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Estimates of Energy Consumption and Selection of Optimal Distillation Sequence for Multicomponent Distillation

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Abstract—An estimate has been obtained of the energy consumption on 1 mol of separated mixture based on thermodynamic balances for processes that use mechanical and heat energy. Only irreversible losses depend on the order of separation for mixtures in mechanical systems, while for the systems using the heat, the order of separation also affects the reversible energy consumption. In the latter case, in order to obtain a reversible estimate of the heat consumption, one should solve the problem of selecting the order of separation. An algorithm has been obtained for its solution that enables one to approximately choose the order of separation at the stage of preliminary calculations knowing only the properties of the feed.

Keywords: systems of separation, rectification, energy costs, optimal order of separation, temperature coefficient

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INTRODUCTION

Upon designing engineering systems, the problem of evaluating their margin emerges. As an example, the maximum performance at the given limitations on the sizes of the apparatus and consumption of the raw material and energy represents the problem of the plot of the feasibility range of a system. The roughest estimate for this range can be obtained by assuming that the processes in the reversible system (the heat machine with the efficiency factor (EF) that exceeds the Carnot EF are compromised; the device that performs the work for separating 1 mol of a mixture that is lower than the Gibbs work of separation is compromised, and so on).

The real feasibility ranges are substantially lower than those that are emphasized by these physical laws. In order to find them, the class of processes should be specified and some limitations should be assumed (on the sizes of units and associated coefficients of heat and mass transfer and the required intensity of flows, and others). The assumption of these limitations gives results that are more real [1–4]. These restrictions make it necessary to find solutions of a critical problem in a class of irreversible processes. The measure of irreversibility is the increment or production of entropy. The optimal solution usually corresponds to the processes with minimum irreversibility.

For the separation systems that use mechanical or electric energy (let us further refer to them as mechanical), irreversible losses can be evaluated by known mass-transfer coefficients, and only these coefficients determine the separation sequence, whereas the reversible work depends only on the contents of input and output flows. For systems that use heat energy (thermal), while reversible losses depend on the temperatures of heat supply and abstraction and, consequently, the order of separation; this allows the selection of this order to be made based on the minimum losses.

The problem of the choice of the order of separation of liquid mixtures in the distillation columns has drawn the attention of many researchers. It was discussed in detail in [5]. The work from [6] is devoted to the computational aspects of this problem, which is solved along with the choice of the design and operation of columns according to the general technical and economic criterion, which assumes the cost of the heat exchangers, mass-exchange plates, and others.

We consider the approach used in [7] to be more efficient; here, the order of separation was chosen according to the estimates of the total heat consumption, based on the suggestion that the design parameters of columns are determined upon subsequent calculations. In this work, the extensional numerical experiment was carried out with the selection of the types of the separation of four components from the mixture. In this case, the minimum heat losses were calculated for each type as the product of the specific heat of vaporization and the vapor consumption from residue at the minimum phlegm number. Considering that this number algorithmically depends on the choice of the cut point, authors were not able to obtain the recommendations on the choice of the order of separation in analytical form. Nevertheless, the results of this work enabled the validity of the heuristic recommendations [5] that were used during design to be evaluated.

Thermodynamic balances were used below to obtain the evaluations of the specific heat losses in simple distillation columns of azeotropic mixtures. In this case, the heat losses also depend on the composition of mixture; however, the order of separation depends only on the boiling points of the components under pressures that were chosen in the columns.

The derivation of the estimates of the effectiveness of the processes assuming the irreversibility requires a priori data on the kinetics of processes and their structure. These data are often absent during the preliminary calculations. The heat losses at high loads cannot be found without them. However, it was determined that the separation sequence at loads that are close to limiting is determined identically to low loads.

WORK OF SEPARATION IN MECHANICAL SYSTEMS

Assumptions and statement of problem. Let us consider the reversible isothermal process of separation and assume that the mixture and its components are similar in their properties to ideal gases or ideal solutions so that the chemical potential of the *i*th component can be written as follows:

$$\mu_i(T,P,C_i) = \mu_{0i}(T,P) + RT\ln C_i, \quad i = 1,2,\ldots,n, \quad (1)$$

where C_i is the concentration of the *i*th component.

If the temperature and pressure in the system prior to and after the end of the separation process did not change and is adiabatically isolated, the work of the separation in this system at arbitrarily slow process corresponds to the change in its Gibbs energy, i.e., the total increment of chemical potentials for 1 mol of the mixture [8]. This can be expressed through the vector of initial concentrations $C_0 = (C_{01},\ldots,C_{0i},\ldots,C_{0n})$ and the vectors of the concentrations of mixture in the products of separation $C_1 = (C_{11},\ldots,C_{1i},\ldots,C_{1n})$ and $C_2 = (C_{21},\ldots,C_{2i},\ldots,C_{2n})$.

