It is obvious that the rate of the diffusional flow during the growth of the crystal, which is governed by diffusion, is equal to the mass rate of growth of the particle. On converting from the mass rate of crystal growth to a linear rate, bearing in mind that X = 2R, it is found that

$$\beta_{dif} = \frac{dx}{d\tau} = \frac{4DM\Delta C}{\delta X}. \quad (11)$$

Here M is the molecular weight of the dissolved material (M = 0.4352 kg.); C and C_0 are, respectively, the actual and equilibrium concentrations of the solution, mole/m^3; D is the diffusion coefficient of the dissolved material in the solvent, m^2/sec.

The diffusion coefficient in 80% ethanol, determined using the method of Norton and Anson (8) at 22°C, is 1.5×10^{-9} m^2/sec. In this case, the "diffusion" rate of growth, with a supersaturation of $\Delta C = 17.391$ mole/m^3, should be equal to

$$\beta_{dif} \cong \frac{2.8\ 10^{-11}}{X}.$$

For these conditions we also have $\beta \cong 8 \times 10^{-9} - 8 \times 10^{-4}X$. Hence, for the same value of X, the values of β_{dif} and β differ from one another by several orders of magnitude. This indicates that, in this case, diffusion is not the limiting step in the deposition of material, but rather that "pseudo-dissolution" of coarse crystals (7–9 microns) occurs in the supersaturated solution (Figure 3b) instead of their expected "diffusion" growth. The simultaneous dissolution of one boundary of a crystal and growth of another under the same solution supersaturation was observed by Andreev (9), and dissolution of coarse and growth of fine crystals by Dulepov (10).

On the basis of this kinetic behavior of the growth of particles during the mass crystallization of thiamine bromide, the assumption can be made that the rate of growth of the particles obviously depends on the circumstances within the crystal itself.

In conclusion, let us consider the change in the dimensions of the crystals during the process of their growth. Equation (7) can be used for this purpose; this is a linear differential equation of the first order. Its general solution is

$$X = \Omega \cdot e^{-\int D(\tau)d\tau} + e^{-\int D(\tau)d\tau} \cdot \int [C(\tau) + \beta_{00}(\tau)] \cdot e^{\int D(\tau)d\tau} \cdot d\tau, \quad (12)$$

where Ω is an integration constant. The functions $C(\tau)$, $D(\tau)$ and $\beta_{00}(\tau)$ are shown in Figure 2.

Let us assume that the crystal in which we are interested has a dimension X_1 at the moment of time τ_1. By substituting X_1 and τ_1 into (12), we determine the values of Ω_1, corresponding to the particular solution. Some of these solutions are shown in Figure 5.

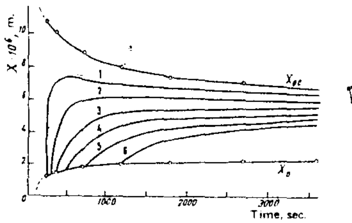

Fig. 5. Change in crystal size during its growth. Curves 1–6 correspond to various times of appearance of the crystal.

It can be seen from Figure 5 that, during the first interval of time after their appearance, the crystals grow rapidly; then, after reaching their maximum size, they practically cease to grow (even some decrease in size can be observed). This picture suggests an ageing process. It can be assumed that during the growth process "defects" accumulate in the crystal, which are related to block growth, together with dislocations, the effects of impurities, etc. These paralyze the process of deposition of material, and the surface of the crystal which is formed at high degrees of supersaturation appears to the thermodynamically unstable at lower degrees of supersaturation.

In the present case this picture cannot be explained by inhibition of the crystals or their disruption by the pump. This is clear from the fact that the results of evaluating the experimental material on the crystallization of the present system in the absence of mixing (circulation) showed a type of dependence on X which does not differ in principle from that described in the present paper. It must also be added that the volume fraction of the solid phase in the circulating suspension reached a maximum of 1.5% in our experiments.

Conclusions

1. It has been shown that the linear rate of growth of thiamine bromide falls as the crystal dimensions increase.
2. It has been shown that, in the present case, diffusion is not the limiting factor in the process of deposition of material on the crystals.
3. It has been shown that there can be "pseudo-dissolution" of coarse crystals and growth of fine crystals in the same supersaturated solution. In this connection, a proposal is made with respect to the ageing of crystals during their growth.

