

Studies on the Multicomponent Distillation

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(Received September 7, 1967)

This paper is the summary of our reseaches on the calculational procedure of the multicomponent distillation which were achieved during these three years.

Introduction

The theories of the continuous multicomponent distillation developed rapidly from those of Lewis¹³⁾, Underwood²¹⁾, and Fenske⁷⁾ to those of Murdoch¹⁴⁾, Acrivos⁴⁾ and Holland¹¹⁾ during these thirty years.

Therefore, for an ideal system we regarded the theory as generally established. But, engaging in the study of this problem, we noticed that there were many more questions, for instance

- i) the treatment of non-distributed components¹⁵⁾
- ii) the development of the high-speed convergence method using the condition of the matching at the feed plate¹⁷⁾²⁶⁾
- iii) the development of the very simplified calculational procedure of the multicomponent distillation¹⁵⁾¹⁷⁾
- iv) the analysis of the system with side cut streams²⁵⁾

On the other hand, for a non-ideal system the step by step calculational procedure proposed by Gilliland⁹⁾ was used in many cases, and the perturbation method proposed by Acrivos³⁾⁴⁾ was the only analytical method. Even Acrivos' method was not useful in practice, because the higher perturbed term was too complicated. Therefore we have proposed Successive Approximation Method and Successive Perturbation Method in § 3²⁸⁾. But these methods are not so simple as the step by step procedure, because these are

deduced using the perturbation theory, so we shall next propose Successive Iteration Method which have merits of both the analytical method and the step by step method¹⁵⁾. Consequently we can simplify the calculational procedures of the azeotropic distillation and the extractive distillation not to mention the ordinary distillation.^{18) 19)}

The exact solution for the case of minimum reflux was discovered by Underwood²²⁾ and, later on, in a more general form, by Murdough and Holland¹⁴⁾. This solution is useful only for the designing problem under the given separate ratio of the key components, therefore we shall propose the calculational method of the terminal compositions at the minimum reflux state under the given reflux ratio.²⁷⁾ On the other hand, for a non-ideal system the solution was unknown until now. But, when nondistributed components don't exist, we can discover the exact solution for the cases of the ordinary distillation and the extractive distillation by the study of the behaviour of the pinch point.^{16) 19)}

On the other hand, the theory of the batch distillation had been developed by Rose²⁰⁾, Croseley⁶⁾, Bowman⁵⁾, Fujita⁸⁾ and Kojima¹²⁾. In this case the still composition is the function of the distillate, namely, it is the problem at the unsteady state. But this problem can be simplified by using the calculational method of the terminal composition from the given composition in a column.

So, we can easily calculate the distillation curve by the method mentioned in §1 and Rayleigh's equation.^{23) 24)}

§1 The calculating method of terminal compositions from the given composition in a column²⁴⁾

For the enriching section Acrivos showed the composition in a column $x_n(i)$ as a function of the terminal composition $x_D(i)$.¹⁾

$$x_n(i) = \frac{x_D(i) \sum_k C_k \lambda_k^{n-1} v_k(i)}{R \sum_k C_k \lambda_k^{n-1}} \dots\dots\dots(1)$$

Where λ_k is the k-th root of Eq.(2), $v_k(i)$ and C_k are defined by Eq.(3) and Eq.(4).

$$\sum_i \frac{P(i) x_D(i)}{\lambda_k - P(i)} = R \quad P(k) < \lambda_k < P(k-1) \dots\dots(2)$$

$$v_k(i) = \frac{P(i)}{\lambda_k - P(i)} \dots\dots\dots(3)$$

$$C_k = \left\{ \sum_i \frac{P(i) x_D(i)}{[\lambda_k - P(i)]^2} \right\}^{-1} \dots\dots\dots(4)$$

In order to get the terminal composition as a function of the composition in a column, we divide both sides of Eq.(1) by $(\lambda_k - P(i))$, and sum up for all components. Then, the following equation can be deduced.

$$\sum_i \frac{x_n(i)}{\lambda_k - P(i)} = \frac{\lambda_k^{n-1}}{K} \quad (K \equiv R \sum_k C_k \lambda_k^{n-1}) \dots\dots(5)$$

On the other hand, the following equation can be deduced from Eq.(2)¹⁾

$$x_D(i) = R \alpha(i) \frac{\prod [\lambda_k - P(i)]}{\prod_k (i) [P(k) - P(i)]} \dots\dots\dots(6)$$

Futher, summing up Eq. (6) for all components,

$$R \sum_i \alpha(i) \frac{\prod [\lambda_k - P(i)]}{\prod_k (i) [P(k) - P(i)]} = 1 \dots\dots\dots(7)$$

Consequently, if $x_n(i)$ is known, we can obtain K and λ_k from Eq. (5) and Eq. (7), and calculate the terminal composition $x_D(i)$ by Eq.(6). On the other hand, for the stripping section we can also deduce analogous equations.

