# The Dependence of the Feasible Separation Region on Feed Quality and Column Equipment

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For zeotropic mixtures with C- or U-shaped distillation lines, the feasible separation region is bound by two elements: a product composition multitude and a generalized distillation limit. The generalized distillation limit demarcates the sloppy splits (i.e., separations in which the composition of at least one product lies inside the composition space) from regions not accessible by distillation and depends on the thermodynamic state of the feed (a mixture of vapor and liquid in equilibrium or saturated vapor/liquid) and column equipment (total/partial condenser and total/partial reboiler). Mathematical relationships for determining the generalized distillation limit are presented, as well as examples of feasible separation regions for different feed quality and column equipment.

## 1. Introduction

Distillation is a widely used process for liquid mixture separation in the modern chemical industry. During the continuous distillation of multicomponent mixtures, components can be variously distributed between the distillate and bottoms. This distribution depends on the mixture properties, column constructional parameters and operating parameters. Determination of feasible separations for arbitrary feed compositions is the key to separation system synthesis. For a given feed composition and its thermodynamic state, feasible separations are described by a set of possible distillate and bottoms compositions, which is called the product composition set (PCS). This set is defined as the feasible separation region (FSR) if it includes all possible product compositions. Determination of the feasible separations for non-ideal and azeotropic mixtures has been the object of many research studies. Reviews of these studies were published by Widagdo and Seider (1966) and recently by Kiva and Krolikowski (2015).

The boundary of the feasible separation region is determined by extreme cases of operating modes of the column. These operating modes do not have much practical meaning, but if they are closely approached, the distillation will approach one of the limit boundaries. For zeotropic mixtures with C- or U-shaped distillation lines [a comprehensive survey of the structure of the distillation line map is given by Kiva et al. (2003)], the feasible separation region is bound by two elements (Figure 1). One of them, according to Serafimov et al. (1971), is a product composition multitude (PCM): i.e., the distillate and bottoms composition points at total reflux and an infinite number of stages (or an infinite height of packing). The second element – namely, the generalized distillation limit (GDL) – demarcates the sloppy splits (i.e., separations where the composition of at least one product lies inside the composition space) from regions not accessible by distillation (Krolikowski, 2017a). A part of the GDL, located between the feed composition point and unstable node of the distillation line map, restricts the distillate compositions, whereas a part limited by the feed composition point and stable node restricts the bottoms compositions. The present work addresses determination of the feasible separation region for a general case where the feed is a mixture of vapor and liquid or saturated vapor/liquid and the column operates with a total/partial condenser and reboiler.

In the current study, continuous distillation in trayed columns was modeled by theoretical stages. The constant molar overflow in each section of the column, the constant pressure along the column, and the products in the form of a saturated liquid or vapor were all assumed. An ideal vapor phase and an activity coefficient model (using the Wilson equation) for the liquid phase were used in all calculations. The references for the vapor–liquid equilibrium data are given in Table 1. MATLAB and Aspen Plus were used for the calculations.
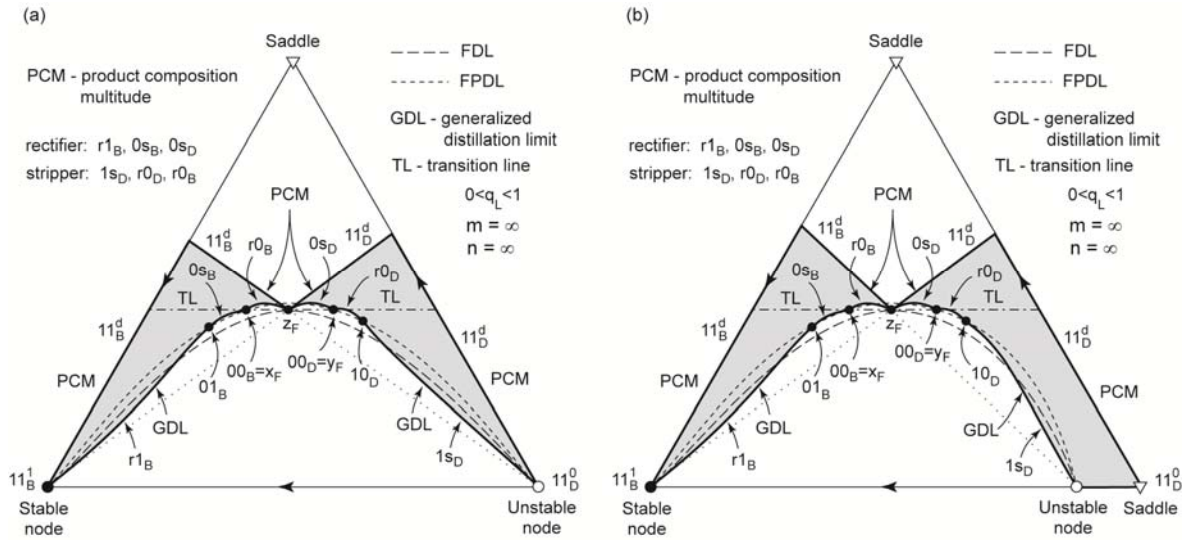
*Figure 1: Feasible separation region for a zeotropic mixture with (a) C-shaped and (b) U-shaped distillation lines (FDL – feed distillation line, FPDL – feed phase distillation line)*