Let us refer to the fraction of feed that was supplied into the first product as ε, while that for the second is (1 – ε). Then, the change of the energy (molar reversible work of separation) corresponds to

$$A_0 = \sum_{i=1}^{n}[\varepsilon C_{1i}\mu_i(T,P,C_{1i}) + (1-\varepsilon)C_{2i}\mu_i(T,P,C_{2i}) - C_{0i}\mu_i(T,P,C_{0i})]. \quad (2)$$

If the equations for chemical potentials (1) are introduced in Eq. (2) and we assume that the conditions of material balance are valid for any component as follows:

$$\varepsilon C_{1i} + (1-\varepsilon)C_{2i} = C_{0i}, \quad i = 1,2,\ldots,n, \quad (3)$$

the components μ_{0i} are reduced and Eq. (2) becomes

$$A_0 = -RT\sum_{i=1}^{n}[C_{0i}\ln C_{0i} - \varepsilon C_{1i}\ln C_{1i} - (1-\varepsilon)C_{0i}\ln C_{0i}] = RT[S_0 - \varepsilon S_1 - (1-\varepsilon)S_2], \quad (4)$$

where $S_j = -\sum_{i=1}^{n} C_{ji}\ln C_{ji}$, ($j$ = 0, 1, 2) is the molar entropy of mixing of the *j*th product.

The analogous equation is obtained for the separation of mixture by *n* rather than two products.

The entropy of mixing (increment in molar entropy upon mixing of individual components) coincides in form with the Shannon function, which determines the amount of information, and it is referred to as the information entropy in some works [9]. When applied to the considered problem, the concept the *entropy of mixing* is considered to be more natural. The transition from mixing entropy to the work of separation requires it to be multiplied by *RT*

At full separation, when each product consists of a single component, its fraction $\varepsilon_i = C_{0i}$, and the concentration is unity, we obtain from Eq. (4) the known relationship for the work of separation of 1 mol of the mixture into pure components in the reversible process:

$$A_0 = -RT\sum_{i=1}^{n} C_{0i}\ln C_{0i} = RTS_0. \quad (5)$$

The determined energy costs due to separation represent the lower estimate of the real consumption.

After dividing the reversible estimate of energy costs by the period of process, we can calculate the reversible estimate of power that is consumed on the separation as well. This evaluation can be approached at a low flow intensity or at finite intensity, but at infinitely high transfer coefficients.

When there is clear separation so that each product of separation (sampling) consists of the fraction of components of the input flow and the components that appeared in one product are absent in others, let us indicate the fraction of *j*th selection as ε_j. This corresponds to the sum of the concentrations of components in the feed that were included in this selection. The reversible work of the separation of each *j*th selection, assuming that its consumption is less by ε_j times than the consumption of feed, whereas the concentrations of the introduced components $C_{ji} = C_{0i}/\varepsilon_j$, is as follows:

$$A_{0j} = -RT\varepsilon_j \sum_{i=1}^{n} \frac{C_{0i}}{\varepsilon_j} \ln \frac{C_{0i}}{\varepsilon_j} = -RT\left(\sum_{i=1}^{n} C_{0i} \ln C_{0i} - \varepsilon_j \ln \varepsilon_j \right). \quad (6)$$

The reversible work of separation for *m* selections is

$$A_0 = RT\left(S_0 - \sum_{j=1}^{m} \varepsilon_j S_j \right) = -RT \sum_{j=1}^{m} \varepsilon_j \ln \varepsilon_j, \quad (7)$$

in other words, each selection can be considered the individual component (Eq. (5)).

The obtained estimates depend only on the compositions of mixture prior to and after separation, while the order of separation does not affect their magnitude. The assumption of kinetic factors and the related irreversibility of processes allows one to evaluate additional energy costs. The work of separation in isothermal process for adiabatically isolated system can be expressed according to the Stodola equation [8] through reversible work A_0, the environmental temperature T, and the increment in entropy of system ΔS as follows:

$$A = A_0 + T\Delta S = A_0 + \delta A. \quad (8)$$

In order to evaluate the energy consumption during separation, one should determine the minimum increment in entropy at the given period of process, the mean intensity of flows, and the heat- and mass-transfer coefficients.

Let us consider the calculation system, which consists of a container with a feed, *m* subsystems in which the flows are fed after separation, and equipment that performs the separation process (let us refer to it as the working medium).

The working medium takes energy from environment and creates the flows of substance. Consider that the feed and the mixture in each *j*th subsystem; the total number of moles N that is subject to separation; as well as the period of process, τ, are specified. The driving force that creates flows of substance is the difference among chemical potentials between the working medium and the container of feed and between the working medium and subsystems. For the sake of simplicity, let us consider only the first subsystem, which indicates the differences of chemical potentials for the *i*th substance as follows:

$$\Delta\mu_{0i} = (\mu_{0i} - \mu_{0i}^{p}),\ \Delta\mu_{1i} = (\mu_{1i}^{p} - \mu_{1i}),\ i = 1,\ldots, n.$$

Here, the index p denotes chemical potentials of working medium upon contact boundaries with the feed and subsystem.

The increment in entropy, which is related to the generation of flow from the container to subsystem, corresponds to

$$\Delta S_1 = \frac{1}{T} \int_0^{\tau} \sum_{i=1}^{n} [g_{0i}(t)\Delta\mu_{0i}(t) + g_{1i}(t)\Delta\mu_{01}(t)]dt. \quad (9)$$

According to the conditions of material balance for working medium, we have

$$\int_0^{\tau} g_{0i}(t)dt = \int_0^{\tau} g_{1i}(t)dt. \quad (10)$$

The total amount of *i*th substance, which was transferred within the period τ to the first subsystem, is specified and corresponds to the product of the number of moles N_1 and the concentration of *i*th component C_{1i}.

