

RESEARCH ARTICLE

Distillation optimization: Parameterized relationship between feed flow rate of a steady-state distillation column and heat duties of reboiler and condenser[†]

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Summary

The paper considers the problem of maximum efficiency for the system of distillation columns. Columns in such systems are connected in parallel or sequential way. The mixture being separated is assumed to be close to ideal one. Authors parameterize the relationship between feed flow rate and heat duties of a steady-state binary distillation column using two parameters: the reversible efficiency and the irreversibility coefficient. This relationship is later being used to solve the problems about optimal distribution of heat and feed flows within the system. The results obtained allow to estimate minimum heat energy demand for distillation of the given feed flow, maximum performance and efficiency of the system.

KEYWORDS:

irreversible separation processes, reachable set, multistage systems, entropy generation, separation sequence, distillation, optimization

INTRODUCTION

Problems of optimal structure of distillation systems are well-known^{1,2,3,9,10,11}. Many authors³ suggest that «methods of distillation system design are based on phase equilibrium diagrams and parameters of a reversible process with some empirical corrections». When choosing the separation sequence researchers often use empirical rules such as²: “The most volatile component should be removed at first” or “The component with the largest molar fraction should be removed at first”. These rules do not have any rigorous justification and often contradict each other.

The use of graphical-analytical methods and algorithmic description of the characteristics of each column makes it impossible to obtain analytical solutions of the optimization problem for a system interconnected columns. This paper uses the results of the authors' previous work on obtaining a relationship between the characteristics of product flows in a binary distillation column and heat consumption, taking into account the irreversibility of the processes occurring in the process (see^{4, 5, 6}) for solving the problem of the optimal distribution of flows in the system of columns with their parallel and sequential structure.

The task of this paper is to answer the following questions:

1. How to distribute the flows of the feed and heat in the system of columns of parallel structure so that at a given flow rate of the feed the total heat consumption is minimal.
2. What is the maximum productivity of parallel-connected columns for a given composition of product flows at the outlet of each of them?

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3. In what order should the separation be carried out in a cascade of successive columns in order to divide the feed stream into fractions of a given composition with a minimum total heat consumption?

4. Within what limits can the consumption of heat change in the problems mentioned above and how to choose a reflux value for the mode of maximum productivity?

5. Under the given structural characteristics of the columns, which of them is expedient to use in the first stage during sequential separation?

6. What is the maximum output for the target product of a cascade of successive columns?

We will assume that compositions of feed and product streams are given. We determine the efficiency of the column as the ratio of the flow of the separated feed to the flow of consumed heat. We will evaluate the irreversibility of the process through the entropy generation, which occurs both in the processes of heat exchange in the reboiler and in the condenser, and in the process of mass transfer between the flows within the column.

In the first section, it is shown that the relationship between the column productivity in terms of the feed flow and the heat consumption can be parameterized by a function that depends only on two parameters, each of which, in turn, depends on the compositions of the flows to be separated, kinetic coefficients, and other factors.

The second section is dedicated to the consequences following from the possibility of such a parametrization.

In the third section, a system of parallel structure for two and for n columns is considered.

The last section is dedicated to systems of sequential structure for three and for n columns. In each case, the answers to the above questions were received.

Most of the equations given in the first section were obtained and published by the authors earlier, but since the further presentation is based on them, the authors considered it expedient not only to give the previously obtained results, but also to remind the scheme of their derivation.

PARAMETERIZATION OF THE DEPENDENCE OF THE COLUMN PRODUCTIVITY ON THE HEAT CONSUMPTION

We will consider the traditional design of the column with heat supply to the reboiler and removal from the condenser. **General**

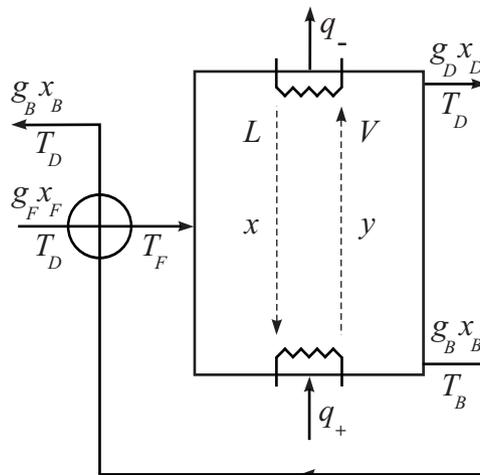


FIGURE 1 Calculation scheme for binary distillation.

assumptions

Let us list the main assumptions used in⁶ when considering a column with a given capacity:

1. Mass transfer is equimolar.
2. In each section along the column height, the pressures and temperatures of the vapor and liquid flows are close to each other (they change from section to section).

3. The column is similar to the packed one, and the flows of steam and reflux travel in a mode close to ideal displacement, so that the effects of diffusion between adjacent sections are negligible.

4. The feed stream entering the column is heated to a temperature close to the reflux temperature in the column section where the reflux composition is close to the feed composition, so that the irreversibility of mixing of these streams can be neglected. The entropy generation in this heat exchanger is independent of the column mode and is much less than the column entropy generation.

5. The liquid phase in the reboiler and in the condenser is continuously stirred.

6. The column is thermally insulated.

The assumptions we made reduce irreversibility, so that the value of the entropy generation obtained in the calculation is a lower estimate for the actual one.

Thus, an idealized model of a packed column is considered, in which two main sources of irreversibility are taken into account: heat transfer when heat is supplied to the reboiler and when it is removed from a condenser and mass transfer between steam and reflux along the height of the column. The tray column is also close to this model with a sufficiently large number of trays. Note that the effective mass transfer coefficient, if it is found from the data of the operating column, indirectly takes into account internal diffusion, mixing on trays, etc.

