REVIEWS

A Review on Minimum Energy Calculations for Ideal and Nonideal Distillations[†]

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The minimum energy requirement of a distillation sets a lower, thermodynamically defined operating limit, which is increasingly important in practice due to growing interest in saving energy. During the conceptual design phase this energy information can also be used to quickly compare distillation configurations. This paper gives a summary of the most important methods published to date for the calculation of the minimum energy requirement. Firstly, the occurrence of so-called pinch zones will be systematically described. These are sections of the column in which at minimum reflux an infinite number of separation stages would be necessary. Then exact and approximating solutions of the problems both for ideal and for nonideal mixtures will be discussed. For ideal mixtures a rapid calculation is possible using the well-known Underwood equations, which can also be applied to complex columns (e.g., several feeds and side products, side stream strippers and enrichers). However, strongly nonideal multicomponent mixtures still require time-consuming simulations of columns having large numbers of plates. In such cases serious convergence problems must often be reckoned with. Recent developments aim at avoiding column simulations and at calculating pinch points directly.

1. Introduction

Distillation is a proven, versatile and intensively investigated unit operation and plays a major role in many chemical processes. This situation is unlikely to change even in the long term, because alternative unit operations are often neither technically feasible nor commercially competitive. The development and continuous refinement of distillation trains are thus important tasks in process design, having a considerable influence on the commercial success of whole production processes. Increases in the costs of primary energy and new government regulations will exert pressure on us—now and in the future—to organize the overall use of energy efficiently and to continually reduce its consumption.

Figure 1 shows schematically the relation between reflux ratio (r) and number of plates (n) for four different degrees of separation. The pressure drop in the column has been ignored. For a constant separation specification the result is a hyperbolic curve. In the limiting case of minimum reflux ratio (r_{min}) the number of separation stages and the investment cost approach infinity. If the reflux is slightly increased, the required number of stages falls rapidly. Operation at total reflux ($r \rightarrow \infty$) defines the minimum number of stages (n_{min}). In practice the optimum operating point for the column, in terms of the overall costs, is usually between 1.1 and 1.5 times the minimum reflux ratio. The approach to the lower, thermodynamically defined operating limit
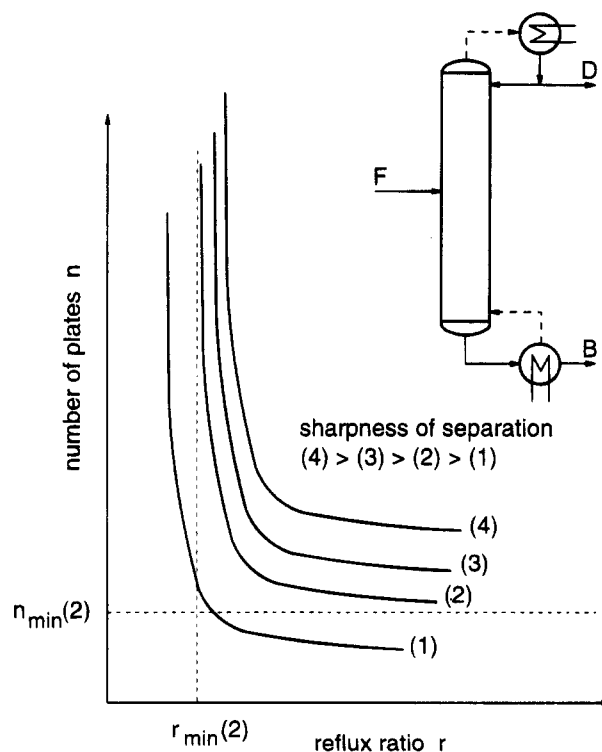

Figure 1. Number of stages and reflux ratio (*B*, bottoms product; *D*, distillate; *F*, feed; n_{min}, minimum number of stages; r_{min}, minimum reflux ratio).

by adding more column stages is confined by the degree of maneuver required for process control in order to handle fluctuations, and also by uncertainties in the physical properties and in the underlying models [1].

