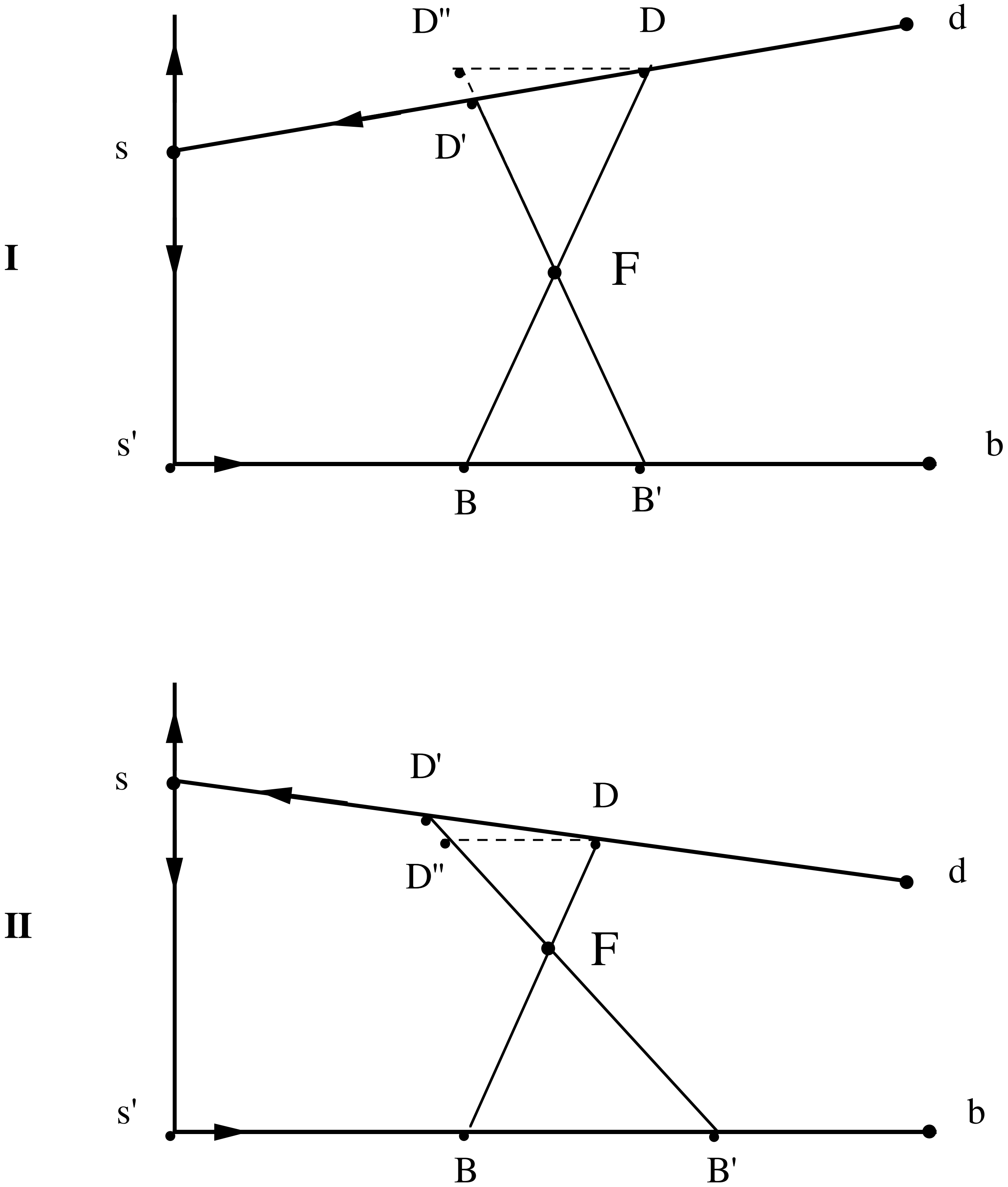

Figure 5a: The geometrical multiplicity condition is
I. not satisfied (*D* increases along the continuation path)
II. satisfied (*D* decreases along the continuation path).

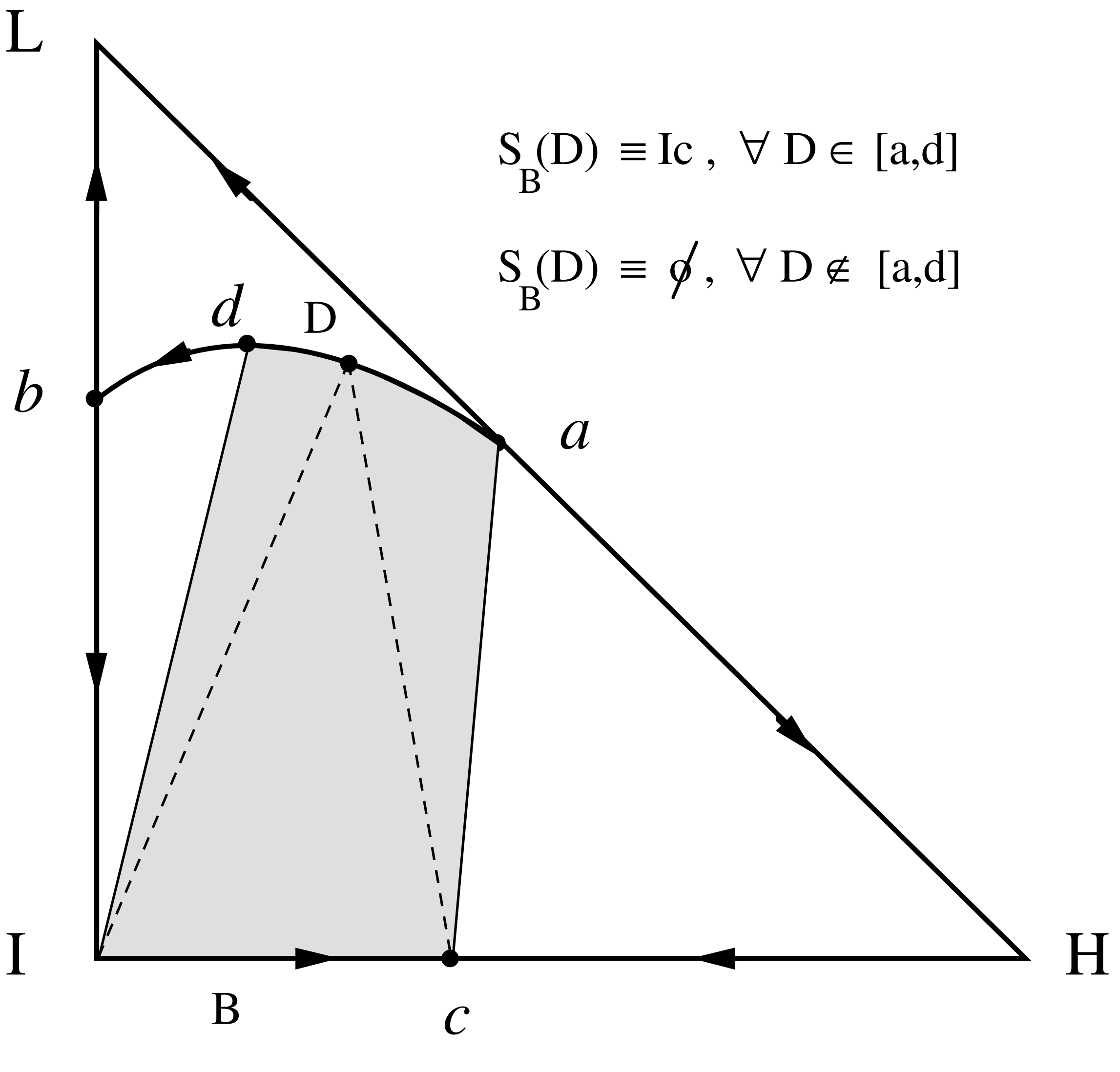

Figure 5b: For any D on the boundary segment *ad* the appropriate feed region is the triangle DI *c*. For this mixture, the region of feed compositions that lead to multiplicities is the union of all these triangles, i.e. the shaded area *ad* I*c*.

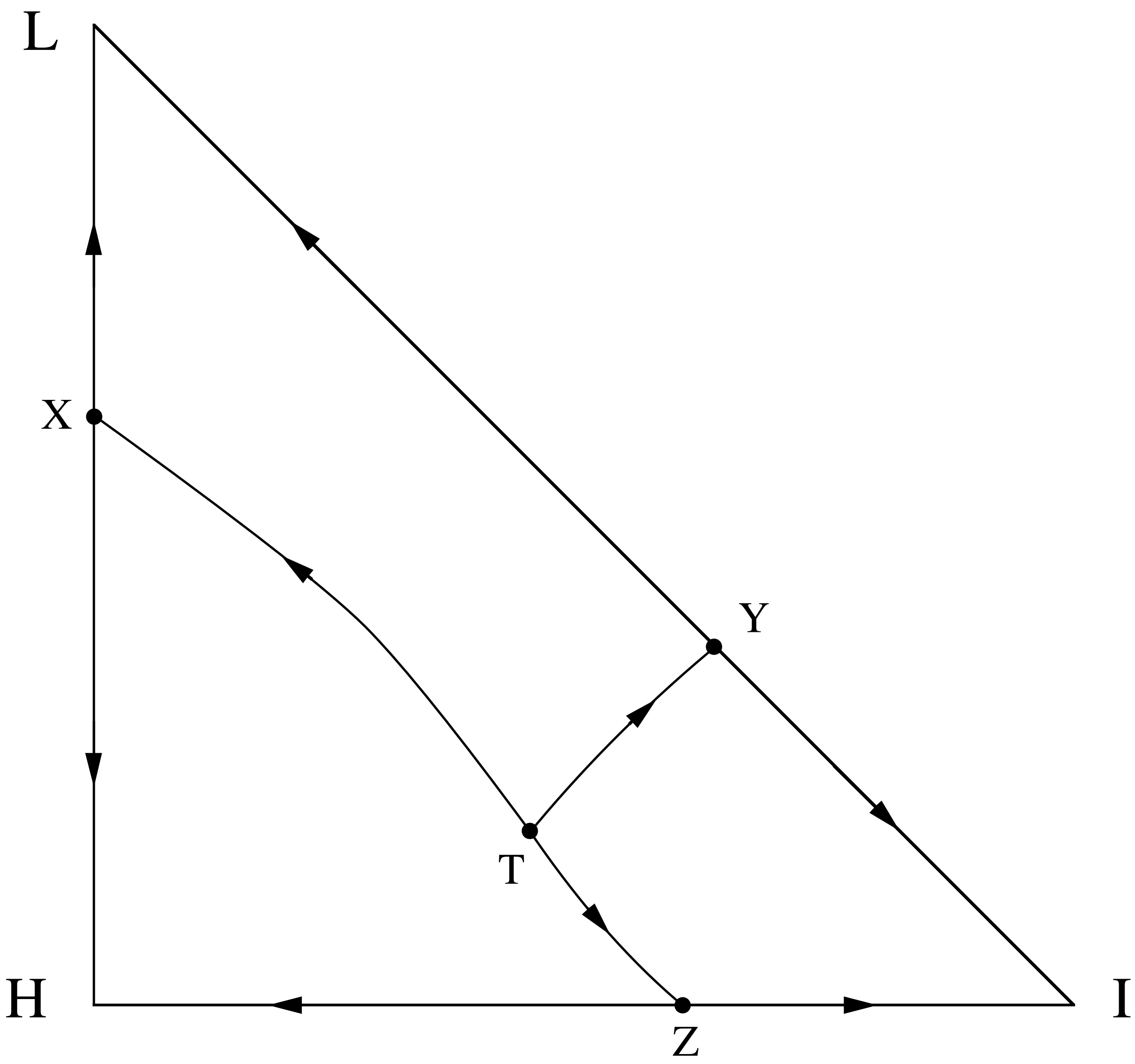

Figure 6a: Packed columns without decanter:
No multiplicities

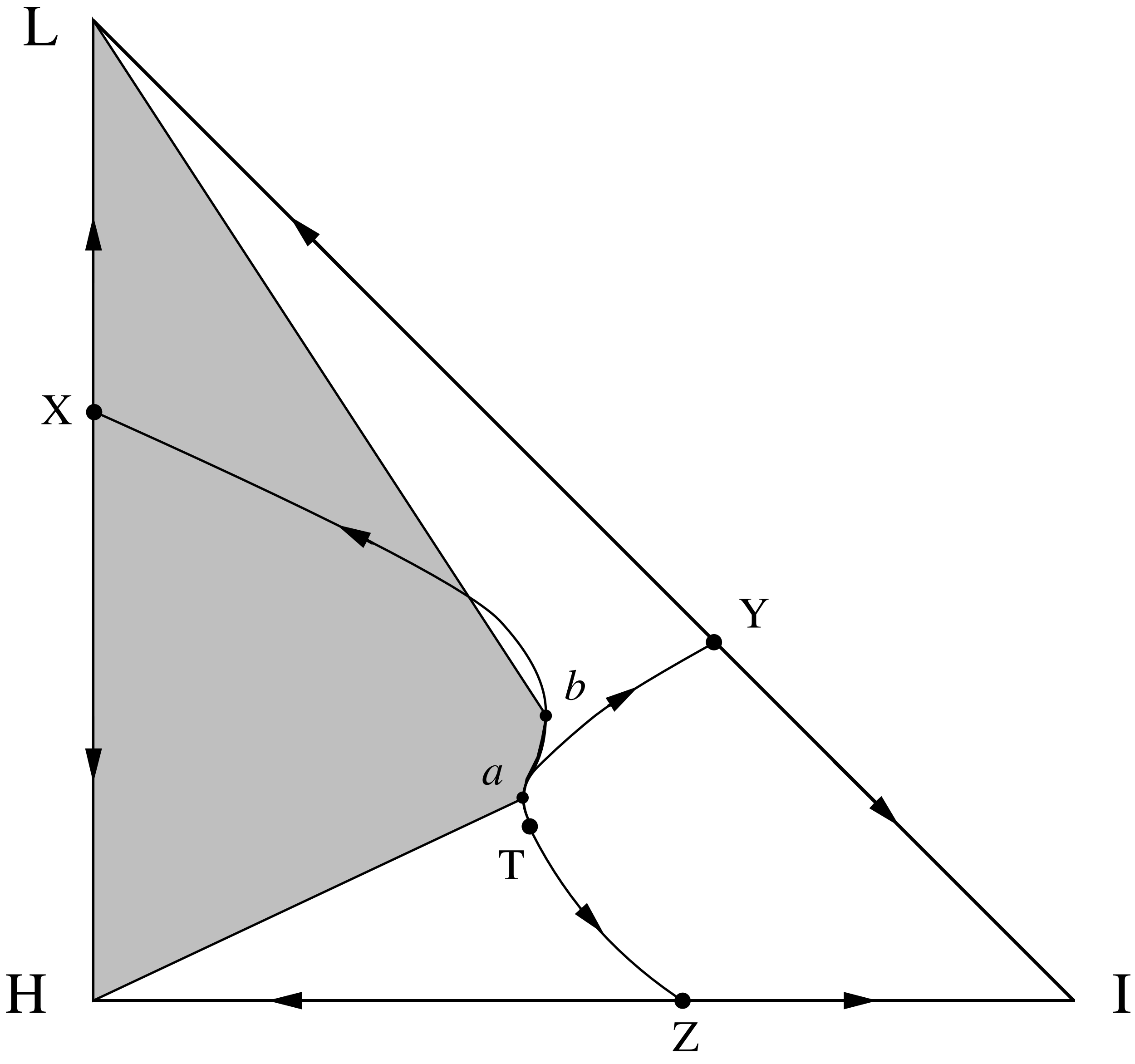

Figure 6b: Tray columns without decanter:
multiplicities for feeds in shaded region.