*Table 1: Sources of Data for Vapor–Liquid Equilibrium Parameters*

| Mixture components 1 – 2 – 3 | 1 – 2 | 1 – 3 | 2 – 3 |
|---|---|---|---|
| methanol – ethanol – n-propanol | I/2e, p.50 | I/2c, p.96 | I/2a, p.340 |
| acetone – benzene – heptane | I/3+4, p.209 | I/3+4, p.243 | I/6b, p.158 |
| acetone – chloroform – methanol | I/3+4, p. 295 | I/2e, pp. 74–75 | I/2e, p. 17 |

Volume, part and page numbers refer to data collected by Gmehling et al. (1977, 1979, 1980, 1982, 1988)

## 2. Boundary of the feasible separation region

### 2.1 Product composition multitude

For a zeotropic mixture with C-shaped distillation lines, a product composition multitude is a simple polygonal chain determined by the following vertices [Figure 1a (Krolikowski, 2017b)]:

- unstable node
- intersection point of the edge (bounded by an unstable node and a saddle) of the composition space with a straight line containing a stable node and feed composition point $z_F$
- feed composition point $z_F$
- intersection point of the edge (bounded by a stable node and a saddle) of the composition space with a straight line containing an unstable node and point $z_F$
- stable node

For a zeotropic mixture with U-shaped distillation lines, two different polygonal chains can determine a product composition multitude. One of them corresponds to cases where an unstable node is located between a stable node and a saddle (on the same edge of the composition space). Its vertices are sequentially listed below (Figure 1b):

- unstable node
- saddle
- intersection point of the edge (bounded by two saddles) of the composition space with a straight line containing a stable node and point $z_F$
- feed composition point $z_F$
- intersection point of the edge (bounded by a stable node and a saddle) of the composition space with a straight line containing an unstable node and point $z_F$
- stable node

The second case occurs when a stable node is located between a saddle and an unstable node on the same edge of the composition space. Then, the shape of the PCM is a mirror image of the previous case. Saddles, stable nodes and unstable nodes are singular points of the distillation line map (Kiva et al., 2003).

## 2.2 Generalized distillation limit

The GDL consists of several curves related to specific types of operating modes of the column (Figure 1). The notation of each curve is a pair of operating parameters of $rs_P$ (where the relative reflux ratio $r = R / (R + 1)$ and the relative reboiler ratio $s = S / (S + 1)$), in which a letter denotes a varying parameter, a digit denotes the value of the constant parameter, and a subscript refers to the appropriate product ($D$ – distillate, $B$ – bottoms). Equations describing the GDL are known (Krolikowski, 2017b). Let us analyze the location of the curves included in the GDL in relation to pinch-point curves that go through feed composition point $z_F$. Curve $1s_D$, which limits the distillate composition, is determined by equations:

$$x_{i,D} = \frac{(x_{i,p} - x_{i,F})y_{i,F} - s(y_{i,p} - y_{i,F})x_{i,F}}{x_{i,p} - x_{i,F} - s(y_{i,p} - y_{i,F})}$$

