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# On the effort of approaching pure components and azeotropes in distillation



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## AUTHOR - HIGHLIGHTS

- We quantify efforts to approach singular points in distillation.
- We propose novel augmented residue curve maps or distillation line maps.
- Empirical findings on the separation effort to remove impurities are confirmed.

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## ABSTRACT

In most distillation problems, the desired products are located at the singular points of the vapor–liquid equilibrium, i.e. pure components or azeotropes. The effort to approach these points depends on the specified purity of the product and tends to infinity as the composition approaches that of a pure component or azeotrope. In the present work, a method to quantify this effort in terms of equilibrium stages is given. It is shown that there is a constant lower bound on the number of stages required to decrease the impurity  $\delta$  of the product by a certain factor  $b$ . Further, it is shown that this lower bound is proportional to the logarithm of  $c$ . The results of the method are valid for ideal and non-ideal systems of any number of components. The information is obtained from the eigenvalues and eigenvectors of the singular points, no process simulations are needed. We propose adding key figures derived from the eigenvalues to distillation line/residue curve diagrams to immediately grasp the effort upon approaching the singular points.

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## 1. Introduction

In conceptual separation process design, two questions have to be answered: First, whether a certain flow sheet is thermodynamically feasible, irrespective of technical limitations. Second, if such a feasible flow sheet is found, whether the technical requirements can be met with an acceptable effort, for which estimates are needed. This contribution focuses on the second task and addresses the number of equilibrium stages needed for separations by distillation.

Diagrams of distillation lines (discrete, also called c-lines) and residue curves (continuous) are widely used in conceptual process design. For a definition, their construction and a survey on the use in conceptual design the reader is referred to the comprehensive review of Kiva et al. (2003). Both distillation lines and residue curves originate

and end in singular points of the vapor–liquid equilibrium (VLE) diagram, either unstable or stable nodes. Further, there may be saddle points which are singular points passed by distillation lines and residue curves (Gurikov, 1958). Singular points, and hence possible nodes or saddles, of the VLE are all pure components and azeotropes of the system (Haase, 1949). The type of a singular point (stable/unstable node or saddle) depends on the signs of the eigenvalues of a matrix derived from the differential equations that describe the residue curves. This was already shown by Russian researchers around Zharov and Serafimov in the late 1960s (Kiva et al., 2003).

The VLE and the topology of the dynamical system described by the residue curve equations determine the location and type of the singular points which are the basis of conceptual process design. A large number of methods which use distillation line and residue curve maps are available to determine the feasibility of a distillation column or the minimum reflux ratio of a column. They are usually based on the limiting cases of an infinite number of equilibrium stages (simply “stages” in the following) and/or total reflux. The minimum reflux ratio, and thus minimum energy demand, is obtained for an

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infinite number of stages (Underwood, 1948; Widagdo and Seider, 1996). Thereby, pinches play a crucial role. Composition pinches are found at column cross-sections where vapor and liquid are in equilibrium, so that a concentration driving force is absent and the column composition profile is unchanging from stage to stage. Studies of the properties of pinches and their loci (pinch curves) in ternary diagrams led to a number of methods to determine minimum reflux ratios for given product specifications, e.g. the boundary value method (Levy et al., 1985), an eigenvector method (Poellmann et al., 1994), the rectification body method (Bausa et al., 1998) or the method of the shortest stripping line (Lucia et al., 2006, 2008). Two ideas among these approaches are of direct relevance to this work. Firstly, Poellmann et al. (1994) linearized the VLE around the pinch point and used eigenvalue theory to calculate volumes inside which the column profiles have to approach the pinch points. As their motivation was different, they did not give measures of how fast the profiles approach the pinch points. This work will finally provide these measures. Secondly, Lucia et al. (2006, 2008) found that the length of the stripping section's profile (defined using the 2-norm in the concentration space) correlates with the energy demand of the column. For the minimum length of this profile, the energy demand (and hence the reflux ratio) of the column is minimized. When approaching the singular points of the VLE, the length of the profile does however not change significantly. Thus, this is an insensitive measure to quantify the separation effort to approach the singular points. This work provides the required measure in terms of the number of stages.

In continuous distillation, the minimum number of stages to meet given product specifications is obtained at total reflux (Stichlmair and Herguijuela, 1992; Widagdo and Seider, 1996). In this case, the profile of the column in the ternary diagram equals a segment of the distillation line connecting both column products (Kiva et al., 2003). The number of vertices of the segment, usually determined by tray-to-tray calculations, equals the number of stages (Stichlmair and Fair, 1998). Thus, the distillation lines provide a direct measure for the difficulty of the separation: the larger the distance (measured by the 2-norm) from stage to stage in the concentration space, the easier the separation (Stichlmair, 1988).

