keyword: Petluyk ; distillation

$$+ 2a_0^2\sqrt{\frac{\text{Fo}}{\pi}}\,\frac{1-n_1}{l_0}\,(\text{Ki}_m l_2 - Al_1),$$

$$\Theta_1(X_1, \text{Fo}) = \text{Pn}_1(X_1-1)\,\text{Ki}_q\,e^{-k\text{Fo}} + (\text{Ki}_m -$$

$$-\text{Pn}_1 A)(X_1-1) + l_1 a_0^2\,\text{Ki}_q\,\frac{1-m_2}{l_0}\cdot\frac{e^{-k\text{Fo}}\,\text{erf}\,(\text{Fo}\sqrt{k\text{Fo}})}{\text{Fo}\sqrt{k}}$$

$$+ 2a_0^2\sqrt{\frac{\text{Fo}}{\pi}}\,\frac{1-m_2}{l_0}\,(\text{Ki}_m l_2 - Al_1),$$

$$T_2(X_2, \text{Fo}) = \frac{a_0^2 b_5}{l_0}\left[l_3\,\text{Ki}_q\,\frac{e^{-k\text{Fo}}\,\text{erf}\,(\text{Fo}\sqrt{k\text{Fo}})}{\text{Fo}\sqrt{k}}\right.$$

$$\left.+ 2\sqrt{\frac{\text{Fo}}{\pi}}\,(\text{Ki}_m l_4 - Al_3)\right] - \frac{a_0 b_5 X_2}{l_0}\,[\text{Ki}_m l_6$$

$$+ (\text{Ki}_q e^{-k\text{Fo}} - A)\,l_5],$$

$$\Theta_2(X_2, \text{Fo}) = \frac{a_0^2 b_5}{l_0}\left[l_7\,\text{Ki}_q\,\frac{e^{-k\text{Fo}}\,\text{erf}\,(\text{Fo}\sqrt{k\text{Fo}})}{\text{Fo}\sqrt{k}}\right.$$

$$\left.+ 2\sqrt{\frac{\text{Fo}}{\pi}}\,(\text{Ki}_m l_8 - Al_7)\right] - \frac{a_0 b_5 X_2}{l_0}\,[\text{Ki}_m l_{10}$$

$$+ (\text{Ki}_q e^{-k\text{Fo}} - A)\,l_9],$$

where

$$l_0 = -b_5 b_6 (v_{21}v_{22}K_\lambda K_{\lambda_m} + a_0^4 v_{11}v_{12}) + a_0^2 v_{22}[b_3 v_{11}(n_3 c_3 K_\lambda$$

$$-c_6 K_{\lambda_m}) - b_1 v_{12}(n_3 c_4 K_\lambda - n_1 c_6 K_{\lambda_m})] + a_0^2 v_{21}[b_4 v_{11}(c_3 K_\lambda$$

$$-c_5 K_{\lambda_m}) - b_2 v_{12}(c_4 K_\lambda - n_1 c_5 K_{\lambda_m})];$$

$$l_1 = K_\lambda(\text{Pn}_1 - \text{Pn}_2)(b_3 n_3 v_{22} + b_4 v_{21}) + K_{\lambda_m}(b_3 c_6 v_{22}$$

$$-b_4 c_5 v_{21}) + a_0 b_6^{-1} c_1 c_3 v_{12};$$

$$l_2 = b_3 n_3 v_{22} K_\lambda + b_4 v_{21} K_\lambda + a_0 b_6^{-1} n_1 c_3 v_{12};$$

$$l_3 = n_3 K_\lambda(\text{Pn}_1 - \text{Pn}_2)(v_{22} - v_{21}) + K_{\lambda_m}(c_6 v_{22} - n_3 c_5 v_{21})$$

$$+ a_0(c_1 v_{12} - n_1 c_2 v_{11});$$

$$l_4 = n_3 K_\lambda(v_{22} - v_{21}) + a_0 n_1(v_{12} - v_{11});$$

$$l_5 = b_5 v_{21} v_{22} K_{\lambda_m} + a_0^2 b_6^{-1} v_{21}(b_2 c_1 v_{12} - b_4 c_2 v_{11})$$

$$+ a_0^2 b_6^{-1} n_3 v_{22}(b_1 c_1 v_{12} - b_3 c_2 v_{11});$$

$$l_6 = a_0^2 b_6^{-1} v_{21}(b_2 n_1 v_{12} - b_4 v_{11}) + a_0^2 b_6^{-1} n_3 v_{22}(b_1 n_1 v_{12} - b_3 v_{11});$$

$$l_7 = K_\lambda(\text{Pn}_1 - \text{Pn}_2)(v_{21} - n_3 m_4 v_{22}) - K_{\lambda_m}(c_5 v_{21} - c_6 m_4 v_{22})$$