If $x_n(i)$ is made small, a useful asymptotic form for $x_D(i)$ is made²⁴⁾.

i) Application to continuous distillation²⁴⁾

Taking the feed rate a unit, the over-all

material balance for i -th component can be changed into the following form.

$$x_f(i) = \frac{x_F(i) x_f(i)}{D x_D(i) + W x_W(i)} \dots\dots\dots(8)$$

Then, if we introduce a parameter θ for the convergence into Eq.(8), and use the value of $x_F(i)$ as a initial value of $x_f(i)$, the value of $x_f(i)$ can be corrected by the following equations.

This iteration must be continued until θ reaches a unit within a certain accuracy.

$$x_f^{(m+1)}(i) = \frac{\theta x_F(i) x_f^{(m)}(i)}{D x_D^{(m)}(i) + W x_W^{(m)}(i)} \dots\dots(9)$$

$$\theta = \left\{ \sum_k \frac{x_F(i) x_f^{(m)}(i)}{D x_D^{(m)}(i) + W x_W^{(m)}(i)} \right\}^{-1} \dots\dots\dots(10)$$

ii) Application to batch distillation²³⁾

We express Rayleigh's equation in the following difference form.

$$\Delta(S x_s(i)) = x_D(i) \Delta S \dots\dots\dots(11)$$

When $D = t \Delta D$, the still composition can be given by the following equation.

$$\dot{x}_s^{(i)}(i) = \frac{S^{(0)} x_s^{(0)}(i) - \sum_{n=1}^i x_D^{(n-1)}(i) \Delta D}{S^{(0)} - t \Delta D} \dots\dots(12)$$

Where $S^{(0)} x_s^{(0)}(i)$ is the initial feed moles of i -th component in a still.

Consequently, we can easily obtain a distillation curve by the above mentioned method with which we can calculate the terminal composition $x_D(i)$ from the still composition $x_s(i)$.

§2 Calculational procedure of the multicomponent distillation with side cut streams for an ideal system

We shall develop the theory for the conventional column into one for the column with side cut streams, for instance the topping in a petroleum refinery, and show the calculational procedure of the composition of each stream under given operating variables.

At this stage now, in order to simplify the problem, let us analyze the column with a side cut stream in each section, and withdraw it in liquid condition.

We can use Acrivos' equations¹⁾ from the

terminal to the side cut plate. On the otherhand, we use the following equations from the side cut plate to the feed plate in the enriching section.

$$x_n(i) = \frac{\eta_E(i) \sum_k C_k \lambda_k^{n-1} v_k(i)}{R \sum_k C_k \lambda_k^{n-1}} \dots\dots\dots(13)$$

Where

$$R \equiv \frac{L}{D+E} \quad (L \equiv L_0 - E) \dots\dots\dots(14)$$

$$\eta_E(i) = \frac{1}{D+E} \{ Dx_D(i) + Ex_E(i) \} \dots\dots\dots(15)$$

$$\sum_i \frac{P(i) \eta_E(i)}{\lambda_k - P(i)} = R \quad P(k) < \lambda_k < P(k-1) \dots\dots\dots(16)$$

$$v_k(i) = \frac{P(i)}{\lambda_k - P(i)} \dots\dots\dots(17)$$

$$C_k = \left[\sum_i \frac{P(i) \eta_E(i)}{\lambda_k - P(i)} + 1 \right] \left[\sum_i \frac{P(i) \eta_E(i)}{(\lambda_k - P(i))^2} \right]^{-1} \dots\dots\dots(18)$$

For the stripping section we can also deduce analogous equations. Further, for non-distributed components we can deduce useful asymptotic expressions.

On the other hand, taking the feed rate a unit we can easily obtain the correcting equations of the terminal compositions from the over all material balance as follows.

$$Dx_D(i) = \frac{x_F(i)}{1 + \theta_1 \left(\frac{Ex_E(i)}{Dx_D(i)} + \frac{E^*x_{E^*}(i)}{Dx_D(i)} + \frac{Wx_W(i)}{Dx_D(i)} \right)} \dots\dots\dots(19)$$

$$Wx_W(i) = \frac{x_F(i)}{1 + \theta_2 \left(\frac{Dx_D(i)}{Wx_W(i)} + \frac{Ex_E(i)}{Wx_W(i)} + \frac{E^*x_{E^*}(i)}{Wx_W(i)} \right)} \dots\dots\dots(20)$$

Where θ_1 and θ_2 are determined by the conditions of $\sum_i Dx_D(i) = D$ and $\sum_i Wx_W(i) = W$ and the terms $x_E(i)/x_D(i)$, $x_E(i)/x_W(i)$, $x_{E^*}(i)/x_D(i)$ and $x_{E^*}(i)/x_W(i)$ are calculated from the initial value of the terminal compositions, but the value of $x_D(i) / x_W(i)$ is determined by the conditions of the feed plate matching as follows.

$$\frac{x_D(i)}{x_W(i)} = \frac{D+E}{W+E^*} \cdot \frac{W + \frac{E^* \sum_k C_k'^* \mu_k'^{-s'-1} v_k'^*(i)}{R'^* \sum_k C_k'^* \mu_k'^{-s'-1}} \cdot \frac{\sum_k C_k^* \mu_k^{-s-1} v_k^*(i)}{R^* \sum_k C_k^* \mu_k^{-s-1}}}{D + \frac{E \sum_k C_k' \lambda_k'^{n'-1} v_k'(i)}{R' \sum_k C_k' \lambda_k'^{n'-1}} \cdot \frac{\sum_k C_k \lambda_k^{n-1} v_k(i)}{R \sum_k C_k \lambda_k^{n-1}}} \dots\dots\dots(21)$$

Finally, we can perform this calculation on the very simplified assumption that the initial values of the terminal compositions are equal to the composition of raw material.