Optimal solution. The problem of the minimum ΔS_1 under the conditions (10) by $g_{0i} \ge 0$, $g_{1i} \ge 0$, and is generally the problem of optimal control because μ_1 depends on the vector of concentrations C_1 of the mixture in subsystem, which conversely varies depending on the capacity of subsystem and the flow intensity $g_1(t)$. However, this problem is substantially facilitated in such a widespread case when the differences of chemical potentials $\Delta\mu_{0i}$ and $\Delta\mu_{1i}$ (driving forces) are unambiguously related to the flows g_{0i} and g_{1i}, respectively.

Assume that $\Delta\mu_{0i} = \varphi_{0i}(g_{0i})$, $\Delta\mu_{1i} = \varphi_{1i}(g_{1i})$, then, Eqs. (9) and (10) are split into $2n$ problems of the following types:

$$\Delta S_{\nu i} = \frac{1}{T} \int_0^{\tau} \sigma_{\nu i}(g_{\nu i})dt \to \min \text{ assuming that} \quad (11)$$
$$\int_0^{\tau} g_{\nu i} dt = N_1 C_{1i}, \quad \nu = 1, 2,\ i = 1, \ldots, n,$$

where $\sigma_{\nu i} = g_{\nu i}\varphi_{\nu i}(g_{\nu i})$ is the function that determines dissipation.

The optimal solution of problems (11) through the equations that relate the driving forces with the change in the composition of subsystems determines the principles of change in the parameters of a working solid that correspond to this solution.

Problems (11) represent the averaged problems of nonlinear programming. Their optimal solution $g_{\nu i}^{*}$ [10] is either constant and corresponds to the specified mean value of flow

$$g_{0i}^{*} = g_{1i}^{*} = \frac{NC_i}{\tau}, \quad (12)$$

or switches at the section $(0, \tau)$ between two values, which are referred to as basic. The latter variant corresponds to the case when, at the point $g_{\nu i}^{*}$, which was determined from Eqs. (12), the convex shell of the function $\sigma_{\nu i}(g_{\nu i})$ is strictly below the plot of this function. For real mass-transfer laws, the driving force monotonically grows with growth in the flow and the function $\sigma_{\nu i}$ (the product of the flow and driving force) is concave downwards so that the optimal consumption $g_{\nu i}$ is initially constant.

In the Onsager case, when the mass-transfer flow linearly depends on the difference of chemical potentials for all i and ν, we obtain

$$g_{\nu i} = \alpha_{\nu i}\Delta\mu_{\nu i} \Rightarrow \phi_{\nu i} = \frac{g_{\nu i}}{\alpha_{\nu i}}. \tag{13}$$

The production of energy is proportional to the square of the flow so that the optimal intensities of flows satisfy Eq. (12).

The minimum increment in entropy for this solution is

$$\Delta S^{\min} = \sum_{i,\nu}\Delta S^{\min}_{\nu i} = \frac{\tau}{T}\sum_{i,\nu}\sigma_{\nu i}\left(\frac{NC_i}{\tau}\right), \tag{14}$$

whereas the minimum work of separation is

$$A_{\min} = A_0 + \tau\sum_{i,\nu}\sigma_{\nu i}\left(\frac{NC_i}{\tau}\right). \tag{15}$$

Because the values of flows are defined by the given initial and final states of system, their introduction into the dependences $\sigma_{ji}(g_{ji})$ enables the specification of estimate (15).

For the process where the flows adhere to the Onsager kinetics (13), it follows from Eq. (15) that

$$\begin{aligned} A_{\min} &= A_0 + \tau\sum_{i=1}^{n} g_i^2\left(\frac{1}{\alpha_{0i}} + \frac{1}{\alpha_{1i}}\right) \\ &= A_0 + \frac{1}{\tau}\sum_{i=1}^{n} N^2C_i^2\big/\bar{\alpha}_i, \end{aligned} \tag{16}$$

where $\bar{\alpha}_i = \alpha_{0i}\alpha_{1i}/(\alpha_{0i} + \alpha_{1i})$ is the equivalent mass-transfer coefficient by the ith component.

The lower estimate for the separation power is

$$\begin{aligned} p_{\min} &= \frac{A_{\min}}{\tau} = \frac{A_0}{\tau} + \frac{1}{\tau^2}\sum_{i=1}^{n} N^2C_i^2\big/\bar{\alpha}_i \\ &= p_0 + g_0^2\sum_{i=1}^{n} C_i^2\big/\bar{\alpha}_i, \end{aligned} \tag{17}$$

where $p_0 = -g_0RT\sum_{i=1}^{n} C_i\ln C_i$.

We should note that the irreversible estimate of the work of separation that was calculated according to Eq. (16) is discontinuous. For poor mixtures, when the concentration of one component is close to unity, whereas it is close to zero for other components, it takes the finite value. This rationalizes the fact that is known in practice that the inaccuracy of the reversible estimates is particularly high for poor mixtures.

Irreversible estimate of power for continuous separation system. Assume that, in a continuous separation system, the feed flow g_0 with the concentration vector C_0 is divided by m flows, g_j ($j = 1,\ldots, m$), with the concentrations C_j. In this case, the temperatures of the separated and output flows are similar.

