Вестник МИТХТ, 2013, т. 8, № 2

ТЕОРЕТИЧЕСКИЕ ОСНОВЫ ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

УДК 620.181

THE LOCALIZATION OF BOUNDARIES OF THE DISTILLATION REGIONS

***L.A. Toro, associate professor, O.O. Usol'tseva, postgraduate student,**
***C.A. Cardona, professor, Yu.A. Pisarenko, professor**

M.V. Lomonosov Moscow State University of Fine Chemical Technology, Moscow, Russia
**Instituto de Biotecnología y Agroindustria, Manizales, Colombia*
**Universidad Nacional de Colombia, Sede Manizales*
**Universidad Autónoma de Manizales, Colombia*
e-mail: latoroc@unal.edu.co

The problem of constructing the boundary lines of distillation are solved using the method of constructing the separatrix line.

Key words: *distillation boundary line, method of constructing the separatrix line, distillation diagrams, distillation regions, nonideal mixtures.*

Distillation diagrams play an important role in creation of technological systems for separation of multicomponent nonideal mixtures by distillation. That diagram of distillation allows us to set the limit composition of product flows obtained in the distillation column, and on this basis to go to the synthesis of process flowsheet [1–3].

This diagram represents a phase portrait for corresponding dynamical system of distillation process. The structure of the phase portrait is defined by the type of singular points (pure components and azeotropes) and by the character of their location in the concentration simplex. Thus in the concentration simplex appear distillation areas, filled with single beam of paths – set of trajectories with common starting and ending point of the special type – unstable and stable nods. The distillation lines that make up the beam can be divided into two classes: those that have a neighborhood that is fully owned by this beam, called the internal distillation lines, the rest – the boundary distillation lines. The set of boundary lines of the beam are the boundary of distillation region.

In the case of ternary mixtures each of the distillation boundary line is the boundary of the region of distillation. In concentration spaces with more higher dimensional, the set of these lines form the separation surface of the distillation region.

The problem of constructing the boundary lines of distillation is relevant and, in this regard, a number of papers have been proposed numerical procedures for the localization of areas of distillation [4–8]. However, these procedures are very cumbersome, requires a large amount of calculation, and at the same time, the justice provisions, on which they are based, are not strictly proved. In return for the construction of distillation boundaries, we offer a simpler and more reliable way.

To solve this problem we use the method of constructing the separatrix line represented in [9].

A merit of the method is that the dynamical system of equilibrium distillation process, carried out at constant pressure ($P = const.$)

$$d\vec{X}/d\tau = \vec{Y} - \vec{X}, \qquad (1)$$

where $\vec{X} = (x_1, x_2, \ldots, x_N)$ – composition of the liquid, mol fractions; $\vec{Y} = (y_1, y_2, \ldots, y_N)$ – composition of the vapor; N – the number of substances that form a mixture; $\tau = \ln M$, M – the number of moles of liquid phase, linearized in the neighborhood of the singular point $X_S = (x_{1,S}, x_{2,S}, \ldots, x_{N,S})$, which is in accordance with the *V. T. Zharov* theorem [1], can be either a node or a saddle, we get a system of linear differential equations

$$d\vec{\xi}/d\tau = B_D\vec{\xi}, \qquad (2)$$

where $\vec{\xi} = (\xi_1, \xi_2, \ldots, \xi_N)$, $\xi_i = x_i - x_{i,S}$, $B_D = \|b_{ij}\|$, $b_{ij} = \left(\partial(y_i - x_i)/\partial x_j\right)_{P=const}$ – the coefficient matrix of the linearized system.

Let's consider the local geometry of the phase trajectories are of course common in the neighborhood of stationary points $\det(B_D) \neq 0$, where B_D – matrix of coefficients of the linearized in the neighborhood of stationary point of a dynamical system of distillation. Since this is a dynamical system of distillation, the stationary point can be either a node or a saddle.

Obviously, in a dynamic system, which has a fixed point X_S, all the trajectories (in the case of a node) or separatrix (in the case of the saddle) are adjacent to X_S and, as supplemented by a stationary point, are tangent in certain directions.

For greater clarity, we consider a dynamical system of second order. In this case, at any regular point X at time t is the slope of the tangent will be equal to

$$\Psi = \left(dx_i / dx_j\right)_D, \qquad (3)$$

and in stationary point

$$\Psi = \lim_{t \to \pm\infty} \left(dx_i / dx_j\right)_D. \qquad (4)$$

It is possible to show that directions (4) coincide with the eigenvectors of the Jacobian matrix of the right sides of the dynamical system.