Of particular practical interest are column products in close vicinity of pure components or azeotropic points, thus in vicinity of the singular points of the VLE. In real columns, the singular points cannot be obtained as column products since an infinite number of stages would be required (even with total reflux provided). While the remainder of the introduction concerns the separation effort for approaching a node singular point, the proposed method is also applicable for separations in which the profile at total reflux and infinite number of stages passes through a saddle. This case is discussed in more detail in the main text.

Consider a distillation column in which one desired product is a pure component which is a node of the VLE diagram and the total amount of impurities  $\delta$  is specified. Upon decreasing  $\delta$  the effort for the separation (expressed in terms of number of stages at total reflux) will increase, with the number of stages approaching infinity as  $\delta$  tends to 0. In the present work, a method to assess that effort without having to carry out process simulations is described. As the analysis underlying the method is based on distillation line/residue curve diagrams, the case of total reflux is considered, and the separation effort is expressed in terms of the required number of stages. Any number of stages given in the present work is therefore a lower bound to the number of stages which would be required for a corresponding separation at finite reflux ratio, i.e. a separation in a real distillation column.

Assume that two design options for the above column with different specifications on  $\delta$  are given, e.g.  $\delta_{\text{spec},1} = 0.01$  mol/mol and  $\delta_{\text{spec},2} = 0.001$  mol/mol. Clearly, additional stages are required to achieve the lower impurity specification  $\delta_{\text{spec},2}$ . We are interested

in quantifying that increase in the number of stages and therefore only consider the transition from points with  $\delta = \delta_{\text{spec},1}$  to those with  $\delta = \delta_{\text{spec},2}$  which lie on the same distillation line or residue curve. The number of stages required for such a transition in the vicinity of a singular point can be obtained from an analysis of the eigenvectors and eigenvalues of the singular point. It is shown that a logarithmic relation exists between the ratio  $\delta_{\text{spec},1}/\delta_{\text{spec},2}$  of the impurities and the number of stages  $N$  required to achieve the desired step in purity, which is of the type  $\ln(\delta_{\text{spec},1}/\delta_{\text{spec},2}) = cN$ . In the literature, this logarithmic dependency was analytically derived for the special cases of systems of constant relative volatilities (Fenske, 1932; Cao et al., 2012) but, to the best of our knowledge, not in a general way. Further, such a logarithmic dependency was found empirically through simulations and experiments for non-ideal systems (Burger and Hasse, 2013; Eduljee, 1975). This work analytically derives the logarithmic dependency for the general case of non-ideal systems. The factor  $c$  depends on the eigenvalues of the singular point which is approached and the direction from which it is approached. The eigenvalues and eigenvectors of the singular points, as well as the value of  $c$  can be readily calculated from the thermodynamic VLE model without tray-to-tray calculations.

The paper is organized as follows. The next section is devoted to the mathematical derivation of a lower bound on the number of stages required to change the impurities of column products. In Section 3 the practical use of the calculated information is demonstrated. In Section 4 an augmented diagram of distillation lines is suggested which contains information about separation complexity.

## 2. Methodology

### 2.1. Basic definitions

The prescription to calculate distillation lines is as follows (Kiva et al., 2003):

$$\mathbf{x}^{(n+1)} = \mathbf{y}(\mathbf{x}^{(n)}) \quad (1)$$

starting from any point  $\mathbf{x}^{(0)}$  in the composition space. The vector  $\mathbf{x} \in \mathbb{R}^{N_C}$  denotes the liquid phase composition (mole fractions) in a system of  $N_C$  components. The vector function

$$\mathbf{y} = \mathbf{y}(\mathbf{x}), \quad \mathbf{y} \in \mathbb{R}^{N_C} \quad (2)$$

maps  $\mathbf{x}$  to the composition  $\mathbf{y}$  of the vapor phase in equilibrium with  $\mathbf{x}$ .

Whereas the stage index  $n$  in Eq. (1) is discrete, residue curves are described by in terms of a continuous parameter  $\tau$  (Van Dongen and Doherty, 1985):

$$\frac{dx_i}{d\tau} = y_i - x_i, \quad i = 1, \dots, (N_C - 1), \quad (3)$$

where in this context, one can think of  $\tau$  as a measure of the normalized column height. The solutions of these differential equations are called residue curves. In this work, we assume total reflux of the column. In this case the pinch points of the column, denoted  $\mathbf{x}_p$ , are equal to the stationary or singular points of Eq. (1). They are the common singular points of (1) and (3) given by

$$\mathbf{x}_p = \mathbf{y}(\mathbf{x}_p). \quad (4)$$

A singular point is either a pure component or an azeotrope, and is either an unstable node, a stable node or a saddle. Its type is defined by the eigenvalues of the matrix  $\mathbf{A}$  on the right side of (3) at the singular point  $P$  which involves the Jacobi matrix with negative sign as follows:

$$A_{ij} := \mathbb{1}_{ij} - \frac{\partial y_i}{\partial x_j} \Big|_P, \quad i, j = 1, \dots, (N_C - 1). \quad (5)$$

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