The minimum power that is required for clear separation in this system can be evaluated by Eq. (17) as follows:

$$p_{\min} = \sum_{j=1}^{m} p_{0j} + g_0^2\sum_{j=1}^{m}\varepsilon_j^2\big/\bar{\alpha}_j, \tag{18}$$

where

$$\varepsilon_j = \frac{g_j}{g_0} \geq 0, \quad \sum_{j=1}^{m}\varepsilon_j = 1, \tag{19}$$

$$p_{0j} = g_0\varepsilon_jRT\sum_{i=1}^{n}\left(C_{ji}\ln C_{ji} - C_{0i}\ln C_{0i}\right), \tag{20}$$

α_j is the coefficient of mass transfer upon the separation of the jth flow.

For strict separation,

$$\sum_{j=1}^{m} p_{0j} = -g_0RT\sum_{i=1}^{n}\varepsilon_j\ln\varepsilon_j.$$

According to the material-balance conditions,

$$\sum_{j=1}^{m}\varepsilon_jC_{ji} = C_{0i}, \quad i = 1,\ldots,n-1, \tag{21}$$

$$\sum_{i=1}^{n} C_{ji} = 1, \quad j = 0,\ldots,m. \tag{22}$$

The number of Eqs. (21) corresponds to $n - 1$ because this relationship is derived from conditions (19) and (22) for the concentration of one component.

Selection of the order of separation for multicomponent mixtures. In practice, the separation of multicomponent mixtures is often performed as the successive separation of mixtures by two flows. For example, during the strict separation, the mixture from three components is initially divided into two flows, the latter of which does not contain any component, and, then, the latter is divided again into two components. It was mentioned that the reversible work (corresponding power is p_0) does not depend on the order of separation, because p_0 is determined by the expenses and the compositions of flows at the input and output of entire system. The irreversible component of the power in Eq. (18) depends on the order of separation of components and allows the choice of this sequence.

Let us consider a mixture that consists of three components with the concentration (C_1, C_2, C_3) and the consumption g. The coefficients of mass transfer during the separation of the first component and the second component are denoted as α_1 and α_2, respectively, and they depend on the design of the apparatus and properties of components. Assume that the components are arranged by their properties so that one cannot isolate the second component without the primary separation of the first or third one.

The following two variants of the separation of three-component mixture are possible:

(1) direct, when the first component is initially separated that is followed by the separation of the second and the third one;

(2) inverse, when the third component is initially separated and then the first and second are separated.

Let us consider that separation upon each step is clear. The irreversible power losses upon the direct order of separation are

$$\Delta p_1 = g^2\left[\frac{C_1^2}{\alpha_1} + \frac{(C_2 + C_3)^2}{\alpha_1} + (1 - C_1)^2\frac{C_2^2 + C_3^2}{\alpha_2}\right] = g^2 a_1. \tag{23}$$

The relation that is given in square parentheses (irreversibility coefficient) is expressed as a_1.

Using the inverse order, we analogously obtain

$$\Delta p_2 = g^2\left[\frac{C_3^2}{\alpha_2} + \frac{(C_1 + C_2)^2}{\alpha_2} + (1 - C_3)^2\frac{C_1^2 + C_2^2}{\alpha_1}\right] = g^2 a_2.$$

The condition of preference of the direct order of separation follows from the inequality $a_1 < a_2$, which looks as follows after simple derivations:

$$\frac{1}{\alpha_1}\left[2C_1^2 - 2C_1 + 1 - \left(C_1^2 + C_2^2\right)\left(C_1 + C_2\right)^2\right] < \frac{1}{\alpha_2}\left[2C_3^2 - 2C_3 + 1 - \left(C_2^2 + C_3^2\right)\left(C_2 + C_3\right)^2\right]. \tag{24}$$

If the right-hand side is less than the left-hand side in this inequality, the inverse order of separation is preferable.

It is easy to show that the equations that are present in square parentheses in the left- and right-hand sides of inequality (24) monotonically decrease at any concentration C_2 with the growth of C_1 and C_3, respectively. Therefore, for the reasonability of the direct order of separation, the simultaneous fulfillment of the following inequalities is sufficient:

$$\alpha_1 \geq \alpha_2,\ C_1 \geq C_3, \tag{25}$$

whereas for inverse order it is sufficient that these inequalities are opposite. When inequalities (25) have a different direction, one should use condition (24).

The condition of preference (24) can be used for multicomponent mixtures in an algorithm that is based on the logic of dynamic programming. In this case, primarily all possible combinations of three-component mixtures are considered, the optimal order of separation is selected for each of them, and the corresponding value of the irreversible work of separation is written to memory.

In order to obtain the optimal solution, one should compare (n–1)th order of separation in the system from two steps. For example, for $n = 4$, one should compare three methods for separation at the first step: (1 + 2 + 3) + 4, 1 + (2 + 3 + 4), and (1 + 2) + (3 + 4). For the first two, the optimal order of the separation of the mixture from three components should be initially determined. For $n = 5$, we should consider two variants of the separation of mixture at the first step into the flows from (4 + 1)th component and two types of separation by (2 + 3) components based on the preliminary determination of the optimal order of separation for flows that contain three and four components, and so on.

Form of the attainability set. As follows from the condition that the dependence of power on performance represents a quadratic parabola that is characterized by two coefficients

$$p_{\min}(g) = p_0 + \Delta p = gA_0 + g^2 a. \tag{26}$$

The form of the attainability set follows for the separation systems that use the mechanical or electric energy, and its cut point is

$$g_{\max}(p) = \frac{-A_0 + \sqrt{A_0^2 + 4pa}}{2a}. \tag{27}$$

The attainable performance is the monotonous upward-convex function of consumed power.