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Thermodynamic analysis of rectification. II. Finite cascade models

A survey-type article concerned with efforts to reduce the degree of irreversibility of existing distillation processes.

Literature review

THE theory of reversible distillation and the minimization of the irreversibility of industrial distillation processes has been the subject of research for roughly one-half a century. In a previous paper, the present author (57) analyzed the characteristics of reversible rectification, emphasizing the practical obstacles to its realization. In the present paper, attempts to reduce the degree of irreversibility of existing distillation processes and to obtain more favorable energy solutions are reviewed, and finite cascade models are analyzed.

Van Nuys (1), in a series of papers published in 1923, first raised the question of the thermal efficiency of distillation and analyzed the process from an energy standpoint. Dodge and Hausen (2) studied a model of an air-separation installation with an infinite number of plates, for the case of adiabatic operation. They found to their surprise that, with an ideal heat pump and minimum reflux ratios (at the head of the column) the energy requirements were still nearly 50% more than the thermodynamic work of reversible separation (Part I, Equation (35)).

In 1932, Hausen (3) proposed a reversible distillation model with an infinite number of plates, with a gradual variation of the liquid and vapor flows required by the reversible process. Variation of the flow of material is assured by the gradual expansion of an auxiliary gas. using gradual cooling in the rectifying zone and gradual heating in the vaporization zone. It is obvious that the infinite dimensions, and the expansion machine for the auxiliary gas needed at each level, make the practical use of such a model impossible.

Benedict (4) classified the operations of the chemical industry from a power standpoint. Three fundamental types are to be distinguished:

—potentially reversible processes in which the energy requirements can theoretically be reduced to the thermodynamic separation work; its value is thus independent of the concentration ratio;

—partially reversible processes in which most of the steps are potentially reversible, but in which a certain part of the operation is irreversible; for example, in extractive distillation the solvent input is always irreversible;

—irreversible processes, in which the amount of work required (exergy devaluation) is inversely proportional to the square of the concentration ratio; for example, diffusion, thermal diffusion, electrolysis, etc.

Based on a thermodynamic examination of a two-component rectifying column, Benedict classified the distillation process as a potentially reversible operation. In a previous article by the present author (57), it was pointed out that, in the general case (for multicomponent mixtures), this statement is not valid

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for the separations used in industrial practice. Benedict's achievement, however, lies in the statement that, in the case of the complete separation of two-component mixtures, the energy requirements for adiabatic rectification are independent of the relative volativity if an ideal heat pump is used.

In the struggle against the irreversibility of the distillation process, the work of Bosnjakovic (14) represented an important step; he proprosed numerous practical possibilities for the approximation of reversible processes, and his discussion called the attention of engineers to the energy viewpoint. The application of the thermodynamic view of distillation processes to industrial installations may be traced in the technical monograph of Ruhemann (5) on the separation of gases.

Researchers arrived at the "ideal cascade" model during an analysis of the efficiency of isotope separation; this model operates with the lowest material flow between levels (6, 11, 15, 20). Although the ideal cascade does not represent a thermodynamically optimum process, it yields a more favorable thermodynamic degree of efficiency than a finite adiabatic rectification installation. In his articles (7, 21), Freshwater proposed recompression of the vapor of the overhead product and the use of heat pumps between the intermediate levels of the column. Hipkin called attention to an error in the graphical representation (22) used by Freshwater. Haselden's work must be mentioned specially (8, 12, 23); he treated the thermodynamic analysis of separation operations in several publications. In a study of the incomplete separation of liquid air, he showed that there is no need for the finite exchange of energy if the energy input is gradual at each level (12). Haselden, however, erroneously generalized the reversible rectification model for two-component mixtures to include multicomponent mixtures. These errors have also been pointed out in References (24, 25).

Grunberg (10) was the first to propose a reversible distillation model for multicomponent mixtures, which was later confirmed on several occasions (16, 17). Grunberg, in his Colorado lectures, in essence laid down the theoretical foundations of the reversible rectification of multicomponent mixtures; this has been described in the first part of the present study. Although in his paper he did not present a mathematical description of the model or demonstrate the uniqueness of his concepts, and although he did not consider the possibility of the coupling of columns, but advanced certain postulates which appear to be superfluous (for example, the postulate of "the continuity of rectification"), the paper is highly important in the history of science, because it opened up the way for the power improvement of industrial distillation systems.

