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Предложен метод расчета наиболее вероятных составов продуктов разделения атермальных смесей в сложных ректификационных системах, к которым относятся системы простых колонн с рециклами и без них, сложные колонны с боковыми отборами, системы со связанными тепловыми потоками и другие. В основе метода лежит расширенная версия принципа максимальной энтропии. В качестве критерия вероятности распределения компонентов в продуктовых потоках системы, которое отвечает максимуму энтропии сложного опыта при соблюдении балансовых ограничений. Показано, что учет атермальных свойств смеси приводит к зависимостям, в которые входят энтропийные коэффициенты активности, связанные с условной энтропией, в характерной для термодинамики форме. Зависимости для идеальных смесей оказываются частным случаем полученных соотношений. Дан способ расчета энтропийных коэффициентов активности как функции относительных объемов молекул компонентов и мольного состава смеси. Предложенный метод ориентирован на проектный вариант расчета ректификационной системы. Он позволяет при заданных ограничениях на качество продуктов определить параметры, характеризующие протяженность процесса (число теоретических ступеней разделения в безотборном режиме), и составы продуктовых потоков. Учет атермальности смеси приводит к увеличению протяженности процесса и не оказывает существенного влияния на составы продуктов. Дано сопоставление результатов расчета составов продуктовых потоков типовой газофракционирующей установки с учетом и без учета атермальных свойств разделаемой смеси с данными промышленного эксперимента.

Ключевые слова: ректификация, атермальная смесь, сложная система, распределение компонентов, принцип максимальной энтропии, энтропия сложного опыта

COMPOSITIONS CALCULATION OF COMPLEX DISTILLATION SYSTEM PRODUCT FLOWS BASED ON THE EXTENDED VERSION OF THE MAXIMUM ENTROPY PRINCIPLE

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A method for calculating the most likely product compositions of athermal mixture separation in complex distillation systems, including systems of simple recycling and non-recycling columns, complex columns with side sampling, systems with joint heat flows, and others. The method is based on an extended version of the maximum entropy principle. The informational entropy of complex experiment involving conditional entropy and conditional probabilities is used as the like-
lihood criterion. The adopted axiomatic allows one to obtain the most probable component distributions in the product flows of the system, which corresponds to the complex experience maximum entropy in accordance with the balance restrictions. It has been demonstrated that athermal properties accounting of the mixture create dependencies that include entropic activity coefficients associated with the conditional entropy in a typical thermodynamics form. Dependencies are a special case of the correlations obtained for ideal mixtures. The method for calculating the entropy activity coefficients as functions of the components molecule relative volumes and the mixture molar composition has been provided. This method is focused on the design version of the distillation system calculation. It allows to determine the parameters characterizing the process length (the number of theoretical separation steps in the non-selective mode) and the product flow composition products under the product quality restrictions. The accounting of mixture athermal nature leads to an increased duration of the process and has a slight impact on the product compositions. A comparison is given of the results of the calculation of the composition of the product flows of a typical gas fractionating unit with and without taking into account the athermal properties of the mixture to be separated with the data of an industrial experiment.

Key words: distillation, athermal mixture, complex system, component distribution, maximum entropy principle, entropy of complex experience

ENTROPIC ACTIVITY COEFFICIENT

As it has been mentioned before, the maximum likelihood criterion, along with Shannon's entropy, also includes conditional entropy and conditional probabilities while accounting the athermal mixture properties. By conditional probability should be meant the probability of randomly detected particle of one type in an athermal mixture, provided that, in the case of an ideal mixture, a particle of another type will be detected in its place. In the reference [16] we can see the relationship between conditional probabilities and relative micro-particle sizes; and the continuity of relation of conditional probability to the component mole fraction \( a \) in a binary mixture has been established:

\[
p_{12} = q x_2, \quad p_{21} = q x_1.
\]  
(1)

Here \( p_{12} \) is the conditional probability that particle 2 will be detected in the sequence of particles randomly extracted from the athermal mixture in place of particle 1 in the case of an ideal mixture; \( p_{21} \) is the same for second type of particle; \( x_1, x_2 \) are the mole fractions of components 1 and 2 in the mixture; \( q \) is the athermal coefficient of a binary mixture, which characterizes the degree of athermality of the mixture and does not depend on the composition just the same like the \( \delta \) relative particle size.

For an ideal binary mixture \( \delta = 1, q = 0 \) are used. For another extreme case, when the particles differ in size by an arbitrarily large value \( \delta = 0, q = 1 \) are used.