(1)

$$s = \frac{x_{i,p} - z_{i,F}}{y_{i,p} - z_{i,F}}$$

(2)

where $x_p$ and $y_p$ are liquid and vapor pinch-point curves, respectively, defined by Eq(2), and $i$ is the component number. Curve $1s_D$ is determined as follows: $z_D = y_D = f_{eq}(x_D)$ for a partial condenser, or $z_D = x_D$ for a total condenser. This curve connects the unstable node with point $10_D$ (Figure 2). In special cases, curve $1s_D$ is part of the vapor pinch-point curve (for partial condenser and saturated vapor feed, and for total condenser and saturated liquid feed) or part of the liquid pinch-point curve (for total condenser and saturated vapor feed). Curves $r0_D$ and $r0_B$, which limit the distillate and bottoms compositions, respectively, are defined as follows:

$$\mathbf{y}_F = r\mathbf{x}_D + (1-r)\mathbf{y}_D$$

(3)

$$\mathbf{x}_B = \frac{q_L \mathbf{x}_F + r(1-q_L)\mathbf{x}_D}{q_L + r(1-q_L)}$$
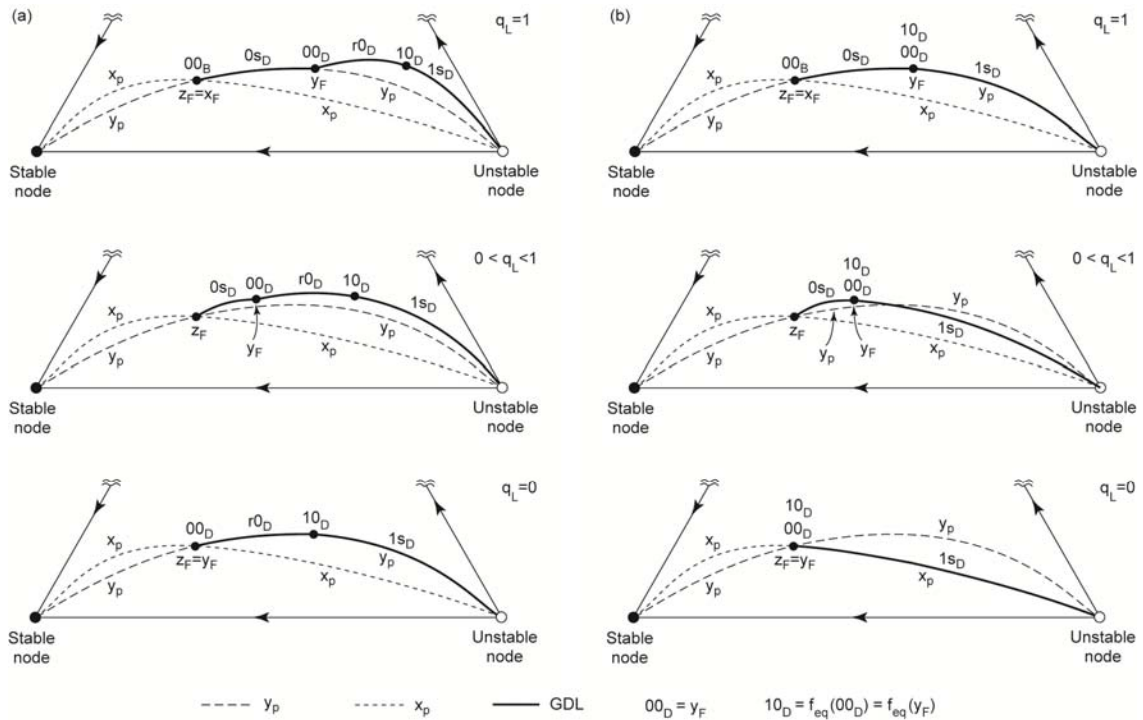
(4)