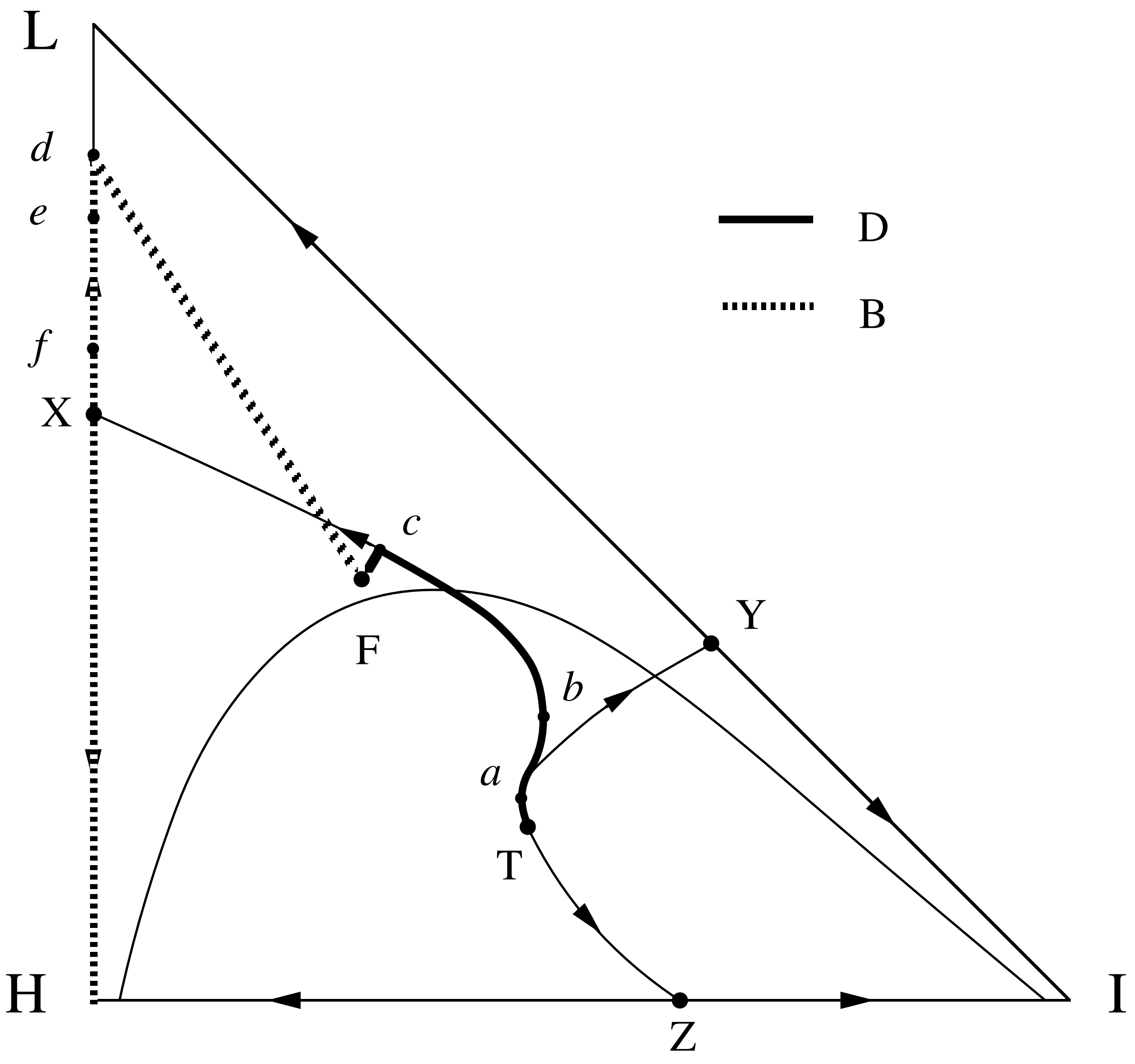

Figure 7: Tray columns without decanter:
the continuation paths for D and B

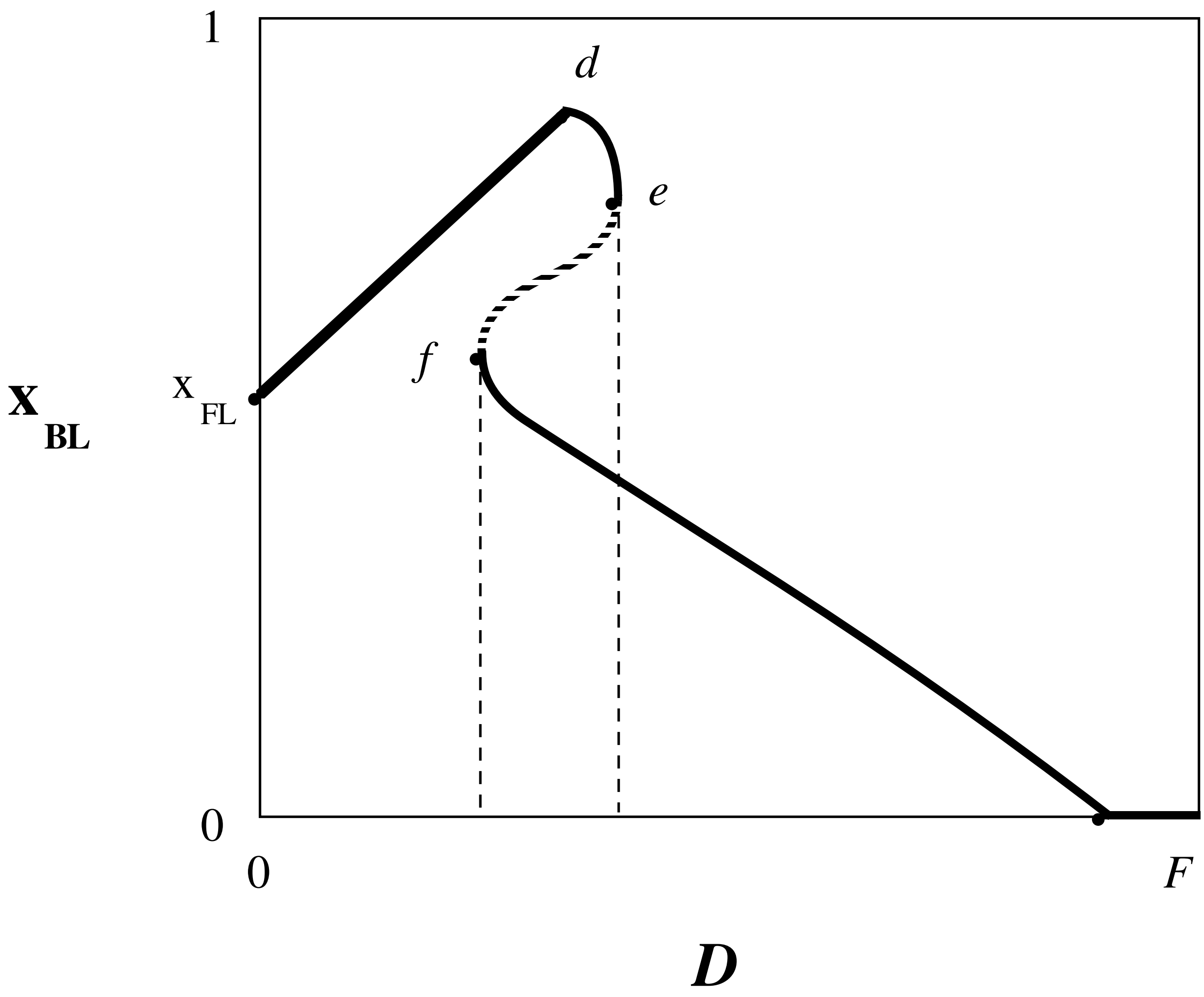

Figure 8: Bifurcation diagram of the mole fraction of L in the bottoms vs. the distillate flow for tray columns without decanter

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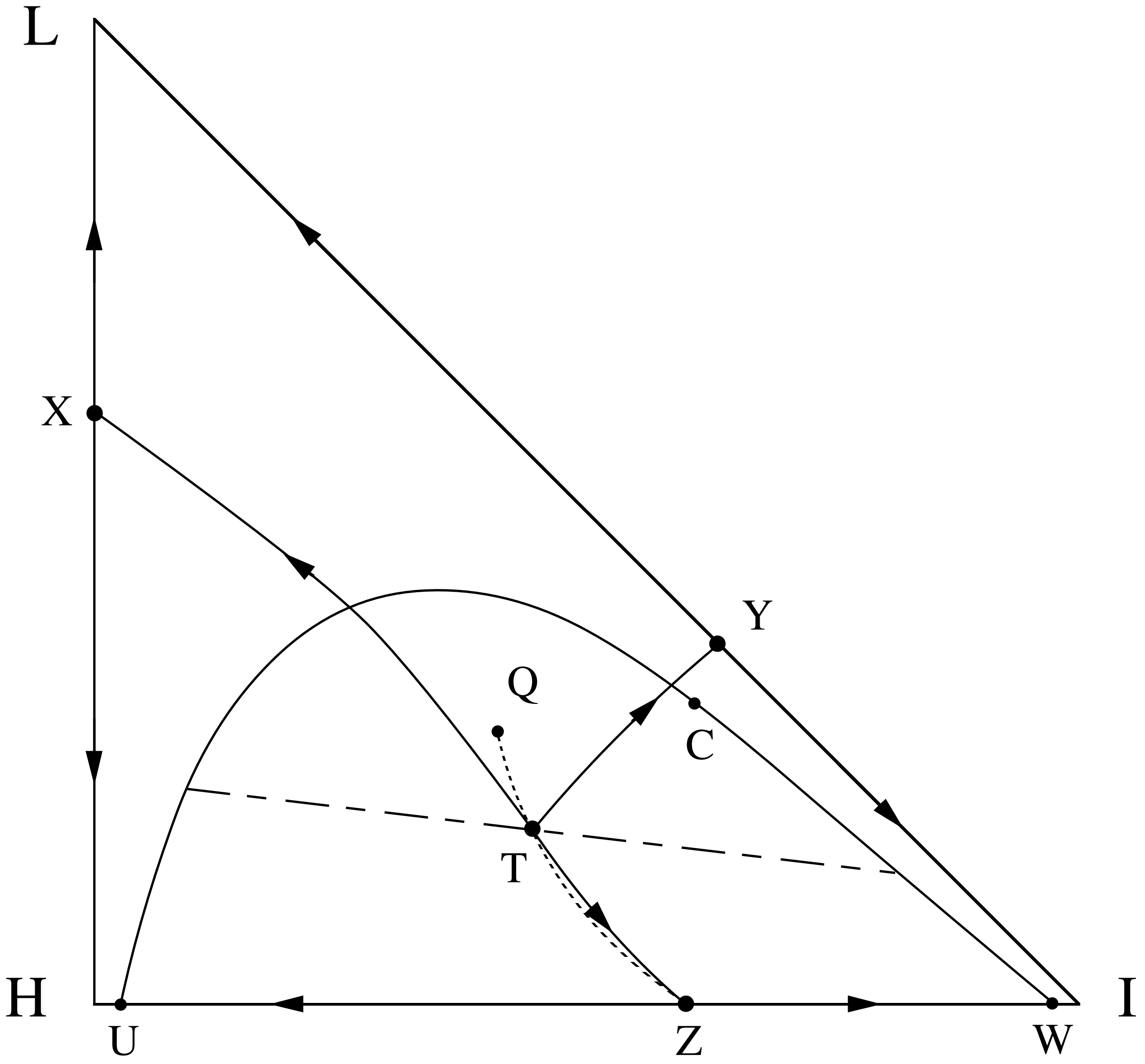

Figure 9: The residue curve boundaries and the vapor line can be used for the qualitative predictions of multiplicities in tray columns without decanter.
For the mixture shown, the different vapor line suggests that no multiplicities exist for tray columns without decanter.

