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DISTILLATION BOUNDARIES IN TERNARY HETEROAZEOTROPIC SYSTEMS

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Abstract

Distillation boundaries are created by saddle azeotropes and divide the composition space into distillation regions. In homogeneous mixtures the distillation regions overlap. The common area of two distillation regions is parametrically sensitive, and it determines the possibilities of crossing (at a finite reflux) the distillation boundaries defined for a total reflux or reboil ratio. In this study was scrutinized whether the distillation regions overlap in heteroazeotropic systems like in homoazeotropic systems. In order to see whether distillation regions overlap, such composition points of the products should be found, for which the rectifying profiles will end in different distillation regions. Calculations were performed for mixture classified under Serafimov's[1] topological class 3.1-2: ethanol – benzene – water.

Keywords: distillation, distillation boundaries, nonideal systems, heteroazeotrope

1. Introduction

Continuous distillation processes are frequently used in industry for the separation of azeotropic mixtures. The processes may dictate a change of operating pressures between columns, the addition of entrainer or the application of recycle or decanter. Such processes can be intricate to design and require new design methods. Moreover the design process of the distillation systems for the separation of highly non-ideal mixtures, with heterogeneous regions, is a complex issue. Examination of separability and selection of attainable process conditions by simulation is very time consuming, despite the application of computational techniques. In this situation, useful are the design methods of distillation columns, which take into account analysis of the entire composition space, its stationary points, distillation boundaries and composition profiles in a distillation column.

Distillation boundaries are created by saddle azeotropes and divide the composition space into distillation regions. There are three varieties of distillation boundaries: *simple distillation boundaries* (SDB), *total reflux boundaries* (TRB) and *pitchfork distillation boundaries* (PDB). Jobson et al.[2] showed that the distillation boundaries depend on the equipment used. An analysis of the distillation boundaries trajectory in the composition space allows identifying which products are obtainable. When combined with geometrical methods of distillation column designing, analysis facilitates, simplifies and accelerates the design process. Unfortunately, the nature of distillation boundaries in heteroazeotropic mixtures is still not precisely understood as it has been made for homogeneous mixtures. The present paper addresses this question.

2. Distillation Boundaries

2.1 Simple Distillation Boundary

A simple distillation process in which a multicomponent mixture is boiled in an open vessel is represented by a residue curve. Vapour whose composition is in equilibrium with the liquid is removed at once after its formation. Changes of the liquid phase composition are described by a system of nonlinear differential equations which have singular points at azeotropes and pure components[3]. In general, all residue curves begin and end at nodes. However, in case of a mixture containing a saddle azeotrope, there is a one residue curve linking it with a node-type singular point – either a pure component or an azeotrope. Such trajectory, dividing the composition space into different pieces, has been called a ***simple distillation boundary*** and abbreviated as ***SDB***. Acrivos and Amundson[4] provided a simple model for a continuous distillation process in packed columns. Their differential equations for composition profiles (see also Laroche et al.[5]) are identical to the residue curve equations for the limit of a total reflux or reboil ratio. Thus, simple SDBs are related to the continuous azeotropic distillation process carried out in packed columns. Van Dogen and Doherty[6] suggested that if a SDB is curved, the composition profile can cross the boundary only from its convex side where the product composition is situated. The crossing of simple distillation boundaries by distillation profiles (for staged columns) from the convex side prompted Fidkowski et al.[7].

2.2 Total Reflux Boundary

In continuous distillation process (Fidkowski et al.[7]), performed in a tray column with theoretical plates, the products of which are saturated liquids, assuming constant pressure and equimolar flow rates in each column section and in conditions of total reflux or reboil ratio, the mass balance equations are simplified to the equalities between vapour and liquid flows and the composition of both phases between the stages. Since balance is assumed between liquid and vapour at each stage, the operating relations and the VLE can be solved starting upwards or downwards the column's composition (for a finite or infinite number of stages) by performing only dew or bubble point calculations. Each such curve is called a *discrete distillation line* (previously referred to *finite differences curve*[3,8]). Similarly to the residue curve map, a finite difference mapping demonstrates an invariant curve which begins at the saddle azeotrope point and links exactly the same singular points, ending at the node. This curve, dividing the composition space into different parts, has been called a ***total reflux boundary***, and abbreviated as ***TRB***. It is generally assumed (Van Dogen and Doherty[9], Wahnschafft et al.[10]) that residue and distillation lines initiating from the same initial point join the same pure component or azeotrope nodes and that the difference between these two kinds of curves is not significant (as it is often the case). The TRB for staged columns has similar properties to those of the simple distillation boundary for packed columns[3,11].