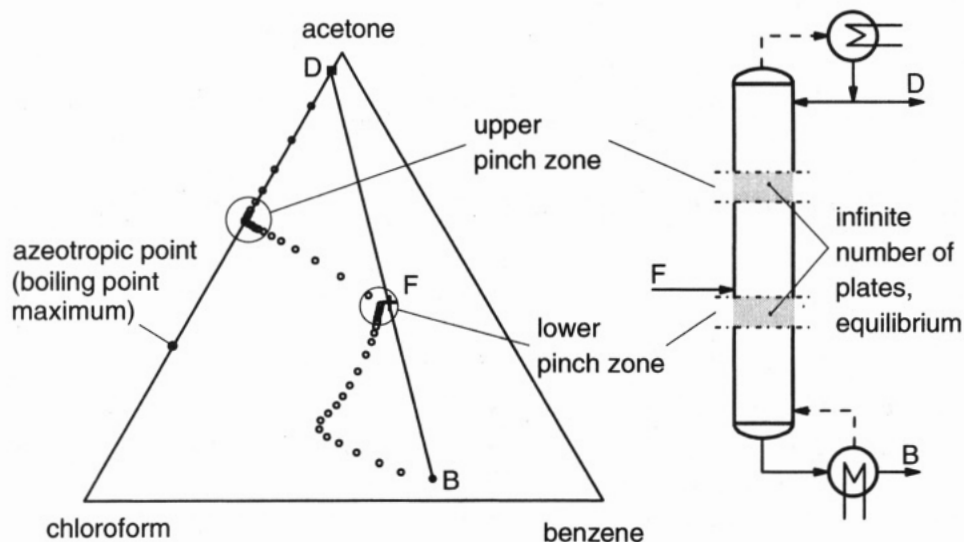Methodical chemical process design consists in gen-

Figure 2. Distillation with minimum energy consumption in a triangular diagram.

eral of the interplay between ideas, which increase the number of possible solutions, and consequent analyses which evaluate the ideas and lead to the early rejection of bad options [2]. During the evaluation steps the minimum energy requirement can also serve as an indicator of the investment costs, since column dimensions such as diameter and heat transfer areas are dependent on the energy input. If we consider further that difficult separations require not only a high consumption of energy but at the same time a large number of separation stages, then it will become clear how the minimum energy requirement of distillation units can be used in an overall feasibility comparison of the various distillation options during the front end engineering [3].

We must not overlook the fact that the minimum flows inside the column are also very useful numerical values for the initialization of rigorous simulation calculations, especially when our goal is to optimize columns with respect to given product specifications.

The rapid and reliable calculation of the minimum energy requirement for a specified sharpness of separation is thus an important task at several stages of the development of a chemical process. However, in spite of a considerable amount of research effort this problem has not been satisfactorily solved for the general case of nonideal multicomponent mixtures. Usually time-consuming calculations using process simulation programs must be tolerated, or alternatively simplifying assumptions must be made. Null [4] puts it in a nutshell: "...there is no corresponding effort to develop reliable and accurate shortcut blocks which give a reasonable approximation of complex columns and of systems which exhibit highly nonideal behavior". This paper offers a systematic analysis of the problem and a critical summary of the approaches available for calculating the minimum energy requirement.

2. Physical and Mathematical Basis

2.1. Occurrence of Pinch Zones. During distillation at minimum reflux ratio zones of constant (stationary) phase composition—so-called pinch zones—would occur in the separation profile. In these column regions vapor and liquid are in equilibrium. Because of the lack of driving forces, in such zones infinitesimal concentration changes require a large number of separation

plates, in the extreme case an infinite number. Figure 2 shows qualitatively in a triangular coordinate system the liquid phase separation profile of a minimum reflux situation in the acetone/chloroform/benzene mixture. Both pinch zones can be recognized by the points which follow each other closely both in the feed region in the stripping section and also in the middle of the rectifying section.

If we consider a distillation in a simple column, where all the components of the feed are present in both products, then at minimum reflux only one pinch will occur, namely in the region of the feed tray [5–7]. In the special case of a potentially reversible split [8], the pinch composition is the same as the feed composition. This very special type of split is named "preferred separation" by Stichlmair [51] and "transitional split" by Levy et al. [91] and Fidkowski et al. [118]. With the exception of the tangent pinch case (cf. section 4.5) all two-component distillations belong to this class of separations, in which the minimum reflux can be determined simply from the feed composition.