If we consider the matrix B_D, as the matrix of the corresponding linear operator realizing the transformation of a linear space, the eigenvector of B_D is a vector $\vec{v} \neq 0$ which satisfies the equation

$$B_D \vec{v} = \lambda \vec{v}, \tag{5}$$

where λ – eigenvalue of B_D.

As can be seen from equation (5), an eigenvector $\vec{v}$ under the action of the matrix does not change direction, and experiences only tensile or compressive.

Column vector of coordinates of the eigenvector (the origin moved to a point X_S), $\vec{\xi}^{(i)} = \left[\xi_1^{(i)}, \xi_2^{(i)}, \ldots, \xi_N^{(i)}\right]^T$ corresponding to the eigenvalue λ_i in the general case of *N*-dimensional phase space can be found solving the system of homogeneous linear equations

$$\left(B_D - \lambda_i E\right)\vec{\xi}^{(i)} = 0. \tag{6}$$

We denote $B - \lambda_i E = A^{(i)}$, and then the system of *N* homogeneous linear equations with *N* variables can be written as

$$\sum_{k=1}^{N} a_{jk}^{(i)} \xi_k^{(i)} = 0,\ j = 1, \ldots, N. \tag{7}$$

This system has a nontrivial solution if and only if $\det\left(A^{(i)}\right) = 0.$ In this case, the equation system (7) is linearly dependent. Denote $r = \operatorname{rank} A^{(i)}$. In the particular case $r = N - 1$. Let the first $N - 1$ equations of (7) are linearly independent, then system (5) can be replaced by an equivalent system

$$\sum_{k=1}^{N} a_{jk}^{(i)} \xi_k^{(i)} = 0,\ j = 1, \ldots, N - 1. \tag{8}$$

We denote the coefficient matrix of these system $\tilde{A}^{(i)}$. The matrix $\tilde{A}^{(i)}$ is obtained from matrix $A^{(i)}$ by deleting from it the last line.

Then the solution of this system (8) can be written as

$$\begin{gathered} \xi_{1i} = (-1)^{1+1} M_1^{(i)} c,\ \xi_{2i} = (-1)^{2+1} M_2^{(i)} c,\ \ldots, \\ \xi_{Ni} = (-1)^{N+1} M_N^{(i)} c, \end{gathered} \tag{9}$$

where $M_j^{(i)}$ – is the minor obtained by deleting from the matrix $\tilde{A}^{(i)}$ of the *j*-th column; *c* – arbitrary constant.

Thus uniquely determined only by the relationship

$$\begin{gathered} \Psi_{jk}^{(i)} = \xi_j^{(i)} / \xi_k^{(i)} = \\ (-1)^{j+1} M_j^{(i)} / (-1)^{k+1} M_k^{(i)} = \\ (-1)^{j-k} M_j^{(i)} / M_k^{(i)}, \end{gathered} \tag{10}$$

As an example, consider a two-dimensional case $N = 2$, corresponding to a ternary mixture. In this case, the system of equations (7) takes the form

$$\begin{gathered} \left(b_{11} - \lambda_i\right)\xi_1^{(i)} + b_{12}\xi_2^{(i)} = 0, \\ b_{21}\xi_1^{(i)} + \left(b_{22} - \lambda_i\right)\xi_2^{(i)} = 0. \end{gathered} \tag{11}$$

The corresponding matrix $A^{(i)}$

$$A^{(i)} = \left\| \begin{matrix} b_{11} - \lambda_i & b_{12} \\ b_{21} & b_{22} - \lambda_i \end{matrix} \right\|. \tag{12}$$

Analogue of the system of equations (8) in this case is a single equation

$$\left(b_{11} - \lambda_i\right)\xi_1^{(i)} + b_{12}\xi_2^{(i)} = 0. \tag{13}$$

For the system (13), consisting of a single equation, the matrix $\tilde{A}^{(i)}$ has the form

$$\tilde{A}^{(i)} = \left\| b_{11} - \lambda_i \quad b_{12} \right\|. \tag{14}$$

From the expression (14)

$$M_1^{(i)} = b_{12},\ M_2^{(i)} = b_{11} - \lambda_i. \tag{15}$$

The solution of equation (13), taking into account the relations (15) and (9), can be written as

$$\begin{gathered} \xi_1^{(i)} = (-1)^{1+1} M_1^{(i)} c = b_{12} c, \\ \xi_2^{(i)} = (-1)^{1+2} M_2^{(i)} c = -\left(b_{11} - \lambda_i\right) c. \end{gathered} \tag{16}$$

