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1 Pinch curves computation using differential 2 continuation algorithm

3 Nataliya Shcherbakova^{a*}, Ivonne Rodriguez-Donis^b, Vincent Gerbaud^a

4 ^a*Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP-ENSIACET, UPS*
5 *Toulouse, France*

6 ^b*Laboratoire de Chimie Agro-industrielle, LCA, Université de Toulouse, INRA,*
7 *Toulouse, France*

8 **nataliya.shcherbakova@ensiacet.fr*

9 Abstract

10 The paper presents a novel algorithm for numerical computation of pinch curves in
11 homogeneous ternary mixtures under assumption of constant molar flow in an infinitely
12 long column. The method is based on the analysis of topological structures of the
13 surfaces associated to the vapor-liquid equilibrium and pinch conditions in the 3D
14 composition - temperature space. The computational problem is formulated in terms of
15 a system of ordinary differential equations. The efficiency of this approach to compute
16 the pinch curves and to detect the bifurcations of their structure is demonstrated with
17 four examples of real mixtures covering ternary diagram classes 1.0-1a, 1.0-2 and 2.0-
18 2b.
19

20 **Keywords:** pinch curves, bifurcation, homogenous extractive distillation, differential
21 continuation

22 1. Introduction

23 Pinch curves are an important concept in the design of extractive distillation process
24 since they are related to limiting operating conditions, which are essential for assessing
25 process feasibility. They represent the set of compositions that remain constant along
26 the increasing number of stages in the column, so that the separation becomes
27 impossible once these compositions are reached. The location of pinch curves delimits
28 the operation domain for a given set of operation parameters (reflux ratio and the
29 entrainer flow rate) allowing to evaluate the performance of the entrainer using the
30 Infinitely Sharp Split (ISS) method as described by Petlyuk et al. (2015) and Rodriguez-
31 Donis et al. (2023).

32 This paper aims to present a new numerical algorithm for pinch curves computation
33 based on the differential continuation method, which reduces the computation to the
34 integration of a system of ordinary differential equations (ODE) instead of solving the
35 systems of algebraic equations by an iterative procedure, as it is usually done. It
36 represents the further development of the new algorithmic approach that was
37 successfully applied to compute univolatility curves (Shcherbakova et al., 2017, Cots et
38 al. 2021) and binodal curves (Shcherbakova et al., 2023) of ternary diagrams.

39 Starting from the code of Poellmann and Blass (1994), there were several attempts to
40 construct the pinch curves via integration of ODE systems (Feldbab, 2012) or
41 differential-algebraic systems of equations (DAE) (Skiborowski et al. 2016). The
42 novelty of our approach comparing to the other authors consist in exploration of the

43 topology and the mutual arrangement of the pair of surfaces associated to the vapor-
 44 liquid equilibrium (VLE) and pinch conditions in a complete 3D composition-
 45 temperature state space, under the standard assumptions of constant molar flow rates
 46 and the infinite height of the column. We show that in this setting the pinch curves are
 47 just projections on the 2D composition space of the intersection of these surfaces, and
 48 their singularities results from the common tangent points of these surfaces.

49 The described geometric model can be formalized in a set of ODE that can be solved by
 50 any conventional ODE solver. This reduces the computation time gaining in the
 51 numerical accuracy and flexibility of the code.

52 This paper is organized as follows. In Section 2 we present the detailed geometrical
 53 model of pinch curves. In particular, we derive the bifurcation condition for the pinch
 54 curves splitting caused by the change of operation parameters. In Section 3 four
 55 examples of different configurations of pinch curves of real ternary mixtures are
 56 presented. In Conclusion we discuss the possible practical issued of the presented
 57 algorithm.

58 **2. Computational method**

59 *2.1. Pinch points and pinch curves in ternary extractive distillation*

60 Assume that the extractive distillation of a ternary homogeneous mixture takes place in
 61 an infinitely high column with constant liquid and molar flow rates L and V . It is also
 62 assumed that the ratio of the entrained molar feed rate E and molar flow rate of the
 63 distillate D is fixed.