$$+ a_0^2 c_2 v_{11} - a_0 c_1 m_2 v_{12};$$

$$l_8 = K_\lambda(v_{21} - n_3 m_4 v_{22}) + a_0(v_{11} - n_1 m_2 v_{12});$$

$$l_9 = b_5 v_{21} v_{22}[K_\lambda(\text{Pn}_1 - \text{Pn}_2) - K_{\lambda_m}\text{Pn}_1]$$

$$+ a_0^2 b_6^{-1} m_4 v_{21}(b_4 c_2 v_{11} - b_2 c_1 v_{12}) + a_0^2 b_6^{-1} v_{22}(b_3 c_2 v_{11}$$

$$-b_1 c_1 v_{12});\ l_{10} = b_5 v_{21} v_{22} K_\lambda + a_0^2 m_4 v_{21}(b_4 v_{11} - b_2 n_1 v_{12})$$

$$+ a_0^2 v_{22}(b_3 v_{11} - b_1 n_1 v_{12});$$

$$b_1 = m_2 - m_4;\ b_2 = 1 - n_3 m_2;\ b_3 = 1 - n_1 m_4;\ b_4 = n_1 - n_3;$$

$$b_5 = 1 - n_1 m_2;\ b_6 = 1 - n_3 m_4;\ c_1 = 1 - n_1\text{Pn}_1;\ c_2 = m_2 + \text{Pn}_1;$$

$$c_3 = m_2 + \text{Pn}_2;\ c_4 = 1 + n_1\text{Pn}_2;\ c_5 = m_4 + \text{Pn}_1;$$

$$c_6 = 1 + n_3\text{Pn}_1.$$

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Thermodynamic analysis of rectification I. Reversible model of rectification

Method for improvement of thermodynamic conditions in the rectification of multicomponent mixtures.

Introduction

THE efficiency of the rectification process can be improved in two ways. One is modification of the design of the distilling installation to intensify its operation. This improves the operating distillation conditions. The other possibility is the improvement of the industrial process, on the basis of other considerations. In this manner, the thermodynamic conditions of the process may be improved.

There are numerous publications dealing with improvement of the distillation process. Usually these have been investigations included in attempts to improve the efficiency of the distillation process. They include the multiple problems of the cross-sectional design of the distilling column, hydrodynamic dimensioning, plate efficiency, modelling, etc. There are comprehensive texts available on the subject in Hungarian, for example, (7, 25).

The present series of papers is concerned with improvement of thermodynamic conditions in the rectification of multicomponent mixtures. In this field, the pertinent literature is much poorer, and the first domestic publications have appeared only recently (26, 31). Deficiencies and unfounded concepts with respect to the fundamental problems of the subject still exist and they lead, from time to time, to incorrect conclusions. Thus, for example, Hopkins in 1966 rigidly rejected the justification for circulation reflux, which had proven itself out for decades in the technology of the petroleum industry. An example of the other extreme is the use of so-called "blind plates" with side discharge (17). The philosophy of its design considers merely the energy aspects of the process and neglects the requirements of product quality and flexibility. The inflexible influence and the unfavorable effect on the quality of the blind-plate discharge process is by now obvious (23, 26).

The purpose of our present discussion is the combination of the thermodynamic concepts of multicomponent rectification systems into a uniform theory and, in the basis of the theory, the presentation of proposals to minimize the degree of irreversibility occurring in industrial distillation installations, keeping in mind the economic aspect (to attain a minimum production of entropy), with consideration of capital investment, capacity, product quality, and flexibility.

Theoretical foundation. Definition of problem.

The separation of components by distillation, in thermodynamic terminology, requires the expenditure of work. The work performed in distillation columns is at the expense of the evolution of heat. In adiabatic distillation, heat flows from the bottom to the top of the column from a higher to a lower temperature level. Maximum work is obtained by the use of the Carnot cycle. The "useful work" or energy of a heat flux Q (9) is:

$$e = Q\left(1 - \frac{T_0}{T}\right). \qquad (1)$$

It can be seen that, with the devaluation of heat, a loss of energy occurs, which in this case, in addition to other thermodynamic losses, covers the work of separation. The theoretically necessary devaluation of energy in the isothermal-isobaric separation in separating n products (one top, one bottom, n-2 side products) is:

$$e = -RT_0\left(a\sum_i x_{ia}\ln x_{ia} + b\sum_i x_{ib}\ln x_{ib} + \dots + n\sum_i x_{in}\ln x_{in} - F\sum_i x_{iF}\ln x_{iF}\right)^*. \qquad (2)$$

The difference between the "useful work" determined from Equation (1) and the "recovered work," calculated by Equation (2), is the internal thermodynamic rectification loss. The internal thermodynamic losses of the column are caused by finite driving forces occurring in the complex, interrelated, mass- and heat-transfer processes, and by the hydrodynamic resistance. In accordance with the theory of irreversible processes, rectification may formally be considered a first-order steady-state system, in which, during evaporation and condensation, combined heat and mass transfer take place at a finite rate, resulting in finite driving forces and irreversibility. Therefore, rectification, based on the theory of associated thermodynamic processes, may be conceived as a process in which a flow of heat is generated in the column under the effect of a temperature gradient (impressed driving force), to be joined by component flows, so that over an uncharged system, the overall component flows are zero (30, 20, 28).