So in the special case where $N = 2$ we can use formula (16) to determine the slopes of the eigenvectors (eigenvalues directions):

$$\begin{gathered} \Psi_{21}^{(1)} = \xi_2^{(1)} / \xi_1^{(1)} = -\left(b_{11} - \lambda_1\right) / b_{12} = \\ \left(\lambda_1 - b_{11}\right) / b_{12}, \\ \Psi_{21}^{(2)} = \xi_2^{(2)} / \xi_1^{(2)} = -\left(b_{11} - \lambda_2\right) / b_{12} = \\ \left(\lambda_2 - b_{11}\right) / b_{12}. \end{gathered} \tag{17}$$

For a saddle singular point equations (15) establish the directions in which the separatrix pairs tend to it or leave it.

Information about eigenvalues directions in the singular saddle point allows us to construct the separatrix without iterations and with sufficient accuracy. To do this, take the initial point X_0 in a small neighborhood of the saddle X_C along direction of the eigenvector. In view of the relations which are valid in the neighborhood of the stationary point of X_S

$$\xi_i = \left(x_k - x_k^S\right);\ \ \xi_k^S = 0;\ \ i = 1, \ldots, N \tag{18}$$

and equations (17) we have:

$$x_{k0}^{(i)} = x_{kC}^{(i)} + \Psi_{kj}^{(i)}\left(x_{j0}^{(i)} - x_{jC}^{(i)}\right). \tag{19}$$

The distance between X_0 and X_C should be chosen so as to satisfy the condition

$$\sqrt{\left(\sum_{k=1}^{N} (x_{k0}^{(i)} - x_{kC}^{(i)})^2\right)} \le 0.01 \text{ mol.frac.} \tag{20}$$

Constructing the separatrix (separation manifold) is carried out by numerical integration from the saddle points along their eigenvectors in the direction of adjacent stable or unstable node.

Now consider the more expressions for the derivatives, which are elements of the matrix B_D. It is known that at low pressures (≤ 1,5 at) and in the absence of vapor phase chemical reactions and molecular association can be considered ideal mixture. In this case in the conditions of phase equilibrium the relation

$$Py_i = P_i^0(T)\gamma_i x_i,\ i = 1, \ldots, N \tag{21}$$

will be true.

From equation (21) it follows

$$y_i = \frac{P_i^0(T)\gamma_i x_i}{P},\ i = 1, \ldots, N. \tag{22}$$

Taken in to account this fact, the system of equations (1) we can be rewritten in the form

$$\frac{dx_i}{d\tau} = y_i - x_i = \\ \frac{1}{P}\left[P_i^0(T)\gamma_i\left(T,\vec{X}\right) - P\right]x_i = \\ \frac{1}{P} f_i\left(P_i^0(T),\gamma_i\left(T,\vec{X}\right),x_i\right),\ i = 1,\ldots,N. \tag{23}$$

As the external pressure P is constant, the elements of the matrix B_D can be written as

$$b_{ij} = \frac{1}{P}\left\{ x_i \left[\begin{array}{l} \gamma_i\left(T,\vec{X}\right)\dfrac{\partial P_i^0(T)}{\partial T} + \\ +P_i^0(T)\left.\dfrac{\gamma_i\left(T,\vec{X}\right)}{\partial T}\right|_{P,\vec{X}} \end{array} \right] \left.\frac{\partial T}{\partial x_j}\right|_{P,x_{k\neq j}} + \right. \\ \left. +\delta_{ij}\left[P_i^0(T)\gamma_i\left(T,\vec{X}\right) - P\right] + \\ x_i P_i^0(T)\left.\frac{\gamma_i\left(T,\vec{X}\right)}{\partial x_j}\right|_{P,T,x_{k\neq j}} \right\}, \\ i, j = 1,\ldots,N, \tag{24}$$

where δ_{ij} – Kronecker delta:

$$\delta_{ij} = \begin{cases} \delta_{ij} = 1, \text{ if } i = j, \\ \delta_{ij} = 0, \text{ if } i \neq j. \end{cases}$$