On the other hand, when the column has side cut streams in each section, we can similarly solve this problem by using Eq.(22) and Eq.(23) in stead of Eq.(14) and Eq.(15).

$$R_z \equiv \frac{L}{D + \sum_z E_z} \quad (L \equiv L' - \sum_z E_z) \dots\dots\dots(22)$$

$$\eta_{E_z}(i) \equiv \frac{1}{D + \sum_z E_z} \{ Dx_D(i) + \sum_z E_z x_{E_z}(i) \} \dots\dots\dots(23)$$

§ 3 Calculational procedure of the multicomponent distillation for non-ideal systems

i) Successive Approximation Method²⁸⁾

The material balance of the enriching section can be expressed in the following equation.

$$y_{n+1}(i) = \frac{R_n}{R_n+1} \cdot \frac{P_n(i) y_n(i)}{\sum_i P_n(i) y_n(i)} + \frac{x_D(i)}{R_n+1} \dots\dots(24)$$

Eq.(24) can now be linearized by the introduction of a generating function $X_n(i)$ defined by the following equations.

$$X_n(i) = P_1(i)/R_1 \dots\dots\dots(25)$$

$$X_{n+1}(i) = R_n P_{n+1}(i) X_n(i) + P_{n+1}(i) \times \sum_i x_D(i) X_n(i) \dots\dots\dots(26)$$

Then, $x_n(i)$ can be expressed in

$$x_n(i) = \frac{x_D(i) X_n(i)}{\sum_i x_D(i) X_n(i)} \dots\dots\dots(27)$$

So, if one is able to obtain the function $X_n(i)$ using Eq.(25) and Eq.(26), one can calculate $x_n(i)$ using Eq.(27). After all, the main object of the problem is a key to solution of Eq.(26).

Acrivos solved Eq.(26) by means of perturbation theory, and showed the first order perturbed solution. But, the higher order solution is necessary to solve the problems of any non-ideal systems. Accordingly, it

is desired that a simplified general form of the higher order solution is deduced.

If we are prepared to neglect the second and higher order correction terms, we can deduce the following ν -th order perturbed solution.

$$X^{(\nu)}_{n+1}(i) = H^{(\nu)} X^{(\nu)}_n(i) + f^{(\nu)}_n(i) \dots\dots\dots(28)$$

Where

$$H^{(\nu)} \equiv R^0 P^0(i) + P^0(i) \sum_j x^{(\nu)}_D(j) \dots\dots\dots(29)$$

$$f^{(\nu)}_n(i) \equiv R^0 [P^{(\nu)}_{n+1}(i) - P^0(i)] X_n(i) + [R^{(\nu)}_n - R^0] P^0(i) X^{(\nu-1)}_n(i) + [P^{(\nu)}_{n+1}(i) - P^0(i)] \sum_j x^{(0)}_D(j) X^{(\nu-1)}_n(j) \dots\dots(30)$$

Finally, we can obtain the solution of the generating function $X^{(\nu)}_n(i)$ in the following form using the linear inhomogeneous difference equation(28).

$$X^{(\nu)}_n(i) = \sum_k C^{(\nu)}_k(n) (R^0 \lambda^{(\nu)}_k)^{n-1} v^{(\nu)}_k(i) \dots\dots\dots(31)$$

Where

$$\sum_i \frac{P^0(i) x^{(\nu)}_D(i)}{\lambda^{(\nu)}_k - P^0(i)} = R^0 \quad P^0(k) < \lambda^{(\nu)}_k < P^0(k-1) \dots\dots\dots(32)$$

$$v^{(\nu)}_k(i) = \frac{P^0(i)}{\lambda^{(\nu)}_k - P^0(i)} \dots\dots\dots(33)$$

$$C^{(\nu)}_k(n) = C^{(\nu)}_k(1) + \sum_{j=1}^{n-1} \frac{Q^{(\nu)}_k(j)}{(R^0 \lambda^{(\nu)}_k)^j} \dots\dots\dots(34)$$

$$C^{(\nu)}_k(1) = \left[\frac{1}{R^0} \sum_i \frac{P_1^{(\nu)}(i) x_D^{(\nu)}(i)}{\lambda^{(\nu)}_k - P^0(i)} \right] \left[\sum_i \frac{P^0(i) x^{(\nu)}_D(i)}{(\lambda^{(\nu)}_k - P^0(i))^2} \right]^{-1} \dots\dots\dots(35)$$

$$Q^{(\nu)}_k(n) = \left[\sum_i \frac{f^{(\nu)}_n(i) x^{(\nu)}_D(i)}{\lambda^{(\nu)}_k - P^0(i)} \right] \left[\sum_i \frac{P^0(i) x^{(\nu)}_D(i)}{(\lambda^{(\nu)}_k - P^0(i))^2} \right]^{-1} \dots\dots\dots(36)$$

On the other hand, for the stripping section analogous equations can be obtained in a similar way. Further, appropriate asymptotic expressions of non-distributed components are used, but we don't discuss these in this paper.

ii) Successive Perturbation Method²⁸⁾

We shall report to an approximation which is useful only where the perturbation is

small. This is a simplified method of Successive Approximation Method for the numerical calculation.