2.3 Pitchfork Distillation Boundary

Since the column concentration profiles have been observed to cross the simple distillation boundary from its convex side, a new distillation boundary has been searched for[10,14-16]. Attempts to define the missing distillation boundary by means of reversible distillation were made by Wahnschafft et al.[10], Davydyan et al.[12], Koehler et al.[14], Poellmann and Blass[15] and Petlyuk[16]. The new boundary has been defined by Davydyan et al.[12]. This boundary is defined by minimal separation energy expenditures in the theoretical process of reversible distillation, in which an infinitely long column with continuous heat exchange along its entire length, runs everywhere at pinch point[12]. It has been called ***pitchfork distillation boundary*** and abbreviated as ***PDB***[3,6,13,14]. Unlike previously discussed distillation boundaries, PDB does not always link azeotrope with another singular point of node type. However, it often crosses the composition space edge at another point, what provides additional opportunities for distillation boundaries crossing[3]. The pitchfork distillation boundary divides also the composition space into separate pieces. In the contradistinction to TRBs and SDBs, the PDB does not depend on the type of applied distillation column; however, together with TRB or SDB, it forms a pair of boundaries which defines the common areas of distillation regions.

3. Relationships Between Distillation Boundaries

Regarding to homogeneous mixtures problems associated with distillation boundaries and their crossing have been systematized by Królikowski[17]. Jobson et al.[2] have demonstrated that distillation boundaries are dependent on the applied equipment. In turn, Królikowski has shown that SDB is associated with packed column, and its counterpart for the staged column is the TRB, while PDB is identical for either column type. In consequence, distillation regions are not inseparable but they overlap. Their common part enclosed between the pair of matching distillation boundaries is parametrically sensitive[18]. The nature of concentration profile within the section of the column which product is located between the corresponding pair of distillation boundaries, depends either on the reflux value or on the reboil ratio. Distillation boundaries created by different azeotropes, present in a mixture, exert mutual effects on each other. These interactions induce (at times radically) a change in behaviour of distillation profiles, in consequence causing a significant change of the shape of distillation regions[18]. With regards to homogeneous solutions, the common part of distillation regions is located between SDB and PDB for a packed column and between TRB and PDB for a staged column. For stable separatrices (SDB and TRB), the SDB lies between the TRB and the PDB[3,8] and it may be crossed from each side by staged column stripping profiles. In the case of unstable separatrices[3,8], the TRB places between the SDB and the PDB and it is obvious that it may be crossed from each side by packed column rectifying profiles. The critical values of the reflux or reboil ratio can be determined during a parametric study. A method of estimating these values was also proposed by Wahnschafft et al.[10].

3. Overlapping Of Distillation Regions

In order to verify whether distillation regions overlap, such composition points of products has to be found, the distillation profiles for which will end in different distillation regions. Studies of this type have been performed for mixture classified under Serafimov's[1] topological class 3.1-2: ethanol – benzene – water. All boundaries (SDBs and TRBs) in the mixture are unstable separatrices – linking the unstable node with the saddle point. It has been assumed that the relations between distillation boundaries are the same as those for homogeneous mixtures[3,8]. Thus, there is TRB on the convex side of SDB, with PDB located still farther on.

It has been discussed here continuous distillation performed in staged column only since the situation for the packed column with simple distillation boundary is similar. The model used in calculations is simplified by assuming constant molar flows in the column sections, and the temperatures on all stages are obtained by bubble point calculations at constant atmospheric pressure P=1atm. The activity coefficients for the phase equilibria are modeled by the NRTL equation with parameters taken from Gmehling and Onken, 1977 and Distil's Internal Database, 2003. The thermodynamic data for the mixtures studied in this paper are given in Table 1 below. It has been assumed perfect mixing and equilibrium in all stages and ideal vapour phase. Column is equipped with total condenser (first stage) and has not got a decanter on top; column is equipped with evaporator (last stage). Distillate and reflux streams are diphase. The resulting mathematical model takes the form of a set of differential and algebraic equations (DAE system) and it is solved in Matlab[19] with the DAE solver ODE15s. Rectification profiles were calculated using Distil[20] with thermodynamic data taken from Table 1.