Even in the relevant literature of the past decade, several examples can be found of the thermodynamic investigation of rectification in which a single aspect is emphasized to the exclusion of all others. This gave birth to the blind-plate design of the distilling columns in the petroleum industry (26). As shown later (41, 50), in its design only energy aspects were considered. Referring to an error in graphical presentation in a paper by Niedzwiecki (31), which extolled the advantages of a recirculating reflux, Hipkin (33) erroneously denies the feasibility of such refluxes in general; they were later reinstated by Niedzwiecki (34).

Among the numerous related subjects found in the literature (for example, (9, 13, 29)), nonadiabatic rectification in separate installations (18, 35) or the proposal of flow diagrams using direct cooling media, are mentioned specifically (28).

The most complete work published to date in the field of the thermodynamic study of distillation of multicomponent mixtures is the monograph of Platonov and Bergo, which has been used as a manual in the writing of the present series of articles (30). The development of the technical scheme of divided column is an important merit of the book. The thermodynamic point of view plays an important role in the analysis of gaseous separation processes (36) in the book by Pratt and King (38, 56) on the processes of separation. Some of the papers which analyze heat transfer and distillation from a thermodynamic standpoint (39, 40, 41, 45, 46, 50, 53, 55) attempt a compromise between thermodynamic requirements and considerations of equipment; and this subject—in the opinion of the author—will be the principal area of research in the improvement of the thermodynamic efficiency of distillation and in its optimum development.

Papers applying the concept of exergy and the theory of associated processes offering coordinating principles (37, 51, 53, 54, 42, 43, 44, 47, 48, 49) are related to thermodynamic analysis of the distillation process. In this field, special attention is merited by the recently published monograph of Szolcsanyi (54), which, as far as is known to the author, is the first to treat operational diffusion units in the chemical industry on the basis of uniform, nonequilibrium principles.

It can be seen from this brief literature review that prior to the selection of efficient processes, in addition to the analysis of reversible distillation—as an ideal model, which can be increasingly approached but never attained—the clarification of certain fundamental concepts is necessary. Some of these are finite distillation models, adiabatic distillation (orthogonal cascades), ideal, stepped and thermodynamically ideal cascades. These models were developed in detail for binary mixtures only, but still offer a suitable basis for further investigations.

Adiabatic distillation (orthogonal cascade)

It has been shown in the foregoing that reversible mass transfer with conventional adiabatic rectification is not feasible. (The values of the material flows do not vary by level in accordance with the relationship corresponding to reversible distillation).

Since presently operating distillation processes are generally adiabatic and a mathematical description of them may be found in texts on unit processes (for example, 32), only two special sets of problems will be discussed here:

—the exergy requirements for an infinite adiabatic distillation column and;

—the problem of the optimum feed rate of a finite adiabatic distillation model.

Exergy requirements for adiabatic rectification

Expressing K_i-t from the material-balance equation of (I. 26)) and forming α_{ip}-t for the volumetric flow of the rectification zone, yields the following expression (47):

$$V=\left[1+\left(\frac{x_{iD}}{x_i}-\alpha_{in}\frac{x_{pD}}{x_p}\right)\frac{1}{\alpha_{ip-1}}\right]D. \tag{1}$$

For the feed plate $x_i = x_{iF}$, and since $x_{iD} >> x_{pD}$ and

$$\alpha_{ip}\approx 1,\ \frac{1}{\alpha_{ip}-1}\to\infty \tag{1a}$$

the following may be written

$$V=\frac{1}{\alpha_{ip}-1}\,\frac{x_{iD}}{x_{iF}}\,D. \tag{2}$$

From the component and complete material balance equation, with the expression

$$D=F\,\frac{x_{iF}-x_{iB}}{x_{iD}-x_{iB}} \tag{2qa}$$

the expression of the mass flow rate of the steam becomes

$$V=\frac{1}{\alpha_{in}-1}\cdot\frac{(x_{iF}-x_{iB})x_{iD}F}{(x_{iD}-x_{iB})x_{iF}} \tag{3}$$