To calculate the derivative $\dfrac{\partial P_i^0(T)}{\partial T}$ using extended Antoine equation in the form

$$P_i^0(T) = \exp\left[\begin{array}{c} A_i + B_i/(C_i + T) + \\ D_i \ln T + E_i T^{F_i} \end{array}\right] [\text{kPa}], \tag{25}$$

In this paper, the calculation of the activity coefficients of the components of the liquid phase was carried out using the equation *NRTL*

$$\ln\gamma_i = \frac{\sum\limits_{j=1}^{N}\tau_{ji}x_jG_{ji}}{\sum\limits_{k=1}^{N}x_kG_{ki}} + \\ +\sum_{j=1}^{N}\frac{x_jG_{ij}}{\sum\limits_{k=1}^{N}x_kG_{kj}}\left(\tau_{ij} - \frac{\sum\limits_{m=1}^{N}\tau_{mj}x_mG_{mj}}{\sum\limits_{k=1}^{N}x_kG_{kj}}\right), \tag{26}$$

$$\tau_{ji} = a_{ij} + b_{ij}/T, [\text{K}];\ G_{ij} = \exp\left(-c_{ij}\tau_{ji}\right).$$

The derivatives $\left.\dfrac{\gamma_i\left(T,\vec{X}\right)}{\partial T}\right|_{P,\vec{X}}$ and $\left.\dfrac{\gamma_i\left(T,\vec{X}\right)}{\partial x_j}\right|_{P,T,x_{k\neq j}}$ may be found from the equation (26).

The calculation of the derivative $\dfrac{\partial T}{\partial xj}\Big|_{P,x_k \neq j}$, presented in the right side of equation (24), carry out, taking into account that the distillation pressure is constant:

$$P = \sum_{k=1}^{N}P_k^0(T)\gamma_k\left(T,\vec{X}\right)x_k = const. \tag{27}$$

From this relation it follows

$$\left.\frac{\partial P}{\partial x_j}\right|_{x_{m\neq j}} = \frac{\partial}{\partial T}\left.\left(\sum_{k=1}^{N}P_k^0(T)\gamma_k\left(T,\vec{X}\right)x_k\right)\right|_{\vec{X}}\left.\frac{\partial T}{\partial x_j}\right|_{x_{m\neq j}} + \\ +\frac{\partial}{\partial x_j}\left.\left(\sum_{k=1}^{N}P_k^0(T)\gamma_k\left(T,\vec{X}\right)x_k\right)\right|_{T,{m\neq j}} = 0. \tag{28}$$

Express the derivative $\left.\dfrac{\partial T}{\partial x_j}\right|_{P,x_{k\neq j}}$ from the relation (28):

$$\left.\frac{\partial T}{\partial x_j}\right|_{P,x_{m\neq j}} = -\frac{\sum\limits_{k=1}^{N}P_k^0(T)\left(\delta_{kj}\gamma_k\left(T,\vec{X}\right) + x_k\left.\dfrac{\partial\gamma_k}{\partial x_j}\right|_{T,x_{m\neq j}}\right)}{\sum\limits_{k=1}^{N}x_k\left(P_k^0(T)\left.\dfrac{\partial\gamma_k\left(T,\vec{X}\right)}{\partial T}\right|_{\vec{X}} + \gamma_k\dfrac{\partial P_k^0(T)}{\partial T}\right)}. \tag{29}$$

It should be noted that when taking the derivative of the activity coefficient and the temperature on the concentrations, the latter acting as the independent variables. However, concentrations expressed in mole or mass fractions, add up to one, hence independent of them can only be (N – 1). We choose as independent variables the first (N – 1) concentrations. In this case $x_N = x_N\left(x_1, x_2, \ldots, x_{N-1}\right)$. Taking into account the relation

$$\sum_{k=1}^{N}x_k = 1. \tag{30}$$

we shall have

$$\left(\frac{\partial x_N}{\partial x_j}\right)_{x_{k\neq N}} = -1. \tag{31}$$

Therefore, the derivatives can be written as

$$\left.\frac{\partial\gamma_i}{\partial x_j}\right|_{T,\hat{x}_{k\neq j}} = \\ \left.\frac{\partial\gamma_i}{\partial x_j}\right|_{T,x_{k\neq j}} + \left.\frac{\partial\gamma_i}{\partial x_N}\right|_{T,x_{k\neq N}}\cdot\left.\frac{\partial x_N}{\partial x_j}\right|_{x_{k\neq N}} = \\ \left.\frac{\partial\gamma_i}{\partial x_j}\right|_{T,x_{k\neq j}} - \left.\frac{\partial\gamma_i}{\partial x_N}\right|_{T,x_{k\neq N}}. \tag{32}$$