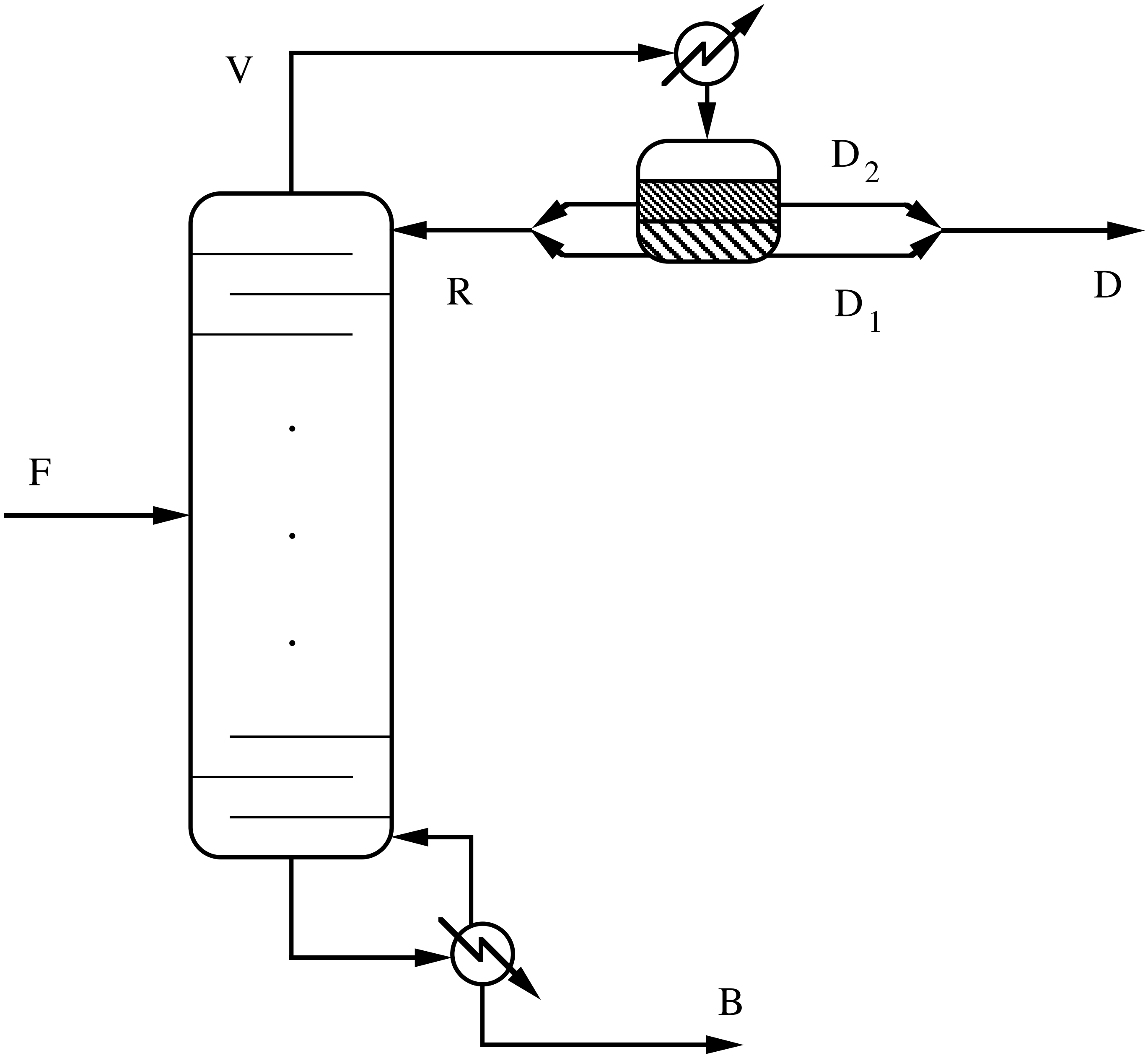

Figure 10: Column with decanter

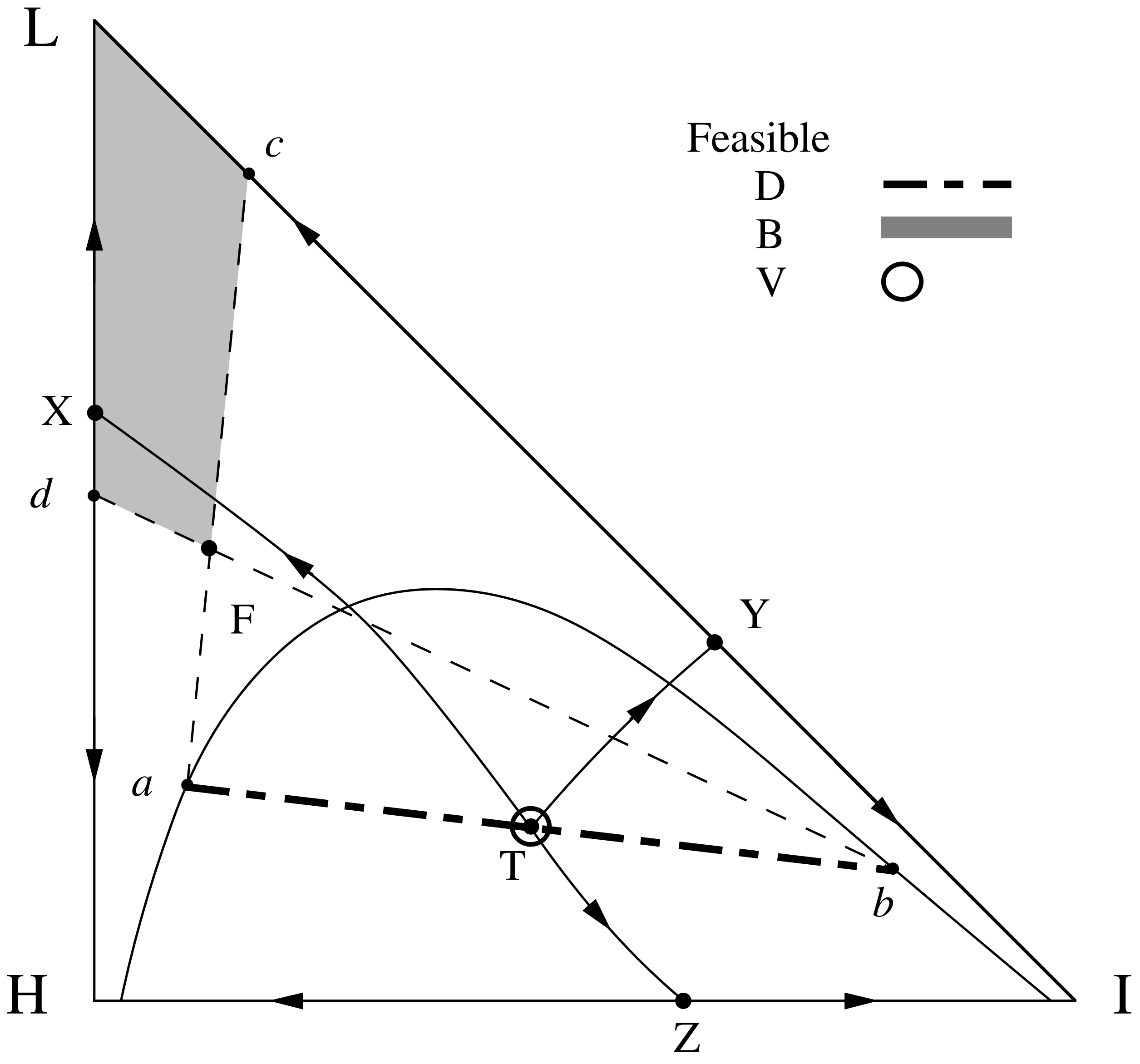

Figure 11a: The feasible overhead vapor V, distillate D and bottom product B regions for a packed column with decanter and given feed F in the ∞/∞ case for:

a. type I profiles.

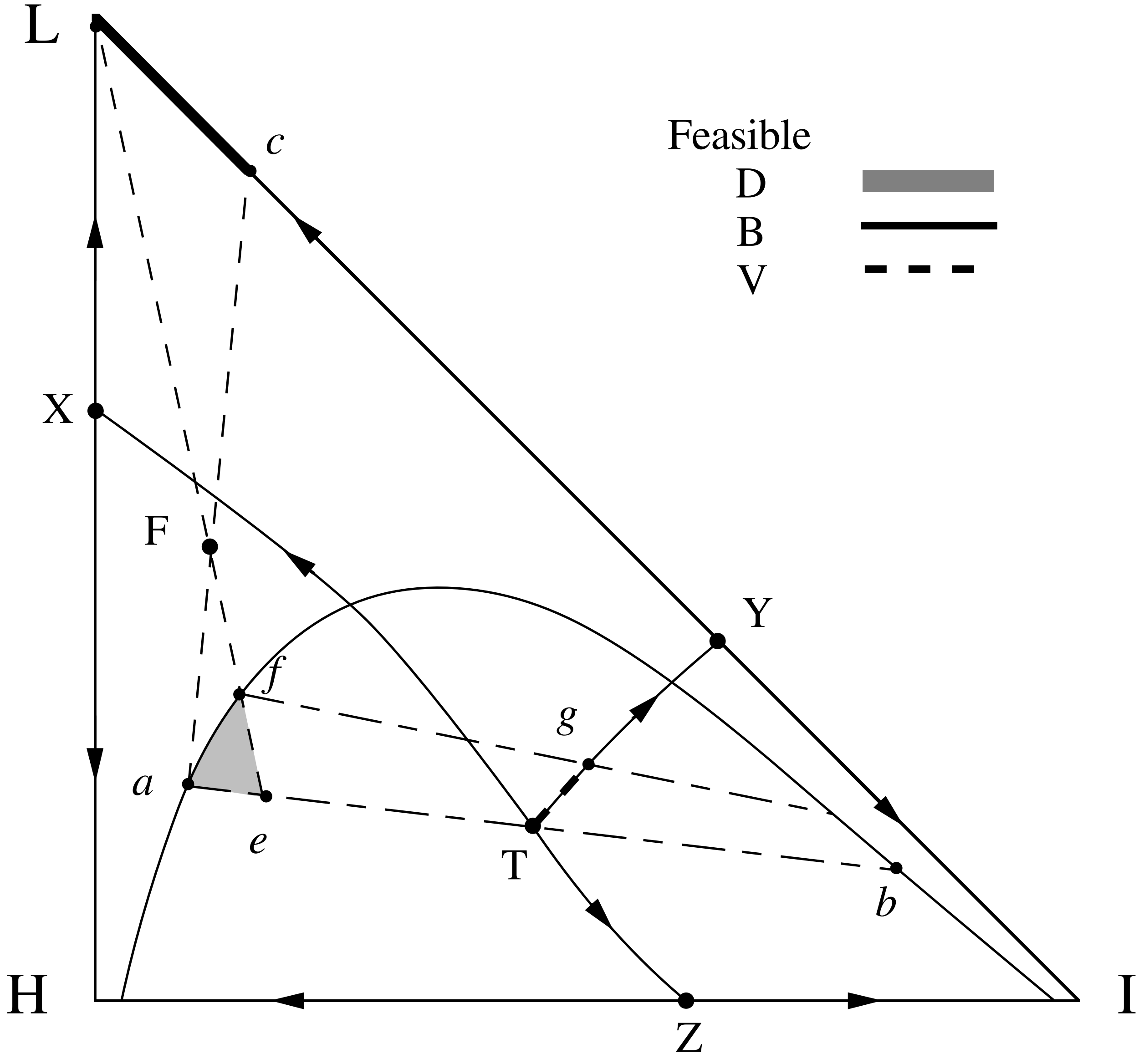

Figure 11b: The feasible overhead vapor V, distillate D and bottom product B regions for a packed column with decanter and given feed F in the ∞/∞ case for:

b. type III profiles with V on TY.

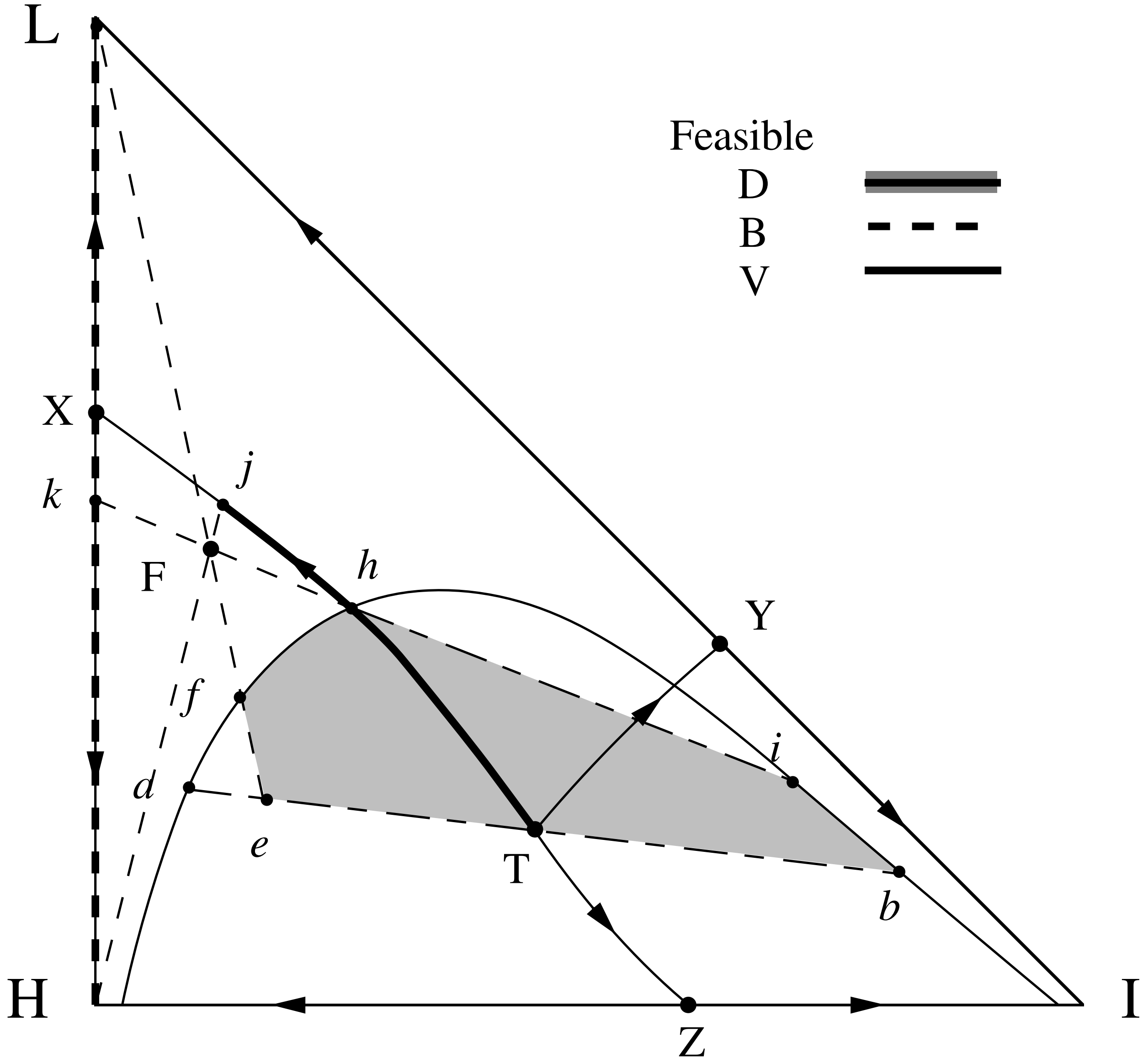

Figure 11c: The feasible overhead vapor V, distillate D and bottom product B regions for a packed column with decanter and given feed F in the ∞/∞ case for:
c. type III profiles with V on TX.