From (I, 19), with a constant value of α, and a temperature difference of ΔT

$$\Delta T=-\frac{RT^2}{\lambda}\sum_{i=1}^{p}(\alpha_{ip}-1)\cdot(x_{iD}-x_{iB}). \tag{4}$$

From Equation (I, 31), assuming that

$$V=\text{const}\quad\text{and}\ \Delta T=\int dT$$

$$e=\lambda V\,\frac{T_0}{T^2}\,\Delta T. \tag{5}$$

The minimum exergy requirements for adiabatic distillation are obtained from the equations (3, 4, 5)

$$e=-RT_0F\sum_{i}^{p}x_{iD}\left(1-\frac{x_{iB}}{x_{iF}}\right). \tag{6}$$

For a binary mixture

$$e=RT_0F\left(1-\frac{1-x_D}{1-x_F}\right)\cdot\left(1-\frac{x_B}{x_F}\right).$$

With complete separation, $1-x_D = 0$ and $x_B = 0$,

$$e=-RTF \tag{7a}$$

for $\alpha \to 1$

Equation (6) is a completely general relationship for the exergy requirements for infinite adiabatic rectification. For the separation of a given mixture, the value obtained in this manner will always be greater than the exergy requirements of a reversible rectification model (I. 35).

The exergy requirements in infinite adiabatic distillation in an actual case can also be calculated from the overall fundamental concepts of distillation technology. For this purpose, the minimum reflux ratio may be calculated from the top and bottom temperatures:

$$e=-T_0\lambda\,\frac{(V_{\min}+D)\cdot(T_B-T_D)}{T_BT_D}. \tag{9}$$

In the case of finite apparatus dimensions, the actual vapor volume must be written for $V_{\min}$.

Optimum feed rate in adiabatic rectification

The costs of finite adiabatic distillation are considerably affected by the choice of the location of the feed (n_F) and of the state (T_F temperature). As in any optimum economic solution, the optimum value of these factors corresponds to the overall minimum of the energy and investment costs. It can be seen that the optimum location and temperature of the feed corresponds only to the energy minimum; the investment costs vary only slightly or not at all with the feed parameters. The coincidence of the economic and thermodynamic optima is demonstrated by Platonov and Bergo (30) using the example of the separation of pyrolysis gas. It is evident that determination of the optimum feed parameters (T_F, n_F) comes down to the minimalization of the total entropy increment function, generated by the concentration and temperature differences of the feed and column material flows being mixed. The form of the function, using the notation of Figure 1, is the following:

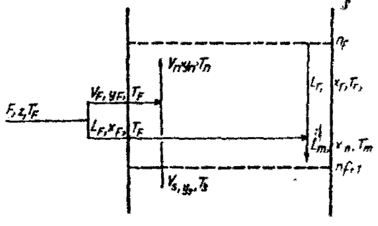

Fig. 1. Feed flow for adiabatic rectification.

$$\Delta s_{\text{total}} = \Delta s_z + \Delta s_T \tag{10}$$

$$\Delta s_z = -L_F R \Sigma x_F \ln x_F - V_F R \Sigma y_F \ln y_F - L_r F \Sigma x_r \ln x_r - V_S R \Sigma y_S \ln y_S + L_m R \Sigma x_m \ln x_m + V_n R \Sigma y_n \ln y_n. \tag{11}$$

$$\Delta S_T = L_F C_{p,L} \ln \frac{T_m}{T_F} + V_F C_{p,V} \ln \frac{T_n}{T_F} + L_r C_{p,L} \ln \frac{T_m}{T_d} + V_S C_{p,V} \ln \frac{T_n}{T_B} \tag{12}$$

The minimum values may be found, under the condition T_F = constant (given feed temperature), in the form of a $\varphi = \varphi(nF)$ single variable function, with the stipulation that the variable nF may assume integral values only. Since the transfer of energy in an adiabatic operation may take place in the condenser or the boiler, the equation contains T_D or T_B.