In accordance with the theory of irreversible processes, the driving force associated with an isothermal-isobaric component flow is:

$$\Delta\left(\frac{G_i}{T}\right) = \frac{1}{T}\Delta G_i = \frac{1}{T}\left(\frac{\partial G_i}{\partial x_i}\right)\Delta x_i,$$

where the partial derivative of G_i is a function of x_i and must thus be calculated at an average concentration of $\bar{x}_i$. Since

$$\frac{\partial G_i}{\partial x_i} = \frac{RT}{\bar{x}_i},$$

the driving force is

$$\Delta\left(\frac{G_i}{T}\right) = \frac{R}{\bar{x}_i}(\Delta x_i)_m.$$

With consideration of the Nernst equation for the component flow:

$$J_i = D_i\,\varrho_i\,\Delta x_i$$

The production of entropy in accordance with the Onsager theorem (driving force times flow) (2) is:

$$\Phi_s = \sum_i J_i\left(\frac{\Delta G_i}{T}\right) = \sum_i D_i \varrho_i R\,\frac{(\Delta x_i)_m^2}{\bar{x}_i}. \qquad (3)$$

The loss of energy in accordance with the Gouy-Stodola equation:

$$\Delta e = T_0(S - S_0) = T_0\Delta S. \qquad (4)$$

Using the equation relating the steady-state change in the entropy with the entropy source density Φs

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*For nonideal mixtures Ln $\gamma_i x_i$ should be written for ln x_i.

Fon 1974

$$\Delta S = \iint \Phi_s \, dt \, dV. \tag{5}$$

It is evident that the loss of energy decreases with decreasing differences in concentration, and is reduced to zero only in the case of an infinitely small difference in concentration (for example, for an infinitely large value of the diffusion coefficient, the value of Δx_i is not finite and $\Phi_s = 0$).

In the course of designing unit processes, however, it must be borne in mind that the dimensions of the installation increase with declining driving forces as do investment costs. The task of the designer is thus to find the optimum value of the driving forces from an economic standpoint.

Study of the thermodynamic losses generated by the driving forces of separation units shows that the lowest losses correspond to the most uniform distribution of driving forces (countercurrent) and that the highest losses occur in complete-mixing elements (16). In the case of countercurrent units, nearly all of the entropy produced is applied to mass transfer (with the exception of finite driving forces and hydraulic resistance); in complete-mixing elements, on the other hand, nearly the entire entropy yield is needed to cover the undesirable "dilution process" (mixing) which takes place with very high driving forces. Direct flow units occupy an intermediate position with respect to thermodynamic losses between the two extremes. On the plates the inefficient use of driving forces (remixing), in industrial installations, thus increases the number of separating units. This statement is supported by other articles, analyzing the degrees of efficiency and remixing, for example (7).

Uniform adjustment of the value of the driving forces is important, not only within a single separation element (plate), but over the entire height of the column. In conventional, so-called adiabatic columns, the distribution of the driving forces over the height of the column in the separation of multicomponent mixtures is extraordinarily uniform, at both ends of the column and in the vicinity of the inlet (in the irreversible mixing of material flows), and large driving forces are generated; this leads to an increase in the overall energy cost of the separation. It can be seen from the above considerations that, in the rectification process, part of the thermodynamic irreversibility occurring as a result of the concentration difference regarded as a driving force, the so-called useful part, which is applied to mass transfer, must be optimized with the counteracting parameter of investment costs; the harmful part, on the other hand, which occurs in the vicinity of the material flow inlet and at the ends of the column during mixing, must be minimized by improving the technical design.

Hydrodynamic resistance, which forms part of the internal thermodynamic losses, is a result of the entropy-producing process of frictional dissipation, in which work performed serves to compensate the energy related to internal friction. The hydraulic resistance encountered in the column increases the temperature difference to be maintained, thus increasing the energy requirements. In the distillation of mixtures to be separated, the hydraulic resistance generally brings about a reduction in relative volatility, thus further raising energy needs. Hydraulic resistance must therefore also be minimized (design improvements).

In addition to the so-called internal losses taking place inside the column, external thermodynamic losses also occur in distillation installations. The most important among these is the production of entropy as a result of the finite temperature differential existing in reflux boilers and condensers (heat exchangers). Since the flow of heat and the associated driving force are related by (30):

$$J_Q = A \cdot \alpha \cdot \Delta T_m$$

it follows that

$$\Delta\left(\frac{1}{T}\right) = \frac{\Delta T}{T_1 T_2} = \frac{\Delta T_m}{T_m^2}.$$

From these, the density of the entropy source is

$$\Phi_s = A \cdot \alpha \cdot \left(\frac{\Delta T}{T}\right)_m^2. \tag{6}$$

It can be seen from Equations (4), (5), (6) that the loss of energy can be reduced in the case of small temperature differences, but that it can be reduced to zero only for infinitely small ΔT values (for example, infinitely large heat-transfer surface areas or infinitely large heat-transfer coefficients). It is evident that in the design of heat-transfer installations, an economic optimum must again be sought through the simultaneous consideration of investment costs and the loss of energy.