According to i), we must calculate $\lambda^{(\nu)}_k$ from the higher order equation (32) at each perturbed state, because the operator $H^{(\nu)}$ contains the function $x^{(\nu)}_D(i)$ for the ν -th perturbed state.

So, we deduce a simplified general form of the higher order perturbation.

$$X^{(\nu)}_{n+1}(i) = H^0 X^{(\nu)}_n(i) + \phi^{(\nu)}_n(i) + g^{(\nu)}_n(i) \dots\dots\dots(37)$$

Where

$$H^0 \equiv R^0 P^0(i) + P^0(i) \sum_j x^{(0)}_D(j) \dots\dots\dots(38)$$

$$\phi^{(\nu)}_n(i) \equiv R^0 [P^{(\nu)}_{n+1}(i) - P^0(i)] X_n^{(\nu-1)}(i) + P^0(i) [R^{(\nu)}_n - R^0] X^{(\nu-1)}_n(i) + [P^{(\nu)}_{n+1}(i) - P^0(i)] \sum_j x^{(0)}_D(j) X_n^{(\nu-1)}(j) \dots\dots\dots(39)$$

$$g^{(\nu)}_n(i) \equiv P^0(i) \sum [x^{(\nu)}_D(j) - x^{(0)}_D(j)] X^{(\nu-1)}_n(j) \dots\dots\dots(40)$$

Finally, the following solution can be obtained corresponding to Eq.(31)

$$X^{(\omega)}_n(i) = \sum_k C^{(\omega)}_k(n) (R^0 \lambda_k)^{n-1} v_k(i) \dots \dots \dots (41)$$

Where

$$\sum_i \frac{P^0(i) x^0_D(i)}{\lambda_k - P^0(i)} = R^0 \quad P^0(k) < \lambda_k < P^0(k-1) \dots \dots \dots (42)$$

$$v_k(i) = \frac{P^0(i)}{\lambda_k - P^0(i)} \dots \dots \dots (43)$$

$$C^{(\omega)}_k(n) = C^{(\omega)}_k(1) + \sum_{j=1}^{n-1} \frac{Q^{(\omega)}_k(j)}{(R^0 \lambda_k)^j} \dots \dots \dots (44)$$

$$C^{(\omega)}_k(1) = \left[\frac{1}{R^0} \sum_i \frac{P^{(\omega)}_1(i) x^0_D(i)}{\lambda_k - P^0(i)} \right] C_k \dots \dots \dots (45)$$

$$Q^{(\omega)}_k(n) = C_k \left[R^0 \Gamma^{(\omega)}(n) + \sum_j \frac{\phi^{(\omega)}_n(j) x^0_D(j)}{\lambda_k - P^0(j)} \right] \dots \dots \dots (46)$$

$$C_k = \left[\sum_i \frac{P^0(i) x^0_D(i)}{(\lambda_k - P^0(i))^2} \right]^{-1} \dots \dots \dots (47)$$

$$\Gamma^{(\omega)}(n) = \sum_j x^{(\omega)}_D(j) - x^0_D(j) \} X^{(\omega-1)}_n(j) \dots \dots \dots (48)$$

iii) Successive Iteration Method I¹⁵⁾

The methods of i) and ii) are more complicated than the step by step procedure for the reason that these methods are deduced by means of perturbation theory. So, we shall now show more simplified method, *i. e.* Successive Iteration Method I, for the case in which the order of size of the relative volatility is not reversible in the column.

If $P_n(i)$, R_n and $x_D(i)$ are known functions, Eq. (26) is an ordinary difference equation. Then, we can calculate the generating function $X_n(i)$ from 1 to n in order by Eq. (25) and Eq. (26). Therefore, in order to regard $P_n(i)$, R_n and $x_D(i)$ as known functions, if we adopt the idea of the perturbation theory into this method, we need not solve Eq. (26).

This method has two merits, first it doesn't need the asymptotic expressions, and secondly it is as simple as the step by step procedure.

iv) Successive Iteration Method II¹⁵⁾

This method is used only for the case in which the order of size of the relative volatility is reversible in the column.

In this case, we use the general form of the ν -th order perturbed equation mentioned in i), *i. e.* Eq. (28), for the reason that the existence of the deviation from the unperturbed state within the radius of convergence

is the only key of the perturbation. Then, as $f^{(\omega)}_n(i)$ is the known function, we can calculate the generating function $X^{(\omega)}_n(i)$ in order by the same process as Successive Iteration Method I.

§ 4 Calculational procedure of the azeotropic distillation¹⁸⁾²⁶⁾

At first, we shall calculate its degree of freedom. When the composition of raw material and the thermal factor of column feed are given, there are four degrees of freedom for the conventional column, but in this case there is one more degree of freedom for the reason that the entrainer feed moles are unknown, that is, the first column has four degrees of freedom and the second column which is constituted only by the stripping section has three degrees of freedom, besides there is a degree of freedom for the whole of the system.