REVERSIBLE ESTIMATE OF HEAT CONSUMPTION FOR THERMAL SEPARATION SYSTEMS

Most separation processes consume the heat energy for the formation of the difference of chemical potentials between working medium and the sources (the driving force of mass transfer).

Assume that the system operates in stationary mode and the mixture is divided into two flows.

Thermodynamic balances of the separation system. Let us write the equations of energy and entropy balances assuming that the mixtures are close to ideal solutions and the heat of mixing can be omitted:

$$q_+ - q_- + q_F h_F - g_F \varepsilon h_D - g_F(1 - \varepsilon)h_B = 0, \tag{28}$$

$$g_F s_F - g_F \varepsilon s_D - g_F(1 - \varepsilon)s_B + \frac{q_+}{T_B} - \frac{q_-}{T_D} + \sigma = 0. \tag{29}$$

Here, q_+ and q_- is the amount of heat fed to the system and taken from it, respectively; T_B and T_D are the temperatures at which the heat flow is supplied and abstracted, respectively; g_F, h_F are the molar flow and the molar enthalpy of separated mixture; ε, h_D, and s_D

are the fraction of the low-temperature product and its enthalpy and entropy; h_B and s_B is the enthalpy and entropy of the high-temperature product; and σ is the production of entropy.

From conditions (28) and (29), after the exclusion of q_-, we obtain following for the heat losses as follows:

$$q_+ = q_F \frac{T_B}{T_B - T_D}[(s_F T_D - h_F) - \varepsilon(s_D T_D - h_D) - (1-\varepsilon)(s_B T_D - h_B)] + \sigma\frac{T_B T_D}{T_B - T_D} = q_+^0 + \sigma\frac{T_B T_D}{T_B - T_D}. \tag{30}$$

The first component in the right-hand side of this equation, which is expressed by q_+^0, represents the heat losses in a reversible process, when the coefficients of heat and mass transfer (sizes of apparatus) are infinitely high; it is proportional to the consumption of the separated mixture g_F The second component corresponds to the dissipative energy costs and is proportional to q^2. for the linear dependence of the flows and driving forces in the heat and mass transfer.

Let us further consider the distillation column for specificity.

Assumptions. The external flows of substance that enter and leave the system usually pass through heat exchangers, where the hot flows are cooled, whereas the raw material flow is warmed to a temperature that corresponds to the temperature in the point of injection. Let us include these heat exchangers in the system. Then, we may consider that the differences of the heat flows that enter and leave with the liquid flows and the heat losses into environment are small compared to the heat flow that is fed with the heating vapor and abstracted in the dephlegmator. This assumption substantially simplifies the analysis of the system. In particular, in this case, $q_+ = q_- = q$. The heat flows differ only by the temperature in the injection and exit points T_B and $T_D < T_B$.

Assuming that the difference $(h - T_D s)$ for each flow corresponds to the molar free energy, that is, the chemical potential, μ, for the mixture at the temperature of T_D, we obtain the relationship of the heat flow with the performance in the following form:

$$q = g_F \frac{T_B}{T_B - T_D}[\varepsilon\mu_D(T_D, P, x_D) + (1-\varepsilon)\mu_B(T_D, P, x_B) - \mu_F(T_D, P, x_F)] + \sigma\frac{T_B T_D}{T_B - T_D}. \tag{31}$$

Here, the concentration vector of the corresponding flow is represented by x_j (j = F, B, D).

For the mixtures that are close to ideal solution, each chemical potential is as follows:

$$\mu_{ji}(T_D, P, x_j) = \mu_{0j}(T_D, P) + RT_D \ln x_{ji}, \quad j = \text{F,D,B}, \quad i = 1, \ldots, n. \tag{32}$$

The right-hand side of Eq. (31) can be expressed through the compositions of flows as follows:

$$q = g_F \frac{T_B}{T_B - T_D}[A_F - \varepsilon A_D - (1-\varepsilon)A_B] + \sigma\frac{T_B T_D}{T_B - T_D} = \frac{p^0}{\eta_C} + \frac{\sigma T_D}{\eta_C}. \tag{33}$$

Here, $A_j = -RT_D\sum_{i=1}^{n} x_{ji}\ln x_{ji} = RT_D S_j$, ($j$ = F, D, B) is the reversible work of the separation of 1 mol of jth flow by pure components. The equation that is given in square parentheses represents the reversible Gibbs work of the separation of 1 mol of flow g_F with the concentration x_F by the flows with the concentrations x_D and x_B at the temperature of T_D. Let us denote it as A_g. The value $\eta_C = (1 - T_D/T_B)$ is the counterpart of the Carnot efficiency.

Equilibrating the production of entropy to zero in Eq. (33), we obtain the reversible estimate of the heat losses $q^0 = g_F A_g/\eta_C$ in the thermal separation system.

The temperatures of heat supply and abstraction depend on the pressure P in column and, consequently, the reversible efficiency depends on the pressure. The aim of the increase in pressure is usually the increase in the temperature T_D to the degree, at which the heat can be abstracted with the water having the temperature that is close to the environmental air temperature. In this case, $T_D(P)$ is nearly 324 K.

Let us solve Eq. (33) relative to g_F and represent it as follows:

$$g_F = q\frac{\eta_C}{A_g} - \sigma(q, g_F)\frac{T_D}{A_g}. \tag{34}$$

Equation (34) shows that the reversible process of thermal separation can be represented as the ideal heat machine, which operates between the reservoirs with the temperatures T_B and T_D and produces the power of separation $p^0 = g_F A_g$. The reversible efficiency of this machine is $b = \frac{\eta_C}{A_g}$.