Since the relation between the conditional probability and the athermal coefficient is very simple (1), it is more convenient to use athermal coefficients, rather than relative particle sizes in practical calculations. To go from \( \delta \) to \( q \), we have compiled a table of athermal coefficients and proposed a transition to multicomponent mixtures [16]. In the latter case, a matrix of athermal coefficients is compiled according to the table \( q_{ik} \) \((i, k = \overline{1,m})\) based on the analysis of the relative particle size values of each pair of multicomponent mixture components \( \delta_{ik} \) \((i, k = \overline{1,m})\). The volume of the largest particle is always considered as a unit.

With the athermal coefficients and the multicomponent mixture composition, it is possible to calculate the conditional probabilities

\[
p_a = \frac{q_{ik} x_i}{x_i + x_i (1-q_{ik})} / \sum_{i=1}^{m} \frac{q_{ik} x_i}{x_i + x_i (1-q_{ik})}, \quad i, k = \overline{1,m},
\]  
(2)

where \( q_{0i} = 1 \).

The formula (2) shows that values \( p_a \) depend on the concentrations. However, when it is about solving the problem of the component distribution in the product flows system, conditional probabilities will be

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assumed to be fixed at each step of the iterative calculation procedure.

By knowing the conditional probabilities, one can calculate the conditional entropies related to each component

\[ H_i = \sum_{i=1}^{m} p_{ij} \ln p_{ij}, \quad i = 1, m, \]

and the component entropic activity coefficients [17]

\[ \gamma_i = \exp(-H_i), \quad i = 1, m. \]

To calculate the entropic activity coefficients, according to (2)–(4), it is necessary to have a matrix of athermal coefficients and composition of the mixture.

**MOST PROBABLE COMPONENT DISTRIBUTION**

Let's consider a distillation system designed to separate the original m-component athermal mixture into p products (flows). Let's define the consumption of the j product, reduced to one mole of the source mixture (relative molar selection of the product),

\[-e_i \quad (j = 1, p); \]

molar concentration of the i component in the source mixture – \( z_i \) \((i = 1, m)\); the molar concentration of the i component in the j product – \( x_{ij} \) \((i = 1, m, \ j = 1, p)\).

Let's formulate the problem of the most probable distribution of components between the product flows of a complex distillation system. Following Jaynes’s model, and taking into account the peculiarities of the similar problem formulation in distillation ideal mixtures [14], we will present the source information in the following form: the molar concentration of the i component in the j product

\[ \sum_{j=1}^{p} e_j x_{ij} = z_i, \quad i = 1, m, \]

\[ \sum_{j=1}^{p} x_{ij} = 1, \quad j = 1, p - 1, \]

\[ e_j \sum_{i=1}^{m} a_{ij} x_{ij} = \langle a_{ij} \rangle, \quad j = 1, p - 1, \]

where \( a_{ij} = a_{ij}^0 - a_{ji} \); \( a_{ij}^0 \) is a phenomenological coefficient that evaluates the problem’s characteristic property of the i component under the conditions (temperature and pressure) of the j product; \( \langle a_{ij} \rangle \) is an average value (mathematical expectation) of coefficients \( a_{ij}^0 \) for the j product.

Equations (5) follow from the material balance of the system, and (6) – conditions for the normalization of concentrations. The equation (6), recorded for the flow \( p \), was not included in the operand because it is not independent.

Equations (7) are typical of the entropic modeling method [13, 14]. They introduce the component properties and fix the separation degree in the system when setting the task. The number of equations (7) corresponds to the number of restrictions that should be imposed on the system (apart from material balances and specified product selections) so that the task acquire physical significance. It is assumed that the coefficients \( a_{ij}^0 \) in equations (7) depend on the type of molecules and external parameters (temperature and pressure) at the product sampling points. The problems with phase transformations of ideal mixtures can be expressed through phase equilibrium constants and the relative volatility component coefficients:

\[ a_{ij} - a_{ji} = (a_{ij}^0 - a_{ji}^0) - (a_{ij}^0 - a_{ji}^0) = \]

\[ = \ln \sqrt{K_{ij}^o K_{ji}^o} - \ln \sqrt{K_{ij}^0 K_{ji}^0} = \ln a_{ij} i = 1, m, \ j = 1, p - 1, \]

where \( K_{ij}^0 \) is a phase equilibrium constant of the i component for the conditions of the j product; \( K_{ij}^0 \) is the same for the reference component \( n \) with the arbitrary choice; \( a_{ij} \) is an effective coefficient of relative volatility of the i component for the j product.

The expression (8) is also true for athermal mixtures, if the phase equilibrium constant is taken not the ratio of equilibrium concentrations, but the ratio of product concentrations to entropic activity coefficients [17, 18].