Table 1. Thermodynamic data for the mixture studied

Class 3.1-2: Ethanol [1] - Benzene [2] - Water [3]

VLE	**A_{ij} (cal/mol)**	**A_{ji} (cal/mol)**	**$\alpha_{ij}=\alpha_{ji}$**
[1-2][21]	775.7625	1118.9759	0.6268
[1-3][20]	-109.6339	1332.3134	0.3031
[2-3][21]	1522.2402	1821.8322	0.3547
Antoine	**A**	**B**	**C**
[1][21]	8.11220	1592.864	226.184
[2][21]	6.87987	1196.760	219.161
[3][21]	8.07131	1730.630	233.426

3.1 Ethanol – Benzene – Water Mixture

The mixture exhibits two binary homoazeotropes, between water–ethanol and ethanol–benzene, one binary heteroazeotrope, between benzene–water, and a ternary heteroazeotrope. The ternary heteroazeotrope is the only unstable node [un]. The three binary azeotropes are saddles [sa] and the three pure components vertices are stable nodes [sn] (Fig. 1).

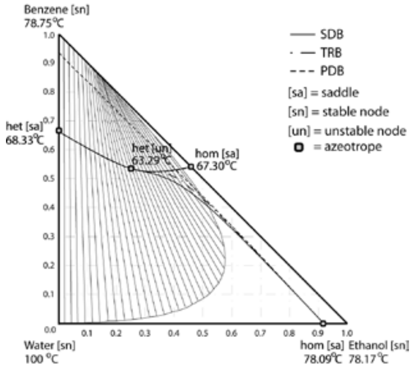

Figure 1. Distillation boundaries for ternary heteroazeotropic mixture ethanol – benzene - water

All distillation boundaries are unstable separatrices. Running from the ternary heteroazeotrope to each one of the binary azeotropes, divide the composition space into regions. As mentioned above - that distillation boundaries are dependent on the applied equipment - a different pair of distillation boundaries is referred to each type of the distillation column. In Fig. 2 have been shown distillation regions created by corresponding distillation boundaries. PDB II and PDB III have been distorted for the purpose of clarity (in fact, they are close to TRB II/SDB II and TRB III/SDB III respectively).

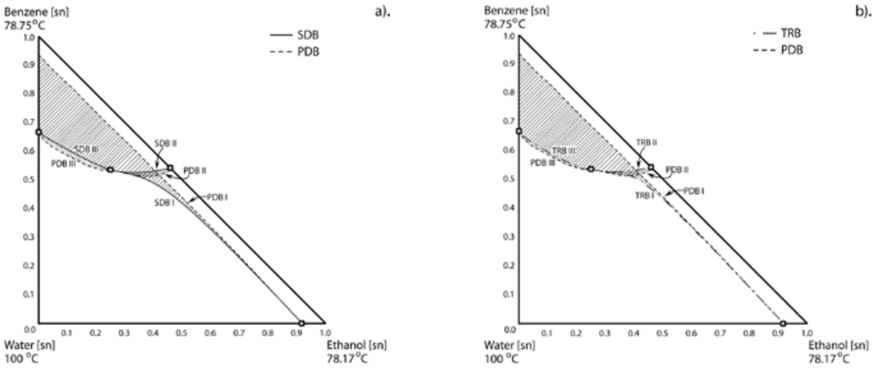

Figure 2. Interaction of boundaries (figures has been distorted):
a). for packed column; b). for staged column

For the staged column, a TRB and a PDB originating from the same saddle azeotrope mark out two distillation regions which overlap. One of the regions situates on the concave side of the PDB and the last one on the convex side of the TRB. The area between the TRB and the PDB is the common part of the two regions. As a result, for examined mixture, there are three regions responsible for the jump of rectifying profiles. One of them extends between TRB I and PDB I, the second one among TRB II and PDB II and the last one broadens between TRB III and PDB III.

A rectifying profile may jump only if the product composition lies between two appropriate distillation boundaries. For the heterogeneous distillate $\boldsymbol{z}_{\mathbf{D}}$ = (0.4719, 0.4542, 0.0739) located between TRB I and PDB I, rectification profiles for the reflux ratios R=42.9 and R=43.0 run appropriately for the stable water and ethanol nodes, respectively (Fig. 3). Therefore, this point is located in the common part of two distillation regions.