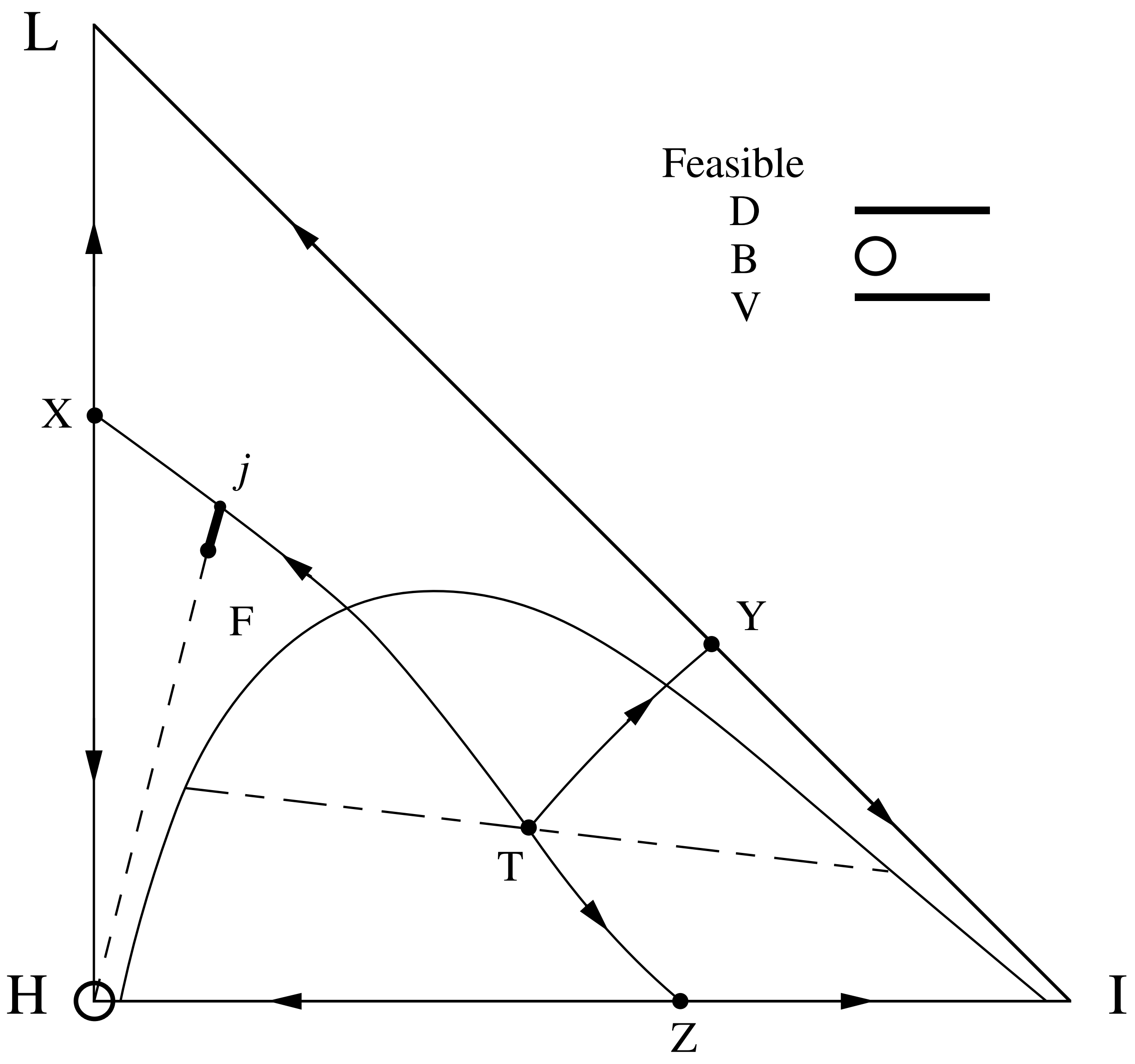

Figure 11d: The feasible overhead vapor V, distillate D and bottom product B regions for a packed column with decanter and given feed F in the ∞/∞ case for:

d. type II profiles.

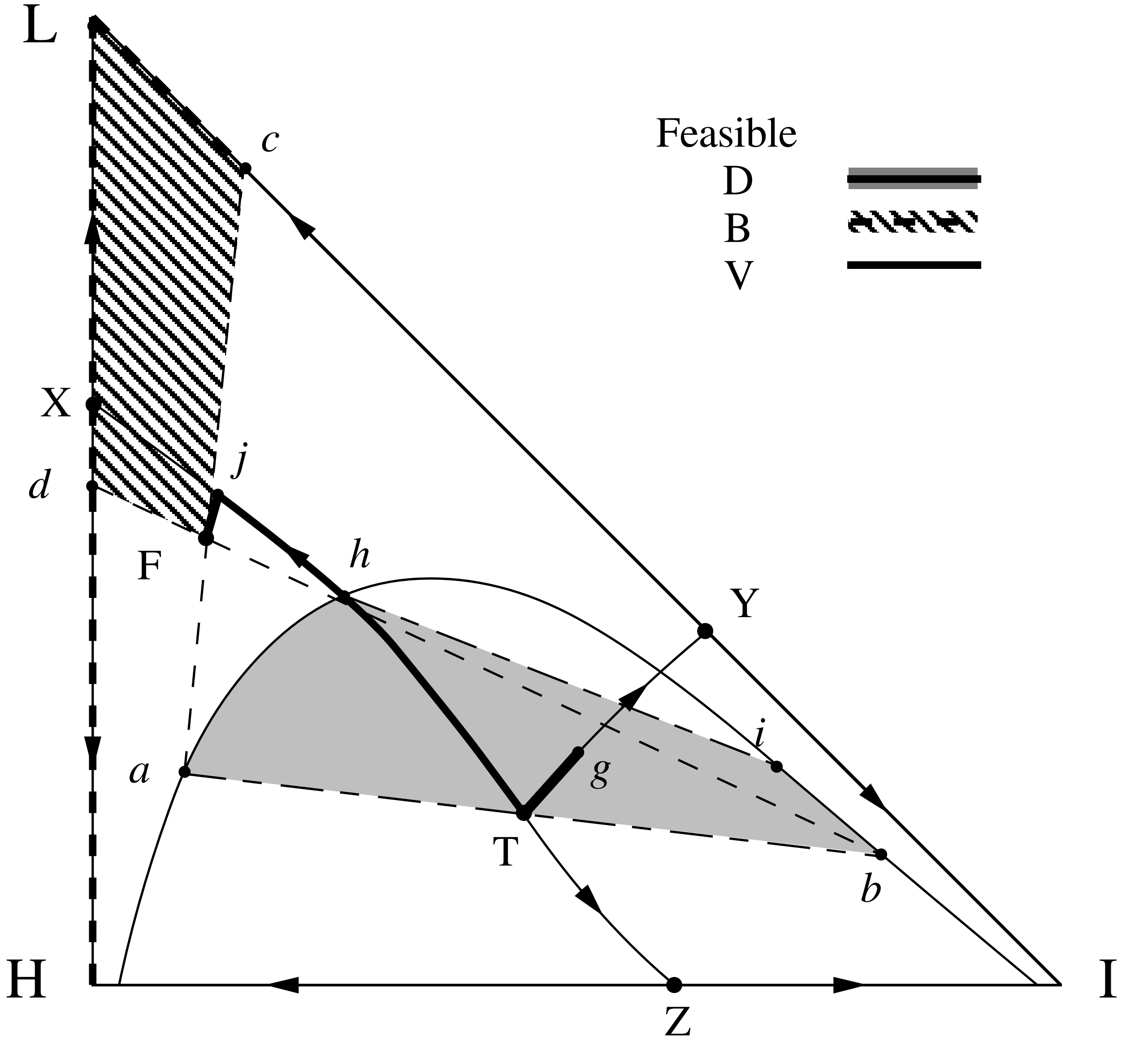

Figure 12: The feasible overhead vapor V, distillate D and bottom product B regions for a packed column with decanter and given feed F in the ∞/∞ case for all acceptable profiles.

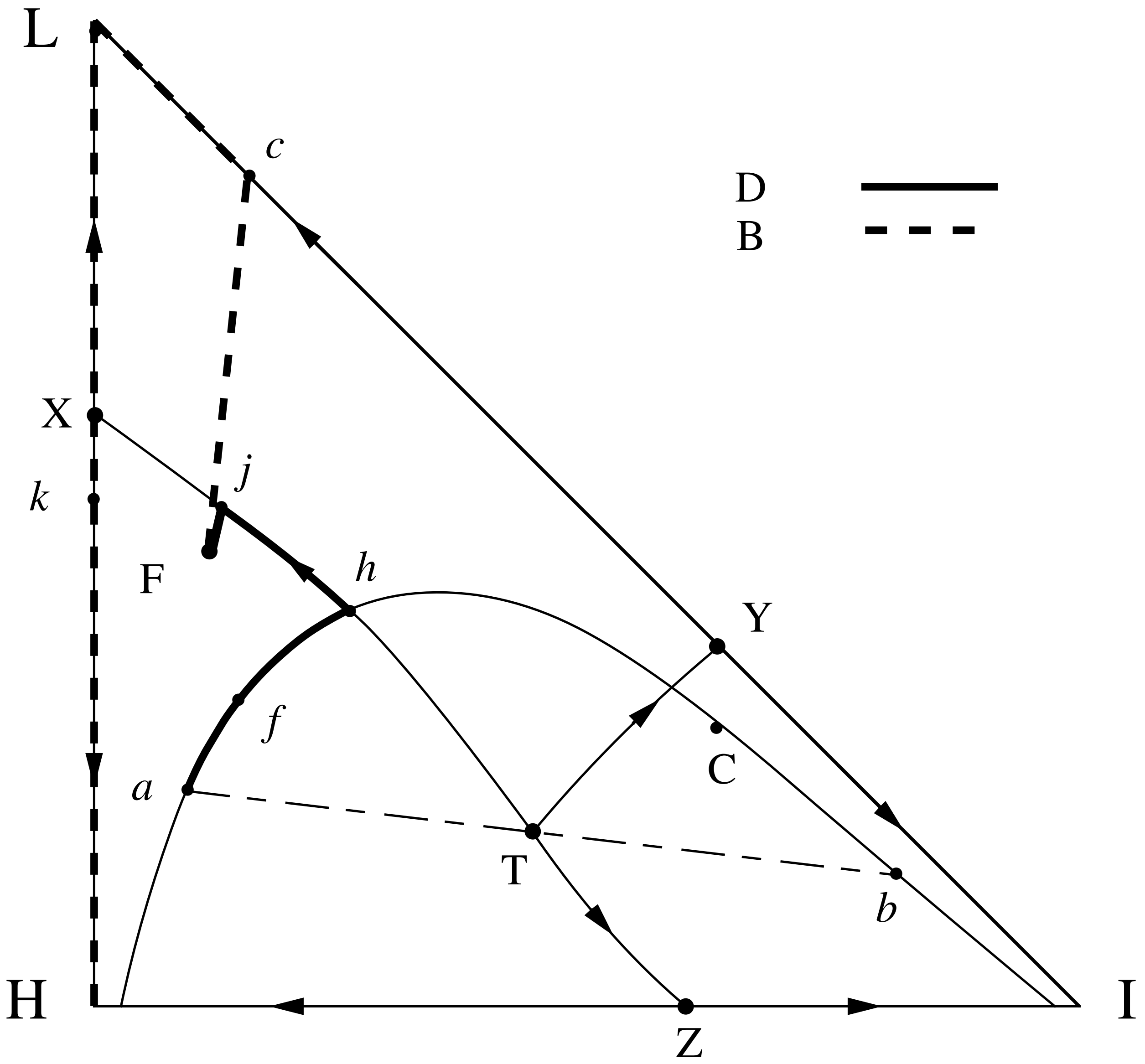

Figure 13: The distillate and bottoms continuation paths for packed columns with decanter and D_2 =0.

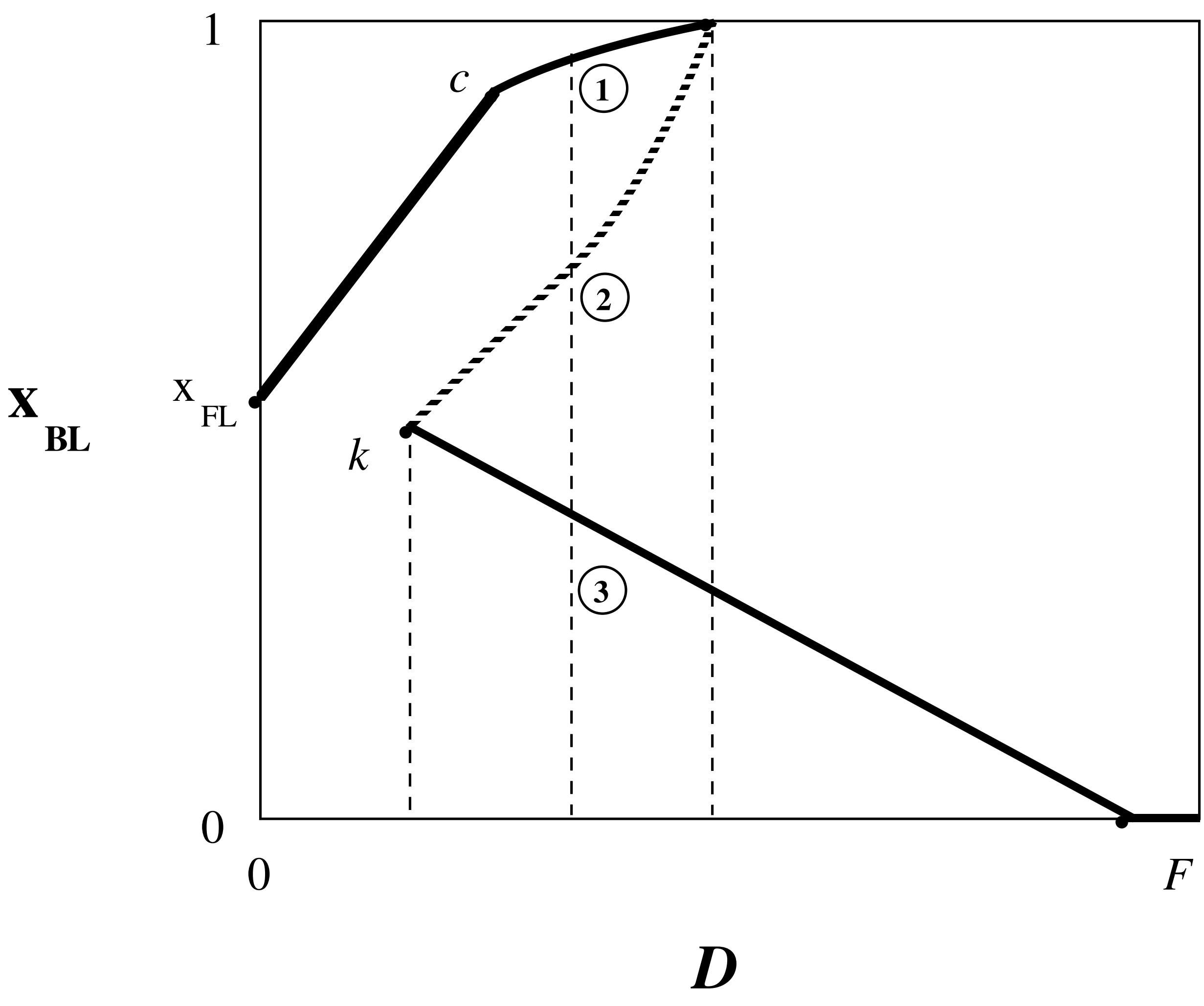

Figure 14: Bifurcation diagram of the mole fraction of L in the bottoms vs. the distillate flow for packed columns with decanter and $D_2 = 0$