Figure 3 shows on a McCabe–Thiele diagram the operating lines for the rectifying and stripping sections for several reflux ratios r in the separation of an ideal, partly vaporized binary mixture. The operating lines for both sections meet on a line which depends on the degree of feed vaporization ($q = L_F/F$) and on the mass balance around the feed tray. At the smallest value of the reflux ($r = r_{min}$) the operating lines of both sections of the column just meet on the equilibrium line. In the pinch area between the operating line corresponding to minimum reflux and the equilibrium line an infinite number of steps can be drawn in as a staircase on both sides.

Most multicomponent separations are in general less sloppy. Apart from exceptions with strongly nonideal mixtures, which will be mentioned later, every minimum reflux separation then exhibits a pinch in each half of the column. As soon as one of the column product streams does not contain one or more of the components of the feed, the pinch in the corresponding half of the column no longer coincides with the feed tray, but moves to somewhere between feed and product outlet. In the part of the column between feed point and pinch the concentrations of the components to be removed fall to zero. In Figure 2 this is shown by the almost straight portion of the concentration profile between the feed
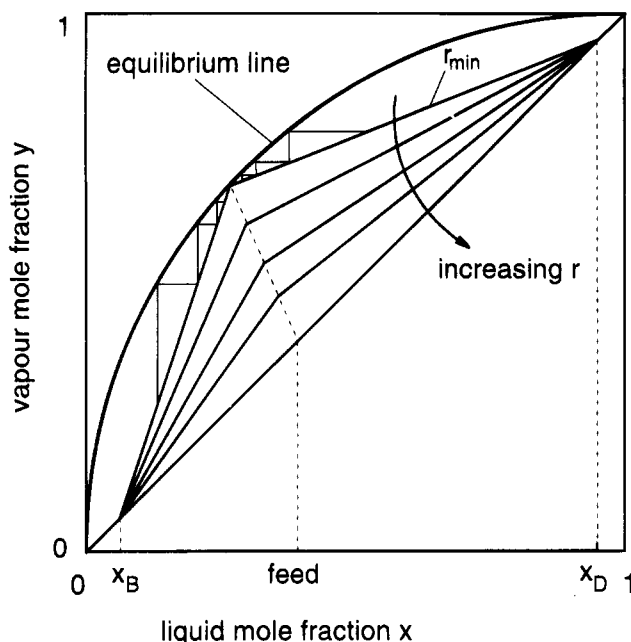
Figure 3. Binary distillation in the McCabe—Thiele plot.

point and the acetone/chloroform side of the triangle, where the concentration of benzene is reduced to zero.

The displacement of the pinch zones from the feed is thus dependent on the key components and the difficulty of separation. Key components are defined by King [9] as components which "appear to a significant extent in both products" of the column, whereas the components boiling lower than the light key or higher than the heavy key are "relegated almost exclusively to one product or the other".

A separation with more than three components can be represented as a profile of mole fractions of one phase along the separation stages. In Figure 4 the mole fractions of the liquid phase are shown for the distillation of an ideal five-component system. The separation takes place between the key components butane and isopentane. The pinch zones can easily be identified as plateaus in the mole fraction profile. In the area between feed point and the pinch under consideration the components boiling lower or higher than the key in question disappear. The enrichment of the product components takes place after this in the zone between pinch and product outlet.

2.2. Pinch Points as "Termination Points of Distillation" and How To Model Them. A column design method recently used by Levy et al. [10] and by Knight and Doherty [11] (see also section 4.3) for nonideal multicomponent mixtures is well suited for illustrating the occurrence of and the search for pinch points with the help of real concentration profiles in columns: The distillation column is divided into stripping section and rectifying section. Both halves of the column are calculated in small differential steps starting from the end of the column. This is done using predetermined product compositions and heat duties. The calculation in each section is carried out by the addition of differential steps until the concentration changes fall below a predetermined minimum value. The point reached is a pinch, where the vapor and liquid streams passing each other are in equilibrium. Hausen [12] evaluated such "termination points of distillation" as long ago as 1935 using the nitrogen/argon/oxygen system as an example.