The relationship between the performance and heat losses, as shown in [11, 12], when the driving force of mass transfer is the difference of chemical potentials, while that for the heat exchange is the temperature difference, is determined by two coefficients, namely, the reversible efficiency of the column b and the irreversibility coefficient a and looks as follows:

$$g_F = bq - aq^2. \tag{35}$$

The relationship between the irreversibility coefficient a and the kinetic parameters of column (heat- and mass-transfer coefficients) was also obtained. At the step of preliminary calculations, the magnitude of the irreversibility coefficient can only be roughly be based on the characteristics of the analogous columns.

We have obtained the following from Eq. (35):

1. The performance of column is restricted by the value $g_F^{\max} = \frac{b^2}{4a}$, which is achieved at the value of heat flow corresponding to $q^{\max} = \frac{b}{2a}$. Further increase in the heat supply decreases the performance due to the growth in the irreversibility.

2. The efficiency of the column in the maximum performance mode $\frac{g_F^{\max}}{q^{\max}}$ does not depend on the irreversibility coefficient and corresponds to one-half of the reversible efficiency. Considering that the reversible efficiency of the system of thermal separation depends not only on compositions, but also temperatures and the order of separation affects the reversible heat losses. This means that, during preliminary calculations, they can be used to select the order of separation. Let us specify the procedure of this choice based on the example of the cascade of simple distillation columns.

SELECTION OF THE ORDER OF SEPARATION FOR A MIXTURE IN A SYSTEM OF SIMPLE DISTILLATION COLUMNS

Reversible heat losses. Assume that the molar composition of the mixture that is fed into separation to the system of distillation columns $x_1,\ldots, x_i,\ldots, x_m$ is known. In this case, all components are arranged such that the boiling point of the ith component T_i is lower than the temperature T_{i+1}.

Let us consider a column of the system, the input flow of which contains the components from ν to μ ($1 \le \nu$, $\mu \le m$). Let us use the concept of the *key component* [13], according to which the separation process is mainly influenced by the difference of the properties of boundary ith and $(i+1)$th components.

Let us consider the separation to be clear [7], i.e., that the upper fraction (distillate) contains all components, the boiling points of which are less than or equal to T_i, while the lower (still) represents all components with the boiling points higher than or corresponding to T_{i+1}. The temperature of the heat supply to the residue T_B is close to T_{i+1}, while the temperature of abstraction from the dephlegmator T_D is close to T_i.

Using Eq. (7), let us write the work of separation that is consumed on 1 mol of input and output flows of column as follows:

$$\begin{aligned} A_{\nu\mu}^{i} &= -RT_i\left(\sum_{k=\nu}^{\mu} x_k \ln x_k - \varepsilon_{\nu\mu}\ln\varepsilon_{\nu\mu}\right) = RT_iS_{\nu\mu},\\ A_{\nu i} &= -RT_i\left(\sum_{k=\nu}^{i} x_k \ln x_k - \varepsilon_{\nu i}\ln\varepsilon_{\nu i}\right) = RT_iS_{\nu i},\\ A_{(i+1)\mu} &= -RT_i\left(\sum_{k=i+1}^{\mu} x_k \ln x_k - \varepsilon_{(i+1)\mu}\ln\varepsilon_{(i+1)\mu}\right) = RT_iS_{(i+1)\mu}. \end{aligned} \tag{36}$$

The upper index i in the first relationship indicates that the work of separation relates to the case when the cut point lies between ith and $(i+1)$th components.

The fractions of these flows out of the input flow of the system are denoted as

$$\varepsilon_{\nu\mu} = \sum_{k=\nu}^{\mu} x_k,\ \ \varepsilon_{\nu i} = \sum_{k=\nu}^{i} x_k,\ \ \varepsilon_{(i+1)\mu} = \sum_{k=i+1}^{\mu} x_k.$$

The entropies of the mixing of corresponding flows that are represented by the concentrations of components in feed are written as follows assuming their fraction in the flow of raw material:

$$\begin{aligned} S_{\nu\mu} &= -\sum_{k=\nu}^{\mu} x_k \ln x_k + \varepsilon_{\nu\mu}\ln\varepsilon_{\nu\mu},\\ S_{\nu i} &= -\sum_{k=\nu}^{i} x_k \ln x_k + \varepsilon_{\nu i}\ln\varepsilon_{\nu i},\\ S_{(i+1)\mu} &= -\sum_{k=i+1}^{\mu} x_k \ln x_k + \varepsilon_{(i+1)\mu}\ln\varepsilon_{(i+1)\mu}. \end{aligned}$$

The reversible heat losses in the column on 1 mol of raw material flow are as follows:

$$\begin{aligned} q_{\nu\mu}^{i} &= R\frac{T_iT_{i+1}}{T_{i+1}-T_i}\left(S_{\nu\mu} - S_{\nu i} - S_{(i+1)\mu}\right)\\ &= -R\frac{T_iT_{i+1}}{T_{i+1}-T_i}\left(\varepsilon_{\nu\mu}\ln\varepsilon_{\nu\mu} - \varepsilon_{\nu i}\ln\varepsilon_{\nu i} - \varepsilon_{(i+1)\mu}\ln\varepsilon_{(i+1)\mu}\right). \end{aligned} \tag{37}$$

Let us refer to the equation that depends on the temperatures of components on the cut point and stays before the square parenthesis as the *temperature coefficient* as follows:

$$K_i = \frac{T_i T_{i+1}}{T_{i+1} - T_i}. \tag{38}$$

The higher the temperature coefficient, the higher the specific heat losses.