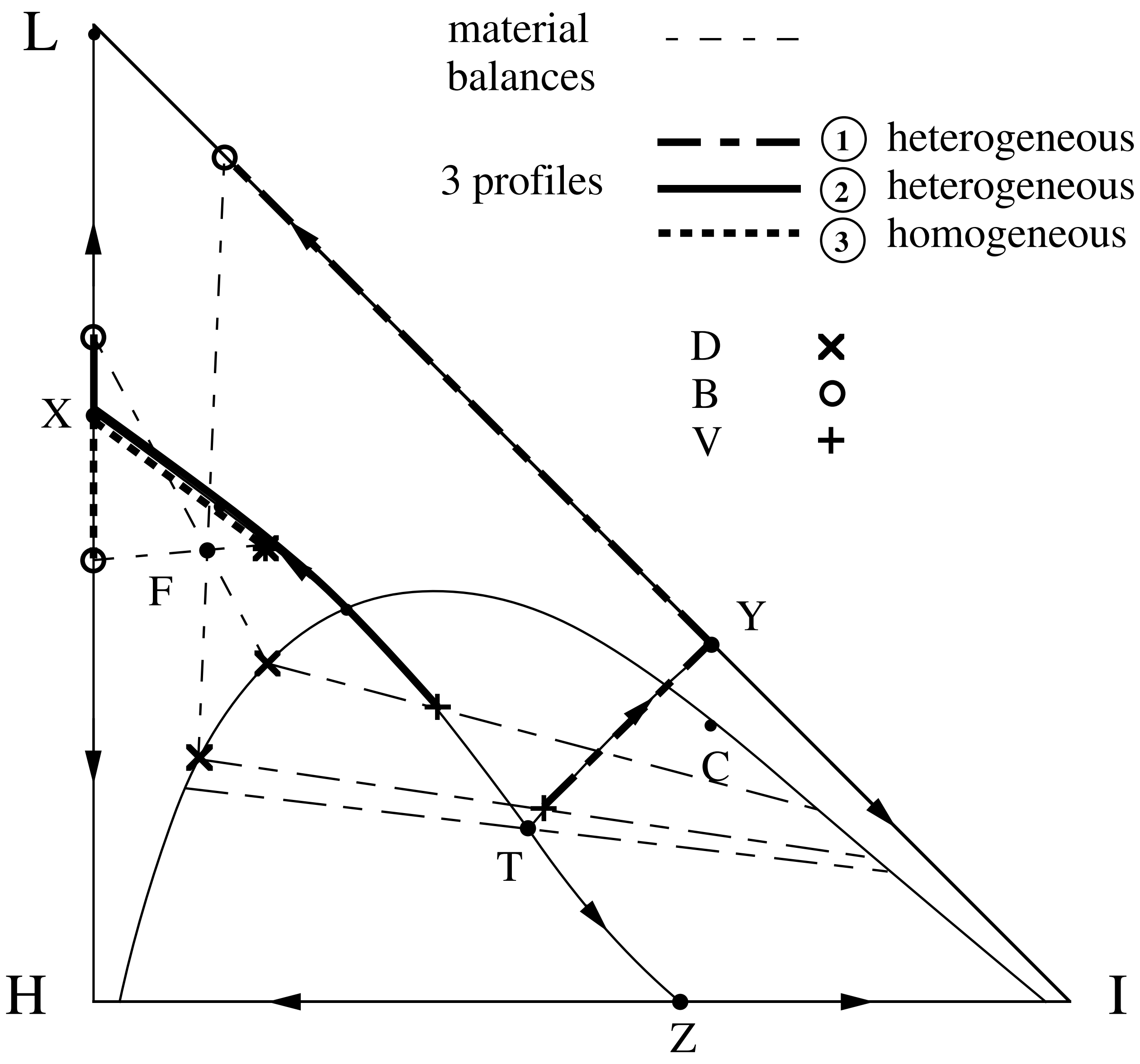

Figure 15: The three steady state profiles with the same distillate flowrate for packed columns with decanter and D_2 =0.

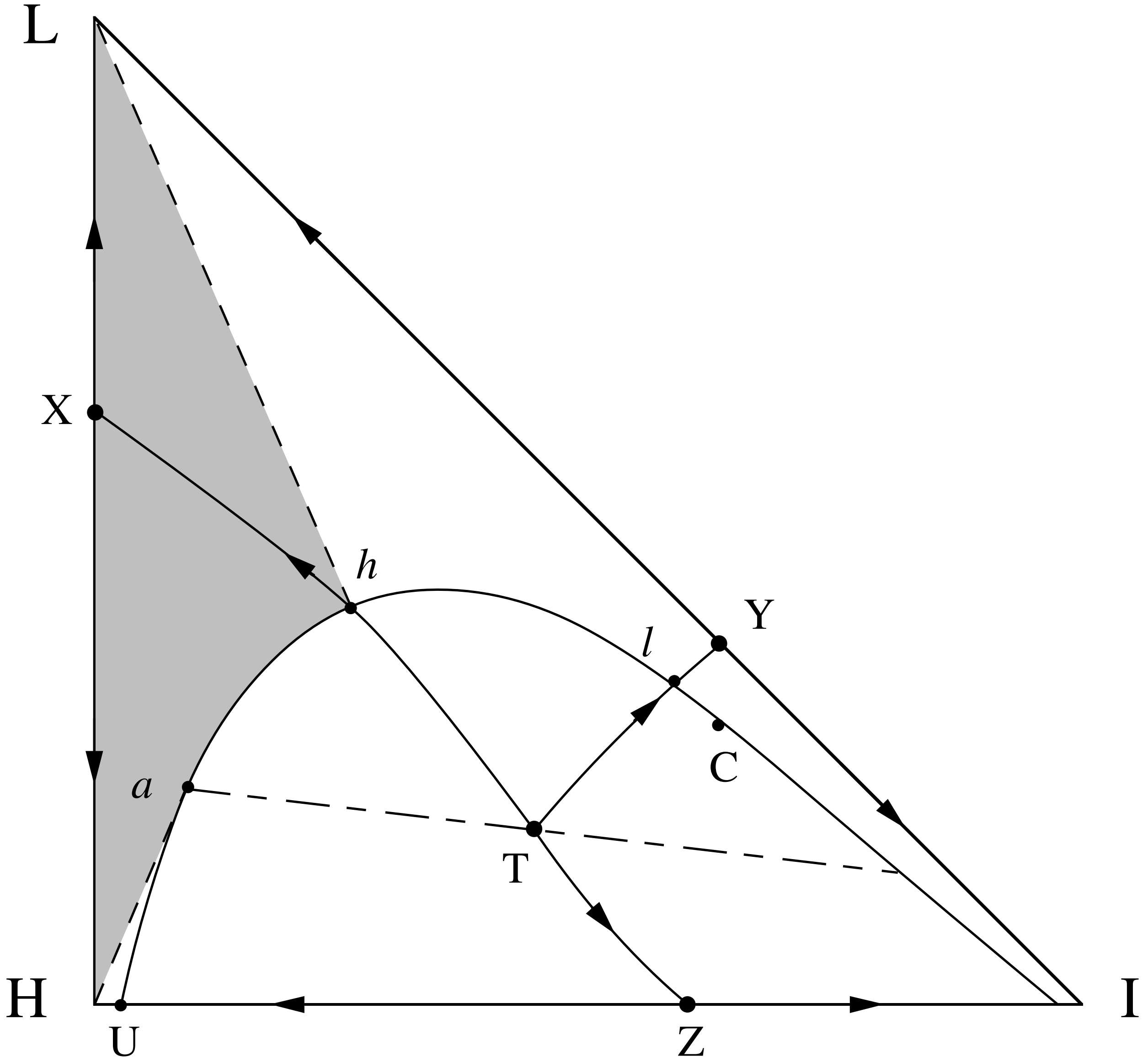

Figure 16: The information required to apply the geometrical condition and the feed composition region (shaded) that leads to multiplicities for packed columns with decanter and D_2=0.

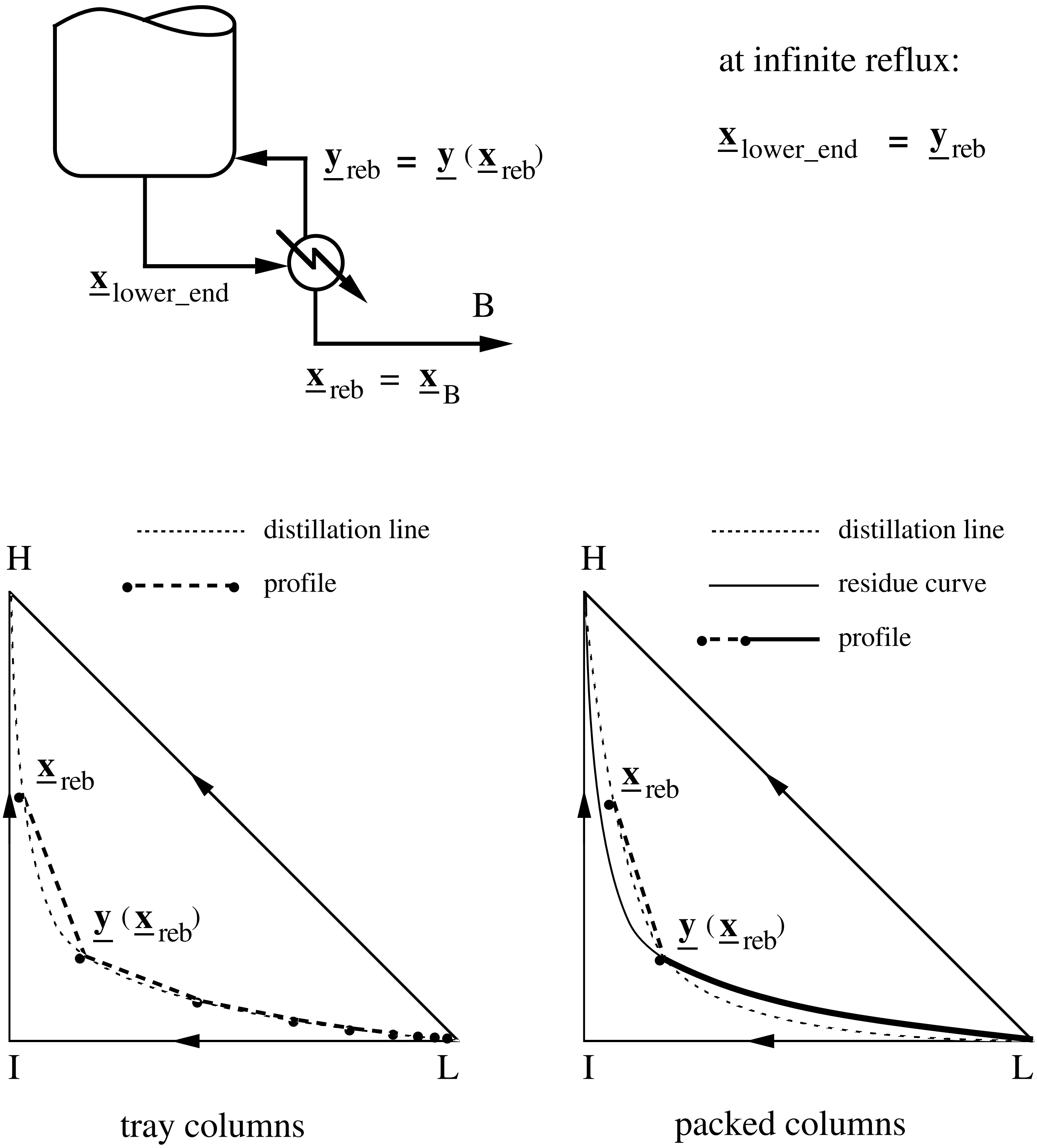

Figure 17: The effect of the use of a typical, partial reboiler on the bottom product composition for tray and packed columns

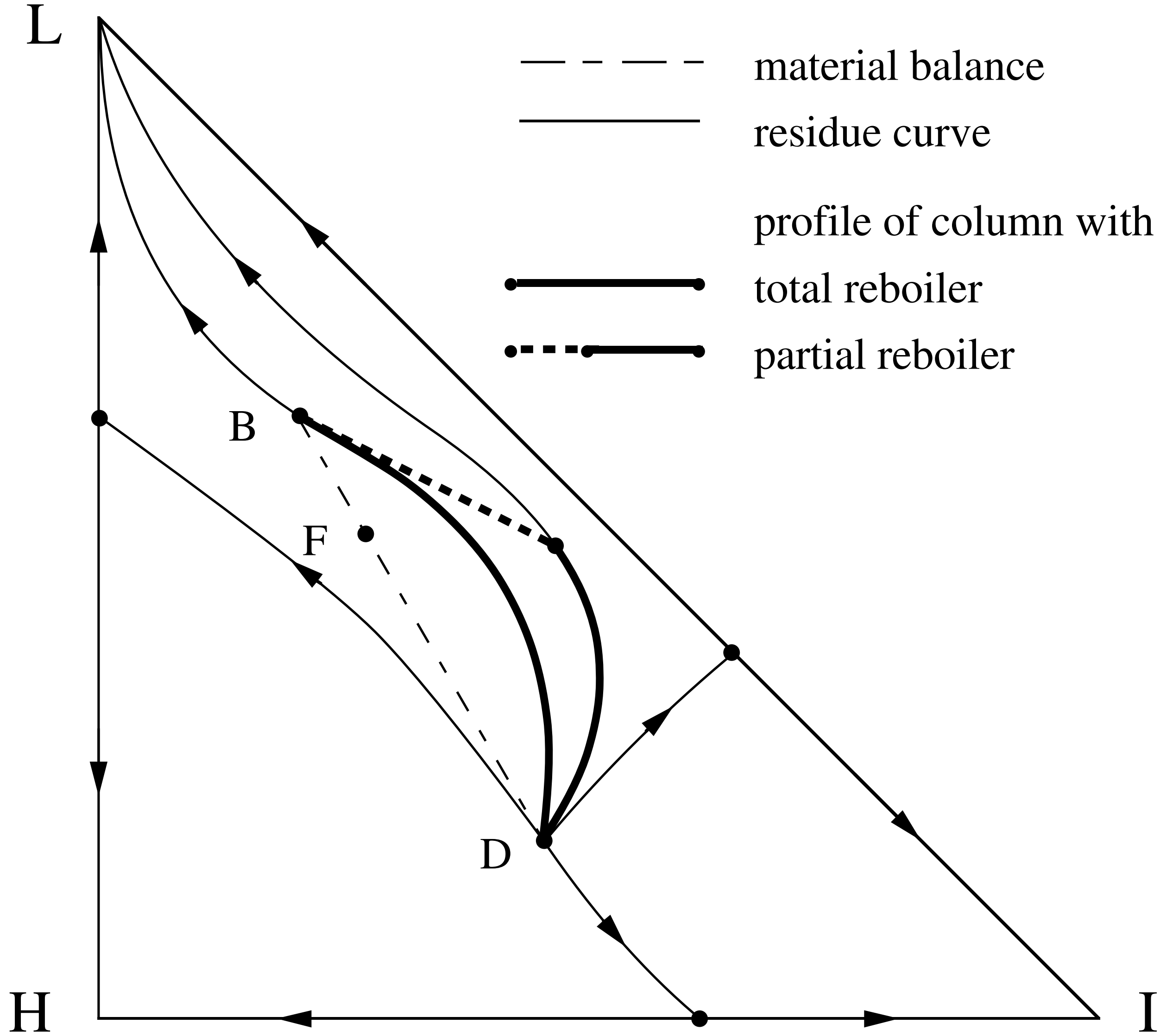

Figure 18a: The effect of the use of a typical, partial reboiler on type I profiles of packed columns.