These degrees of freedom are given as follows.

1-st column : bottoms of all components and reflux ratio of the stripping section

2-nd column : bottoms of the key components and reflux ratio of the stripping section

the whole of the system : the determinant condition of the optimum feed plate

Now, we show the calculational procedure of the azeotropic distillation using Successive Iteration Method.

i) Stripping section of the 1-st column

$$X_0(i) = 1 \dots\dots\dots(49)$$

$$X_{s+1}(i) = (R_{s+1} - 1)\alpha_s(i)X_s(i) + \sum_i \alpha_s(i)x_w(i)X_s(i) \dots\dots\dots(50)$$

$$x_s(i) = \frac{x_w(i)X_s(i)}{\sum_i x_w(i)X_s(i)} \dots\dots\dots(51)$$

Where $R_s \equiv L_s/W$. We can calculate $x_s(i)$ from the bottom in order by the equation above and a vapor-liquid equilibrium.

ii) Enriching section of the 1-st column

$$X_0(i) = x_f(i) \dots\dots\dots(52)$$

$$X_{n+1}(i) = (R_{n+1} + 1)\alpha_n(i)X_n(i) - \eta(i) \sum_i \alpha_n(i)x_w(i)X_n(i) \dots\dots\dots(53)$$

$$x_n(i) = \frac{x_w(i)X_n(i)}{\sum_i x_w(i)X_n(i)} \dots\dots\dots(54)$$

Where

$$R_n \equiv \frac{L_n}{1 - W} \dots\dots\dots(55)$$

$$\eta(i) \equiv \frac{x_f(i) - Wx_w(i)}{(1 - W)x_w(i)} \dots\dots\dots(56)$$

We can calculate $x_n(i)$ from the feed plate in order by the same process as i).

iii) Stripping section of the 2-nd column

$$X_0^*(i) = 1$$

$$X_{s+1}^*(i) = (R_{s+1}^* - 1)\alpha_s^*(i)X_s^*(i) + \sum_i \alpha_s^*(i)x_w^*(i)X_s^*(i) \dots\dots\dots(57)$$

$$x_s^*(i) = \frac{x_w^*(i)X_s^*(i)}{\sum_i x_w^*(i)X_s^*(i)} \dots\dots\dots(58)$$

Where $R_s^* \equiv L_s^*/W^*$. And, we correct the ungiven $W^*x_w^*(i)$ by the following equation deduced from the condition of the matching at the top of the 2-nd column.

$$W^*x_w^*(i) = \frac{L_D^*x_L^*(i)}{1 + \frac{V_D^*y_D^*(i)}{W^*x_w^*(i)}} \dots\dots\dots(59)$$

$$\frac{y_D^*(i)}{x_w^*(i)} = \frac{\alpha_s^*(i)X_s^*(i)}{\sum_i \alpha_s^*(i)x_w^*(i)X_s^*(i)} \dots\dots\dots(60)$$

iv) The boundary condition at the top

When the liquid on the plate is one-layered, it is the boundary condition that the distillation curve just crosses the binodal curve at the top. On the other hand, when the liquid on the plate is two-layered, it is the boundary condition that the distillation curve just crosses the given tie-line at the top.

v) Calculation of the activity coefficient of the two-layered liquid

In this case, as these layers are in equi-

brium each other, their chemical potentials are equal each other, that is, $\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}$ but $\gamma_i^I \neq \gamma_i^{II}$. Consequently each relative volatility is not equal, but the vapor compositions in an equilibrium with these liquid layers are equal each other. In this case, the operating line denotes the relation of the apparent composition, on the other hand, the vapor-liquid equilibrium denotes the relation of the true composition. Therefore, we must deduce the special calculational

procedure, which is different from the one-layered case, for the two-layered case. But, if we take care to calculate the activity coefficient of the two-layered liquid, we can express the vapor-liquid equilibrium of the apparent composition using $\gamma_i = \gamma_i^I x_i^I / x_i = \gamma_i^{II} x_i^{II} / x_i$.

Consequently, if we take care of the calculation of the activity coefficient, we can also use the above mentioned Successive

Iteration Method in this case.

§ 5 Calculational procedure of extractive distillation¹⁹⁾

We have shown the calculational procedure of the multicomponent distillation for a conventional column using Successive Iteration Method in § 3. This method is also applicable to the extractive distillation system.

i) Solvent recovery section

$$X_1(i) = P_1(i) / R_1 \dots\dots\dots(61)$$

$$X_{n+1}(i) = R_n P_{n+1}(i) X_n(i) + P_{n+1}(i) \sum_j x_D(j) X_n(j) \dots\dots\dots(62)$$

$$x_n(i) = \frac{x_D(i) X_n(i)}{\sum_j x_D(j) X_n(j)} \dots\dots\dots(63)$$

ii) Enriching section

Solvent is generally more non-volatile than key components, so, if we are prepared to

consider the composition of solvent in the enriching section to be constant, the following results can be obtained.