Ideal cascade

Recently, the pertinent literature, in addition to a reversible rectification model, is showing much interest in an ideal-cascade model for binary mixtures (6, 11, 15, 20). This represents a finite cascade, and has the lowest possible mass flow between levels, thus requiring the lowest column volume.

$$I = \int_0^N V(j)\,dj = \text{Min} \tag{13}$$

Attempts have been made to apply the theory to multicomponent rectification (19). A detailed analysis of ideal cascades goes beyond the scope of this paper; thus, only the most important characteristics, necessary for the further investigation, are described. In an ideal cascade, the composition of the liquid and vapor arriving at any plate is identical (6):

$$x_{j+1} = y_{j-1} \tag{14}$$

It can be shown that the equation of the working line of an ideal cascade is

$$y_{j-1} = \frac{\sqrt{\alpha}\,x_j}{1 + (\sqrt{\alpha} - 1)x_j}. \tag{15}$$

Since the equilibrium relationship is

$$y_{j-1} = \frac{\alpha x_{j-1}}{1 + (\alpha - 1)x_{j-1}} \tag{16}$$

it can be seen that equation of the working line for an ideal cascade coincides with the hyperbolic equation of a binary mixture with a relative volatility of $\sqrt{\alpha}$ (Figure 2). It follows that an ideal cascade contains twice the minimum number of plates ($R = \infty$) in a given rectification problem (11):

$$N_{N_{\text{cascade (ideal)}}} = 2N_{\min} \tag{17}$$

Based on the parameters listed above, the material flows in the ideal cascade can easily be derived for each level (11):

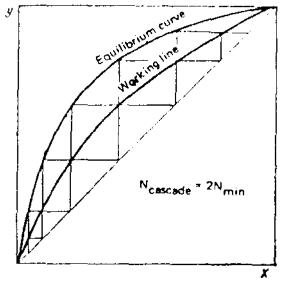

Fig. 2. Working line of ideal cascade and its steps.

For the rectification zone:

$$\frac{L_j}{D} = \frac{1}{\sqrt{\alpha} - 1}\left\{[x_d(1 - \sqrt{\alpha})^{j-N}] - (1 - x_d)\sqrt{\alpha}[(\sqrt{\alpha})^{N-j} - 1]\right\} \tag{18}$$

For the stripping zone:

$$\frac{V_j}{B} = \frac{1}{\sqrt{\alpha} - 1}\left\{x_W\sqrt{\alpha}[(\sqrt{\alpha})^{j-1}] + (1 - x_W)[1 - (\sqrt{\alpha})^{-j}]\right\} \tag{19}$$

Since, in the equations, j is the number of plates, in an ideal cascade the thermal and cold energies—similarly to reversible rectification, but not to the same degree—must be fed to the stripping concentrating sections along the entire height of the column (only in this manner can the variations of the vapor and liquid flows be obtained for each level).

The production of entropy in the ideal cascade can be determined from an integral calculated over the entire width of the cascade:

$$\Delta S = \lambda \int_0^{V_{\max}} \frac{T_T - T_A}{T_T \cdot T_A} \cdot dV, \tag{20}$$

where T_T and T_A are the absolute temperatures of the upper and lower temperature levels, between which heat transfer on the magnitude of $\lambda \Delta V$ takes place.

Numerous publications regard an ideal cascade as a model of minimum exergy requirements. This concept is, however, incorrect. Minimum exergy requirements are insured by a minimum total entropy production, and not by a minimum value of the sum of the material flows between levels. The latter is proportional to the total volume of the column; an ideal cascade thus yields minimum column volumes. In rectification operations, the exergy requirements for separation are not directly proportional to the sum of the material flows between levels. (Such a direct proportionality exists only for elemental irreversible processes (for example, gaseous diffusion). In distillation, on the other hand, in addition to the value of the material flows, the varying temperature difference also plays a decisive role.

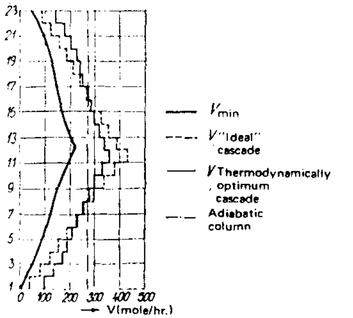

Fig. 3. Comparison of thermodynamically optimum cascade vapor flow with reversible, ideal, and adiabatic cascades.

Thermodynamically optimum cascade.

The exergy requirements of this cascade depend significantly on the properties of the mixture to be separated, and the course of the L(x) function also differs from the relationships for equilibrium distillation.