The molar fractions of the low-boiling component in the feed flow x_F and in the flows taken from the condenser and the reboiler x_B and x_D will be assumed to be given, as are the temperatures of the reboiler T_B and in the condenser T_D .

The fraction of the upper product ε depends on the composition of the input and output flows. Indeed, from the material balance for the low-boiling component, we obtain

$$\varepsilon = \frac{x_F - x_B}{x_D - x_B}. \quad (1)$$

Relationship between heat input and column performance

From the equations of energy and entropy balances, assuming that the mixtures are close to ideal solutions and neglecting the heat of mixing, we obtain:

$$q_+ - q_- + g_F h_F - g_F \varepsilon h_D - g_F (1 - \varepsilon) h_B = 0, \quad (2)$$

$$g_F s_F - g_F \varepsilon s_D - g_F (1 - \varepsilon) s_B + \frac{q_+}{T_B} - \frac{q_-}{T_D} + \sigma = 0. \quad (3)$$

Here $\sigma > 0$ is the entropy generation within the column.

From equations (2), (3) after elimination of q_- it follows that

$$q_+ = g_F \frac{T_B}{T_B - T_D} \left[(s_F T_D - h_F) - \varepsilon (s_D T_D - h_D) - (1 - \varepsilon) (s_B T_D - h_B) \right] + \sigma \frac{T_B T_D}{T_B - T_D} = q_+^0 + \sigma \frac{T_B T_D}{T_B - T_D}. \quad (4)$$

The first term on the right-hand side of this expression, which is denoted by q_+^0 , is the heat consumption in a reversible process, when the heat and mass transfer coefficients (column size) are arbitrarily large. It only depends on parameters of input and output flows and is proportional to the productivity g_F , the second term corresponds to dissipative energy losses.

Let us denote by C_F, C_D, C_B the heat capacities of the feed, upper product and bottoms. The feed flow, before entering the column, usually passes through a regenerative heat exchanger, in which it contacts the bottoms flow. In this case, the temperature of the feed flow at the inlet to the heat exchanger is close to T_D , in the heat exchanger (see assumption 4) the heat balance equation is fulfilled

$$C_B (1 - \varepsilon) (T_B - T_D) = C_F (T_F - T_D),$$

so that the bottoms flow leaves the heat exchanger at a temperature of T_D .

Taking into account the fact that the difference $(h - T_D s)$ for each of the flows is equal to the molar free energy, i.e. to the chemical potential μ of the mixture at $T = T_D$, the relationship between the heat flux and productivity takes the form

$$q = g_F \frac{T_B}{T_B - T_D} \left[\varepsilon \mu_D(T_D, x_D) + (1 - \varepsilon) \mu_B(T_D, x_B) - \mu_F(T_D, x_F) \right] + \sigma \frac{T_B T_D}{T_B - T_D}. \quad (5)$$

Each of the chemical potentials has the form

$$\mu_i(T, P, x_i) = \mu_{i0}(P, T) + RT \ln x_i, \quad i = D, B, F. \quad (6)$$

Since the chemical potentials in each section of the column correspond to the same temperature and pressure, their difference for the vapor phase is

$$\begin{aligned}\mu_1(T, y^0) - \mu_1(T, y) &= RT \ln \frac{y^0}{y}, \\ \mu_2(T, 1 - y) - \mu_2(T, 1 - y^0) &= RT \ln \frac{1 - y}{1 - y^0}.\end{aligned}$$

Substituting these equalities into (5), we obtain:

$$q = g_F \frac{T_B}{T_B - T_D} \left[A_F - \varepsilon A_D - (1 - \varepsilon) A_B \right] + \frac{\sigma T_D T_B}{T_B - T_D} = \frac{p_0}{\eta_K} + \frac{\sigma T_D}{\eta_K}. \quad (7)$$

Here

$$A_i = -RT_D \left[x_i \ln x_i + (1 - x_i) \ln(1 - x_i) \right], \quad (i = F, D, B), \quad (8)$$

is the reversible work of separating one mole of the i th flow into pure components, and the expression in (7) in square brackets is the Gibbs reversible work of separating one mole of the feed flow of composition x_F into product flows of compositions x_B and x_D at a temperature of T_D . We will designate it as A_G . The value $\eta_K = (1 - T_D/T_B)$ is an analogue of the Carnot efficiency. Equating in (7) the entropy generation to zero, we obtain a reversible estimate $q^0 = \frac{g_F A_G}{\eta_K}$ of heat consumption in the distillation process.

Let us solve the equation (7) for g_F . We obtain:

$$g_F = q \frac{\eta_K}{A_G} - \sigma(q, g_F) \frac{T_D}{A_G}. \quad (9)$$

Let us find a lower bound for the second term in this equality (see⁶). To do this it is necessary to determine the entropy generation in the processes of heat transfer in the reboiler and condenser, as well as in the process of mass transfer between the flows of steam and reflux.

Irreversible energy losses

Irreversibility of heat transfer. Let the heat fluxes in the reboiler and condenser be proportional to the temperature difference

$$q = rV = \beta_B (T_+ - T_B) = \beta_D (T_D - T_-). \quad (10)$$

Here V is the steam flow leaving the reboiler, r is the molar heat of vaporization.

The entropy generation due to thermal processes in the reboiler and condenser, taking into account (10), is equal to

$$\sigma_q = q \left[\frac{1}{T_B} - \frac{1}{T_+} + \frac{1}{T_-} - \frac{1}{T_D} \right] = q^2 \left[\frac{1}{\beta_B T_B T_+} + \frac{1}{\beta_D T_D T_-} \right], \quad (11)$$

where β_B and β_D are the heat transfer coefficients proportional to the heat transfer surfaces, T_B and T_D are the temperatures of the liquid in the reboiler and condenser respectively, which we assume to be known, T_+ , T_- are temperatures of the heating steam in the reboiler and the cooling water in the condenser.