Figure 5 shows the separation profiles in the stripping

section of a ternary distillation for one bottoms product composition and for several reboiler loads. The termination points of the separation profiles (P_s) lie on a chain dotted line starting from the bottoms product. This curve is known as the pinch point curve of the bottoms product. In the example shown the pinch point curve for the distillate ($P_{r,j}$) runs along the side of the triangle.

The termination points of distillation and the pinch point curves can be quickly found using a system of equations which has roughly the same order of difficulty as a flash calculation: Figure 6 gives the control volume for modeling a pinch point in the rectifying section. The system of equations corresponds to the calculation of a reversible distillation and is as follows:

material balances:

$$Vy_i = Lx_i + Dx_{D,i} \quad (i = 1, ..., C) \quad (1)$$

concentration summations: $\sum_{i=1}^{c} x_i = 1, \ \sum_{i=1}^{c} y_i = 1$ (2)

equilibrium condition: $y_i = K_i x_i \quad (i = 1, ..., C)$ (3)

energy balance: $Vh^V - Lh^L - Dh_D^L = Q_C$ (4)

pressure constancy: $p = p_D$ (5)

physical properties:

$$K_i = K_i(\vec{x}, \vec{y}, T, p) \quad (i = 1, ..., C) \quad (6)$$

$$h^L = h^L(\vec{x}, T, p), \quad h^V = h^V(\vec{y}, T, p) \quad (7)$$

The system consists of material and energy balances, summations of mole fractions, and physical property relationships. The additional condition, which characterizes the pinch, is the equilibrium of the vapor and liquid phases flowing across the cross section of the column. An analogous set of equations can be written for the pinch in the stripping section. Assumptions concerning the number of components or the boiling or enthalpy behavior—for example constant relative volatility and constant molal overflow—are not required.

Koehler et al. [8] deduce that the degree of freedom of the system of equations for a completely specified distillate is 1. We can therefore, theoretically, solve the system of equations after fixing one more variable (e.g., temperature, quantity of energy exchanged, one mole fraction). This is, however, an extremely difficult undertaking, since we are dealing with a nonlinear system of equations and in practice solution methods only converge if reliable starting values—close to the true values—are available for the remaining variables and in particular for the mole fractions. The remaining degree of freedom also prevents us from solving the minimum energy problem using the system of equations: in the general case it is not known, a priori, where on the two pinch point curves the pinch points lie at minimum reflux. It should be mentioned here that the Underwood method implies the solution of the system of pinch equations—explained in section 3—given certain simplifying assumptions.