In addition to the loss of energy caused by the finite temperature difference existing in heat exchangers, compressor and pump losses, thermal losses to the environment, hydraulic losses, etc., are unavoidable in heat exchangers. As a demonstration, we present certain examples of the thermodynamic efficiency of distillation plants:*

Separation of liquid air: 18% (11);
atmospheric and vacuum distillation in the petroleum industry: 12% (16);
Separation of pyrolysis gas: 5% (11);
isotope separation: 0.01—0.001% (13).

The low thermodynamic efficiency of rectification processes represents an incentive for researchers to seek novel, more economical, technologies through detailed analysis.

External losses in heat exchangers, for example, can be reduced by the application of heat pumps (12, 15). The method, however, is economical only in the separation of mixtures with boiling points which are close together. Further decreases in external thermodynamic losses are obtainable in connection with the design and fabrication of insulation, heat-exchanger systems, compressors, pumps and other ancillary installations. The present paper is concerned only with internal thermodynamic losses in rectification and specifically only with the analysis and possible reduction of losses due to excessively large driving forces, reduction of the hydraulic resistance being associated with improvement of the kinetic conditions of the distillation process (design modifications).

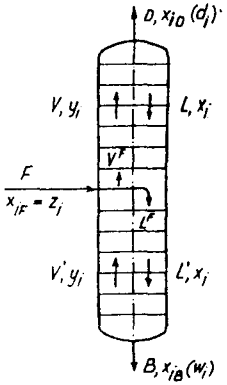

Fig. 1. Nomenclature used in the description of a reversible distillation model.

Thermodynamic reversibility, mathematical description of a multicomponent distillation column and its characteristics.

In order to carry out a detailed analysis of industrial distillation installations, an ideal installation must first be examined, that is, model column for reversible multicomponent distillation.

Using the notation of Figure 1, the material balance equations for any cross section of the column are (8):
For concentrating sections:

$$V y_i - L x_i = d_i \geq 0, \; i = 1,2 \ldots p \tag{7}$$

For stripping sections:

$$L' x_i - V' y_i = w_i \geq 0, \; i = 1,2 \ldots p \tag{8}$$

The equations express the fact that the mole fraction of the components leaving with the overhead and bottoms products may have positive values or may be equal to zero, depending on the sharpness of the separation. In addition to Equations (7) and (8), in reversible distillation the phase equilibrium relationship must be valid at all points of the column cross sections for all of the components (14):

$$K_i = \frac{y_i}{x_i} = \frac{\alpha_i}{\sum\limits_{i=1}^{p} \alpha_i x_i}, \quad i = 1,2, \ldots, p \tag{9}$$

At any cross section of the column, the maximum reflux value is determined by the complete "depletion" of the least volatile component from the concentrating section ($d_p = 0$), and maximum evaporation by the complete depletion of the most volatile component from the stripping section ($w_1 = 0$), since the material-balance equation and the equilibrium relationship cannot be valid simultaneously for multiple components. (For the rest of the components the inequalities of (7), (8) are valid). The complete removal of the remaining components from the top or bottom products requires high reflux or boiling values, since

$$\frac{y_p}{x_p} < \frac{y_{p-1}}{x_{p-1}} < \ldots < \frac{y_1}{x_1} \tag{10}$$

It may be seen that, for example, assignment of the following values

$$\frac{y_2}{x_2} = \frac{L}{V}, \quad \text{or} \quad \frac{y_{p-1}}{x_{p-1}} = \frac{V'}{L'}$$

for all of the heavier components requires more evaporation and condensation than necessary in the vicinity of the inlet, so that the distillation is not reversible. (The driving forces between the coexisting vapor and liquid are greater).

It follows that, in the thermodynamically reversible distillation of multicomponent mixtures (in contrast to the direct separation of binary mixtures), the sharpness of the separation is greatly limited; only the heaviest component can be removed completely from the overhead product and the lightest from the bottoms product; other components are divided between the overhead and bottoms products. The scientific literature defines separations of this type or one with reduced sharpness, that is, which is potentially reversible, as first class and sharper separations as second class (6). If more components are to be completely separated, that is, a more complete separation, irreversibility is unavoidable (6). Relating Equation (7) to the first and p-th component, and assuming a degree of condensation equal to

$$q = \frac{L^F}{F}$$

the following relationships may be written for the rectification zone (32):

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*In rectification, in a thermodynamic sense a spontaneous process and an associated forced process taken place. The desired entropy-producing process (component separation) is made possible by an entropy-producing transfer of heat. The separating operation becomes more favorable from an energy point of view with decreasing overall entropy production. Thermodynamic efficiency is the ratio of the reversible work of separation to the energy put into the system.