Similarly

$$\left.\frac{\partial T}{\partial x_j}\right|_{\hat{x}_{k\neq j}} = \left.\frac{\partial T}{\partial x_j}\right|_{x_{k\neq j}} - \left.\frac{\partial T}{\partial x_N}\right|_{x_{k\neq N}}. \tag{33}$$

Now we explain the conditions under which the partial derivatives are taken. Subscript for the partial derivative $T, x_{k\neq j}$ indicates that the derivatives are taken at constant temperature and constant concentration of all substances, except substances with the number *j*. Subscript $T, \hat{x}_{k\neq j}$ denotes, that in addition to a constant temperature, the concentrations of first (n – 1) substances remain constant, except the concentration of the substance to the number *j*.

Based on the considerations made by us, (32) and (33) can be conveniently written as

$$\left.\frac{\partial\gamma_i}{\partial x_j}\right|_{T,x_{m\neq j}} = \left.\frac{\partial\gamma_i}{\partial x_j}\right|_{T,x_{k\neq j}} - \left.\frac{\partial\gamma_i}{\partial x_N}\right|_{T,x_{k\neq N}}, \tag{34}$$

$$\left.\frac{\partial T}{\partial x_j}\right|_{x_{m\neq j}} = \left.\frac{\partial T}{\partial x_j}\right|_{x_{k\neq j}} - \left.\frac{\partial T}{\partial x_N}\right|_{x_{k\neq N}} . \tag{35}$$

Where the index m changes from 1 to $(n-1)$ and appropriate to independent concentration the total number of which is equal to $(n-1)$. At the same time, the index k varies from 1 to N, and corresponds to the concentration of any of the substances, the total number of which is N.

The following is the algorithm used in this paper for localization and construction of separation manifolds of the distillation diagrams in ternary systems.

Background information: a mixture, the pressure, the *NRTL* and extended Antoine equation coefficients .

To find singular points. To do this, it is necessary to solve the nonlinear system

$$d\vec{X}/d\tau = \vec{Y} - \vec{X} = 0. \tag{36}$$

This is a nonlinear equation system of second order, which is solved using both equilibrium relation and the *NRTL* equation, means Newton method.

Linearization of the dynamical system given by Eq. (1) in each singular point. The linearized dynamical system is:

$$d\vec{\xi}/d\tau = B_D\vec{\xi}, \tag{37}$$

The elements of B_D, the Jacobian matrix of the system, are calculated analytically means both equilibrium relation (1) and the *NRTL* model given by equations (25)–(26). For each singular point, the Jacobian matrix is calculated (see equations (27)–(35)).

Once the dynamical system is linearized, the next step is to find the eigenvalues and eigenvectors for each singular point. To do this, for each singular point their eigenvalues $(i = 1, 2)$ are calculated by solving the equation:

$$\det(B_D - \lambda) = 0. \tag{38}$$

Since the analyzed dynamical system is for a distillation process, the critical points can be either a node or a saddle [1]. **Case 1***:* Both eigenvalues are positive. This is the point reached as τ tends to $-\infty$, and is where all residue curves in a given region terminate. Thus, it is the pure component or azeotrope with the highest boiling point in the region. This point is a stable node because it is like the low point of a valley, in which a rolling ball finds a stable position. **Case 2**: Both eigenvalues are negative. This is the point where all residue curves in a region originate, and is the pure component or azeotrope with the lowest boiling point in the region. This point is an unstable node because it is like the top of a mountain from which a ball rolls toward a stable position. **Case 3.** One eigenvalue is positive and one is negative. Residue curve maps within the triangle move toward and then away from such saddle point. For a given region, all pure components and azeotropes intermediate in boiling point between the stable node and the unstable node are saddles. The eigenvectors $\vec{\xi}^{(i)}$ $(i = 1, 2)$ can be found solving the system of homogeneous linear equations

$$\left(B_D - \lambda_i E\right)\vec{\xi}^{(i)} = 0, \tag{39}$$

where E is the identity matrix of second order.