The pinch point curve will be obtained when the system of equations is solved repeatedly starting at the product and by increasing the reboiler or condenser load or by varying one of the mole fractions. Therefore the calculation of pinch points does not require the compu-
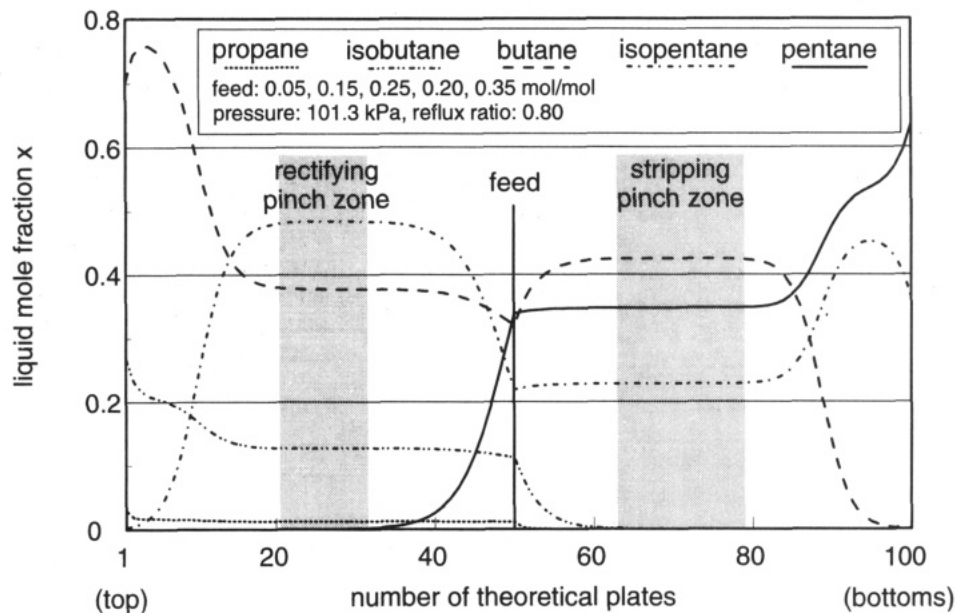
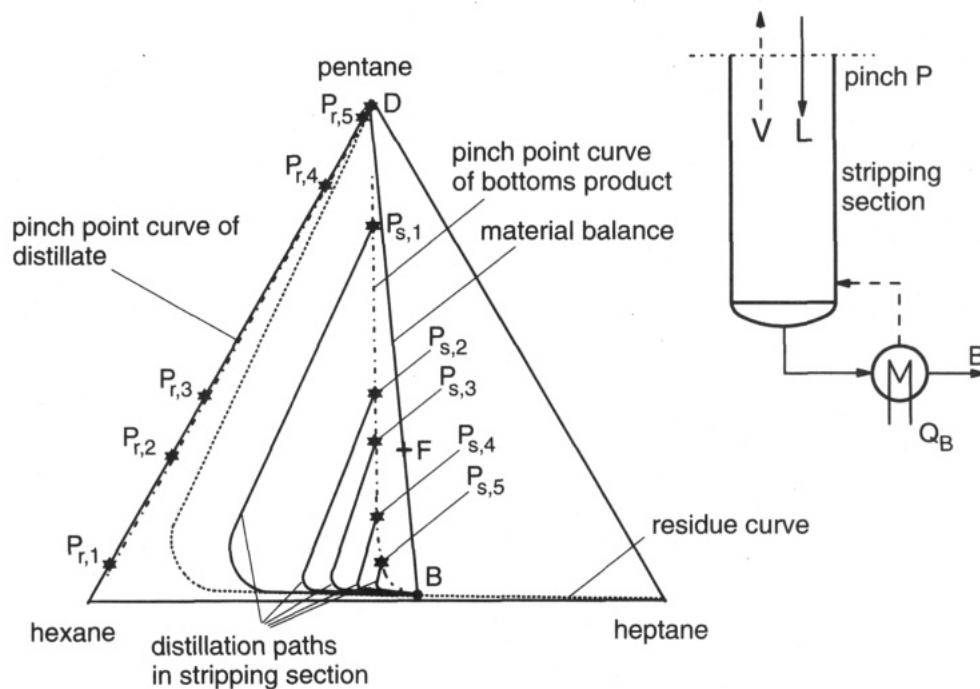**Figure 4.** Five-component distillation under minimum reflux.

Figure 5. Concentration profiles and pinch curves (L, liquid; V, vapor; P, pinch point; Q_B, reboiler duty; r, rectifying section; s, stripping section).

tation of numerous multistage adiabatic separation profiles. This statement applies also to nonideal systems.

If we consider a complete column instead of half a column, then the solutions of the systems of pinch equations for the rectifying section and the stripping section are not independent of each other. They are linked via the energy balance over the column because each condenser load corresponds to a given reboiler load:
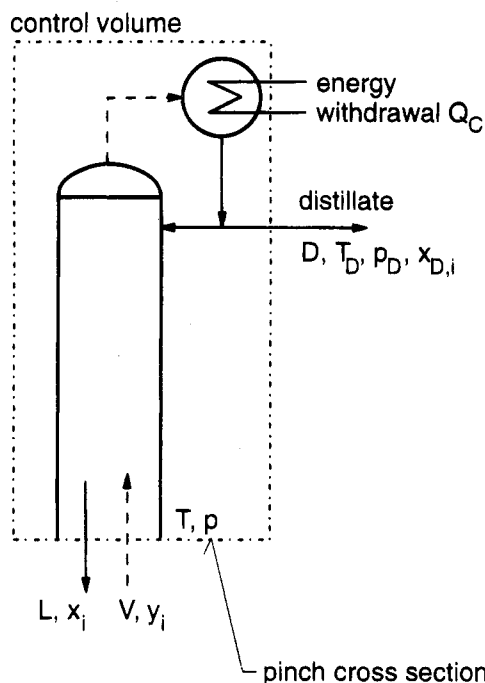
$$Q_B - Q_C = H_D + H_B - H_F \qquad (8)$$

Provided that no multiple solutions of the system of pinch equations occur (see also section 4.5), every solution in the rectifying section determines exactly one solution in the stripping section, as is indicated in Figure 5, in which corresponding pinch points have the

same index numbers. Each estimated reflux ratio and respectively each estimated energy quantity give a solution of the system of pinch equations in both halves of the column. In principle the problem now consists in identifying which of the infinite number of pinch point pairs gives the minimum energy requirement for the given separation.