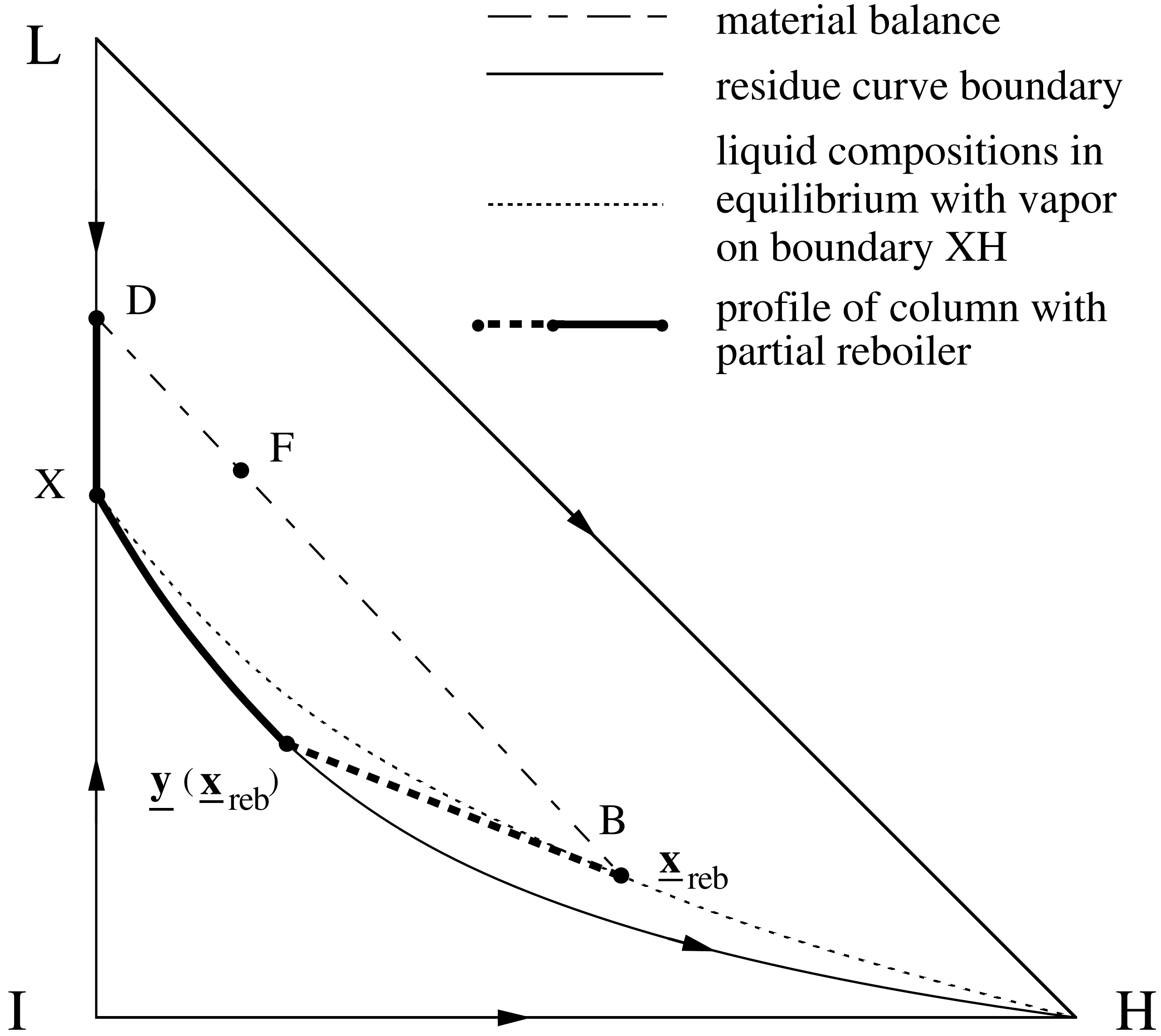

Figure 18b: The effect of the use of a typical, partial reboiler on the bottom product composition of type III profiles of packed columns.

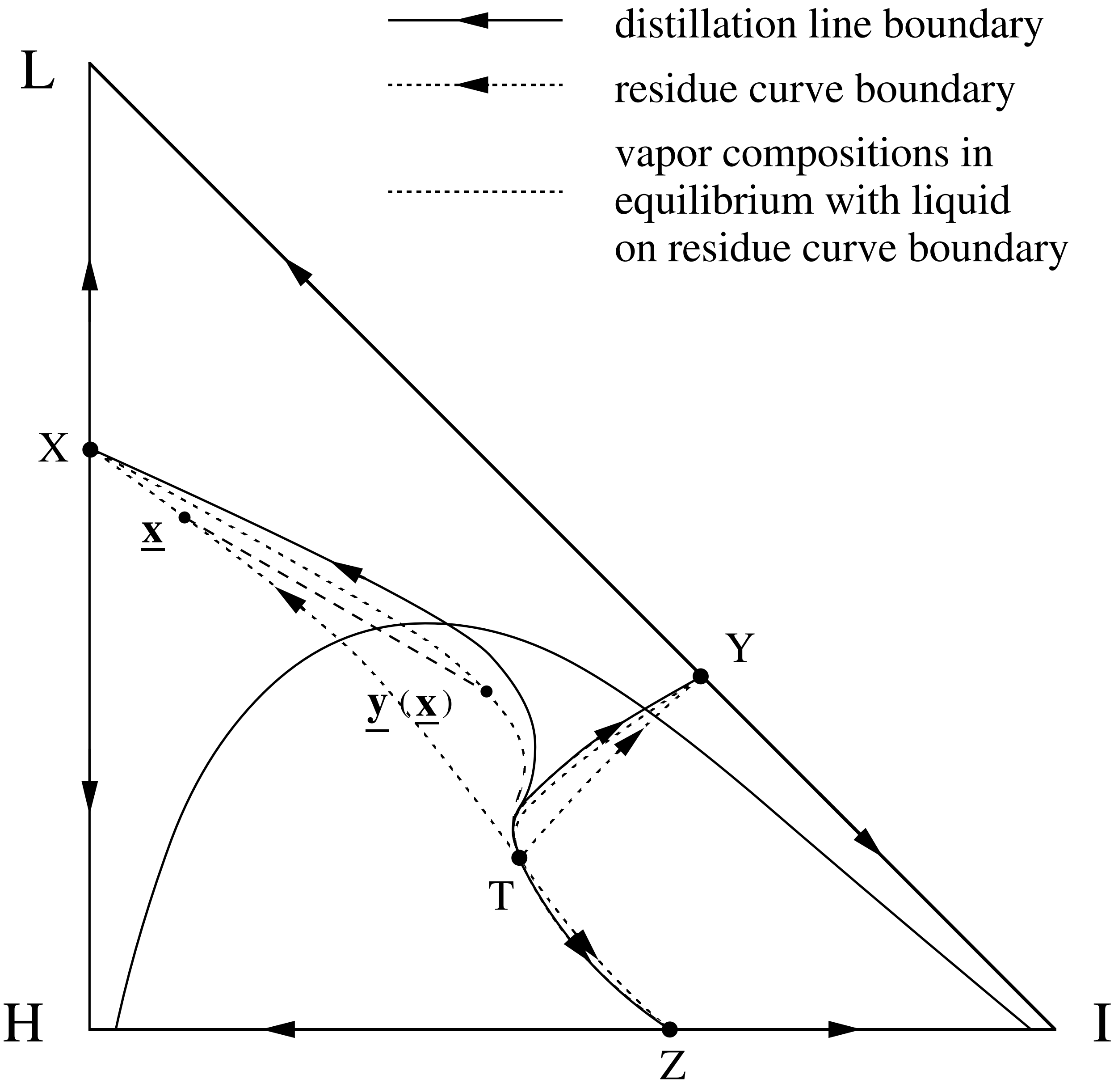

Figure 18c: The effect of the use of a partial condenser on the feasible distillate product composition of type III profiles of packed columns without decanter.

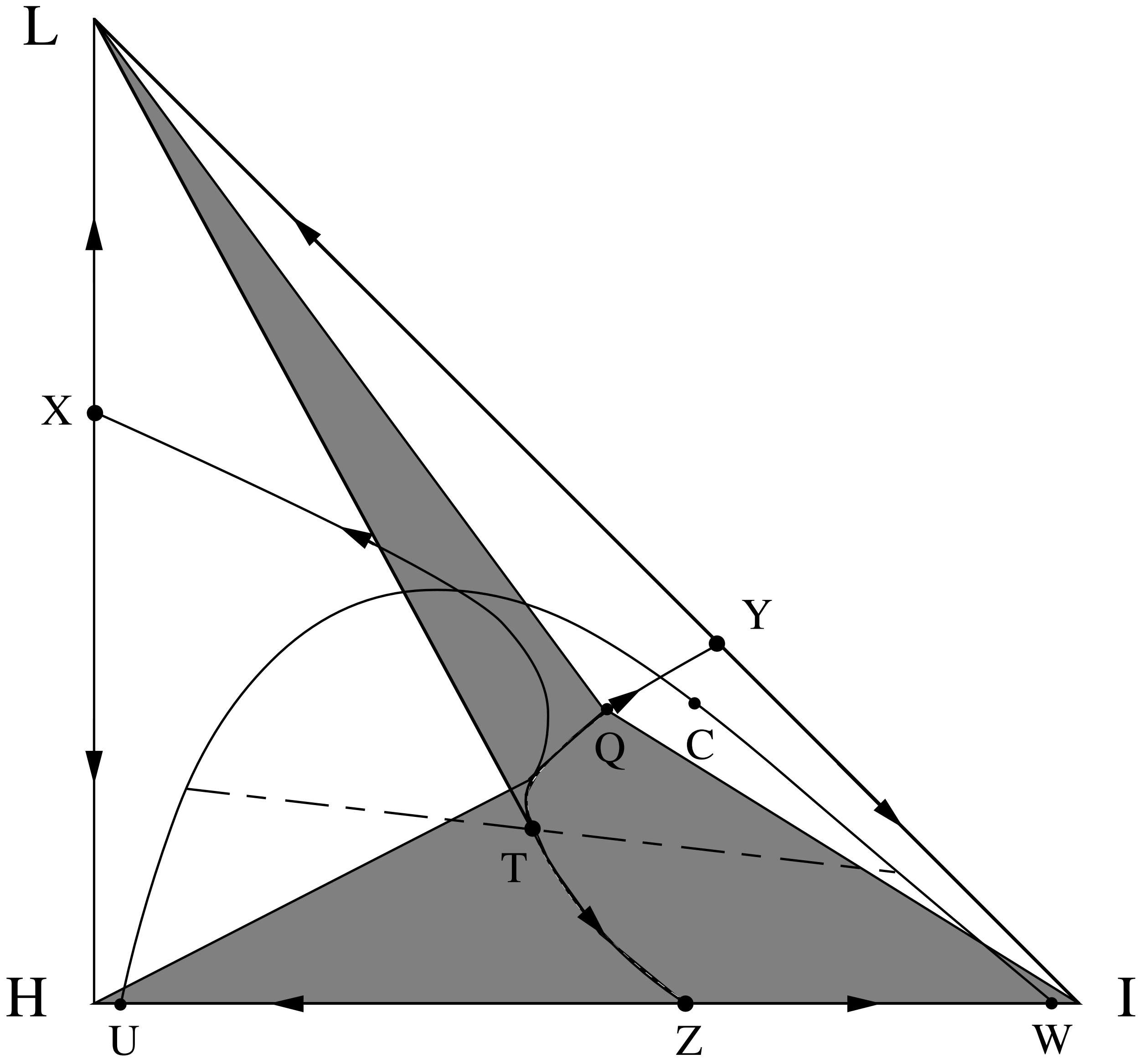

Figure 19: The region of feed compositions that lead to the degenerate type of multiplicities for tray columns without decanter.