For a given heat flux, the temperatures T_+ and T_- depend on the selected values of the temperature differences in the reboiler and condenser. After substitution of these temperatures into (11), the value of σ_q is determined.

Irreversibility of mass transfer. To calculate the entropy generation in the process of mass transfer, we will use a model corresponding to a packed column with countercurrent flow of steam and reflux in a mode close to the ideal displacement. The steam flow rate $V = \frac{q}{r}$ at equimolar mass transfer does not change along the column height and is related to the reflux flow L by the equalities:

for the rectifying section

$$L_D = \frac{q}{r} - g_D, \quad (12)$$

for the stripping section

$$L_B = \frac{q}{r} + g_B. \quad (13)$$

As an independent variable, instead of the column height, we choose the concentration of the low-boiling component x , which monotonically depends on the height.

Taking into account the fact that for binary distillation the concentration high-boiling component in liquid and vapor streams are equal to $1 - x$ and $1 - y$, respectively, and the driving force of the process is determined by the difference between the

current concentration $y(x)$ and the equilibrium concentration $y^0(x)$, entropy generation associated with mass transfer, expressed in terms of fluxes and chemical potentials, is

$$\sigma_g = \int_{x_B}^{x_D} \frac{1}{T(x)} \{g_1(y, y^0)[\mu_1(T, y^0) - \mu_1(T, y)] + g_2(1 - y, 1 - y^0)[\mu_2(T, 1 - y) - \mu_2(T, 1 - y^0)]\} dx, \quad (14)$$

where g_j and μ_j ($j = 1, 2$) are mass transfer flows and chemical potentials of the components.

Expression (14), taking into account the form of chemical potentials (6) and equimolarity of mass transfer ($g_1(y, y^0) = -g_2(1 - y, 1 - y^0) = g$), will be rewritten in the form

$$\sigma_g = R \int_{x_B}^{x_D} g(y, y^0) \ln \frac{y^0(1 - y)}{y(1 - y^0)} dx. \quad (15)$$

Using equations of material balance for rectifying and stripping sections we obtain:

$$\frac{q}{r}y(x) - g_D x_D - x L_D = 0, \quad (16)$$

$$L_B x - \frac{q}{r}y(x) - g_B x_B = 0. \quad (17)$$

Taking into account (12), (13) we have operating lines for rectifying and stripping sections, after substitution $g_D = g_F \varepsilon$, $g_B = g_F(1 - \varepsilon)$:

$$y^D(x, \frac{q}{r}, g_F) = \left(1 - \frac{g_F \varepsilon r}{q}\right) x + \frac{x_D g_F \varepsilon r}{q}, \quad (18)$$

$$y^B(x, \frac{q}{r}, g_F) = \left(1 + \frac{g_F(1 - \varepsilon)r}{q}\right) x - \frac{x_B g_F(1 - \varepsilon)r}{q}. \quad (19)$$

From these equations it follows that $y^D(x_D) = x_D$, $y^B(x_B) = x_B$, $y^D(x_F) = y^B(x_F) = y_F$, and $y_F - x_F = \frac{g_D r}{q}(x_D - x_F)$.

Substitution of expressions (18), (19) into equality (15) determines the entropy generation $\sigma_g(q, g_F)$ for a given law mass transfer. In this case, the sum of the integrals is calculated on the intervals from x_B to x_F , when $y(x) = y^B(x, \frac{q}{r}, g_F)$, and from x_F to x_D , when $y(x) = y^D(x, \frac{q}{r}, g_F)$, that is possible only numerically.

To obtain the results in analytical form, we find the lower bound of σ_g , adopting the law of mass transfer proportional to the driving force

$$g(y, y^0) = k \frac{[\mu_1(T, y^0) - \mu_1(T, y)]}{T}, \quad (20)$$

After eliminating the chemical potential difference through the flow $g(y, y^0)$, the equality (15) takes the form

$$\sigma_g(q, g_F) = \frac{2}{k} \int_{x_B}^{x_D} g^2(y, y^0) dx. \quad (21)$$

Here, the factor 2 is associated with the equimolar flux of the high-boiling component from vapor to liquid.

We denote the average value of the flow as:

$$\bar{g} = \frac{1}{x_D - x_B} \int_{x_B}^{x_D} g(y, y^0) dx \quad (22)$$

and using (21) we obtain a lower bound for σ_g ⁶:

$$\sigma_g \geq \frac{2(x_D - x_B)\bar{g}^2}{k}. \quad (23)$$

Inequality (23) turns into equality when the mass transfer flow between steam and reflux does not change along the column height.

The steam consumption along the column height is constant and for the total amount of the low-boiling component, transferred from liquid to vapor, we have the material balance condition

$$\int_{x_B}^{x_D} g(y, y^0) dx = V[y^D(x_D) - y^B(x_B)] = \frac{q}{r}(x_D - x_B). \quad (24)$$

We obtain that $\bar{g} = \frac{q}{r}$. After substitution of this value into (23) we get:

$$\sigma_g \geq \frac{2(x_D - x_B)q^2}{kr^2}. \quad (25)$$

We will use the right-hand side of this inequality to estimate the irreversibility of mass transfer.

Substitution of the total entropy generation into the expression (9) allows one to obtain an estimate for the productivity of binary distillation depending on the heat flow in a parameterized form:

$$g_F \leq bq - aq^2. \quad (26)$$

This relationship will be called *column load characteristic*.