$$X_{o'}(i) = X_N(i) \dots\dots\dots(64)$$

$$X_{n'+1}(i) = R_{n'} P_{n'+1}(i) X_{n'}(i) + P_{n'+1}(i) \sum_j x_D(j) X_{n'}(j) \dots\dots\dots(65)$$

$$x_{n'}(i) = (1 - x_{sf}(1)) \frac{x_D(i) X_{n'}(i)}{\sum_j x_D(j) X_{n'}(j)} \quad (i \neq 1) \dots\dots\dots(66)$$

iii) Stripping section

$$X_0^*(i) = \alpha_0^*(i) \dots\dots\dots(67)$$

$$X_{s+1}^*(i) = (R_{s+1}^* - 1) \alpha_{s+1}^*(i) X_s^*(i) + \alpha_{s+1}^*(i) \sum_j x_W(j) X_s^*(j) \dots\dots\dots(68)$$

$$x_s^*(i) = \frac{P_s^*(i) x_W(i) X_s^*(i)}{\sum_j P_s^*(j) x_W(j) X_s^*(j)} \dots\dots\dots(69)$$

iv) Convergence method

$$\frac{x_D(1)}{x_W(1)} = \frac{P_f^*(1) X_f^*(1)}{X_{sf}(1)} \cdot \frac{\sum_j x_D(j) X_{sf}(j)}{\sum_j P_f^*(j) x_W(j) X_f^*(j)} \dots\dots\dots(70)$$

$$\frac{x_D(i)}{x_W(i)} = \frac{P_f^*(i) X_f^*(i)}{[1 - x_{sf}(1)] x_f(i)} \cdot \frac{\sum_j x_D(j) X_f(j)}{\sum_j P_f^*(j) x_W(j) X_f^*(j)} \quad (i \neq 1) \dots\dots\dots(71)$$

$$Dx_D(i) = \frac{x_F(i) + Sx_{SF}(i)}{1 + \frac{\theta_1 Wx_W(i)}{Dx_D(i)}} \dots\dots\dots(72)$$

$$Wx_W(i) = \frac{x_F(i) + Sx_{SF}(i)}{1 + \frac{\theta_2 Dx_D(i)}{Wx_W(i)}} \dots\dots\dots(73)$$

Where the symbol (1) denotes solvent.

§ 6 Minimum reflux calculation of the ideal multicomponent distillation²⁷⁾

Underwood²²⁾ and Acrivos²³⁾ discovered the exact solution for the case of minimum

reflux which was only useful to calculate minimum reflux ratio under the given separate ratio of two arbitrary components.

We shall here derive the method which is useful to calculate the terminal compositions

under the given reflux ratio and infinite plate number, and discuss the behaviour of pinch points. At this stage now, we are in a position to extend the treatment given on § 1.

We first note that the functional properties of G_k in $n \rightarrow \infty$ was given as the following relations by Acrivos²⁾.

- 1) $G_k \rightarrow 0 \quad k > h$
- 2) $G_k \rightarrow 1$
- 3) $G_k \rightarrow \text{finite} \quad k < h$

Where G_k is defined by

$$G_k \equiv \frac{C_k}{C_h} \left(\frac{\lambda_k}{\lambda_h} \right)^{n-1} \dots\dots\dots(74)$$

We can easily derive the determinant equations of λ_k in $n \rightarrow \infty$ using Eq.(5), Eq(7), and above.

- 1) $k < h$

$$\sum_i \frac{x_f(i)}{\lambda_k - P(i)} = 0 \dots\dots\dots(75)$$
- 2) $k < h \quad \lambda_k = P(k) \dots\dots\dots(76)$
- 3) $k = h$

$$\lambda_k = \frac{\frac{1}{R} + \sum_i \frac{\prod(h) [\lambda_k - P(i)]}{\prod(i) [P(k) - P(i)]}}{\frac{\prod(h) [\lambda_k - P(i)]}{\sum_i \alpha(i) \frac{1}{[P(k) - P(i)]}}} \dots\dots\dots(77)$$

Consequently, we can calculate $x_D(i)$ in $n \rightarrow \infty$ under the given reflux ratio and $x_f(i)$ using Eq.(6). On the other hand, for the stripping section we can similarly derive analogous equations. Further, the correcting method of $x_f(i)$ is the same as Eq.(9) and Eq.(10).

While, when non-distributed components do not exist, we can next show that a pinch point exists around the feed plate and its composition is identical with that of the liquid part of raw material.

First, the composition of the liquid part of raw material is given by the following equation.

$$x_{1q}(i) = \frac{x_F(i)}{q + (1-q)\alpha(i) \sum_i \alpha(i)x_{1q}(i)} \dots\dots\dots(78)$$

Substituting Eq. (78) into Underwood's determinant equation of, λ_k , *i. e.* into

$$\sum_i \frac{P(i) x_F(i)}{\lambda_k - P(i)} = -q \dots\dots\dots(79)$$

We can easily obtain the following equation.

$$\sum_i \frac{x_{1q}(i)}{\lambda_k - P(i)} = 0 \dots\dots\dots(80)$$

So, if we compare Eq.(80) with Eq.(75), we immediately obtain the following result.

$$x_{1q}(i) = x_f(i)$$

§ 7 Minimum reflux ratio of a non-ideal multicomponent distillation¹⁶⁾

If we assume that for the enriching section a pinch point exists below the E-th plate from the top and for the stripping section above the E*-th plate from the bottom, we can obtain the same fundamental equation as that of the ideal system, because relative volatilities of each component and molar flow rate are constant through the pinch zone.