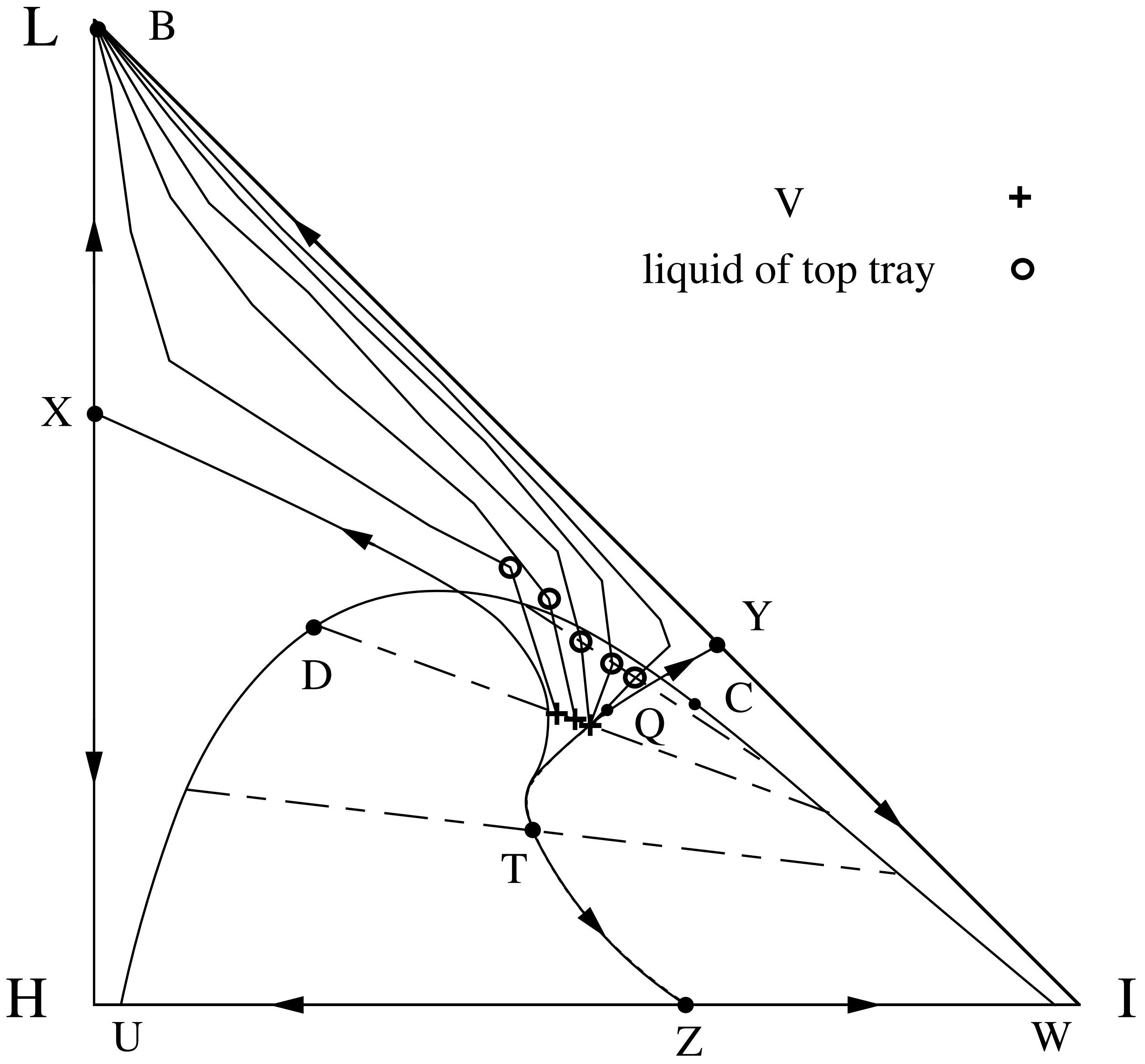

Figure 20: Five different column profiles with identical B and D (degenerate multiplicity) for a tray column with decanter and $D_2 = 0$.

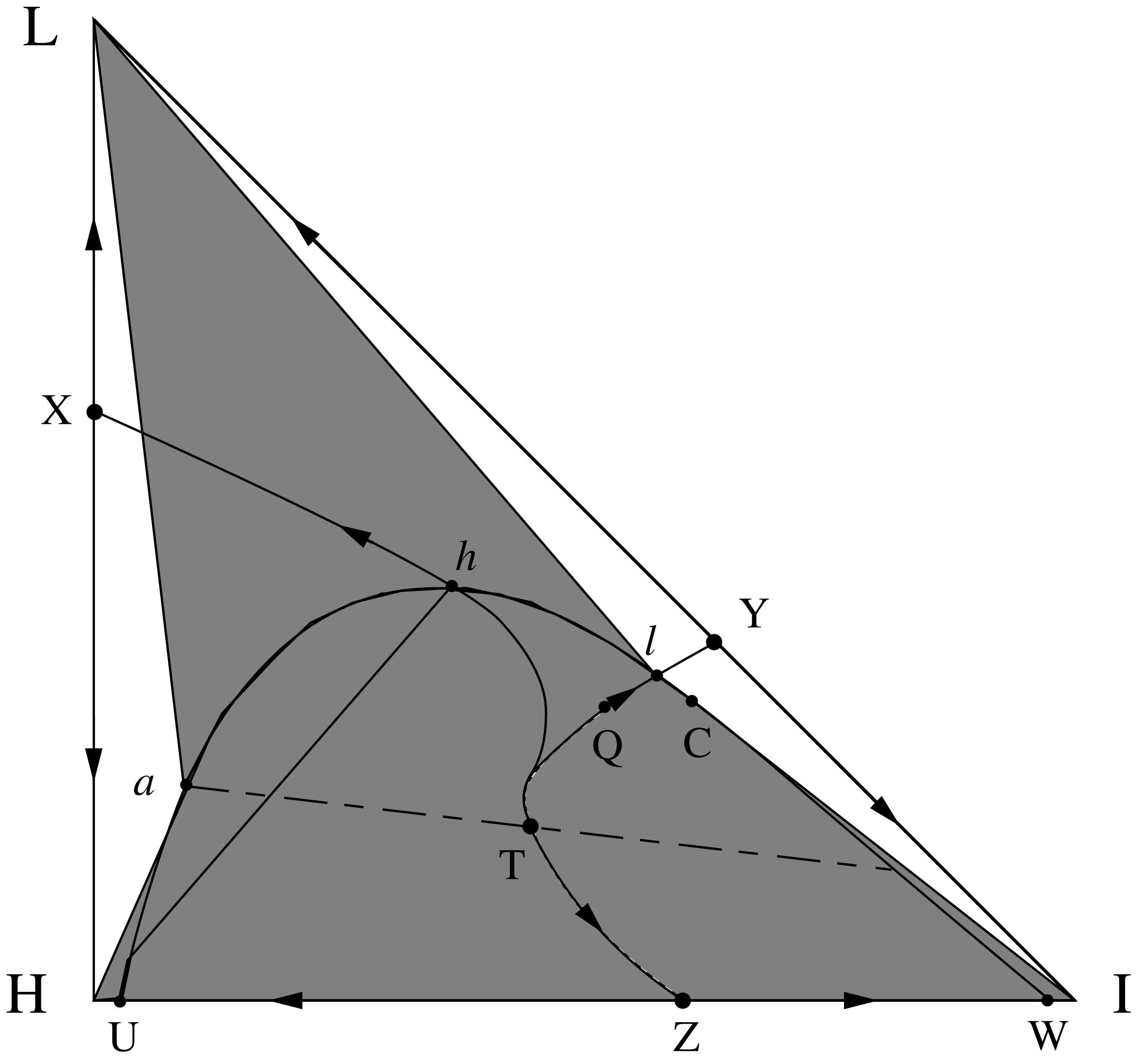

Figure 21: The region of feed compositions that lead to the degenerate type of multiplicities for tray columns with decanter and $D_2=0$.

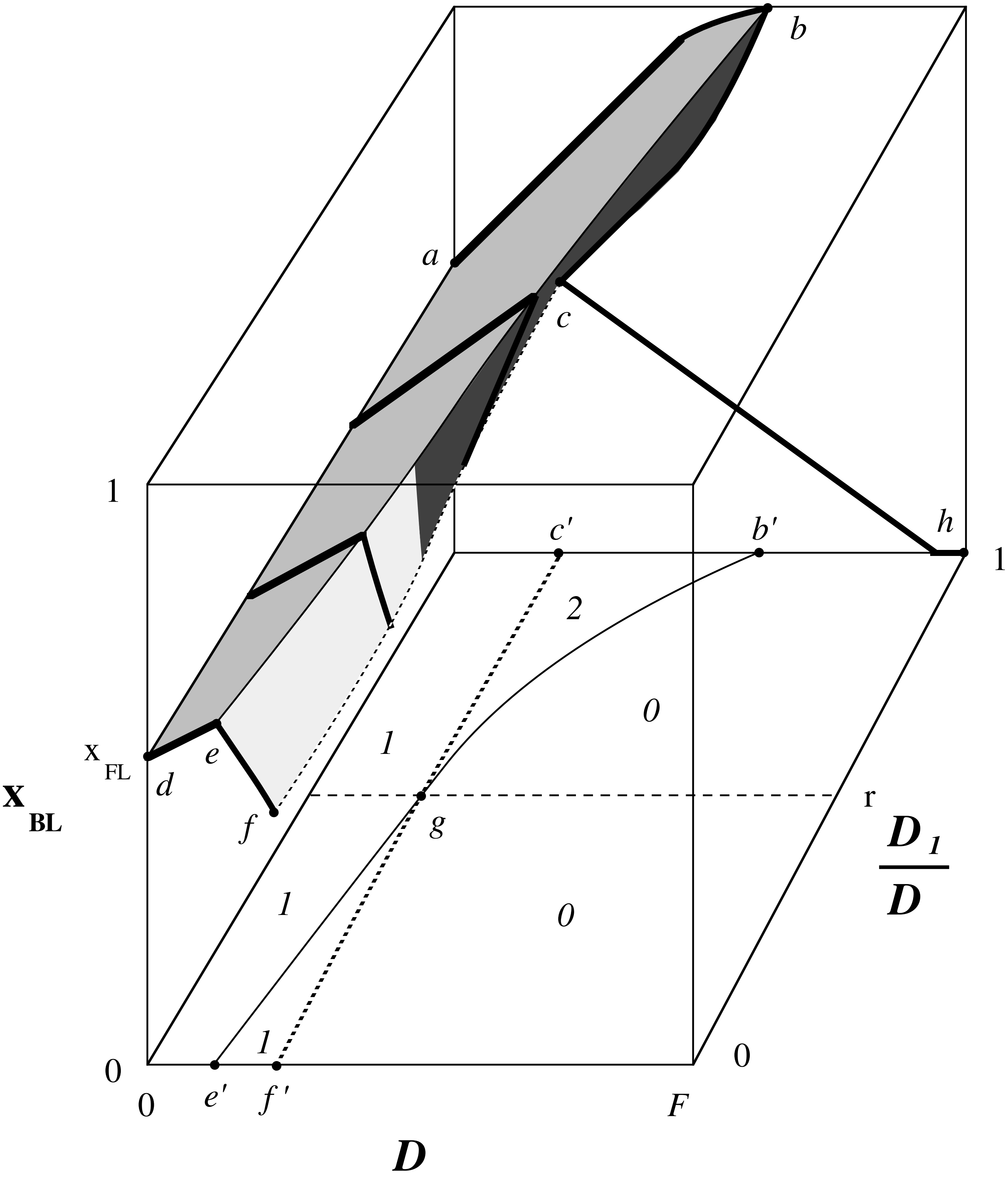

Figure 22: The mole fraction of L in the bottoms vs. the distillate flow and the ratio D_1/D for packed columns with decanter.

Numbers in italics: the number of heterogeneous steady states in the parameter space.

$D - D_1/D$

	$F_1 = 100.00$	$F_2 = 45.32$
Ethanol (L)	89.00	9.90
Benzene (I)	0.00	33.62
Water (H)	11.00	1.80

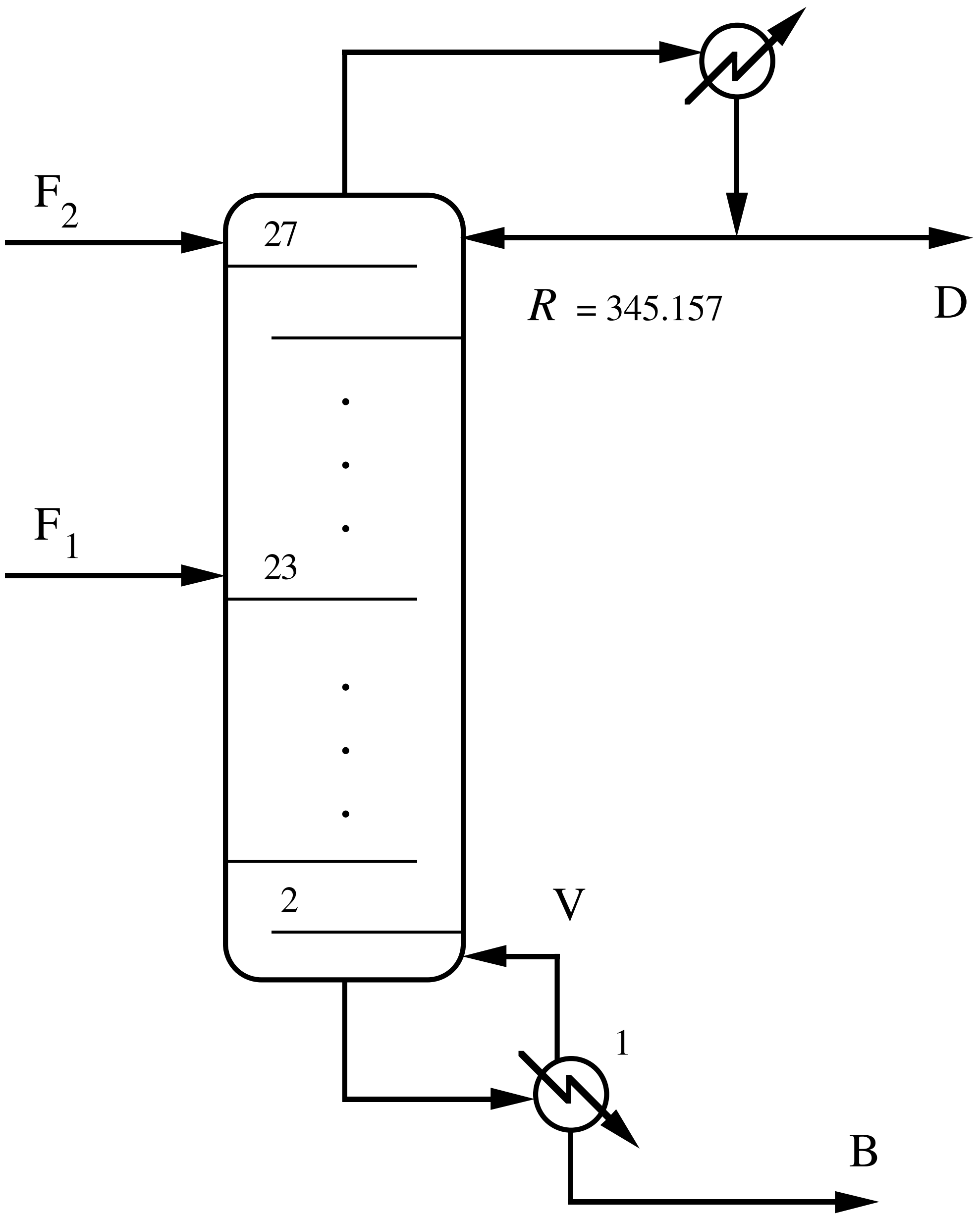

Figure 23: The column without decanter used in the numerical continuation calculations.