Comparison of the parameterized load characteristic with the expression (9) leads to the fact that the characteristic parameters a, b should depend on the kinetics of the processes, the composition and properties of the substances to be separated as:

$$b = \frac{T_B - T_D}{T_B A_G} = \frac{\eta_c}{A_G}, \quad (27)$$

$$a = \left[\frac{1}{\beta_b T_B T_+} + \frac{1}{\beta_d T_D T_-} + \frac{2(x_D - x_B)}{kr^2} \right] \frac{T_D}{A_G}. \quad (28)$$

Here η_c is an analogue of the Carnot efficiency, if we consider the distillation column as a heat machine that converts thermal energy into separation work. With a complete separation, the concentration of low-boiling component in the bottoms x_B in the equation (27) is zero, the concentration in the condenser it is equal to one, and the fraction of withdrawal is equal to x_F .

We will call the parameter b the *reversible efficiency*, and the parameter a the *irreversibility coefficient*. The first of them depends only on the compositions of the mixture to be separated and the product flows, the second one also depends on the kinetics of the process, and therefore on the design features of the column. Reversible efficiency corresponds to the efficiency of a column having arbitrarily large heat and mass transfer coefficients. Since the compositions of the flows are usually given, its value is known.

CONSEQUENCES FROM THE PARAMETERIZATION OF THE LOAD CHARACTERISTIC

The fact that the relationship between the maximum performance and the feed flow rate can be parameterized by two coefficients allows one to solve some problems using these parameters. Below are solutions for several such problems.

Limiting performance

The most expedient heat consumption and maximum productivity are determined through the characteristic parameters. From (26) it follows that the productivity reaches its maximum when the heat consumption is:

$$q^0 = \frac{b}{2a} \quad (29)$$

and it reaches the maximum value of

$$g_F^m = \frac{b^2}{4a}. \quad (30)$$

A further increase in the heat flux is impractical, since, due to the increase in dissipation, it leads to a decrease in productivity, therefore q^0 is the boundary of the operating part of the load characteristic. At the operating part, the heat consumption monotonously depends on the productivity as:

$$q = \frac{b}{2a} - \sqrt{\frac{b^2}{4a^2} - \frac{g_F}{a}}. \quad (31)$$

Column efficiency in the mode of maximum productivity

Let us introduce the parameter $z = \frac{q}{q_0}$ — the degree of the column load, varying from zero to one. Then the efficiency of the binary distillation column (see (26)) after elimination of a through z will take the form:

$$\eta(z) = \frac{g_F}{q} = b(1 - 0.5z). \quad (32)$$

At full load, when $z = 1$, the column efficiency does not depend on irreversible factors and is equal to $0.5b$ (half of the reversible efficiency). The value of the maximum productivity and the corresponding heat consumption depend on these factors. This circumstance corresponds to the well-known fact⁷ that the value of the efficiency of the cycle of an irreversible heat engine corresponding to its maximum power (Novikov-Curzon-Alburn efficiency) does not depend on the kinetics of heat transfer of the working fluid with sources (the maximum power of the machine depends on this kinetics).

Changing the column dimensions, the ratio between the heat transfer surfaces in the reboiler and in the condenser affects the value of the heat and mass transfer coefficients, which affect the productivity through the irreversibility parameter a . The family of dependencies $g_F(q)$ for different values of a turns out to be such that the maxima of all parabolas lie on one straight line drawn from the origin with slope $b/2$ (see Fig. 2).

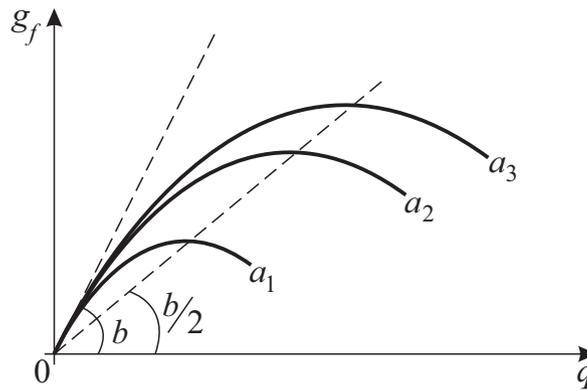


FIGURE 2 Column productivity versus heat consumption for different heat and mass transfer coefficients . $a_1 > a_2 > a_3$

General assumptions

Since the efficiency of the column monotonously decreases with increasing load, it satisfies the inequality in the operating section of the load characteristic

$$b \geq \eta \geq b/2$$

. Calculation of the irreversibility coefficient using the experimental data

The reversible efficiency is usually given, but the irreversibility coefficient is much more difficult to compute by the formula (28), since the expression (28) includes the effective mass transfer coefficient k , which, like the heat transfer coefficients β_B, β_D depends on the design and dimensions of the column. Therefore, the irreversibility coefficient for an operating column can be found from the results of experimental measurements of the actual heat consumption q^{ex} and the actual feed flow rate g_F^{ex} . From (26) it follows:

$$a = \frac{bq^{ex} - g_F^{ex}}{(q^{ex})^2}. \quad (33)$$

The obtained value of a allows one to compute the boundary of the operating section, the efficiency of the column taking into account irreversibility and, as shown below, the reflux ratio. Through the condition (28), the value of a relates to each other the kinetic coefficients included in its right-hand side.

Relationship between reflux ratio, column load and characteristic parameters

The reflux ratio R , equal to the ratio of the reflux flow returned to the column to the withdrawal of the product from the condenser, is an important control factor. Let us express it in terms of characteristic parameters. To do this, we write down the material balance equation for the flows entering and leaving the reflux condenser

$$V = L + g_F \epsilon.$$

Here L is the reflux flow returning to the column.