3. Ideal Mixtures

3.1. Basis of the Underwood Method. The most important shortcut in the calculation of the minimum reflux ratio for a simple distillation originated in a publication by Underwood in the year 1932 [13] and several in the years 1945–1948 [14–17]. The principles of the calculation method widely used today are contained in the last three of these papers on which the

Figure 6. Control volume to model pinch points in the rectifying section.

Figure 7. Geometric interpretation of the Underwood method for separating the heavy component c from the mixture abc (b, light key; c, heavy key).

following summary of Underwood's key ideas is also based. Underwood gave a completely general solution to the problem of minimum energy requirement for mixtures, subject to the assumptions of constant relative volatility and constant molal overflow. These assumptions are also made in the next paragraphs. The results are often qualitatively valid for real mixtures.

The components are numbered in order of boiling points. The separation factors of the vapor–liquid equilibrium should be referred to the highest-boiling component C:

$$\alpha_i = \frac{y_i/x_i}{y_C/x_C} = \frac{K_i}{K_C} \qquad (9)$$

With the equations

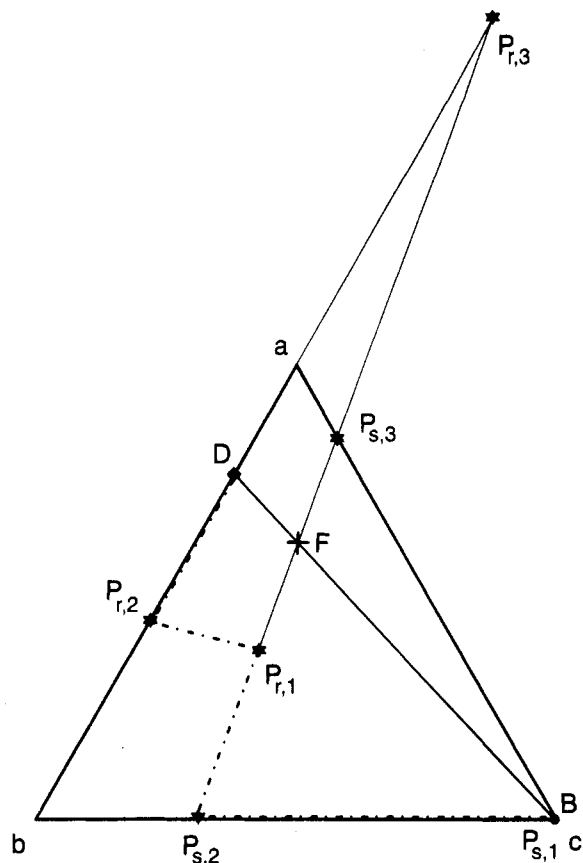$$\sum_{i=1}^{c} \frac{\alpha_i x_{D,i}}{\alpha_i - \varphi} = r + 1 \qquad (10)$$

$$\sum_{i=1}^{c} \frac{\alpha_i x_{B,i}}{\alpha_i - \psi} = -s \qquad (11)$$

Underwood defines for formal reasons the parameters φ of the rectifying section and ψ of the stripping section.

The physical interpretation of parameter φ can be obtained from material balance and equilibrium at a pinch point in the rectifying section (eqs 1 and 3), which give

$$\frac{\alpha_i x_{D,i}}{\alpha_i - L/(VK_C)} = (r + 1)y_{P,i} \qquad (12)$$

when they are combined. When this expression is summed for all components, the result is eq 10. The parameter $\varphi = L/(VK_C)$ contains the ratio of the flow of the phases and the equilibrium and is commonly known as the stripping factor.