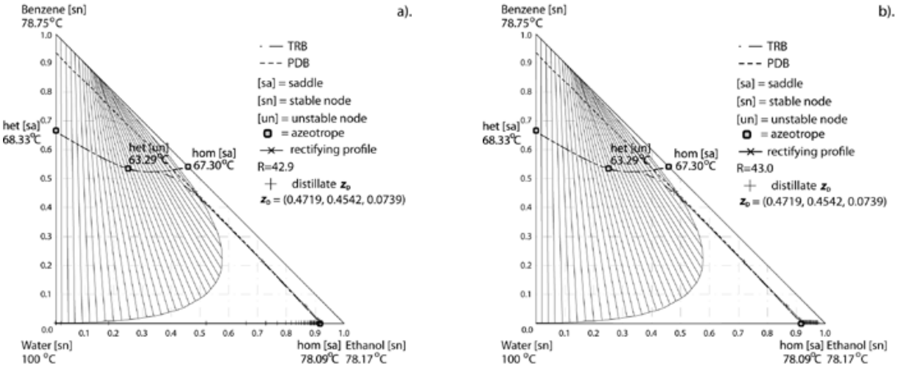

Figure 3. Rectifying profiles for the distillate placed on the distillation region determined by TRB I & PDB I

If we take now the heterogeneous distillate $\boldsymbol{z}_{\mathbf{D}}$ = (0.4279, 0.5345, 0.0376) located between TRB II and PDB II, rectification profiles run appropriately for the stable benzene and ethanol nodes after changing the reflux ratios from R=4.51 to R=4.52, respectively (Fig. 4). Therefore, also this point is located in the common part of two distillation regions.

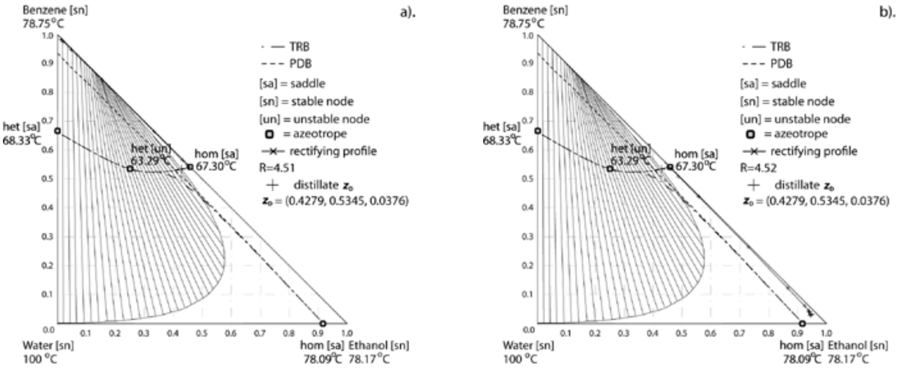

Figure 4. Rectifying profiles for the distillate placed on the distillation region determined by TRB II & PDB II

Sometimes regions between different total reflux boundaries and pitchfork distillation boundaries overlap. Then they interact in two possible ways. The first type of interaction occurs in the common area of two regions between certain TRBs and PDBs. The common piece is bounded by TRB I, PDB I, TRB II and PDB II (Fig. 2b). Thus for the heterogeneous distillate $\boldsymbol{z}_\mathbf{D}$ = (0.3355, 0.5231, 0.1414) located in this area, for various values of the reflux ratio rectifying profile may end in three different distillation regions running towards stable nodes represented by pure components vertices in composition space (Fig. 5).

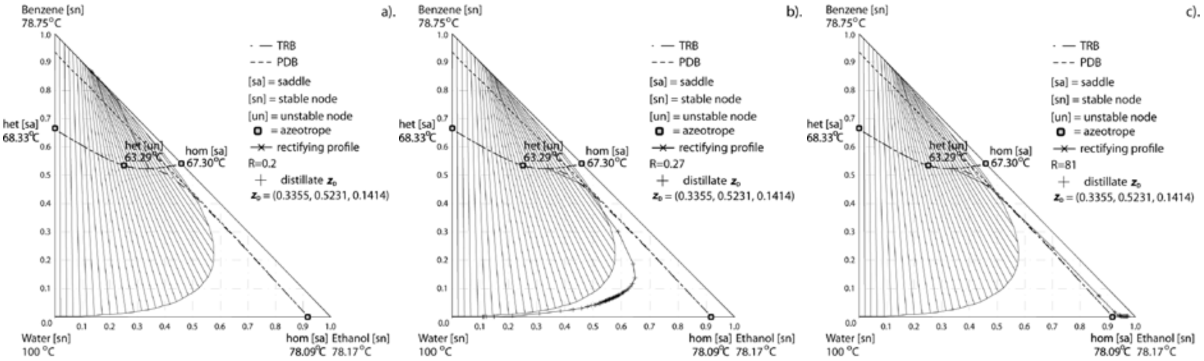

Figure 5. Rectifying profiles for the distillate located in the common area of two regions