We will assume the separation is complete. In this case for a binary mixture $\varepsilon = x_F$, and for a multicomponent x_F is the molar fraction of the fraction separated as the upper product. Taking into account that $q = Vr$, and $R = \frac{L}{g_F x_F}$, we get:

$$\frac{1}{\eta(z)} = \frac{Vr}{g_F} = \frac{1}{b(1-0.5z)} = rx_F(R+1).$$

So we obtain:

$$R = \frac{1}{b(1-0.5z)rx_F} - 1 = \frac{1}{(b-aq)rx_F} - 1. \quad (34)$$

In the mode of maximum productivity, the degree of the column load is $z = 1$ and

$$R = R_{max} = \frac{2}{brx_F} - 1. \quad (35)$$

If the reflux ratio is measured on a operating column, then the formula (34) can be used to calculate the irreversibility factor.

OPTIMIZATION OF THE PARALLEL STRUCTURE

A parallel structure of distillation columns is a structure that consumes a limited flow of heat energy. The feed flow g_{Fi} arrives at the inlet of each column, the composition of these flows, like the compositions of the flows leaving the column, is known. The total feed flow will be denoted as g_F . The columns differ in their design characteristics, temperatures of the flows that heat the mixture of components in the reboiler and cool it in the condenser, etc. This circumstance leads to the fact that for each i th column the characteristic parameters a_i, b_i , found by the formulas (27), (28) or calculated from experimental data (see (33)) are different.

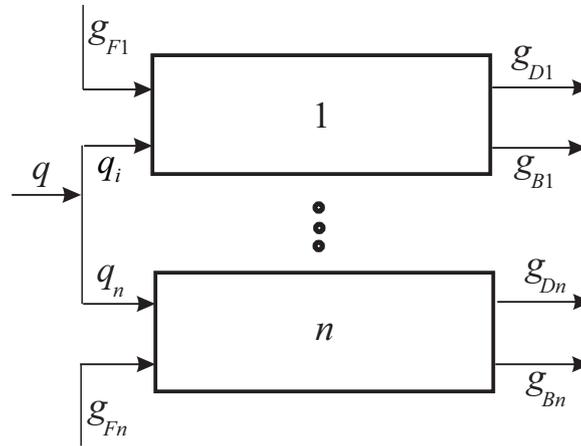


FIGURE 3 Parallel structure of distillation columns

Let us express the limiting capabilities of such a structure through the characteristic parameters of the columns.

Reversible efficiency and maximum productivity

Let the distribution of feed flows g_{Fi} between the columns be given, and γ_i is the fraction g_{Fi}/g_F . Then the reversible efficiency of a parallel structure is equal to:

$$b = \frac{g_F}{q_\Sigma} = \frac{1}{\sum(\gamma_i/b_i)}. \quad (36)$$

Maximum productivity of the system of parallel columns and the corresponding heat consumption, taking into account irreversibility:

$$g_F^{\max} = \sum_i \frac{b_i^2}{4a_i}, \quad q_\Sigma^{\max} = \sum_i \frac{b_i}{2a_i}. \quad (37)$$

Optimal distribution of heat flows

Let us consider the problem of such a distribution of heat fluxes between the columns so that for a given total heat consumption q_Σ the productivity n of the parallel columns g_F is maximum. The problem will take the form:

$$g_F = \sum_i (b_i q_i - a_i q_i^2) \rightarrow \max, \quad \sum_i q_i = q_\Sigma < q_\Sigma^{\max}. \quad (38)$$

Since the function $g_{Fi}(q_i)$ is monotonic and convex on the operating section of the load characteristic, the problem (38) has the same solution as the dual problem of the minimum heat consumption for a given total productivity.

The Lagrange function of the problem (38) for a non-degenerate solution has the form:

$$L = \sum_i (b_i q_i - a_i q_i^2 - \lambda q_i)$$

Its stationarity conditions for q_i are:

$$b_i - 2a_i q_i = \lambda, \quad i = 1, 2, \dots, n. \quad (39)$$

After substituting $q_i = \frac{b_i - \lambda}{2a_i}$ in (38) and excluding λ we obtain:

$$q_i^* = \frac{b_i}{2a_i} - \frac{\sum_j \frac{b_j}{2a_j} - q_\Sigma}{a_i \sum_j \frac{1}{a_j}}, \quad i, j = 1, \dots, n. \quad (40)$$

OPTIMIZATION OF THE SEQUENTIAL STRUCTURE

To separate multicomponent mixtures into individual components or into fractions consisting of several components, a cascade of columns connected sequentially is used.

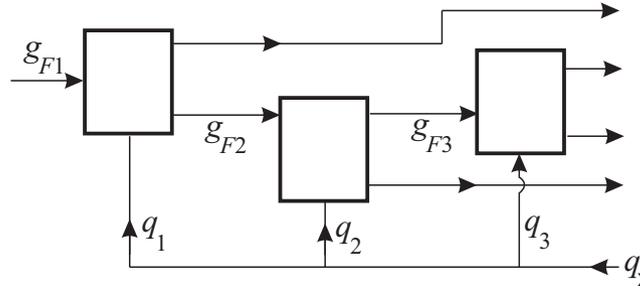


FIGURE 4 Sequential structure of distillation columns

Initially, let us consider in more detail a cascade of two successive columns, in which it is necessary to separate the mixture into three components or three fractions. In particular, such a problem arises when one component or fraction with an intermediate boiling point is separated from a mixture.