For the enriching section solving the equation, we can express the liquid composition of the n-th plate from the E-th plate in the following form.

$$x_n(i) = \frac{x_D(i) \sum_k C_k \lambda_k^{n-1} v_k(i)}{R \sum_k C_k \lambda_k^{n-1}} \dots\dots\dots(81)$$

Where

$$\sum_i \frac{P(i)x_D(i)}{\lambda_k - P(i)} = R \dots\dots\dots(82)$$

$$v_k(i) = \frac{P(i)}{\lambda_k - P(i)} \dots\dots\dots(83)$$

$$C_k = \left[\sum_i \frac{P(i)y_E(i)}{\lambda_k - P(i)} \right] \left[\sum_i \frac{P(i)x_D(i)}{(\lambda_k - P(i))^2} \right]^{-1} \dots\dots(84)$$

At this paper, we shall discuss the minimum reflux ratio of the case in which non-distributed components don't exist.

For an ideal system we have already shown that a pinch point exists around the feed plate and its composition is equal to that of the liquid part of raw material.

At this stage now, we shall advance the analysis of this problem on the assumption that the above mentioned fact holds good for a non-ideal system.

As we have shown in Eq. (84), although the definition of C_k is different from that of an ideal system, the functional properties of G_k in $n \rightarrow \infty$ is identical with that of an

ideal system, and the determinant equation, *i. e.* Eq.(82), of minimum reflux ratio is also identical with that of an ideal system.

Consequently, when non-distributed components don't exist, the minimum reflux ratio of a non-ideal system can be calculated by the same method as that of an ideal system using $P(i)$ calculated from the composition of the liquid part of raw material.

And further, the behaviour of a pinch point is also identical with that of an ideal

system. But when non-distributed components exist, for the reason of, $P(i) \neq P^*(i)$, at this stage now we can't make clear the problem of this case.

§ 8 Minimum reflux ratio of the extractive distillation¹⁹⁾

Hitherto, when a system is not so non-ideal, the following equations have been used on the assumption that a pinch point exists around the feed plate.¹⁰⁾

$$\sum_i \frac{P(i)x_F(i)}{\lambda_k - P(i)} = -q \quad P(k) < \lambda_k < P(k-1) \dots \dots \dots (85)$$

$$R_m + \frac{S}{D} = \sum_i \frac{P(i)[x_D(i) - S/Dx_{SF}(i)]}{\lambda_k - P(i)} \dots \dots \dots (86)$$

But, as the result of calculating its degree of freedom, we discovered that the above mentioned method is not correct and a pinch point exists all over the enriching section and around it.

Using this facts, we deduce the determinant equations of the minimum reflux ratio by the same technique mentioned in § 7.

Then, the following results are obtained.

$$\sum_i \frac{P(i)[x_F(i) + Sx_{SF}(i)]}{\lambda_k - P(i)} = -(S+q) \quad 2 \leq k \leq m \dots \dots \dots (87)$$

$$P(i) Dx_D(i) = B(i) \left\{ RD - \frac{P(1) Dx_D(1)}{B(1)[P(i) - P(1)]} \right\} \quad 2 \leq i \leq m \dots \dots \dots (88)$$

Where

$$B(i) = \frac{\prod_{k=2}^m [\lambda_k - P(i)]}{\prod_{k=2}^m [P(k) - P(i)]} \dots \dots \dots (89)$$

$$B(1) = \frac{\prod_{k=2}^m [\lambda_k - P(1)]}{\prod_{k=2}^m [P(k) - P(1)]} \dots \dots \dots (90)$$

$P(i)$ in the equations above is the value calculated from the composition of the pinch point. Now, we assume that the composition of the pinch point is given by the following equation.

$$x_\infty(i) = \frac{1}{S+q} \{ Sx_{SF}(i) + qx_F(i) \} \dots \dots \dots (91)$$

$$\sum_i \frac{P(i)[qx_F(i) + Sx_{SF}(i)]}{\lambda_k - P(i)} = -(S+q)$$

Consequently, if we compare Eq.(87) with Eq.(93), when $q=1$, it is clear that these equations are identical. Namely, when $q=1$, the composition of the pinch point is given by Eq.(91).

And, we substitute Eq.(91) into the determinant equation of λ_k in, $n \rightarrow \infty$, *i. e.* into

$$\sum_i \frac{x_\infty(i)}{\lambda_k - P(i)} = 0 \quad 2 \leq k \leq m \dots \dots \dots (92)$$

The following equation can be obtained.

$$2 \leq k \leq m \dots \dots \dots (93)$$

But, when $q \neq 1$, we must calculate the composition by trial and error using the minimum reflux calculation mentioned in § 6.