With a known theoretical number of plates, a real cascade ($N_{\text{real}} > N_{\min}$) obtainable with a heat removal of $\pm Q_j$ per j levels, is thermodynamically optimum if the following entropy integral is at a minimum:

$$S = \int_{j=1}^{N} \frac{dQ_{j-j'}}{T_j \cdot T_{j'}}(T_j - T_{j'}) = \text{Min}\,!, \tag{21}$$

where $dQ_{j-j'}$ is the amount of heat transferred from the T_j temperature level to the $T_{j'}$ temperature level. This entropy integral is directly proportional to the energy requirements for the separation and assures minimum irreversibility of the process. With the introduction of amounts of heat having discrete values per level, the minimum of the following sum

$$\sum_{j=1}^{N} \frac{Q_j}{T_j} = \text{Min}\,! \tag{21a}$$

will correspond to a minimum of the integral.

Such an optimation is demonstrated by Platonov and Petljuk (45, 30) for binary mixtures, with dynamic programming. Here only the most important relationships needed for the further discussion are given; they were obtained from examples of gaseous separation with respect to a binary mixture having a given relative volatility.

In Figure 3, the vapor flow is given as a function of the number of plates, as a comparison, for the case of minimum vapor flow (reversible rectification), adiabatic rectification, ideal cascades, and thermodynamically optimum cascades. The figure shows that the material flows of a thermodynamically optimum cascade occupy an intermediate position between the values of an adiabatic column for an ideal cascade.

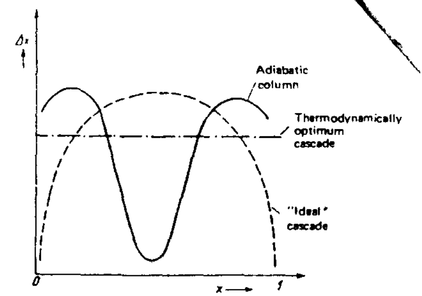

Fig. 4. Distribution of driving forces in various cascade models.

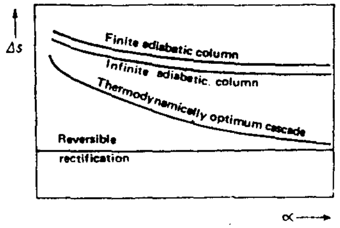

Fig. 5. Variation of entropy as a function of relative volatility.

Figure 4 shows the distribution of the driving forces over the height of the column (binary mixture) for the finite rectification model under discussion. It can be seen that the distribution of the driving forces in the case of a thermodynamically optimum cascade is uniform over the height of the column; thus, their use is the most favorable.

Figure 5 displays the variation of the entropy of separation as a function of α. The separation entropy production of an optimum cascade from an energy standpoint, in the case of $\alpha \to \infty$, approaches the entropy production of reversible separation asymptotically (the same is true for $N \to \infty$).

As far as is known to the author, no description of a thermodynamically optimum cascade for multicomponent mixtures has even been developed. The two-component model also considers only the losses of distillation due to the driving forces; in the general case, other thermodynamic losses must also be minimized.

The problem is further complicated by the fact that practical design requires the development of an overall economic optimum flow model which, in addition to exergy factors, considers investment costs also. In searching for a generally optimum solution, one of the problems to be investigated is, for example, the determination of the intermediate inlet points of thermal and cold energy, together with their number. (It can readily be seen that the thermodynamically most favorable solution, that is, realization of material flow variation for each plate, is not economically profitable). Optimization of this type has been shown for binary mixtures by Dipak and Ray (27) in their investigation of stepped cascades; this has a very restricted applicability. As a comparison, Figure 6 shows material flows developed in the concentrating sections of ideal orthogonal (adiabatic) and stepped cascades as a function of the number of plates.

It can be seen that a majority of the problems remains to be solved by researchers and designers. The discussion presented in the foregoing yields the decisively important assertion that, with constant reflux over the height of the column, distillation with good thermodynamic efficiency cannot be achieved.

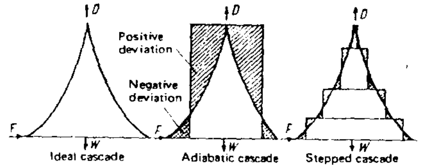

Fig. 6. Ideal, adiabatic, and stepped cascades: variation of material flow (in the condensing section) as a function of plate number.