Three-component mixture. Reachable set and selection of optimal separation sequence

Formulation of the problem

Representation of the load characteristic of a column through characteristic parameters allows one to use these parameters to optimize a cascade of two columns. The values of characteristic parameters must be previously obtained using the formulas (27), (28) or from experimental data.

As above, we will choose a separation sequence according to the condition of the minimum total heat consumption q_Σ for a given productivity and flow compositions. As above, we will assume a complete separation in each column.

Let the components of the mixture be ordered and marked with indices 0, 1, 2. Their molar fractions in the flow of the separated mixture x_0, x_1, x_2 are given. Evaporating temperatures $T_0 < T_1 < T_2$. Let us introduce designations for the characteristic parameters of each of the columns for each of the separation orders:

- The direct one, when the zeroth component is separated in the first column, and the first and the second ones are separated in the second column. The characteristic parameters corresponding to this case will be denoted by the index d . For example, b_{d1} is the reversible efficiency in the direct order of separation for the first column.
- The indirect one, when the second component is separated in the first stage, and the remaining mixture is divided by half in the second column. Accordingly, b_{r1} is the reversible efficiency in the indirect order of separation for the first column, and b_{r2} — for the second.

Consider the feed mixture with the molar fractions of components x_0, x_1, x_2 , where x_0 is the molar fraction of the most volatile component, and x_2 is a molar fraction of the least volatile one. Let the molar heats of vaporization of most volatile r_0 and medium volatile components r_1 be known. The molar heat of vaporization of a mixture of the most volatile and medium volatile component will be determined as a weighted average $r_{01} = (r_0x_0 + r_1x_1)/(x_0 + x_1)$.

In the direct order of separation on the first column $T_D = T_0$, and the temperature in the reboiler, where the first and second components fall, is close to the boiling point of the first $T_B = T_1$. In the second column $T_D = T_1, T_B = T_2$.

In the indirect separation order for the first column we have $T_D = T_1, T_B = T_2$. For the second column we have $T_D = T_0, T_B = T_1$.

Initially, we obtain an inequality that determines the condition under which the total reversible heat consumption for the direct order of separation is less than for the indirect one. Then we will solve the problem of the boundary of the reachable set for the cascade taking into account irreversibility. This solution determines the optimal separation order taking into account irreversible factors.

Choosing the order of separation in the reversible approximation

Reversible column efficiency values for the direct order of separation in accordance with (28), (8) are:

$$b_{d1} = -\frac{T_1 - T_0}{RT_1T_0(x_0 \ln x_0 + (1 - x_0) \ln(1 - x_0))}, \quad (41)$$

$$b_{d2} = -\frac{T_2 - T_1}{RT_2T_1(x_1 \ln x_1 + x_2 \ln x_2 - (x_1 + x_2) \ln(x_1 + x_2))}.$$

Similarly, for the indirect order of separation, we obtain:

$$b_{r1} = -\frac{T_2 - T_1}{RT_2T_1(x_2 \ln x_2 + (1 - x_2) \ln(1 - x_2))}, \quad (42)$$

$$b_{r2} = -\frac{T_1 - T_0}{RT_1T_0(x_0 \ln x_0 + x_1 \ln x_1 - (x_0 + x_1) \ln(x_0 + x_1))}.$$

In these two expressions, the efficiency is calculated as the ratio of the flow at the inlet to the cascade per unit of heat expended, taking into account that the second column receives a flow equal to $g_F(x_1 + x_2)$ for direct and $g_F(x_0 + x_1)$ for indirect order of separation.

The flux of the separated flow does not affect the reversible parameters, as well as the universal gas constant R in (41), (42). The inequality that determines the condition under which the direct order of separation corresponds to lower heat consumption has the form:

$$(1/b_{d1} + 1/b_{d2}) < (1/b_{r1} + 1/b_{r2}). \quad (43)$$

If we substitute in this inequality the values of reversible efficiency, expressed by the formulas (41), (42) through the temperatures and molar fractions of the components, it becomes simpler and, after simple calculations, leads to a condition that includes only the boiling points of the components:

$$\frac{T_0}{T_1 - T_0} < \frac{T_2}{T_2 - T_1}. \quad (44)$$

The inequality (44) is certainly satisfied if the differences between the boiling points $T_1 - T_0$ and $T_2 - T_1$ are small. This explains the fact that in most cases, volatile components are initially separated.

The reachable set of the three-component mixture separation cascade

Let us write the relations that determine the form of the reachable set for the cascade. This form will be determined by the characteristic parameters of the columns in the direct and in the indirect order of separation, taking into account irreversible factors. The limiting value of the heat flux and the limiting productivity of the column are inversely proportional to a . Since the feed flow entering the first column is greater than the feed flow of the second one, it is advisable to lower the irreversibility coefficient of the first column.

The limiting performance of the cascade g_F^* depends on the order of separation. For direct order:

$$g_{Fd}^* = \min \left(\frac{b_{d1}^2}{4a_{d1}}; \frac{b_{d2}^2}{4a_{d2}(1-x_0)} \right). \quad (45)$$

For the indirect one:

$$g_{Fr}^* = \min \left(\frac{b_{r1}^2}{4a_{r1}}; \frac{b_{r2}^2}{4a_{r2}(1-x_2)} \right). \quad (46)$$

The productivity of the g_F cascade is related to the heat consumption.