For each saddle: (a) For every eigenvector corresponding to a positive eigenvalue, integrate Eq. (1) backward in τ from the saddle(i) in a direction along the eigenvector and(ii) in a direction opposite to the eigenvector, omitting directions in the integration that point outside the composition space; (b). For each eigenvector corresponding to negative eigenvalue repeat the previous step, but integrate forward in τ. The integration procedure is started for cdoncentration value of the saddle point that is being considered and is stopped when the residue curve approaches any singular point (other than the one it started from) withtin a Euclidean distance given by Eq. (20). For each eigenvector direction of each saddle point the residue curve may connect a stable node or an unstable node, but no another saddle point (Peixoto's Theorem [10, 11]), except when the two saddle points are located in the vertices of concentration triangle (in this cause the dimension of the space of concentration, which owns the separatrix, is unity). This kind of connection is a edge (of part of it) that is boundary of the adjoining distillation regions (separation manifolds) in which the concentration triangle is divided. If the saddle point is a binary azeotrope, one of its corresponding residue curve is a straight line that connects it with the nodes located in the vertices of the corresponding edge, that constitutes a boundary for the regions created by de saddle point, and this is because the direction of one of its eigenvectors coincides with the edge that connects the two singular points; the residue curve that corresponds to another eigenvector may connect either a stable or an unstable node. If the saddle point is a ternary azeotrope it may reaches an unstable node that also is interior or unstable o stable nodes locate in triangle vertices or edges (binary azeotrope). If a binary azeotrope is a stable or unstable node, it is connected by a straight line to the adjacent vertices of the concentration triangle. These lines are boundaries of two adjacent separation manifolds. If an unstable node is interior to the triangle it is reached by at least a saddle point or by a stable node. If the saddle point is a vertex of the concentration triangle it is connected to other vertices by straight lines, because the directions of its eigenvectors coincide with the directions of the two sides. In this form, the concentration triangle is divided in finitely many of different separation manifolds perfectly located and defined by their respective boundaries. A separation manifold contains a stable node, and unstable node and at least a saddle point.

To construct the equilateral triangle of concentrations, display separation lines and boundary of triangle. This lines together form boundaries of distillation regions.

To construct some residue curve for each region means the usual procedure of integrating the dynamical system (1).

The algorithm previously described was used for writing down a Matlab® based program. This algorithm, and the program based on it was used to construct the boundaries of distillation 76 ternary mixtures. Here we present results of a study of some diagrams, namely the system Acetone–Chloroform–Methanol, Dichloroethane–Trichloroethane–Propanol and Methylethylketone–Benzene–Isopropanol. Tables 1–4 show the parameters of the ternary mixtures needed to build the corresponding distillation diagrams.

Table 1. Parameters six parametric Antoine equation, see equation (25)

	AC	CLF	MET	DCLE	TCLE	PR	MEK	BNZ	IPR
A_i	71.3031	73.7058	59.8373	73.2566	93.2846	79.4625	73.6555	169.6500	83.6370
B_i	-5952.00	-6055.60	-6282.89	-6499.80	-7360.26	-8294.91	-6465.24	-10314.8	-8249.01
C_i	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
D_i	-8.5313	-8.9189	-6.37873	-8.7177	-11.7913	-8.9096	-8.7920	-23.5895	-9.5452
E_i	7.82E-06	7.74E-06	47.6E-06	6.45E-06	9.08E-06	1.82E-06	6.90E-06	2.09E-05	2.00E-06
F_i	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

AC – Acetone; **CLF –** Chloroform; **MET –** Methanol; **DCLE –** Dichloroethane; **TCLE –** Trichlo-roethane; **PR –** Propanol; **MEK–** Methylet-hylketone; **BNZ –** Benzene; **IPR –** Isopropanol

Table 2**.** NRTL equation parameters for the system Acetone (1)–Chloroform (2)–Methanol (3)

	12	13	23
a_{ij}	0.00	0.00	0.00
a_{ji}	0.00	0.00	0.00
b_{ij}	151.9297	149.1131	-67.6285
b_{ji}	-327.7751	59.4353	686.8933
c_{ij}	0.3054	0.3003	0.2932
c_{ji}	0.3054	0.3003	0.2932

Table 3. NRTL equation parameters for system Dichloroethane (1)–Trichloroethane (2)–Propanol (3)