Figure 2: Distillate composition limit for (a) partial and (b) total condensers

For $0 < r < 1$, the set of points $\boldsymbol{y}_D$, as obtained from Eq(3), creates curve $r0_D$ (in the case of a partial condenser). The curve connects points $00_D$ and $10_D$. For saturated vapor feed, curve $r0_D$ is part of vapor pinch-point curve $\boldsymbol{y}_p$ (Figure 2a). For a total condenser, points $00_D$ and $10_D$ are superimposed and curve $r0_D$ is reduced to point $00_D = 10_D = \boldsymbol{y}_D$ (Figure 2b). Points $\boldsymbol{x}_B$, which are calculated from Eq(4), form curve $r0_B$ (Figure 3), which connects point $00_B$ with feed composition point $\boldsymbol{z}_F$. In special cases, curve $r0_B$ is part of liquid pinch-point curve $\boldsymbol{x}_p$ (for saturated vapor feed and a partial or total condenser).
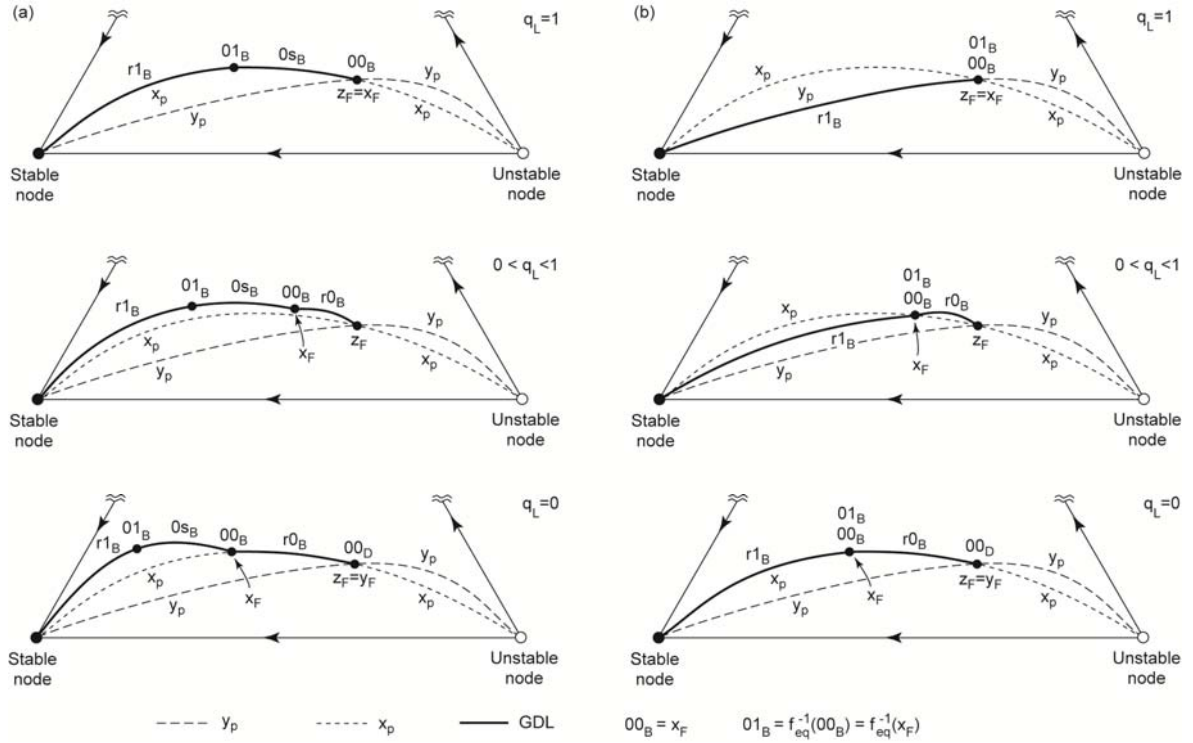


*Figure 3: Bottoms composition limit for (a) partial and (b) total reboilers*

Curves $0s_D$ and $0s_B$, which limit the distillate and bottoms compositions, respectively, are defined as follows:

$$\boldsymbol{x}_F = (1-s)\boldsymbol{x}_B + s\boldsymbol{y}_B \tag{5}$$

$$\boldsymbol{y}_D = \frac{(1-q_L)\boldsymbol{y}_F + sq_L\boldsymbol{y}_B}{1-q_L + sq_L} \tag{6}$$

For $0 < s < 1$, the set of points $\boldsymbol{y}_D$, as obtained from Eq(6), creates curve $0s_D$, which connects feed composition point $\boldsymbol{z}_F$ with point $00_D$ (Figure 2). In the case of saturated liquid feed, curve $0s_D$ is part of vapor pinch-point curve $\boldsymbol{y}_p$. For saturated vapor feed, points $\boldsymbol{z}_F$ and $00_D$ are superimposed and curve $0s_D$ is reduced to point $00_D = \boldsymbol{z}_D$. Points $\boldsymbol{x}_B$, which are calculated from Eq(5), form curve $0s_B$, which connects points $01_B$ and $00_B$ (Figure 3). For a partial reboiler and saturated liquid feed, curve $0s_B$ is part of vapor pinch-point curve $\boldsymbol{y}_p$. For a total reboiler, points $01_B$ and $00_B$ are superimposed and curve $0s_D$ is reduced to point $01_B = 00_B$.