64 Pinch points of the distillation diagram associated to this process represent the critical
 65 state inside the column corresponding to the VLE between the vapor and the liquid
 66 phases at the same stage of the column, so that their further separation becomes
 67 impossible. The geometrical loci of such points form the pinch branches or pinch curves
 68 of the diagram. Pinch curves play the central role in the infinitely sharp split (ISS)
 69 method to identify the possible splits in a given mixture. For the detailed description the
 70 pinch points and the ISS method we refer the reader to papers cited above and
 71 references therein. In this paper we focus on the purely computational aspects, and to
 72 this end we first need to recall the main mathematical formulae used in the
 73 computations.

74 In what follows T is the temperature of the mixture, $x_i, y_i \in [0,1]$, $i=1,2,3$ denote
 75 the molar fractions of the three component mixtures in liquid and vapor phases so that
 76 $y_i = K_i(x_1, x_2, x_3, T)x_i$, where the functions K_i represent the distribution
 77 coefficients of the component i . Since $\sum_{i=1}^3 x_i = 1$, only two of molar fraction are
 78 independent, so that below x_3 will be replaced by $x_3 = 1 - x_1 - x_2$. The VLE
 79 condition then takes the form

$$x_1 K_1(x_1, x_2, T) + x_2 K_2(x_1, x_2, T) + (1 - x_1 - x_2) K_3(x_1, x_2, T) = I \quad (1)$$

80 According to Petlyuk et al. (2015), the pinch point condition associated to the first
 81 component that should be separated from the second one (using the third one as an
 82 entrainer) can be written in the form

$$x_1^\Delta = \frac{K_1(x_1, x_2, T) - K_2(x_1, x_2, T)}{1 - K_2(x_1, x_2, T)} x_1 \quad (2)$$

83 Here $x^\Delta \notin [0,1]$ denoted the difference or delta point, it lies outside of the
 84 concentration triangle and represents a virtual concentration corresponding to the
 85 composition of the difference between the distillate and the entrainer feed of the column.
 86 Once the ratio E/D is fixed, the delta point is defined by the relation

$$\frac{E}{D} = \frac{x^\Delta - 1}{x^\Delta} \quad (3)$$

87 The set of points on the composition space verifying conditions Eqs. (1, 2) is called the
 88 pinch curve associated to the operating conditions expressed by Eq. (3). These curves
 89 are bounded by the binary sides of the composition triangle and by the univolatility
 90 curves $\alpha_{ij} = 1$ that represent the points where $K_i(x_1, x_2, T) = K_j(x_1, x_2, T)$.
 91 The pinch and univolatility curves can intersect only at azeotropic points of the diagram.

92 2.2 Geometrical model of pinch curves and their singularities

93 Eqs.(1-3) admit a very clear geometric interpretation. Indeed, denote by $\Omega = \{x_i \in$
 94 $[0,1], x_1 + x_2 \ll 1, i = 1,2\}$ the composition triangle associated to the ternary
 95 mixture and consider a 3D cartesian space $\Sigma = \{z = (x_1, x_2, T) : (x_1, x_2) \in \Omega\}$
 96 over Ω endowed with the coordinates x_1, x_2 and T . Define two functions

$$\begin{aligned} \Phi(x_1, x_2, T) &= \sum_{i=1}^3 x_i K_i(x_1, x_2, T) - 1 \\ \Psi(x_1, x_2, T) &= x_1^\Delta (1 - K_2(x_1, x_2, T)) - x_1 (K_1(x_1, x_2, T) \\ &\quad - K_2(x_1, x_2, T)) \end{aligned} \quad (4)$$