$$V y_{1F} - L x_{1F} = F z_1. \tag{11}$$

$$V y_{pF} - L x_{pF} = 0 \tag{12}$$

$$z_1 = q x_{1F} + (1-q)\frac{\alpha_{1F} x_{1F}}{\sum_{i=1}^{p} \alpha_i x_i}. \tag{13}$$

From Equations (11), (12) and (13), the mass flows may be determined for the point of input:

$$L_F = F\frac{\alpha_{pF}}{\alpha_{1F} - \alpha_{pF}} \cdot \frac{q\left(\sum_{i=1}^{p} \alpha_{iF} x_{iF}\right) + (1-q)\alpha_{1F}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}}, \tag{14}$$

$$V_F = F\frac{1}{\alpha_{1F} - \alpha_{pF}} \cdot \frac{q\left(\sum_{i=1}^{p} \alpha_{iF} x_{iF}\right) + (1-q)\alpha_{1F}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}}. \tag{15}$$

Writing Equation (8) in a similar manner for the first and the p-th component and using Equation (13), the material flows for the stripping section at the point of input are obtained:

$$L'_F = F\frac{\alpha_{1F}}{\alpha_{1F} - \alpha_{pF}} \cdot \frac{q\left(\sum_{i=1}^{p} \alpha_i x_{iF}\right) + (1-q)\alpha_{pF}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}}, \tag{16}$$

$$V'_F = F\frac{1}{\alpha_{1F} - \alpha_{pF}} \cdot \frac{q\left(\sum_{i=1}^{p} \alpha_i x_i\right) + (1-q)\alpha_{pF}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}} \tag{17}$$

It is evident from the equations that in reversible rectification the maximum material flows in the column are inversely proportional to the difference in volatility of the key components. (In reversible rectification the lightest and the heaviest components are considered as the key components).

Since $d_i = Vy_i - Lx_i$ and $w_i = L'x_i - V'y_i$, the distribution of the components by product may be obtained using Equations (7), (14), (15) and (8), (16), (17):

$$d_i = F x_{iF}\left(\frac{\alpha_{iF} - \alpha_{pF}}{\alpha_{1F} - \alpha_{pF}}\right) \cdot \frac{q\sum_{i=1}^{p} \alpha_{iF} x_{iF} + (1-q)\alpha_{1F}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}}, \tag{18}$$

$$w_i = F x_{iF}\left(\frac{\alpha_{1F} - \alpha_{pF}}{\alpha_{1F} - \alpha_{pF}}\right) \cdot \frac{q\sum_{i=1}^{p} \alpha_{iF} x_{iF} + (1-q)\alpha_{1F}}{\sum_{i=1}^{p} \alpha_{iF} x_{iF}} \tag{19}$$

It is evident that in multicomponent reversible distillation each component is distributed between the overhead and bottoms products in proportion to its deviation from the volatility of the heaviest or lightest component and to the difference in the relative volatility of the key components. Equations (18) and (19) also indicate that the distribution of the components in the overhead and bottoms products is a function not only of the composition of the input, but also of its thermal state (q).

Since in reversible rectification the material balance and equilibrium relationships must hold, the following is obtained:
for the concentrating section:

$$\sum_{i=1}^{p} x_i = \sum_{i=1}^{p} \frac{d_i}{K_i(L+D) - L} = 1, \tag{20}$$

for the stripping section:

$$\sum_{i=1}^{p} y_i = \sum_{i=1}^{p} \frac{w_i}{\frac{1}{K_i}(V'+B) - V'} = 1 \tag{21}$$

In the reversible model, the liquid flow in the concentrating section is determined at all levels by the disappearance of the heaviest component ($d_p = 0$):

$$K_p(L+D) - L = 0, \quad L = \frac{DK_p}{1 - K_p}. \tag{22}$$

The vapor flow in the stripping section is determined at all levels by the disappearance of the lightest component ($w_1 = 0$):

$$\frac{1}{K_1}(V'+B) - V' = 0, \tag{23}$$

$$V' = \frac{B}{K_1 - 1}.$$

At the intermediate levels of the column the values of the material flows expressed by Equations (22) and (23) decrease gradually toward the extremeties of the column, since the K values are functions of temperature and pressure and thus vary along the height of the column. (In this respect, pressure changes in the column may in general be neglected).

Liquid and vapor flows attain their minimum values at the ends of the column; however, if Equations (7), (8), (9) are applied at the points of complete depletion of the key components, then

$$\lim_{x_p \to 0} \frac{L}{V} = \frac{\alpha_p}{\sum_{i=1}^{p} \alpha_i x_i} \neq 0, \tag{24}$$

$$\lim_{x_1 \to 0} \frac{V'}{L'} = \frac{\sum_{i=1}^{p} \alpha_i x_i}{\alpha_1} \neq 0. \tag{25}$$

In reversible columns therefore, the material flows at the ends of the column cannot be equal to zero, with complete separation of the key components by section; thus, at both ends of the column a finite amount of reflux or boiling is necessary. It may be shown that in a separation less sharp than this (all the components are divided between the bottoms and overhead products), at the ends of the column the value of the material flows become equal to zero, that is, reflux or boiling is not necessary (19).