For the direct order of separation, we obtain the relations that determine q_{d1} , q_{d2} and q_d for a given mixture flow rate:

$$q_{d1} = \frac{b_{d1}}{2a_{d1}} - \sqrt{\frac{b_{d1}^2}{4a_{d1}^2} - \frac{g_F}{a_{d1}}}, \quad (47)$$

$$q_{d2} = \frac{b_{d2}}{2a_{d2}} - \sqrt{\frac{b_{d2}^2}{4a_{d2}^2} - \frac{g_F(1-x_0)}{a_{d2}}}, \quad q_{d1} + q_{d2} = q_d.$$

Similarly, for the indirect order we obtain:

$$q_{r1} = \frac{b_{r1}}{2a_{r1}} - \sqrt{\frac{b_{r1}^2}{4a_{r1}^2} - \frac{g_F}{a_{r1}}}, \quad (48)$$

$$q_{r2} = \frac{b_{r2}}{2a_{r2}} - \sqrt{\frac{b_{r2}^2}{4a_{r2}^2} - \frac{g_F(1-x_2)}{a_{r2}}}, \quad q_{r1} + q_{r2} = q_r.$$

These costs are limited by inequalities resulting from the dimensions of the operating area of each column:

$$q_{d1} \leq \frac{b_{d1}}{2a_{d1}}, \quad q_{d2} \leq \frac{b_{d2}}{2a_{d2}}, \quad (49)$$

$$q_{r1} \leq \frac{b_{r1}}{2a_{r1}}, \quad q_{r2} \leq \frac{b_{r2}}{2a_{r2}}. \quad (50)$$

The order of separation, for which, at a given value of productivity, the heat consumption is less, is optimal, which leads to the inequality,

$$q_{d1} + q_{d2} < q_{r1} + q_{r2}. \quad (51)$$

determining the choice of the direct order of separation, taking into account the irreversibility of the processes. If the right-hand side of this inequality is greater than the left-hand side, then the optimal order is the indirect one.

At the operating area, the performance of the cascade monotonously depends on the total heat consumption, therefore, the solution to the problem of the minimum heat consumption at a given productivity coincides with the solution to the problem of the maximum productivity at a given heat consumption.

Note that the left and right sides of the inequality (51) through the conditions (47), (48) depend on the flow rate of the mixture to be separated g_F , and it may turn out that for one productivity it is more profitable to use direct, and in the case of another, the reverse order of separation.

The maximum performance for the intermediate product is $x_1 g_F^*$.

Example

Let us give an example of calculating a cascade of columns using the relationships obtained above.

1. Initial data:

- Component molar fractions and boiling points:

$$x_0 = 0.5, \quad x_1 = 0.3, \quad x_2 = 0.2, \quad T_0 = 393\text{K}, \quad T_1 = 438\text{K}, \quad T_2 = 458\text{K}.$$

- The heats of vaporization for two of the most volatile components, and their mixture:

$$r_0 = 50000 \text{ J/mol}, \quad r_1 = 70000 \text{ J/mol}, \quad r_{01} = 57500 \text{ J/mol}.$$

- Coefficients of mass and heat transfer in columns for both separation orders:

$$k_{d1} = 13 \frac{\text{mol}^2\text{K}}{\text{J} \cdot \text{s}}, \quad k_{d2} = 11 \frac{\text{mol}^2\text{K}}{\text{J} \cdot \text{s}}, \quad k_{r1} = 15 \frac{\text{mol}^2\text{K}}{\text{J} \cdot \text{s}}, \quad k_{r2} = 13 \frac{\text{mol}^2\text{K}}{\text{J} \cdot \text{s}}.$$

$$\beta_1^B = 70000 \frac{\text{W}}{\text{K}}, \quad \beta_2^B = 20000 \frac{\text{W}}{\text{K}}, \quad \beta_1^D = 75000 \frac{\text{W}}{\text{K}}, \quad \beta_2^D = 22000 \frac{\text{W}}{\text{K}}.$$

$$\text{Productivity required: } g_F = 1 \frac{\text{mol}}{\text{s}}.$$

2. Characteristic parameters for each column:

- Reversible work of separation of the mixture:

$$A_{Gd1} = -RT_0(x_0 \ln x_0 + (1 - x_0) \ln(1 - x_0)) = 2258 \frac{\text{J}}{\text{mol}},$$

$$A_{Gd2} = 1223 \frac{\text{J}}{\text{mol}}, \quad A_{Gr1} = 1819 \frac{\text{J}}{\text{mol}}, \quad A_{Gr2} = 1720 \frac{\text{J}}{\text{mol}}.$$

- Reversible efficiency, after substituting the values given above into the formulas (41), (42):

$$b_{d1} = 4.55 \cdot 10^{-5} \frac{\text{mol}}{\text{J}}, \quad b_{d2} = 3.57 \cdot 10^{-5} \frac{\text{mol}}{\text{J}},$$

$$b_{r1} = 2.40 \cdot 10^{-5} \frac{\text{mol}}{\text{J}}, \quad b_{r2} = 5.97 \cdot 10^{-5} \frac{\text{mol}}{\text{J}},$$

- The irreversibility coefficients for the direct and indirect order of separation are calculated by the formula (27), assuming the temperatures T_+ , T_- are close to T_B , T_D , respectively:

$$a_{d1} = 3.38 \cdot 10^{-11} \frac{\text{mol} \cdot \text{s}}{\text{J}^2}, \quad a_{d2} = 18.0 \cdot 10^{-11} \frac{\text{mol} \cdot \text{s}}{\text{J}^2},$$

$$a_{r1} = 4.27 \cdot 10^{-11} \frac{\text{mol} \cdot \text{s}}{\text{J}^2}, \quad a_{r2} = 13.3 \cdot 10^{-11} \frac{\text{mol} \cdot \text{s}}{\text{J}^2}.$$

3. The inequality (43), which determines the order of separation in the reversible approximation, up to a constant factor 10^5 , takes the form:

$$(1/4.55 + 1/3.57) < (1/2.4 + 1/5.97).$$

It is satisfied; therefore, in the reversible approximation, the direct order of separation is preferable.