To demonstrate the sources of thermodynamic losses, let us analyze the following gaseous fractionation problem (30). To produce ethylene, 100 mole/hr. of a mixture in the form of a saturated liquid is fed into a column under a pressure of 30 atm. The composition data is presented in the following table.

Parameters used and obtained in a computer solution of the problem:

Minimum number of plates: N_{min} = 17;

Minimum reflux (liquid flow): L_{min} = 95.4 mole/hr. (R = 3.97);

Heat of evaporation of the mixture: 8856.4 kJ/kmole;

Top temperature: T_d = 263°K;

Bottom temperature: T_W = 350°K;

Value of actual liquid flow: L_{val} = 114 mole/hr.;

Temperature difference at heat exchanger surfaces: ∇T = 7°C;

Let us approach, step by step, the entropy production from the separation entropy production of the reversible distillation column (insulation, compressor, heat-exchanger, hydraulic and other slight external losses are neglected) (Table 1). The standard thermodynamic efficiency, calculated directly for the distillation process, is low: 23.2%; if other external losses are included, it will decline further.

Table 1

Calculation of the thermodynamic efficiency of a distillation

Number	Gradual approximation step	Relationship used in calculation of entropy production	ΔS, (kJ/°C)	Entropy efficiency of gradual transition
1	Infinite, thermodynamically reversible distillation	$\Delta S_1 = D\,\Delta S_D + B\,\Delta S_B - F\,\Delta S_F$	348	
2	Infinite adiabatic distillation	$\Delta S_2 = \frac{\lambda(V_{\min}+D)\cdot(T_B-T_D)}{T_B\cdot T_D}$	1001	$\eta_1 = \frac{\Delta S_1}{\Delta S_2} = 0.35$
3	Finite adiabatic distillation	$\Delta S_3 = \frac{\lambda(V_{\mathrm{val}}+D)\cdot(T_B-T_D)}{T_B\cdot T_D}$	1207	$\eta_2 = \frac{\Delta S_2}{\Delta S_3} = 0.83$
4	Finite adiabatic distillation with hydraulic resistance	$\Delta S_4 = \Delta S_3 + \Delta S_{\mathrm{hydr.}}$	1240	$\eta_3 = \frac{\Delta S_3}{\Delta S_4} = 0.97$
5	Finite adiabatic distillation with resistance and with finite ΔT in heat exchangers	$\Delta S_5 = \Delta S_4 + Q\frac{\Delta T_m}{T_m^2}$	1503	$\eta_4 = \frac{\Delta S_4}{\Delta S_5} = 0.825$
6	Overall thermodynamic efficiency			$\eta_{\mathrm{comp}} = \frac{348}{1503} = 0.232$
	Ideal cascade for comparison	$\Delta S_{\mathrm{id}} = \int_0^{V_{\max}} \frac{T_T - T_A}{T_T\cdot T_A}\,dV$	1014	

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*Standard thermodynamic efficiency.

Composition	Feed mole %	Overhead product, mole %	Bottoms product, mole %
C_2H_4	25	96	2.63
C_2H_6	15	4	18.42
C_3	20	—	26.32
C_4	40	—	52.63
Total	100	100	100.00
Amount, mole % ..	100	24	76

It can be seen from the table that among the steps investigated, the greatest irreversibility is due to the transition to adiabatic distillation (η_1), that is, the introduction and removal of thermal energy at the ends of the column. The transition from an infinite column to a finite column, for practical reasons, cannot be reduced (η_2). On the other hand, losses due to hydraulic resistance are relatively slight (η_3).

The increase in entropy due to the finite temperature difference produced in the condenser and the boiler (η_4) is generally considerable; its value can be reduced by increasing the surface area of the heat exchangers, or by establishing direct contact in the design of the industrial installation.

The above discussion clearly indicates that the highest degree of irreversibility is due to:

—transition to the adiabatic column and;

—transition to finite condensers and boilers.

In multicomponent distillation, additional sources of irreversibility are produced by:

—second order separation requirements and;

—the nonequilibrium compositions of the recycled reflux and vapor.