Curve $r1_B$, which limits the bottoms composition, is described by equations:

$$r = \frac{y_{i,p} - z_{i,F}}{x_{i,p} - z_{i,F}} \tag{7}$$

$$y_{i,B} = \frac{(y_{i,p} - y_{i,F})x_{i,F} - r(x_{i,p} - x_{i,F})y_{i,F}}{y_{i,p} - y_{i,F} - r(x_{i,p} - x_{i,F})} \tag{8}$$

Curve $r1_B$ is determined as follows: for a partial reboiler, $z_B = x_B = f_{eq}^{-1}(y_B)$, and for a total reboiler, $z_B = y_B$. For $0 < r < 1$, the set of points $z_B$ creates curve $r1_B$. This curve connects the stable node with point $01_B$ (Figure 3). In special cases, curve $r1_B$ is part of a vapor pinch-point curve (for a partial condenser and saturated liquid feed, and for a total condenser and saturated vapor feed) or part of a liquid pinch-point curve (for a total condenser and saturated liquid feed).

## 3. Feasible separation region

The shape of the feasible separation region depends mainly on the thermodynamic state of the feed and the column equipment. A set of bottoms compositions is the largest for a total condenser and saturated liquid feed, and is the smallest for a partial reboiler and saturated vapor feed (Figure 4).
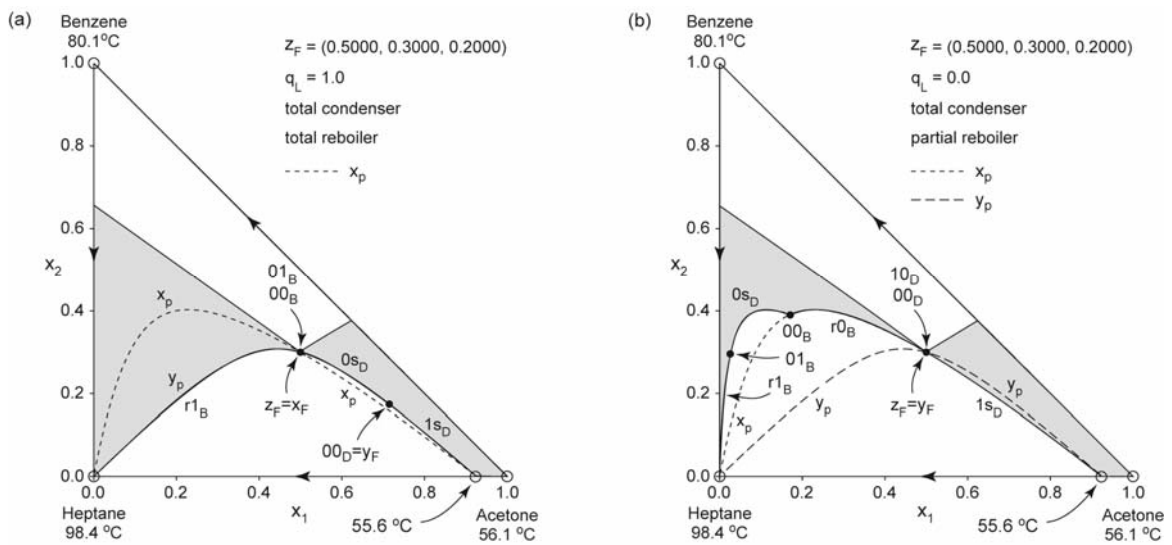