Rule of the choice of the order of separation for a ternary mixture. Assume that the composition of the mixture that is fed to the separation is known, where $x_1, x_2, x_3 = 1 - x_1 - x_2$ are the molar fractions of components. Let us write the total heat losses in direct and inverse orders of separation according to Eq. (37) as follows:

$$\begin{aligned} q_1 = q_{11} + q_{12} = -R\frac{T_1T_2}{T_2 - T_1} \\ \times \left[x_1 \ln x_1 + (x_2 + x_3)\ln(x_2 + x_3)\right] \qquad (39) \\ - R\frac{T_2T_3}{T_3 - T_2}\left[x_2 \ln x_2 + x_3 \ln x_3 - (x_2 + x_3)\ln(x_2 + x_3)\right], \end{aligned}$$

$$\begin{aligned} q_2 = q_{21} + q_{22} = -R\frac{T_2T_3}{T_3 - T_2} \\ \times \left[x_3 \ln x_3 + (x_1 + x_2)\ln(x_1 + x_2)\right] \qquad (40) \\ - R\frac{T_1T_2}{T_2 - T_1}\left[x_1 \ln x_1 + x_2 \ln x_2 - (x_1 + x_2)\ln(x_1 + x_2)\right]. \end{aligned}$$

The sign of the difference $\Delta_{12} = q_1 - q_2$ determines the order of separation. If $\Delta_{12} < 0, < 0$, the total heat losses are lower upon the direct order of separation. If the difference is positive, the inverse order is more favorable.

After simple derivations, Δq_{12} is

$$\begin{aligned} \Delta_{12} \\ = R\left(\frac{T_1T_2}{T_2 - T_1} - \frac{T_2T_3}{T_3 - T_2}\right)F_{12}(x) = R(K_1 - K_2)F_{12}(x), \end{aligned} \tag{41}$$

where $F_{12}(x) = x_2 \ln x_2 - (1 - x_1)\ln(1 - x_1) - (1 - x_3) \times \ln(1 - x_3)$.

Assuming that $x_2 = 1 - (x_1 + x_3)$, the function $F_{12} = (x_1, x_3)$ corresponds to zero on the nodes and along the coordinate axes of the x_1x_3 plane of the concentration simplex, which is limited by the inequalities $x_1 \geq 0$, $x_3 \geq 0$, $(x_1 + x_3) \leq 1$. Inside the simplex, this function is always positive and achieves a maximum on the line $x_1 = x_3 = 0.5(1 - x_2)$. The order of separation is determined only by the sign of the first comultiplier in Eq. (41), which corresponds to the difference of the temperature coefficients. The direct order is preferable if $K_1 < K_2$. If this inequality has an opposite sign, the inverse order of separation is favorable. Each temperature coefficient is calculated under the pressure set in the column.

Analogously, the problem of the order of separation can be considered in the cascade from two columns, which is intended for the separation of one component or a group of components with intermediate boiling points. Assume that the lower boiling point of the intermediate target sampling is T_{i+1}, while the highest is T_j. The order of separation is determined identically to that for the mixture of three components. Instead of concentrations, the fractions of corresponding selections are considered.

A flow containing several substances can be considered to be a component, the fraction of which corresponds to the total concentration of the substances in it, whereas the boiling point corresponds to the that of the component on the cut point. Therefore, the medium component during the direct order of separation in the first column has the temperature T_{i+1}, and T_j, in the second one, while it becomes inverse upon inverse order. The direct order of separation, when it is reasonable to separate the components with the boiling points that are less or equal to T_i, on the first column of cascade, while those are from T_{i+1} to T_j on the second one, is preferable if the following inequality is fulfilled:

$$K_i < K_j \Rightarrow \frac{T_iT_{i+1}}{T_{i+1} - T_i} < \frac{T_jT_{j+1}}{T_{j+1} - T_j}, \tag{42}$$

Example 1. As an example, let us choose the order of separation and determine the reversible heat losses for separating the mixture from three components, namely, benzene, toluene, and xylene [14]. In addition, the latter consists of three isomers. The molar concentration and the boiling point of benzene are $x_1 = 0.4$, $T_1 = 353.1$ K, while for toluene they are $x_2 = 0.3$, $T_2 = 383.6$ K. The total concentration of xylene and the boiling point of the low-boiling isomer is $x_3 = 0.3$, $T_3 = 411.35$ K. The pressure in the columns is equivalent and close to atmospheric.

Let us determine the order of separation according to Eq. (42). After introducing the boiling points, its right-hand side corresponds to 380.0 K, while the left-hand side is 383.62 K. Thus, the inequality is fulfilled and it is reasonable to separate benzene on the first column of cascade, as is performed in real systems of separation.

Reversible heat losses on 1 mol of the mixture during direct and inverse orders of separation (Eqs. (39), (40)) are $q_1 = 44.516$ kJ/mol and $q_2 = 46.537$ kJ/mol.