97 and consider the pair of surfaces associated to zero levels of these functions: $W_\Phi =$
 98 $\{z \in \Sigma : \Phi(z) = 0\}$ and $W_\Psi = \{z \in \Sigma : \Psi(z) = 0\}$. The intersection of
 99 these surfaces defines a smooth curve Γ in Σ . Comparing Eqs. (1, 2) with Eq. (4) one
 100 can easily see that Γ projects on a pinch curve on Ω . Indeed, since $\Gamma = W_\Phi \cap W_\Psi$, it
 101 is generated by some vector field which is orthogonal to both normal vectors $N_{W_\Phi} =$
 102 $\nabla\Phi(z)$ and $N_{W_\Psi} = \nabla\Psi(z)$. In other word, at each point $z \in \Gamma$, the vector

$$U(z) = \nabla\Phi(z) \times \nabla\Psi(z) \quad (5)$$

103 belongs to the tangent space Γ . Therefore, knowing one pinch point $z_0 \in \Gamma$ would be
 104 enough to construct the whole pinch curve by solving the following system of ODE

$$\dot{x}_1 = U_1(x_1, x_2, T), \quad \dot{x}_2 = U_2(x_1, x_2, T), \quad \dot{T} = U_3(x_1, x_2, T) \quad (6)$$

105 where, according to Eq.(5),

$$\begin{aligned} U_1 &= \frac{\partial\Phi}{\partial x_2} \frac{\partial\Psi}{\partial T} - \frac{\partial\Phi}{\partial T} \frac{\partial\Psi}{\partial x_2}, \quad U_2 = \frac{\partial\Phi}{\partial T} \frac{\partial\Psi}{\partial x_1} - \frac{\partial\Phi}{\partial x_1} \frac{\partial\Psi}{\partial T}, \\ U_3 &= \frac{\partial\Phi}{\partial x_1} \frac{\partial\Psi}{\partial x_2} - \frac{\partial\Phi}{\partial x_2} \frac{\partial\Psi}{\partial x_1} \end{aligned} \quad (7)$$

106 Observe, that if W_Φ and W_Ψ have a common tangent plane at z , then $U(z) = 0$ and
 107 such a point is a singular point of Γ . Moreover, due to Eq.(4), the gradient of the at any
 108 point of W_Φ verifies $\frac{\partial T}{\partial x_i} = -\frac{\partial\Phi}{\partial x_i} / \frac{\partial\Phi}{\partial T}$, $i = 1,2$. Combining this expression with Eq. (7)
 109 yields

$$U_3 = U_1 \frac{\partial T}{\partial x_1} + U_2 \frac{\partial T}{\partial x_2} \quad (8)$$

110 Hence the singular points of Γ are in one-to-one correspondence with the singularities
 111 of the underlying pinch curve. Such isolated singular points can be of elliptic of
 112 hyperbolic type. The first case corresponds to a pinch curve shrinking into an isolated
 113 pinch point under certain operation conditions, whereas in the hyperbolic case there are
 114 four pinch branches meeting at the singular point. Examples of such configurations will
 115 be given in Section 3.

116 The topology of the pinch diagram is entirely determined by the value of E/F (and
 117 hence by x^Δ) and by the pressure in the column. The modification of one of these
 118 parameters will cause the transformation of the shape and of the mutual arrangement of
 119 the surfaces W_Φ and W_Ψ , leading to the transformation of the topological structure of
 120 the underlying pinch diagram. In particular, it may cause its bifurcation. According to
 121 the geometrical model described above, the bifurcation occurs when the curve Γ has a
 122 critical point. In view of Eq. (8), the corresponding pinch point and operating conditions
 123 can be found by solving the following system of four equations

$$\begin{aligned} \Phi(x_1, x_2, T) = 0, \Psi(x_1, x_2, T) = 0, \\ U_1(x_1, x_2, T) = 0, U_2(x_1, x_2, T) = 0 \end{aligned} \quad (9)$$

124 with respect to x_1, x_2, T, P or x_1, x_2, T, x^Δ , according to the type of bifurcation.

125 *2.3 Numerical computation of pinch curves*

126 Using Eq. (6) the whole pinch curve can be computed numerically using the standard
 127 Runge-Kutta schemes for ODE integration. Initial points for such integration can be
 128 found by solving Eqs. (1,2) on the binary sides of the composition triangle, by an
 129 iteration procedure. The dot symbol in the left-hand side of Eq. (6) has the meaning of a
 130 derivative with respect to some scalar parameter. In practical computations, it would be
 131 convenient to normalize the vector field U and thus rewrite Eq. (6) with respect to arc
 132 length s . This will also avoid an eventual stiffness problem along the integration.