Since, in the preceding relationships, the material flows are represented as functions of the relative volatility and the equilibrium, which, in turn, are functions of temperature and pressure, the parameters of distillation columns can be determined for arbitrary pressures and temperatures. The profile of the vapor and liquid flows in the column is not affected by a variation of the heat of evaporation, it affects merely the amount of heat and cold energy introduced at various sections of the column.

It is evident from the mathematical description of a thermodynamically reversible column that, in the rectification of multicomponent mixtures, the material flows in the column (and also the concentration of the components) must be varied continuously along the column from point to point (Figure 2). This can be effected only by the addition of infinitely small amounts of heat at all intermediate points of the concentrating section and the removal of heat in infinitely small amounts from all intermediate points of ths stripping section, even in the case of a column with an infinite number of separating steps (which provide infinitely small values of the driving force). It is evident therefore that, with "adiabatic distillation" (heat transfer takes place at the ends of the column only), a thermodynamically reversible distillation cannot be approximated.

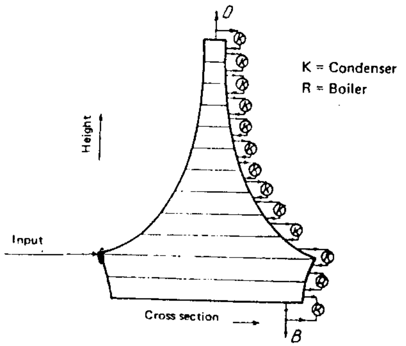

Fig. 2. Material flow distribution in a reversible distillation column (The column is infinitely high with a infinite number of condensers (K) and boilers (R)).

In the case of products with more than one component, equilibrium reflux and boiling material flows cannot be obtained with a single condensation or evaporation of the vapor or liquid leaving the column (the liquid or vapor obtained in this manner is not in equilibrium with the vapor and liquid flows leaving at the ends of the column).

This statement with respect to the distillation of multicomponent mixtures, in addition to the sharpness limitation of the separation, represents the other highly important deviation from the rectification of binary mixtures, and indicates that the equilibrium reflux and boiling-material flows in reversible rectification must be attained in some other way, for example, by recycling from the next column or by auxiliary rectification.

In the distillation processes generally used in industrial practice, the generation of harmfully excessive driving forces, and thus the irreversibility of the rectification process, is mainly due to two causes:

—Irreversibility at the input (second order separation cannot be reversible even potentially; also, continuous variation of the material flows over the height of the column is not assured);

Irreversibility at the ends of the column (reflux and recycled vapors are not in equilibrium with the output products).

It is the task of the designer to minimize both sources of irreversibility.

Based on the above considerations, the characteristics of a reversible rectification model may be summarized as follows:

—provision of an infinite number of degrees of separation;

—removal of infinitely small amounts of heat at all intermediate points of the concentrating section and the addition of infinitely small amounts of heat at all intermediate points of the stripping section, thus establishing phase equilibria along the entire length of the column;

—in any given section only one component can be completely separated (the product can be freed of one component only). This means that only the heaviest component can be completely removed from the overhead product and only the lightest from the bottoms product;

—at the points of the depletion of the key components, the values of the reflux and vapor flows cannot be equal to zero and their equilibrium composition cannot be attained by a single condensation

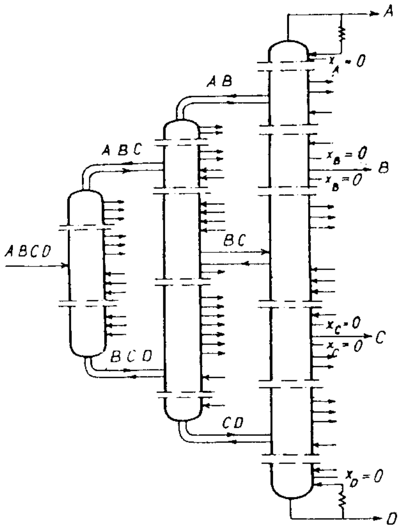

Fig. 3. Flow diagram of the reversible distillation of a four component mixture (infinite column dimensions).

or evaporation, except by the use of auxiliary distillation;

—in the column, an infinitely small pressure drop must be established across an infinite plate.

On the basis of the above, an industrial process involving reversible rectification for a four-component mixture is illustrated in Figure 3. It is shown that it is convenient to take the reflux and boiling material flows from the next column at an equilibrium composition; in such a case, the amount of energy transferred is less (Columns 1, 2) than if established in the column (by increasing the dimensions) (Column 3), although the work of separation is the same in both cases (19).