Nomenclature

Common

D : moles of distillate per unit feed
 L : molar flow rate of liquid
 $P(i)$: reciprocal relative volatility of i -th component
 m : number of components
 q : thermal factor of column feed
 V : molar flow rate of vapor
 W : moles of bottoms per unit feed
 $x(i)$: molar fraction of liquid of i -th component
 $y(i)$: molar fraction of vapor of i -th component
 $\alpha(i)$: relative volatility of i -th component based on the most non-volatile component

§ 1

C_k : function defined by Eq.(4)
 K : function defined by Eq.(5)
 n : number of plates from the column top
 S : moles remained in the still
 $v_k(i)$: function defined by Eq.(3)
 θ : correcting parameter defined by Eq.(10)
 λ_k : k -th root of Eq.(2)

§ 2

C_k : function defined by Eq.(18)
 E : moles of side cut product of enriching section
 E^* : moles of side cut product of stripping section
 n : number of plates from the side cut plate of enriching section
 n' : number of plates from the column top
 R^* : modified reflux ratio ($\equiv L^*/(W+E^*)$)
 s : number of plates from the side cut plate of stripping section
 s' : number of plates from the column bottom
 $v_k(i)$: function defined by Eq.(17)
 $\eta_E(i)$: function defined by Eq.(15)
 θ : correcting parameter defined by Eq.(19),(20)
 λ_k : k -th root of Eq.(16)
 R : modified reflux ratio defined by Eq.(14)

§ 3

C_k : function defined by Eq.(47)
 $C^{(\nu)}_k(1)$: function defined by Eq.(35), or(45)
 $C^{(\nu)}_k(n)$: function defined by Eq.(34), or(44)
 $f^{(\nu)}_n(i)$: function defined by Eq.(30)
 $g^{(\nu)}_n(i)$: function defined by Eq.(40)
 H^0 : operator defined by Eq.(38)
 $H^{(\nu)}$: operator defined by Eq.(29)
 n : number of plates from the column top
 $C^{(\nu)}_k(n)$: function defined by Eq.(36), or(46)

R_n : reflux ratio ($\equiv L_n/D$)

$v^{(\nu)}_k(i)$: function defined by Eq.(33)
 $v_k(i)$: function defined by Eq.(43)
 $X_n(i)$: function defined by Eq.(25),(36)
 $\Gamma^{(\nu)}(n)$: function defined by Eq.(48)
 $\lambda^{(\nu)}_k$: k -th root of Eq.(32)
 λ_k : k -th root of Eq.(42)

§ 4

L^*_D : molar rate of 2-nd column feed
 R_n : modified reflux ratio defined by Eq.(55)
 R_s : modified reflux ratio ($\equiv L_s/W$)
 R^*_s : modified reflux ratio ($\equiv L^*_s/W^*$)
 V^*_D : molar rate of vapor at the top of the 2-nd column
 W : moles of bottoms of the 1-st column per unit feed
 W^* : moles of bottoms of the 2-nd column per unit feed
 x_i : molar fraction of liquid
 γ_i : activity coefficient of i -th component
 $\eta(i)$: function defined by Eq.(56)

§ 5

R_n : modified reflux ratio ($\equiv L_n/D$)
 $R_{n'}$: modified reflux ratio ($\equiv L_{n'}/D$)
 R^*_s : modified reflux ratio ($\equiv L^*_s/W$)
 S : solvent feed moles per unit raw material
 θ : correcting parameter defined by Eq.(72),(73)

§ 6, § 7, § 8

$B(i)$: function defined by Eq.(89), (90)
 C_k : function defined by Eq.(84)
 G_k : function defined by Eq.(74)
 n : number of plates from the column top
 R : reflux ratio ($\equiv L/D$)
 R_m : minimum reflux ratio
 S : solvent feed moles per unit raw material
 $v_k(i)$: function defined by Eq.(83)
 $y_E(i)$: molar fraction of vapor on the E -th plate

Subscript

Common

D : distillate
 F : raw material
 f : feed plate
 i, j, k : kind of component
 W : bottoms

§ 1, § 2, § 3

E : side cut product of enriching section
 E^* : side cut product of stripping section
 n : n -th plate from the column top
 S : still pot

§ 4

D^* : top of the 2-nd column

L^* : a layer of the 2-nd column feed

n : n -th plate from feed plate of the 1-st column

s : s -th plate from bottom of the 1-st column

s^* : s^* -th plate from bottom of the 2-nd column

S^* : number of plates of the 2-nd column

W : bottoms of the 1-st column

W^* : bottoms of the 2-nd column

§ 5

n : n -th plate from the column top of solvent recovery section

n' : n' -th plate from the solvent feed plate of enriching section

s : s -th plate from the column bottom of stripping section

SF : solvent

sf : solvent feed plate

§ 6, § 7, § 8

h : heavy key component

l : light key component

lq : liquid part of raw material

SF : solvent

∞ : pinch point

Superscript

§ 1

(0): initial value

(m): m -th corrected value

(t): value at $D=tAD$

§ 2

' : section from terminal to the side cut plate

* : stripping section

§ 3

* : stripping section

v : v -th perturbed term

(v): approximate value determined by summation up from 0-th to v -th perturbed term

§ 4

* : 2-nd column

I, II : sign of layer

§ 5

' : enriching section

* : stripping section

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