Therefore, the solution of this problem lies in the determination of the product flow compositions \( x_{ij} \) given \( e_j, z_i, a_{ij}, \langle a_{ij} \rangle \). Since generally the number of dimensionalities is greater than the number of equations (5)–(7), it is possible to find only the most probable (likely) component distribution law. To evaluate the uncertainty of the determinates we will use an extended version of the maximum entropy principle, in which the likelihood criterion is the complex experience entropy

\[ H = -\sum_{j=1}^{p} \left[ e_j \left( \sum_{i=1}^{m} x_{ij} \ln x_{ij} + \sum_{i=1}^{m} x_{ij} H_{ij} \right) \right]. \]

Here \( H_{ij} \) is a conditional entropy related to the i component in the j flow.

Formally, the problem is as follows: when the values are known \( z_i \) \((i = 1, m)\) and \( e_j \) \((j = 1, p)\), as well as given values \( a_{ij} \) \((i = 1, m, \ j = 1, p)\), \( \langle a_{ij} \rangle \), \( p d' \) \((i, k = 1, m, j = 1, p)\), the task is to find such values \( x_{ij} \) \((i = 1, m, \ j = 1, p)\), which would afford the maximum entropy (9) subject to restrictions (5)–(7).

We use the Lagrange multiplier method to solve the problem. Introducing undetermined multipliers \( \alpha_i \) \((i = 1, m)\), \( \mu e_i, \lambda_j \) \((j = 1, p)\) for restrictions (5)–(7), you can come up with the following solution:

\[ -e_j (1 + \ln x_{ij}) + e_j H_{ij} + \sigma e_j + \mu e_j + \lambda e_j a_{ij} = 0, \]

\[ i = 1, m, \ j = 1, p. \]
In the used notation \( \lambda_p = \mu_p \varepsilon_p = 0 \). After that, we have a closed system of equations (5)–(7) and (10) to determine the unknown concentrations and Lagrange multipliers.

The solution of the obtained system of algebraic equations is similar to [14]. Using (5), from the expressions (10) it is possible to exclude the multipliers \( \sigma_i \):

\[
x_j = z_i \exp(\mu_j + \lambda_j a_y + H_y) \frac{\sum_{i=1}^{p-1} e_j \exp(\mu_j + \lambda_j a_y + H_y)}{\sum_{i=1}^{p-1} e_j},
\]

where \( \sigma_i = \frac{1}{1, m}, \quad j = 1, p \).

In order to determine multipliers \( \mu_j, \varepsilon_j \) we could use equations (6) or (7), however, we will go the other way. In the practice of calculations, it can happen there are no values \( a_p \) given that limit the degree of separation according to the original formulation of the problem, but the concentration of individual components in the system product flows. Therefore, instead of \( p-1 \) equations (7), we introduce \( p-1 \) equations (11), recorded for given concentrations \( x_j \). These new restrictions can be brought to a linear equation system for \( \exp(\mu_j) \):

\[
\sum_{j=1}^{p-1} e_j \exp(\lambda_j a_y) \exp(\mu_j) = -e_j \exp(\lambda_j a_y) \exp(\mu_j),
\]

where \( f = 1, p-1 \),

\[
C_j \begin{cases} \exp[\lambda_j (a_y - a_m) + H_y], & \text{if } j \neq l, \\ \frac{1 - x_j e_j}{x_j e_j}, \exp[\lambda_j (a_y - a_m) + H_y], & \text{if } j = l. \end{cases}
\]

When solving system of linear equations (12), we find

\[
\exp(\mu_j) = \frac{e_j}{\exp(\lambda_j a_y - a_m) \exp(\mu_j) D_j} D_j,
\]

where \( D_p = \det C_j; \quad D_j = -\sum_{j=1}^{p-1} A_j C_j; \quad f = 1, p-1 \); \( A_{j} \) - algebraic matrix complement with elements \( C_j \) in the determinant \( D_p \).

Substituting the value \( \exp(\mu_j) \) into the equations (11), taking into accounting (4) and (8), we get the final solution:

\[
x_j = z_i a_i \gamma_{i j} D_j e_j \sum_{j=1}^{p-1} a_i \gamma_{i j} D_j, \quad i = 1, m, \quad j = 1, p \),
\]

where

\[
C_j = \begin{cases} a_i \gamma_{i j}, & \text{if } j \neq l, \\ \frac{1 - x_j e_j}{x_j e_j}, a_i \gamma_{i j}, & \text{if } j = l. \end{cases}
\]

For \( p = 2 \), we have formulas to calculate the compositions of the athermal mixture product separation in a simple (two-product) column.