In the flow diagram, the two-section columns are so connected that all the products are obtained at a single point; this reduces the total amount of energy to be fed in and also the number of columns. Grunberg (8), who was the first to outline the fundamental limits of the reversible distillation of multicomponent mixtures, did not consider the possibility of combining the columns and thus obtained, instead of the necessary (p—1) number of columns, a greatly increased number:

$$\frac{1}{2}\sum_{2}^{p} 2^{p-1}$$

Although it is not possible to carry out in practice the reversible rectification process described above —due to the fact that the necessary conditions cannot be satisfied—a knowledge of it is indispensable, since it opens up the way to improvements to thermodynamic conditions of distillation installations. As emphasized by B. F. Dodge in his classic thermodynamic work (4): "The reversible process represents the highest possible efficiency which we must strive to approach, but which can never be completely attained. Without such an absolute standard of comparison the efforts of an engineer charged with improving the efficiency of the process would represent merely empty, aimless searching in the dark."

The work of separation of reversible multicomponent rectification (energy needs).

Using the notation of Figure 1, the application of component and mass-balance equations to the rectification section and rearranging, the vapor flow (24) is:

$$V = \frac{1}{K_i - 1}\left(\frac{x_{iD}}{x_i} - 1\right)D. \qquad (26)$$

Similarly, for the stripping section, the vapor flow:

$$V' = \frac{1}{K_i - 1}\left(1 - \frac{x_{iB}}{x_i}\right)B. \qquad (27)$$

The form of the Clausius-Clapeyron equation, neglecting the liquid volume is:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda P}{RT^2}. \qquad (28)$$

From Raoult's law, the complete pressure differentials is:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \sum_i p_i \frac{\mathrm{d}x_i}{\mathrm{d}T} + \sum_i x_i \frac{\mathrm{d}p_i}{\mathrm{d}T} = 0. \qquad (29)$$

From Equations (28) and (29), with consideration of reaction

$$K_i = \frac{p_i}{P} \quad \text{and} \quad \sum \mathrm{d}x_i = 0$$

$$\mathrm{d}T = \frac{RT^2}{\lambda} \sum_i (K_i - 1)\,\mathrm{d}x_i. \qquad (30)$$

the Carnot relationship yields, at the transition of $Q = V$, $T_1 \to T_2$, if $T_1 \approx T_2 \approx T$:

$$de = \lambda V_{\text{total}} \frac{T_0}{T^2}\,\mathrm{d}T. \qquad (31)$$

At all cross sections of the column, using minimum reflux and vapor mass flow values, the differential change in energy is:

$$de = RDT_0 \sum_i \left(\frac{x_{iD}}{x_i} - 1\right)\mathrm{d}x_i, \qquad (32)$$

$$de' = RBT_0 \sum_i \left(1 - \frac{x_{iB}}{x_i}\right)\mathrm{d}x_i. \qquad (33)$$

Integration of the equations yields the Van't Hoff expression for the energy requirements of machines, known from thermodynamics (4, 10, 30). (As is known, a Van't Hoff machine requires the minimum theoretical energy for a change of state of the chemical components).

$$e = -RT_0\left\{D \sum_i \int_{x_{iF}}^{x_{iD}} \left(\frac{x_{iD}}{x_i} - 1\right)\mathrm{d}x_i + B \sum \int_{x_{iB}}^{x_{iF}} \left(1 - \frac{x_{iB}}{x_i}\right)\mathrm{d}x_i\right\} \qquad (34)$$

Table 1

Relationships in the reversible rectification of binary mixtures

Identification numbers of equations obtained for a multicomponent reversible rectification model	Corresponding equations for the binary reversible rectification model
(7)	$Vy - Lx = Fz;\quad V(1-y) - L(1-x) = 0$
(8)	$L'x - V'y = 0;\quad L'(1-x) - V'(1-y) = F(1-z)$
(9)	$y = \frac{\alpha x}{1 + (\alpha - 1)x}$
(13)	$z = qx + (1-q)\frac{\alpha x}{1 + (\alpha - 1)x}$
(14)	$L = F\frac{z}{\alpha - 1}\cdot\frac{1}{x}$
(15)	$V = F\frac{z}{\alpha - 1}\cdot\frac{1 + (\alpha - 1)x}{x}$
(16)	$L' = F\frac{1 - z}{\alpha - 1}\cdot\frac{\alpha}{1 - x}$
(17)	$V' = F\frac{1 - z}{\alpha - 1}\cdot\frac{1 + (\alpha - 1)x}{1 - x}$
(35)	$e = -RT_0\left\{D\left[x_D \ln\frac{x_D}{x_F} + (1 - x_D)\ln\frac{(1 - x_D)}{(1 - x_F)}\right] + B\left[x_B \ln\frac{x_B}{x_F} + (1 - x_B)\ln\frac{1 - x_B}{1 - x_F}\right]\right\}$