133 The same computation can be performed with respect to another component, yielding
 134 other types of pinch curves. To this end, in Eq. (2) x_1 should be replaced by x_2 or x_3 ,
 135 modifying the indexes of distribution coefficients accordingly. Taking into account that
 136 a pinch curve may be composed of two branches, the complete pinch diagram of a given
 137 mixture can be obtained by the following steps:

- 138 - build a list of all pinch points on the boundary of Ω .
- 139 - for each binary pinch point from in the list compute the pinch curve issued from this
 140 point with an appropriate choice of the initial direction. The numerical integration
 141 should be continued until the boundary of Ω is attained.
- 142 - exclude both initial and final points of the already computed pinch curve and
 143 continue until the list of binary pinch points is emptied.

144 The described algorithm allows to compute all pinch branches of the given ternary
 145 mixture that start from the binary pinch points. However, in some rare cases the mixture
 146 may have closed pinch curves entirely lying in the interior part of Ω . An example of
 147 such a situation is presented in the next section. In this case the pinch curve still can be
 148 computed by solving Eq. (6), but it will require to detect a pinch point in the inner part

149 of Ω . The clear indicator of such a configuration is the existence of a bifurcation point
 150 of elliptic type inside Ω for some value of E/D or pressure.

151 A numerical implementation of Eq. (7) requires the access to the derivatives of the
 152 expressions defining the thermodynamical model of the mixture: activity coefficients,
 153 vapor-temperature equation, etc. The complexity of such a computation is the main
 154 reason for which the differential continuation algorithms are very poorly used in
 155 Process Engineering compared to the other fields. In fact, the use of difference formulae
 156 for the derivatives do not satisfy the necessary accuracy requirements to guarantee the
 157 numerical stability and accuracy of computation. On the other hand, the automatic
 158 differentiation technology (Hasco and Pascual, 2012), already implemented in many
 159 other applications, can successfully build these expressions. A working example of a
 160 code based on the coupling of the differential continuation with automatic
 161 differentiation of the thermodynamic model is described in Cots et al. (2020) for the
 162 univolatility curves computation. For academic use, any package of symbolic
 163 computation can be employed. The results of pinch curves computation presented in the
 164 next section were done with Mathematica.
 165

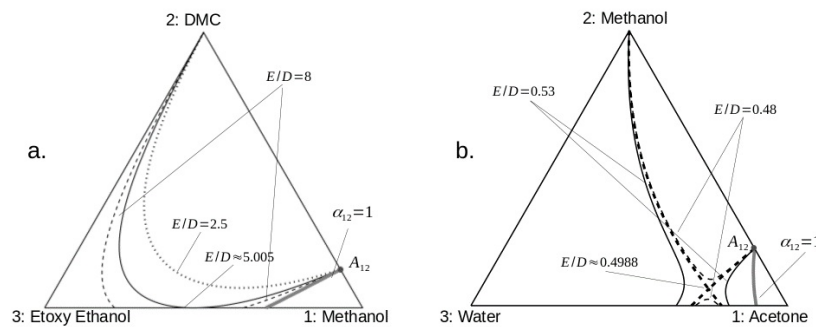


Figure 1. Serafimov's class 1.01-a. Examples of possible evolution of the pinch diagrams with the variation of E/D parameter. Case a: regular splitting of the pinch curve. Case b: splitting caused by a saddle-type bifurcation.