The distribution (13) corresponds to the linear relation

\[
\lambda_j = \ln \left( \frac{X_i Y_m X_j Y_p}{X_m Y_i X_p Y_j} \right) / \ln \frac{a_j}{a_j}, \quad i, k = 1, 2, \quad i \neq k,
\]

which is a generalization of the known in the distillation theory of the Fenske-Underwood equation. The latter is obtained as a special case for ideal mixtures with \( \gamma_{i j} = 1 \) (\( i = 1, m, \quad j = 1, p \)). Therefore, the Lagrange multipliers \( \lambda_j \) have the physical significance of the minimum number of theoretical contact stages necessary to separate the source mixture into products from \( j \) to \( p \) from the point of view of the equilibrium distillation theory.

Since the final calculated dependencies contain only the difference of phenomenological coefficients \( a_i^0 \), their point of reference does not affect the structure of the final formulas, but leads only to a new reference system of Lagrange multipliers introduced for restrictions (7). This work provides the reference coefficients \( a_i^0 \) with their values sampled at temperature and pressure of \( p \) flow. It is convenient to use such a reference system when the concentrations of target components in flows are set from 1 to \( p-1 \). Under the statement of the problem the component concentration in one of the intermediate product flows of the system is not fixed, then the point of reference of the coefficients \( a_i^0 \) would be more convenient to transfer to the temperature and pressure of this flow [14].

**Algorithm and Calculation Sample**

The dependencies (13) are focused on the design version of the complex system calculation. Together with (6) they allow us to determine the conditional depth of system elements (sections of complex column) \( \lambda_j \) and distribution of components in product flows \( x_j \) at known parameter values \( z_i, e_j, a_{ij}, q_{ik} \) (\( i, k = 1, m, \quad j = 1, p \)), as well as predetermined concentrations of target components \( x_{li} \) in \( p-1 \) separation products. The coefficients of the component relative volatility at the beginning of the calculation are taken for the temperature of the output flowed at the approximate estimation. Having determined the composition of the output flows, these temperatures are elaborated and, if necessary, recalculated.

Since the entropic activity coefficients in expressions (13) depend on the product flow compositions, which are yet to be determined, the calculation algorithm becomes iterative:

1. originally, all activity coefficients are taken equal to one, i.e. the mixture is considered ideal;
2. parameter values are found \( \lambda_j \) as a result of solving the system of equations (6) and (13);
3) the composition of product flows is calculated according to the formulas (13);
4) the activity coefficient values are specified by formulas (2)–(4), using the compositions calculated in the previous step;
5) the calculation is repeated, starting from point 2, until there is a coincidence of the compositions obtained in two successive iterations with a preset accuracy.

Below you can find a comparison of the calculation results of the product flow composition of an ordinary gas fractionation unit (complex system) according to the offered model (6), (13) with the data of an industrial experiment. The installation consists of three distillation columns and divides the initial hydrocarbon mixture into four products: 1 – propane fraction \( \epsilon_1 = 0.279, T_1 = 325 \text{ K}, P_1 = 1.67 \text{ MPa} \), 2 – isobutane fraction \( \epsilon_2 = 0.113, T_2 = 327 \text{ K}, P_2 = 0.80 \text{ MPa} \), 3 – butane fraction \( \epsilon_3 = 0.225, T_3 = 344 \text{ K}, P_3 = 8.3 \text{ MPa} \) and 4 – pentane fraction \( \epsilon_4 = 0.383, T_4 = 387 \text{ K}, P_4 = 0.65 \text{ MPa} \). The source mixture composition, the experimental compositions of the separation products, as well as other primary source data are given in Table 1. The volumes of the component molecules needed to calculate the relative particle size \( \delta \) are determined by the method of molecular models [20].

**Table 2** shows the calculation results of this system including and excluding the accounting of separated mixture athermal properties. The effective coefficients of the component relative volatilities of the in both cases are assumed to be identical. The preset concentrations are specified in bold letters. The results analysis show that accounting of the mixture athermality leads, first of all, to increased values of the Lagrange multipliers, \( \lambda_j \), characterizing duration of the process, and has no significant impact on the composition of the products. At the same time, the distributions calculated considering the athermal properties of the mixture and assuming that mixture is ideal are similar to the data of an industrial experiment.

**CONCLUSION**

The offered calculated composition of the athermal mixture separation products in complex distillation systems is quite similar to the thermodynamic method. The method is based on an extended version of the maximum entropy principle, with the introduction of complex experience information entropy as the likelihood criterion. The extended version allows to carry out the multicomponent distillation calculation of both ideal and non-ideal (athermal) mixtures on a uniform methodological basis.

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