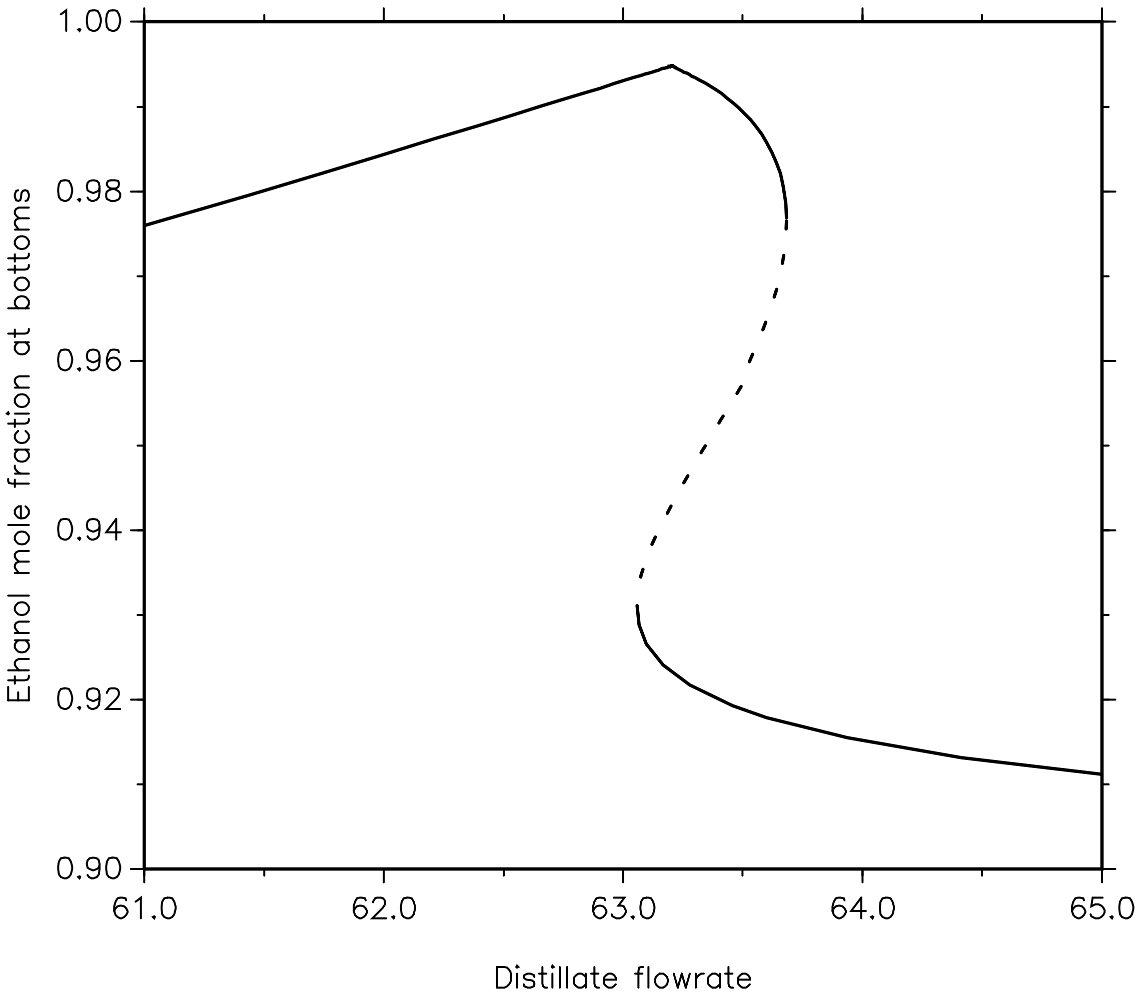

Figure 24: Bifurcation diagram with the distillate flow as the bifurcation parameter for the column without decanter depicted in Figure 23.

	$F_1 = 100.00$	$F_2 = 1.962$
Ethanol (L)	89.00	0.00
Benzene (I)	0.00	1.962
Water (H)	11.00	0.00

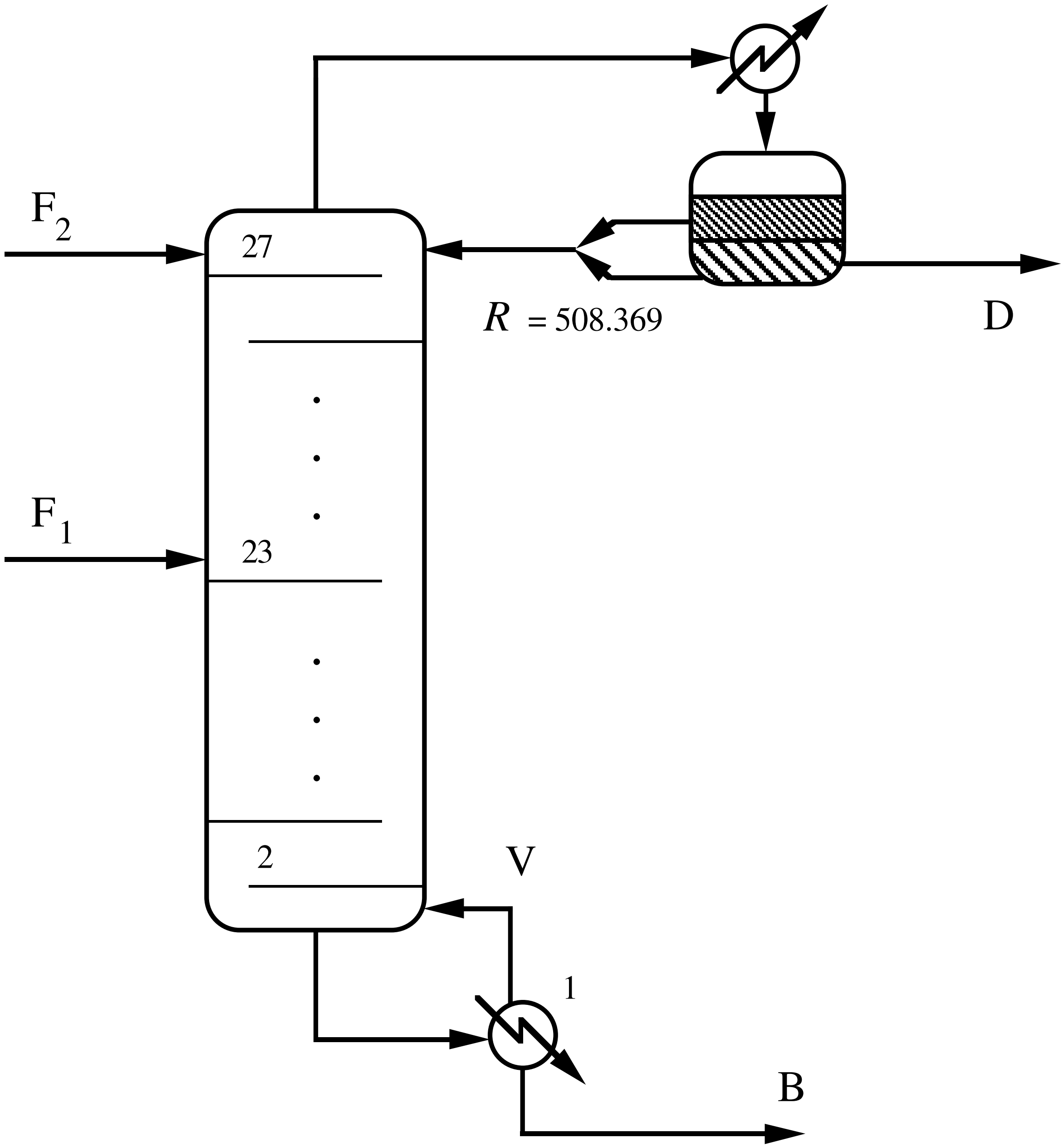

Figure 25: The column with decanter used in the numerical continuation calculations.

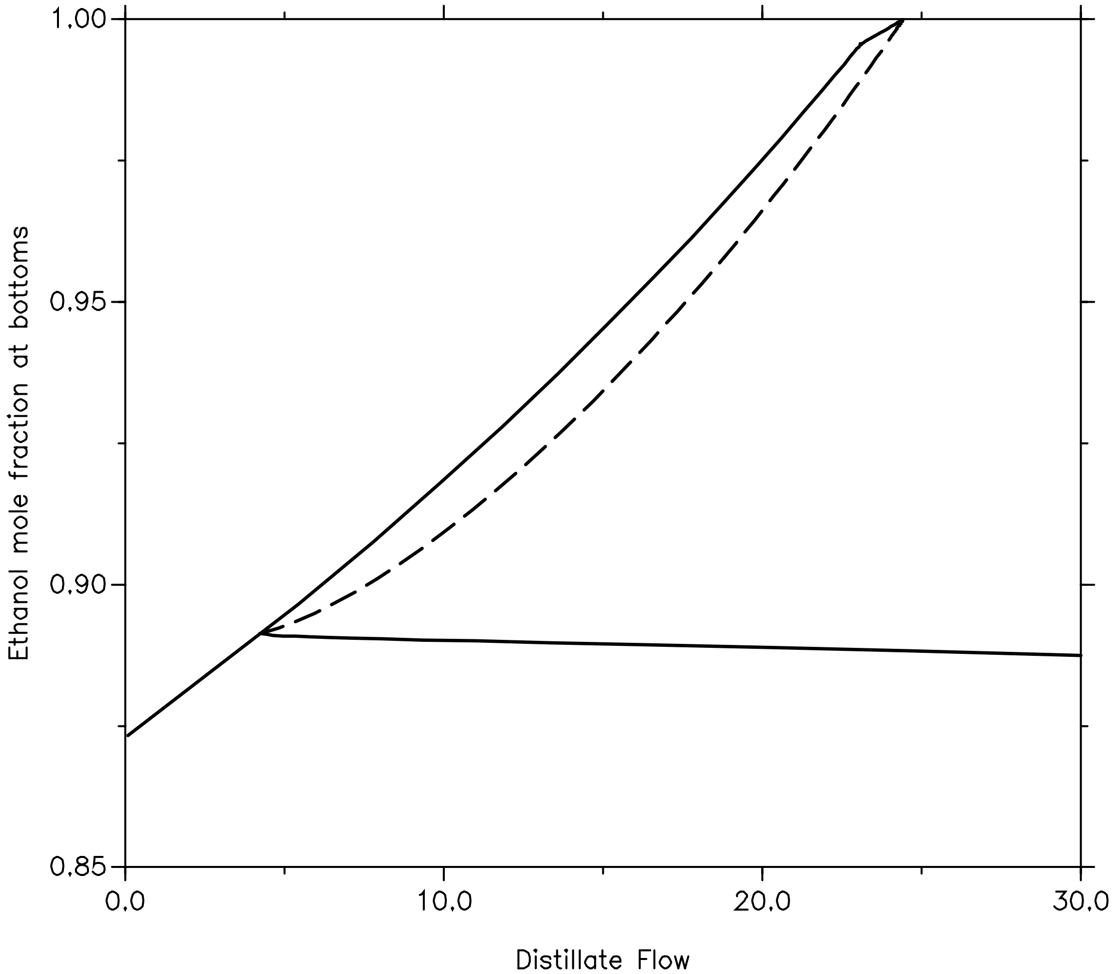

Figure 26: Bifurcation diagram with the distillate flow as the bifurcation parameter for the column with decanter depicted in Figure 25.

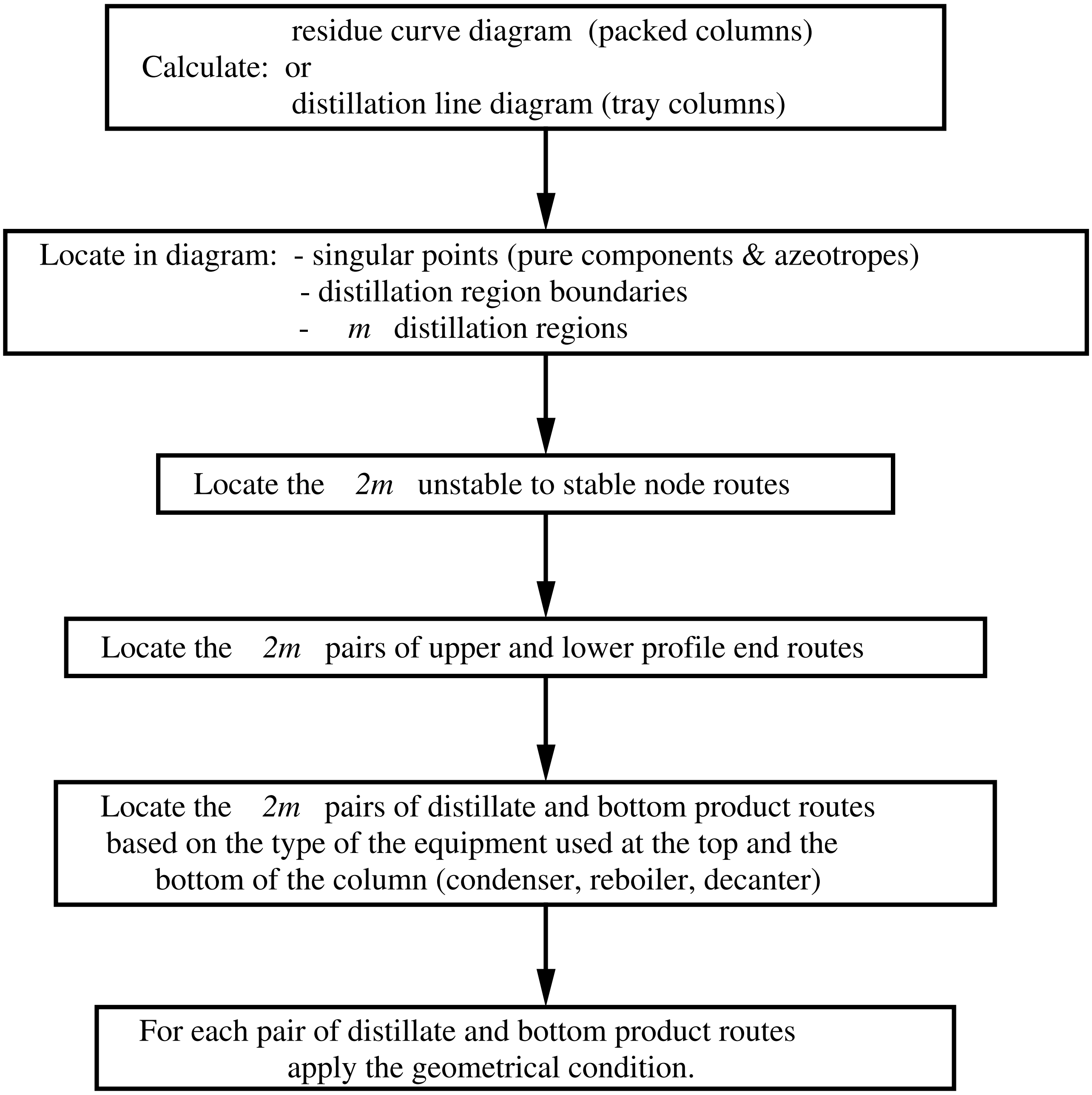

Figure 27: The general procedure for checking the existence of multiple steady states in the ∞/∞ case of any ternary mixture.