	12	13	23
a_{ij}	0.00	0.00	0.00
a_{ji}	0.00	0.00	0.00
b_{ij}	108.3451	132.8825	-28.1331
b_{ji}	12.1599	328.3886	632.7492
c_{ij}	0.3015	0.2971	0.2925
c_{ji}	0.3015	0.2971	0.2925

Table 4. NRTL equation parameters for systemMethylethylketone (1)–Benzene (2)–Isopropanol (3)

	12	13	23
a_{ij}	0.00	0.00	0.00
a_{ji}	0.00	0.00	0.00
b_{ij}	184.3350	-12.9325	166.8225
b_{ji}	-99.8608	170.2266	392.1955
c_{ij}	0.3093	0.3017	0.2913
c_{ji}	0. 3093	0. 3017	0. 2913

Tables 5–7 present the report about the number of the singular points and their characterization given by program for each system. The characterization consists of: (a) type of singular point (stable node, unstable node and saddle point), (b) molar fraction of the singular point which indicates if the singular point is pure component, binary or ternary and (c) its temperature.

Table 5. Singular point report for system Acetone (1)–Chloroform (2)–Methanol (3), P = 101.00 kPa

№	x_1, *mol.f.*	x_2, *mol.f.*	x_3, *mol.f.*	T, ºC	Point type
1	1.000	0.000	0.000	55.99	Saddle
2	0.421	0.579	0.000	63.88	Stable node
3	0.000	1.000	0.000	61.11	Saddle
4	0.790	0.000	0.210	55.15	Unstable node
5	0.368	0.162	0.469	56.87	Saddle
6	0.000	0.487	0.513	54.48	Unstable node
7	0.000	0.000	1.000	64.40	Stable node

Table 6. Singular point report for system Dichloroethane (1)–Trichloroethane (2)–Propanol (3), P = 101.00 kPa

№	x_1, *mol.f.*	x_2, *mol.f.*	x_3, *mol.f.*	T, ºC	Point type
1	1.000	0.000	0.000	83.32	Stable node
2	0.680	0.320	0.000	82.20	Saddle
3	0.000	1.000	0.000	86.97	Stable node
4	0.543	0.221	0.236	80.65	Unstable node
5	0.742	0.000	0.258	81.20	Saddle
6	0.000	0.626	0.374	83.26	Saddle
7	0.000	0.000	1.000	97.09	Stable node

Table 7. Singular point report for system Methylethylketone(1)–Benzene(2)–Isopropanol (3), P = 101.00 kPa

№	x_1, *mol.f.*	x_2, *mol.f.*	x_3, *mol.f.*	T, ºC	Point type
1	1.000	0.000	0.000	79.63	Stable node
2	0.461	0.539	0.000	77.77	Saddle
3	0.000	1.000	0.000	78.68	Stable node
4	0.626	0.000	0.374	78.04	Saddle
5	0.000	0.556	0.444	71.14	Unstable node
6	0.000	0.000	1.000	82.18	Stable node

Figure 1 (a, b ,c) presents for each ternary system the separation manifolds with the respective boundaries as they are predicted by step 5 of the proposed algorithm.