Figure 4: Feasible separation region with (a) the largest and (b) the smallest bottoms composition set
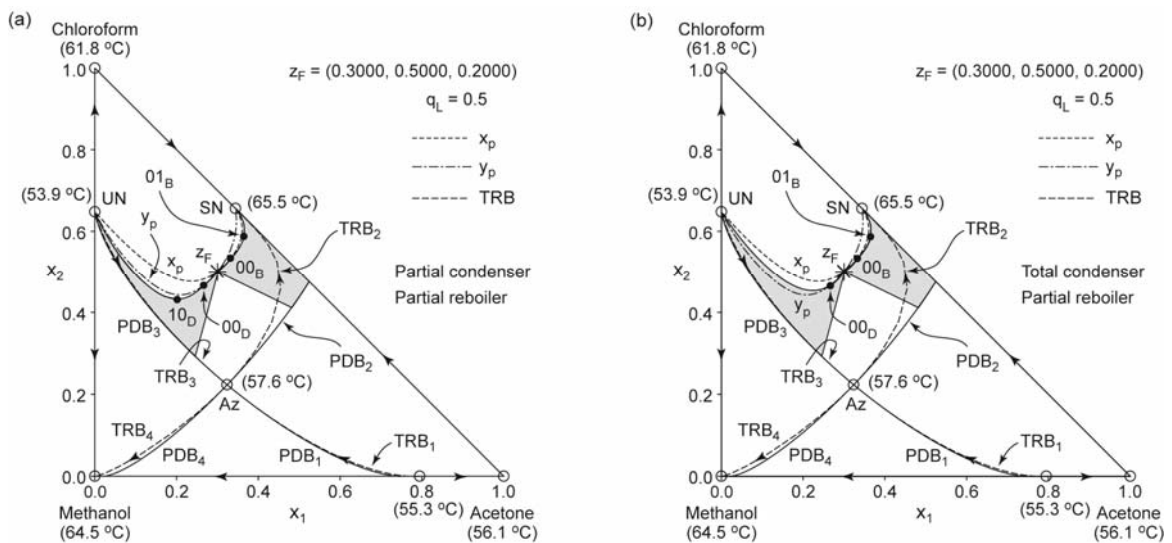


Figure 5: Feasible separation regions for a mixture with distillation boundaries and the feed being a mixture of vapor and liquid in equilibrium

Similarly, the distillate composition set is the largest for a total condenser and saturated vapor feed, and is the smallest for a partial condenser and saturated liquid feed.

Examples of feasible separation regions for an azeotropic mixture with distillation boundaries, and columns with a partial reboiler and partial/total condenser where the feed is a mixture of vapor and liquid in equilibrium, are presented in Fig. 5. In this case, the feed composition point is located on the U-shaped distillation line. Two pitchfork distillation boundaries modify the product composition multitude (Krolikowski, 2006). Pitchfork distillation boundary $PDB_2$ significantly expands the area of possible bottoms compositions, whereas boundary $PDB_3$ expands the area of distillate compositions. This last extension is irrelevant because total reflux boundary $TRB_3$ and pitchfork distillation boundary $PDB_3$ are located very close to each other. A part of the generalized distillation limit that bounds the distillate composition lies below the vapor pinch-point curve for a partial condenser or approximately between the liquid and vapor pinch-point curves for a total condenser (both pinch-point curves go through the feed composition point).

## 4. Conclusions

The feasible separation region depends on the thermodynamic state of the feed (a mixture of vapor and liquid in equilibrium or saturated vapor/liquid), the column equipment (total/partial condenser and total/partial reboiler), and the existence of distillation boundaries. Its shape may change substantially; nevertheless, every FSR is included in the set, which is determined by:

- a vapor pinch-point curve connecting a stable node to a feed composition point
- a liquid pinch-point curve connecting a feed composition point to an unstable node, and
- the product composition multitude (which can be modified by the pitchfork distillation boundary).

The generalized distillation limit is the most variable element of the FSR's boundary. The distillate composition limit lies approximately between the liquid pinch-point curves and the curve consisting of the vapor composition points in equilibrium with the liquid composition that is the same as the vapor pinch-point curve. Similarly, the bottoms composition limit is located approximately between the vapor pinch-point curve and the curve consisting of the liquid composition points in equilibrium with the vapor composition that is identical to the liquid pinch point curve. Suitable selection of condenser/reboiler type and the feed thermodynamic state may extend distillate of bottoms composition set and facilitate crossing of the distillation boundary when the boundary lies inside the feasible separation region.

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