In reduction of the internal thermodynamic losses of separation, the following industral processes are the most effective:

—the use of intermediate reflux condensers in the concentrating section and of intermediate boilers in the stripping section;

—installation of a heat pump in the intermediate zone of the column;

—introduction of additional feed and removal points;

—use of divided columns;

—development of a countercurrent condensation-evaporation installation;

—use of flow sheets with reversible mixing of material flows.

In these variants, the transfer of energy in general takes place at certain intermediate locations within the column or along the entire mass transfer surface; this results in a stepped variation of the interlevel material flows (or continuous variation); or this is aimed at reversible mixing of the material flows.

Nomenclature

B .... mass flow of bottoms product;
C_p .... molar heat at constant pressure;
D .... mass flow rate of overhead product;
e .... exergy;
F .... mass flow rate of feed;
I .... sum of material flows between levels;
j .... j-th plate of column;
K_i .... equilibrium proportion;
L .... liquid flow in column;
N .... number of plates in column;
Q .... heat flux;
R .... gas constant;
R .... reflux ratio;
S .... entropy;
T .... absolute temperature;
T_0 .... ambient temperature;
V .... vapor flow in column;
x_i .... mole fraction of i-th component in liquid;
y_i .... mole fraction of i-th component in vapor;
α .... relative heat of evaporation, volatility;
η .... thermodynamic efficiency;

Subscripts

B .... bottoms product;
D .... overhead product;
F .... feed plate;
i .... i-th component of mixture;
j .... j-th plate of column;
T .... upper temperature level;
A .... lower temperature level;

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A co-current mass-transfer apparatus with separated fluid streams

It is shown that division of the liquid flow into two streams significantly improves the hydrodynamic conditions for the operation of the contact stages of mass-transfer equipment.

THE development of the chemical and petrochemical industries has led to the creation of new types of mass-transfer equipment designed for absorption and rectification processes; among these, the types distinguished by the highest efficiency and throughput include equipment with co-current contacting of the phases in the contact zones (1). The use of such equipment in industry makes it possible to reduce significantly the capital expenditures for column equipment and its pay-out time.

Below we shall consider the hardware, operating features, and design methods for one variant of this type of apparatus (2).

The mass-transfer equipment shown in Figure 1 consists of a cylindrical shell 1 and an internal cylinder 2, between which is fixed a spiral strip 3 with a rising angle of 10—15°, which forms a spiral channel of rectangular cross-section. Each turn of the spiral channel has slit-like apertures which connect it with the external channels for the overflow of liquid 4. In this way, the individual turns of the spiral represent contact stages in which the overflow channels are connected not with the adjacent contact stages, but to every other stage, that is, the first with the third, the second with the fourth, etc. (Figure 2a). This arises as a result of the fact that at the succeeding junction of the contact stages (Figure 2b) the height of the overflow channel is insufficient to create in it the required column of liquid to bring about normal overflow operation.

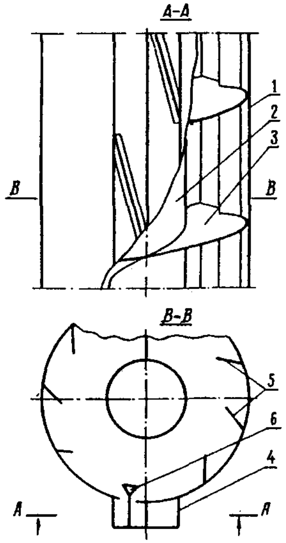

Fig. 1. Mass-transfer apparatus with separated liquid streams. 1—shell; 2—inner cylinder; 3—spiral strip; 4—liquid overflow; 5—dispersing plates; 6—separator baffle.

The vapor (gas) is fed into the lower part of the apparatus and moves upwards along the spiral channel, passing through all the contact stages in turn. The liquid is fed to the top of the apparatus, and is divided into two streams, which pass to the inlets of the first and second contact stages. On emerging from the narrow slots in the column wall, the liquid is picked up by the gas (vapor) stream and is entrained by it in the direction of its flow. The centrifugal force arising with the motion of the two-phase stream along the spiral channel tends to force the liquid toward the inner wall of the shell of the apparatus. In order to distribute the liquid more uniformly over the cross section of the contact zone, and also to ensure the development of the interfacial area and its repeated renewal, several plates 5 are fixed in each contact stage to disperse the liquid. The layer of liquid moving along the wall of the apparatus in the same

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