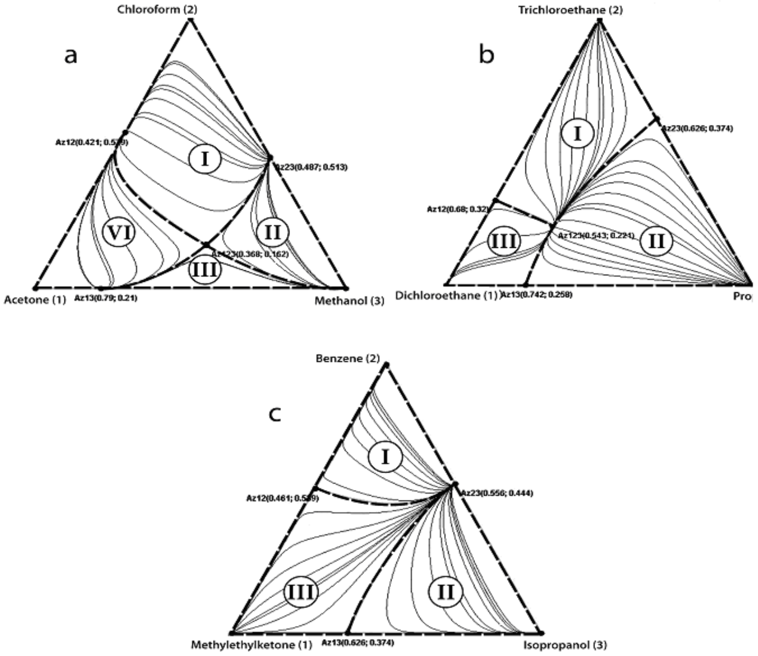

Figure 1. Distillation regions of three-component systems: a – Acetone (1)–Chloroform (2)–Methanol (3);
b – Dichloroethane (1)–Trichloroethane (2)–Propanol (3);
c – Methylethylketone(1)–Benzene(2)–Isopropanol(3).

The calculation shows (see Figure 1a) that in the ternary system Acetone (1)–Chloroform (2)–Methanol (3) has seven critical points: pure components Acetone (1) and Chloroform (2) are saddles, while Methanol is a stable node; the binary azeotrope Acetone (1) –Chloroform (2) is a stable node; the binary azeotrope Chloroform (2)–Methanol (3) is an unstable node; the binary azeotrope Acetone(1)–Chloroform (3) is an unstable node; the ternary azeotrope is a saddle. The ternary azeotrope is connected to the binary azeotropes and to the stable node Methanol (3). The connections are made in the increasing temperature. In this way, the ternary diagram for the system under study is divided in four manifolds perfectly located and defined by their respective boundaries as shown in Figure 1,a. Any separation manifold contains a stable node, and unstable node and at least a saddle point. The boundaries of distillation areas are ternary saddle separatrix together with the elements which locate of the boundary of the triangle diagram.

The diagrams, shown in Figure 1b and Figure 1c, are interpreted in a similar way. In the ternary system Dichloroethane (1)–Trichloroethane (2)–Propanol (3), Figure 1b, three distillation areas have one a common point – ternary azeotrope, acting as an unstable node. Ternary system Methylethylketone (1)–Benzene (2)–Isopropanol (3), Figure 1c, also includes three distillation areas with the total singular point that is a binary azeotrope of benzene-isopropanol.

On the diagrams shown in Figure 1, almost all of the separatrix are very nonlinear curves, however, the algorithm, presented in this paper, can reproduce them with a high degree of accuracy. The latter indicates the simplicity and reliability of the algorithm and the program that implements it.

REFERENCES:

1. Zharov V.T., Serafimov L.A. Physico-Chemical Fundamentals of Distillation and Rectification. L.: Chemistry, 1975. 239 p.

2. Doherty M.F, Malone M.F. Conceptual Design of Distillation System. NY: McGraw-Hill, 2001. 586 p.

3. Petlyuk F.B. Distillation Theory and Its Application to Optimal Design of Separation Units. Cambridge: Cambridge University Press, 2004. 336 p.

4. Van Dongen D.B, Doherty M.F. On the dynamics of distillation processes vs. the topology of the boiling temperature surface and its relation to azeotropic distillation // Chem. Eng. Sci. 1984. V. 39. P. 883–892.

5. Foucher E.R., Doherty M.F, Malone M.F. Automatic screening of entrainers for homogeneous azeotropic distillation // Ind. Eng. Chem. Res. 1991. V. 29. P. 760–772.

6. Peterson E. ., Partin L.R. Temperature sequences for categorizing all ternary distillation boundary maps // Ind. Eng. Chem. Res. 1997. V. 36. P. 1799–1811.

7. Rooks R.E., Julka V., Doherty M.F., Malone M.F. Structure of distillation regions for multicomponent azeotropic mixtures // AIChE J. 1988. V. 44. P. 1382–1391.

8. Pöpken T., Gmehling J. Simple method for determining the location of distillation region boundaries in quaternary systems // Ind. Eng. Chem. Res. 2004. V. 43. P. 777–783.

9. Mozguhin A.S., Mitropolskaya V.A., Tihonova N.K. Analysis of the vapor–liquid equilibrium diagrams structures. M.: MITHT, 1988. 93 p.

10. Peixoto M.M. On structural stability // Ann. Mathematics. Second Ser. 1959. V. 69. № 1. P. 199–222.

11. Peixoto M.M. Structural Stability on Two-Dimensional Manifolds. Topology: Pergamon Press, 1962. 46 p.