Similar situation exhibits for the heterogeneous distillate $\boldsymbol{z}_\mathbf{D}$ = (0.1269, 0.5870, 0.2861) situated on the convex side of TRB III in region determined by TRB III and PDB III. This region is influenced by PDB I. Once rectifying profile runs towards stable node – water (R=0.1), secondly for reflux ratio in range R=0.2 to R=744 profile approaches to saddle – benzene-water azeotrope, while for R=745 rectifying profile comes up to stable node – represented by pure benzene vertex.

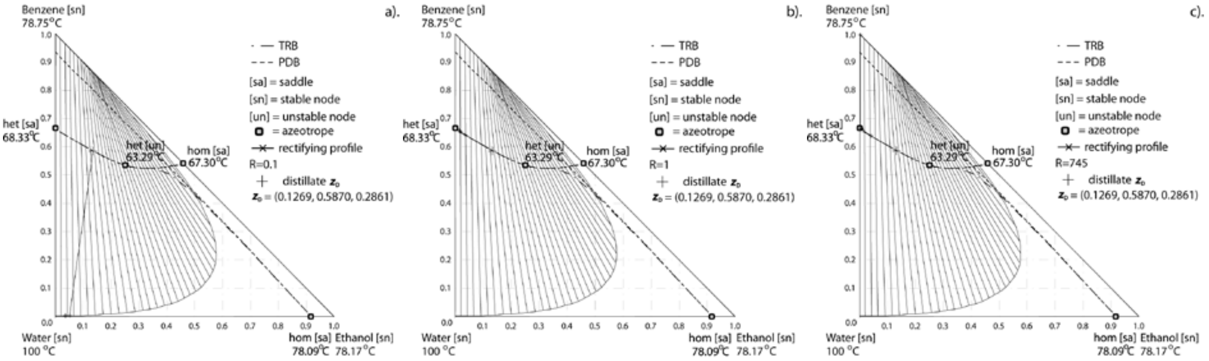

Figure 6. Rectifying profiles for distillate $\boldsymbol{z}_\mathbf{D}$ = (0.1269, 0.5870, 0.2861)

Additionally, it has been observed for this distillate point $\boldsymbol{z}_\mathbf{D}$ = (0.3355, 0.5231, 0.1414), that critical values of reflux ratio shown on Fig. 5 are not the only critical values, for which rectifying profile may end in another distillation regions. For the reflux ratios R=(0.5, 0.8, 1, 4, 6, 8, 14, 20, ..., 79) distillation profile approaches the stable node – benzene, while for values of R=(0.6, 0.9, 2, 5, 7, 9, 18, ..., 78) it runs in the direction of vertex represented by water in the composition space. For critical value of R=81 rectifying profile ends close to the ethanol vertex. Further increase of reflux ratio value results in jumping of distillation profile once towards to the benzene, once to the ethanol.

The second kind of interaction occurs when region between TRB and related PDB is crossed by another TRB. This is the case, where occurs “cut-off effect” by the other TRB. For ethanol-benzene-water mixture TRB II cuts the region between TRB I and PDB I. Normally by changing the reflux ratio, the rectifying profile would jump for the distillate composition in this entire region, but it does not in the area enclosed in TRB II and the benzene-water edge in the composition space.

4. Conclusions

An overlapping of distillation regions in heteroazeotropic mixtures has been scrutinized. To prove it, such composition points of the products (distillate points) have been found for which the rectifying profiles have been jumped into different distillation regions. Different distillation boundaries are assigned to the particular types of distillation column (staged or packed). For both columns’ types pitchfork distillation boundary exists. The area between related boundaries is parametrically sensitive. The area represents the common part of two overlapped distillation regions. When a product is located in such area, the second product may occur in different distillation regions. When the product is located in the common area between regions assigned by two pairs of appropriate distillation boundaries, the second product may occur in three distillation regions. For a product localized in the cut-off region, the second product occurs in the same distillation region.

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