Table 2

Differences between models of binary and multicomponent reversible rectification

Designation	Binary mixture	Multicomponent mixture
Separation of components by reversible rectification	Possible to the fullest extent	**Only the heaviest component can be separated completely from the overhead product and only the lightest from the bottoms product**
Equilibrium reflux	Can be produced by single condensation	**Cannot be produced by single condensation, but with auxiliary distillation only**
Equilibrium boiling	With single evaporation	**Cannot be produced by single evaporation, but with auxiliary distillation only**
Rectification used in industrial practice	Potentially reversible in all cases	**Not reversible even potentially, because separation sharpness is mainly "of second order"**

$$e = -RT_0\,\Delta S = -RT_0\left\{D\sum_{i=1}^{P} x_{iD}\ln x_{iD} + B\sum_{i=1}^{P} x_{iB}\ln x_{iB} - F\sum_{i=1}^{P} x_{iF}\ln x_{iF}\right\}. \tag{35}$$

Since the "work of separation" obtained from the mathematical description of the distillation column under discussion is in agreement with the sum of the isothermal compression work through specific membranes (30, 33), it follows that, with the use of the scheme presented in Figure 3, the work of separation, in principle, can be made to approach the thermodynamical minimum as closely as desired.

Comparison of a two-component and a multicomponent reversible rectification model.

Summing up the discussion of reversible rectification, let us review the principal relationships derived for the particular case of rectification in the separation of binary mixtures. The results are summarized in Table 1.

It is evident from the table that relationships relating to binary mixtures have structures similar to those describing multicomponent operations. Table 2 presents various characteristics, derived logically from a discussion of reversible binary and multicomponent rectification.

As is evident from Table 2, the opinions to be found in the literature, in accordance with which rectification is, in general, potentially reversible, are incorrect (1, 3, 5, 16, 29). This statement is not valid for a large part of the techniques employed in modern processes in the chemical industry, the petroleum industry isotope separation, etc, since in these fields, almost without exception, multicomponent mixtures are separated and the sharpness of the separation is generally of "second order." Such statements are based on investigations of binary mixtures. In many cases, the attainment of the low separation sharpnesses required by nearly reversible distillation would increase capital costs disproportionally and is thus not economic.

The purpose of the investigation the power requirements of industrial chemical process is thus primarily to find installations and flow diagrams which will prevent the generation of harmfully excessive driving forces in the column, with relatively small increases in capital costs.

Nomenclature

a, b, ..., n .... mass flow rate of products;
A .... surface area;
B .... mass flow rate of bottoms product;
D .... mass flow rate of overhead product;
d_i .... amount of i-th component in overhead product ($D \cdot x_{iD}$);
e .... energy (useful work);
F .... mass flow rate of input;
G .... free enthalpy;
I_Q .... heat flux;
J_i .... component flow;
K_i .... equilibrium ratio;
L, L′ .... liquid flow rate in column, in concentrating or stripping section;
P .... compression;
p .... vapor pressure;
R .... gas constant;
Q .... heat flux;
q .... thermal state of input (L^F/F);
T .... absolute temperature;
T_0 .... ambient temperature;
t .... time;
V .... volume;
V, V′ .... vapor flow rate in the column, concentrating or stripping section;
w_i .... amount of i-th component in the bottoms product ($B \cdot x_{iB}$);
z_i .... mole fraction of i-th component in input;
$\bar{x}_i$ .... average mole fraction (concentration);
$(\Delta x_i)_m$ .... logarithmic mole fraction (concentration), average difference;
x_i .... mole fraction of i-th component in liquid;
y_i .... mole fraction of i-th component in vapor phase;
α .... heat-transfer coefficient or relative volativity (according to context);
λ .... heat of evaporation;
ρ .... density of component transported;
Φ_s .... entropy source density;

Subscripts and superscripts

$-_B$ .... boiling;
$-_D$ .... condenser;
$-_F$ .... feed plate;
$-^F$ .... input material flow;
$-_i$ .... i-th component of mixture;
$-'$ .... refers to stripping section

The equations are written in dimensionless form, their dimensional homogeneity must be obtained by substitution.

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POLAND

Filtration study -- practical application of test data

A calculating procedure for determining the surface area requirements for batch and continuous filters.

FILTRATION operations rank among the oldest operations specific to the chemical industry. Most often, slurry separation is a purely physical phenomenon. Even so, it is a frequent bottleneck in a continuous processing scheme. Therefore, prudent filtration equipment selection and its proper utilization permit operating cost reduction and product quality improvements. Through numerous studies, relationships useful in solving practical problems have been developed. Nonetheless, the present filtration knowhow is still inadequate. In fact, in most applications, it falls short of the users needs. Furthermore, literature data is frequently inconsistent. The problem is compounded by the vast variety of commercial slurries encountered. The latter point adds to the complexity of process optimization.

The essential concepts in filtration are: the slurry and the filter. In the simplest terms, the filter is a porous membrane which, under conditions of imposed differential pressure, separates the slurry into a filtrate and a filter cake.

The parameters characterizing the slurry are: solid phase concentration and particle size, temperature, viscosity, and density. All of the above are governed by fixed process considerations. The equipment designer is forced to accept these conditions and to select equipment which in no way affects the chemical parameters of the overall process. At the same time, the method of slurry preparation, the conditions of precipitate preparation, time, mixing

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