Each of the eqs 10 and 11 has—for a given product composition and a given reflux ratio—as many solutions as there are components in the mixture. The solution parameters fit into the order of relative volatilities as follows:

$$0 < \varphi_1 < \alpha_C < \varphi_2 < \alpha_{C-1} < ... < \alpha_2 < \varphi_C < \alpha_1 \qquad (13)$$

$$\alpha_C < \psi_1 < \alpha_{C-1} < ... < \alpha_2 < \psi_{C-1} < \alpha_1 < \varphi_C \qquad (14)$$

Equation 12 contains, in the form given, the vapor mole fraction at the pinch point, and there is also an analogous equation for the stripping section. Because of these equations pinch compositions can be calculated for each parameter, i.e., for every value of product composition and reflux flow. Some concentrations can even assume a negative value, and the corresponding pinches then have merely a theoretical meaning. The polyhedron obtained from the straight lines joining the compositions of the pinches is called the "distillation space". In the case of three-component mixtures the expression "distillation triangle" is used.

Figure 7 gives an example from Underwood [15]: from a mixture having components a, b, and c and composition F the high boiler c is to be almost completely separated. The light key is component b, the heavy key is c. For the chosen product compositions B and D (mass balance line shown dashed) and the reflux ratio, the distillation triangle for the rectifying section is fixed by the pinch points $P_{r,1}$, $P_{r,2}$, and $P_{r,3}$, and that of the stripping section by $P_{s,1}$, $P_{s,2}$, and $P_{s,3}$. The edges of the two distillation triangles appear in a slightly different context as distillation separatrices [18–21, 124]. (Not to be confounded with the product region boundaries of

section 4.6.) The chain dotted line shows the liquid phase concentration profile in the column at minimum reflux, which coincides with a separatrix.

Underwood's great achievement is to have provided a method which determines, from the great number of pinch points, the ones which follow from the given separation under minimum energy consumption. He proved that, at minimum reflux, these two parameters φ and ψ from the rectifying section and from the stripping section coincide, which lie between the relative volatilities of the key components; he proved that $\varphi_2 = \psi_1$ in the example. It is this identity which makes possible the geometric interpretation of a minimum energy rectification shown in Figure 7. Because of the common parameters the pinch points $P_{r,1}$ and $P_{r,3}$ of the rectifying section lie together with the pinch points $P_{s,2}$ and $P_{s,3}$ of the stripping section on a straight line, i.e., they are colinear. Levy et al. [10] write that this colinearity is an assumption by Underwood. We believe it would be more precise to say that the colinearity is a consequence of the minimum energy condition. To illustrate the problem several authors (e.g., ref 25) show for one specified separation distillation triangles with a smaller and with a larger reflux than the minimum. In the one case the triangles do not reach each other; in the other case they penetrate each other and the distillation triangle corners of the rectifying and stripping sections are no longer colinear.

Geometric relationships of this kind, in part generalized to four-component mixtures, and illustrated by concentration tetrahedra, are to be found in the excellent interpretation of Underwood's papers by Franklin [22–25]. The four pinches in each column section then form two unsymmetrical tetrahedra, which, according to the separation being considered and at minimum reflux, have points, edges, side surfaces, or parts of tetrahedra in common. Vogelpohl [26] gives the relationships necessary for calculating the distillation "spaces" for arbitrary numbers of components of ideal mixtures. White has written a series of papers [27–35], in which he treats very clearly the calculation and interpretation of concentration profiles for ternary and quaternary distillations of ideal mixtures. He also deals several times with the case of minimum reflux and the location of pinch points.

The common roots of the systems of pinch equations of the rectifying and of the stripping sections allow us to combine eq 10 with the aid of the material balance around the whole column ($x_{F,i}F = x_{D,i}D + x_{B,i}B$):

$$\sum_{i=1}^{c} \frac{\alpha_i x_{F,i}}{\alpha_i - \Theta} = 1 - q \tag{15}$$

where q is the liquid fraction of the feed and Θ one of the common roots.

To calculate the minimum reflux ratio, Underwood proposes evaluating all the common roots of the last equation and putting each into eq 10. This gives a linear system of equations for the minimum reflux ratio (or for the minimum boilup ratio). It also gives the product concentrations of all components lying between the key components. The number of equations is the same as the number of common roots Θ.