Using the molar weights of the components ($M_1 = 78.0$ g/mol, $M_2 = 92.14$ g/mol, and $M_3 = 106.16$ g/mol), one can evaluate the heat losses on one kilogram of mixture (molar weight of the mixture $\bar{M} = x_1M_1 + x_2M_2 + x_3M_3 = 90.16$ g/mol): $q_1^m = 493.74$ kJ/kg and $q_2^m = 516.16$ kJ/kg.

After multiplying by the consumption of mixture in kg/s, we obtain a lower estimate of the heat flow in kilowatts.

Rule of a nondecrease in temperature coefficients. Condition (42) may be considered to be a necessary condition of the reasonability of the problem of the order of separation. A comparison of two possible cut points leads to a simple rule for choosing the order of separation of a multicomponent mixture in thermal systems. *In order to make reversible energy costs on the separation of multicomponent mixture in the cascade of binary separation systems minimum, the temperature coefficients should monotonically increase from the first to the further steps of cascade*. This rule does not require the procedure of dynamic programming and overcome of the associated computational difficulties.

Each possible cut point determines the pressure in the column and the related temperatures of heat supply and abstraction and, consequently, the temperature coefficient. First, one should separate the mixture by the cut point, which corresponds to minimum temperature coefficient.

Upon a shift in the cut point to high-boiling components, the temperature coefficient usually increases (the numerator grows in proportion to square, whereas the denominator grows in proportion to the first degree of temperature). Therefore, in most cases, but not always, the heuristic rule that the low-boiling components should be sequentially separated [5] is valid. This also corresponds to the results of a numerical experiment that was performed in [7], when in two out of twelve cases, the direct order of separation was not best.

To the roughest approximation, one can assume the effect of the losses from irreversibility in thermal systems was due to the fact that they are proportional to the square of the flow of separated mixture. The sum of the squares of the output flows for each column at the given total flow is minimal on its input when these flows are close to each other. Therefore, the best cut point should be the one from the viewpoint of the necessary consumption that the input flows in each column would be nearly equivalent. This corresponds to the dichotomy rule suggested in [15].

Assuming this fact, the rule postulated above for selecting the order of separation can be complemented as follows: if the temperature coefficients for two types of separation coincide or differ slightly from each other, the one for which the fractions of selections are closer to each other is favorable.

Example 2. As an example, let us analyze the order of separation that was accepted in the typical gas-fractioning setup of one of the oil-refining plants. The equipment is intended for the separation of the mixture of hydrocarbons into four fractions, namely, methane containing hydrogen sulfide, carbon dioxide, methane, ethane, and propane ($i = 1$); isobutane ($i = 2$); butane ($i = 3$); and pentane that contains pentane and hexane ($i = 4$).

The pressure in columns is maintained at such a level that the temperature of heat abstraction in dephlegmators would be 324 K. In the first column, the most volatile (methane) fraction is separated. The temperature of the heat supply to the residue of the first column is 424 K, whereas the pressure in column is 1.7 MPa. In the second column, the fourth fraction is separated, the pressure is 0.65 MPa, and the temperature in residue is 389 K. Finally, in the third column of separation, the second and third fractions are separated under the pressure of 0.72 MPa. The temperature in residue is 341 K. We should note that the heuristic principle of the successive separation of low-boiling components is violated in the second column [5].

The temperature coefficients in the existing order of separation were as follows:

$$K_1 = \frac{324 \times 424}{100} = 1373.8,$$

$$K_2 = \frac{324 \times 389}{65} = 1939.0,$$

$$K_3 = \frac{324 \times 341}{17} = 6499.0.$$

Thus, the order of separation that is accepted on the plant corresponds to the rule of growth in the temperature coefficients. If the low-boiling second fraction was isolated in the second column and the fourth and third fractions were isolated in the third column, the temperature coefficients K_2 and K_3 would replace each other and the growth rule would be violated, which would imply growth in the energy costs.

Because the efficiency corresponds to one-half of the reversible efficiency in the limiting performance mode, the choice by the rule of temperature coefficients is also valid for this mode.

CONCLUSIONS

The rules for preliminary calculations of the optimal order of separation were obtained for multicomponent mixtures. For systems that use mechanical or electric energy (membranes, centrifuges, and others), the order of separation is determined only by irreversible losses. For thermal systems (rectification, absorption, and others), the reversible energy costs also depend on the order of separation. The order of separation that corresponds to maximum reversible efficiency is determined by the temperature coefficients for the distillation columns.

The obtained recommendations have an approximate character and are only valid because the aforementioned assumptions are close to real; in addition, the separated mixtures are close to an ideal solution and the conditions in the column are close to the displacement mode.

NOTATION

A_0	reversible molar work of separation, J/mol;
a	irreversibility coefficient, mol s/J^2;
C, x	concentration, mol/mol;
g	consumption, mol/s;
h	molar enthalpy, J/mol;
K	temperature coefficient, K;
P	pressure, Pa;
p	power, W;
q	heat flux, W;
R	universal gas constant, J/(mol K);
S	entropy of mixing;
s	molar entropy, J/(mol K);
T	temperature, K;
α	mass-transfer coefficient, mol^2 K/(s J);
ε	fraction of product withdrawal;
μ	chemical potential, J/mol;
σ	production of entropy, W/K.

SUBSCRIPTS AND SUPERSCRIPTS

B	variables that are related to bottoms;
D	variables that are related to the dephlegmator;
F	variables that are related to feed;
i	number of the component of mixture;
j	number of selection of product.

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