4. The maximum productivity of the cascade for the direct and indirect order of separation according to the formulas (45), (46):

$$g_F^{*I} = \min \left[\frac{(4.55)^2 10}{43.38}; \frac{(3.57)^2 10}{4180.5} \right] = 3.54 \frac{\text{mol}}{\text{s}},$$

$$g_F^{*II} = \min \left[\frac{(2.4)^2 10}{44.27}; \frac{(5.97)^2 10}{413.30.8} \right] = 3.37 \frac{\text{mol}}{\text{s}}.$$

The required performance is less than the maximum one for both separation options.

5. For each of the options, the total heat consumption according to the formulas (47), (48) for $g_F = 1$:

$$q_{d1} = 23\text{kW}, \quad q_{d2} = 16\text{kW}, \quad q_d = 39\text{kW},$$

$$q_{r1} = 45.2\text{kW}, \quad q_{r2} = 57.5\text{kW}, \quad q_r = 202.7\text{kW}.$$

So according to (51) and taking into account irreversibility, the direct order of separation is preferable.

Generalization to a multicomponent mixture

The results obtained can be generalized to the case of separating a mixture of n components with a molar fraction of each equal to x_i into three fractions with concentrations $X_0 = \sum_0^v x_i$, $X_1 = \sum_{v+1}^j x_i$, $X_2 = \sum_{j+1}^v x_i$ assuming a complete separation.

In order for the mixture in the condenser to contain all the components of the separated fraction, the temperature in it must be equal to the highest boiling point of the component of this fraction. Similarly, so that the liquid in the reboiler contains all the components of the fraction separated into the cube, its temperature cannot be higher than the minimum boiling point of the component of the fraction in the cube. As a result, all the results obtained above are valid after replacing the concentrations of the components with the concentrations of fractions and calculating the temperatures in the still and in the reflux condenser as the boiling points of the most and least volatile components of those included in the separated fraction. Taking this circumstance into account, we will not further distinguish between the problems of separation into components and into fractions.

Structure of n consecutive columns

More than two columns are connected in series, in the case when in each column one of the output streams does not require further separation, and the second stream enters the next column of the cascade. If both outlets of the first column are connected to two subsequent columns, then we arrive at the parallel structure discussed above.

Let us take a look on the sequential structure. When separating a mixture of n components, the cascade consists of $n - 1$ columns. The columns are arranged so that the corresponding irreversibility coefficients a_i increase, since the flow rate of the mixture decreases in the course of the separation process.

To optimize such a structure, the Bellman dynamic programming algorithm⁸ can be used, which takes the following form:

1. For the last two columns, all possible fractions of three components with close boiling points are taken into account (their amount is equal to $n - 2$). For each such fraction, using the conditions (44)–(51), the optimal separation order and the corresponding minimum heat consumption are found.
2. A third column from the end is added to this cascade, and for the resulting cascade, all fractions from four components close in boiling points are sorted out (their amount is $n - 3$). Of the two possible options - the direct and indirect order of separation of each such fraction, the best is chosen, taking into account the fact that each order of separation corresponds to the optimal parameters of the cascade of the last two columns. Thus, each mixture of four components close to each other is put in correspondence with the order of its separation and the minimum required heat consumption.
3. The fourth column from the end of the cascade is added and all five-component fractions are sorted out in the same way, and so on.

The calculation is completed when the size of the fraction becomes equal to $n - 1$, and the number of options turns out to be equal to two. The limiting productivity of the cascade is determined by the limiting productivity of the first column, when the difference between the total heat consumption and its minimum consumption on all other columns of the cascade is $\frac{b_1}{2a_1}$ for the order of separation, which is found using the described algorithm.

CONCLUSION

We have shown that for optimization problems of structures consisting of several distillation columns, a parameterized representation of its load characteristic can be used. In this representation the relationship for the load characteristic is determined by only two characteristic parameters. These parameters can be calculated both from the characteristics of the mixture and the kinetics of the process, and directly from the experimental data. Problems that can be solved knowing only the characteristic parameters of the columns are considered. Such problems include the problem of the maximum productivity, the dependence of the efficiency of the column on its productivity, the optimal distribution of flows in the parallel structure, and the order of separation in the sequential structure. The dependence of the reflux ratio on the characteristic parameters is obtained. The results make it possible to optimize complex systems by dividing them into subsystems, each of which can be represented as a parallel or sequential structure.

NOTATION

g — material flux, mol/s;
 h — molar enthalpy, J/mol;
 \bar{k} — effective mass transfer coefficient, $\frac{\text{mol}^2 \text{K}}{\text{J} \cdot \text{s}}$;
 β — heat transfer coefficient, $\frac{\text{W}}{\text{K}}$;
 P — pressure, Pa;
 p — power output, W;
 q_+, q_- — heat fluxes in the reboiler and condenser respectively, W;
 $R = 8.31 \text{ J}/(\text{mol} \cdot \text{K})$ — universal gas constant; reflux ratio;
 s — molar entropy, J/(mol·K);
 T_+, T_- — temperatures of the heating fluid in the reboiler and cooling fluid in the condenser respectively, K;
 V — the vapor flux, mol/s;
 x — molar fraction of a component in the liquid phase;
 y — molar fraction of a component in the vapor phase;
 y^0 — equilibrium molar fraction of a component in the vapor phase;
 α — relative volatility;
 r — molar vaporization heat, J/mol;
 ε — upper product fraction;
 μ — chemical potential, J/mol;
 σ — entropy generation, W/K.

INDICES

B — related to the reboiler;
 D — related to the condenser;
 F — related to the feed;
 i, j — related to the component or order of separation.

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