166 3. Case studies

167 All the pinch diagrams presented below were computed using Mathematica 9 package.
 168 We present here 4 examples corresponding to Serafimov's classes 1.01-a (Fig. 1), 1.02
 169 and 2.02-b (Fig. 2). The DIPPR equation and database were used for the vapor pressure
 170 computation. For the mixtures shown in Fig. 1 and Fig. 2 a the non-random two-liquid
 171 (NRTL) thermodynamic model was used, the VLE binary coefficients of mixtures were
 172 taken from the Simulis Thermodynamics (Prosim, 2023). For the case shown in Fig. 2b
 173 the binary coefficients were estimated using the UNIFAC modified Dortmund 1993
 174 model (Gmehling et al., 1993). The pressure is assumed constant and equal to 1 atm.

175 Fig1. shows two examples of ternary mixtures of Serafimov's class 1.01-a. (Kiva et al.,
 176 2003). In the first case methanol is separated from dimethyl carbonate (DMC) using the
 177 ethoxy ethanol as an entrainer. The pinch curve is bounded from the right by the
 178 univolatility curve α_{12} (thick grey curve) issued from the binary azeotrope A_{12} . A
 179 unique pinch curve exists for E/D smaller than 5.005. For greater values a part of the

180 pinch curve lies behind of the composition triangle, causing the regular splitting of the
 181 unique pinch curve into two disjoint branches. The situation shown in Fig.1b is different.
 182 This example describes the separation of the acetone from methanol using water as the
 183 entrainer. Near the value 0.48 of E/D , the diagram has 2 pinch branches that meet each
 184 other when $E/D=0.4988$ in the interior of Ω , and then they split again in the other
 185 direction. This is the saddle-type splitting caused by the presence of the bifurcation
 186 point of hyperbolic type verifying Eq. (9).

187 Fig. 2a provides an example of a mixture of class 2.0-2b with two binary azeotropes. It
 188 shows the evolution of the pinch curve associated to the separation of component 2
 189 from component 3 using component 1 as the entrainer. The pinch curves are limited
 190 from the left and from the right by two univolatility curves α_{13} and α_{23} . Fig. 2b shows
 191 an example of class 1.0-2 exhibiting closed type pinch curves in the zone comprised
 192 between two branches of the same univolatility curve α_{13} . Here toluene is separated
 193 from ethanol using acetone as an entrainer. The elliptic type bifurcation at the critical
 194 value $E/D=0.017$ causes the vanishment of the pinch curve for the greater values of
 195 E/D .

196 4. Conclusion

197 The new computational method presented in this paper assures an easy computation of
 198 pinch curves of ternary mixtures with high accuracy. It can be naturally generalized to
 199 compute the curves of more than three component mixtures. It is based on a geometrical

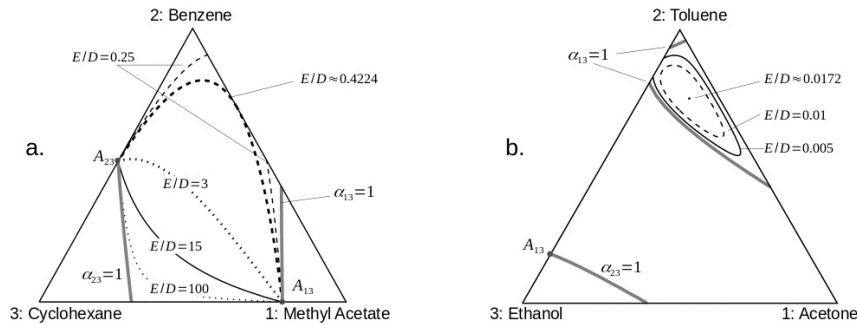


Figure. 2. Case a: Serafimov's class 2.0 – 2b. Pinch curves associated to the separation of benzene from cyclohexane using methyl acetate as the entrainer. Case b : Serafimov's class 1.0-2, pinch separation of toluene from acetone using ethanol as an entrainer. Elliptic-type bifurcation: closed pinch curves shrink into a single pinch point before disappearing.

200 model that allows to predict the bifurcation in the topological structure of pinch
 201 diagrams related to the change of operational conditions. Accurate computation of
 202 pinch branches facilitates the synthesis and design of an extractive distillation column
 203 since they give access to limiting values of reflux ratio and entrainer flow rate that help
 204 select entrainer and assess process feasibility.

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