Shiras [5] remarked that it can be difficult to predict—in the case of narrow-boiling mixtures—how the components are distributed in the products. If, however, during the solution of the system of equations we

assume incorrectly that a certain component is distributed in the products, then the result will be that the quantity of the component in the distillate is greater than the quantity in the feed stream if in actual fact it is a lighter component. On the other hand, if it is really a heavier component than assumed, then the result will be a negative mole fraction in the distillate. This indicates how we should improve the product specification for further iterations. The well-known methods for estimating the distribution of the components in the product for ideal mixtures [36–39] can also be helpful here: these are given in detail in the textbook by King [9] and in the paper by Wagner [40].

Finally it should be mentioned that Vogelpohl [26] and Norden et al. [41] have in other ways derived equations which correspond to Underwood's. Acrivos and Amundson [42–47] devote a series of papers to the calculation of ideal distillations of continuous mixtures, i.e., of mixtures which are described not as discrete components, but rather as a distribution of properties. They also report a method equivalent to Underwood's for calculating the minimum reflux. Cerda and Westerberg [48] also develop a simple method for the determination of the minimum energy requirement. This method can be extended to columns having side stream strippers and side stream rectifiers. The derivations, however, make further assumptions besides those of Underwood, e.g., for sharp multicomponent separations, that the pinch points in both column halves always occur exactly two stages above and below the feed tray. Although the authors present several satisfactory results of comparative calculations with the Underwood method, the simplification probably causes unnecessary inaccuracies. Lestak et al. [49] demonstrate this using a statistical analysis of comparative calculations and mention further that several of Cerda's equations contain mistakes. Glinos and Malone [50] give approximations to the Underwood equations for ternary distillations and propose the formation of pseudocomponents for use with multicomponent mixtures. The idea of substituting the very fast and established Underwood method by procedures with additional simplifications must however be critically examined. For several special cases of ideal three-component distillations (complete removal of the light boiler or of the heavy boiler) Stichlmair [51] gives the analytical solutions of the Underwood equations.

Figure 8 shows a short summary of the most important offspring of the Underwood method, of which some are touched upon below. In practice, the relatively easy modifications for so-called complex columns are significant (sections 3.2 and 3.3). Some publications deal with extentions of the Underwood procedures to enable calculations of nonideal mixtures with a higher accuracy. Particularly interesting is the proposed introduction of "enthalpy fractions" by Hausen [52] to deal with the influence of the differing heats of evaporation of the components. The "enthalpy share" of a component in a mixture is defined by

$$x'_i = \frac{x_i \Delta h_{V,i}}{\sum_{j=1}^{c} (x_j \Delta h_{V,j})} \tag{16}$$

using the enthalpies of vaporization of the components. King [9] also proposes using the Underwood method with these transformed mole fractions. In two consider-
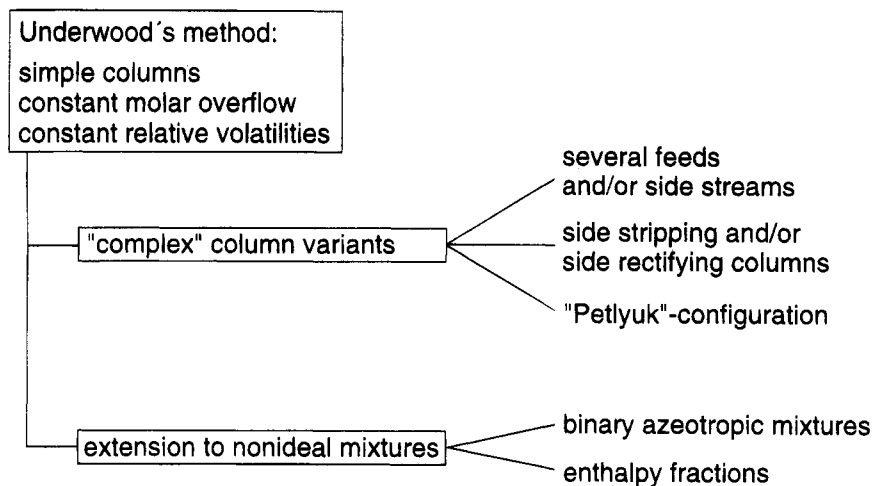
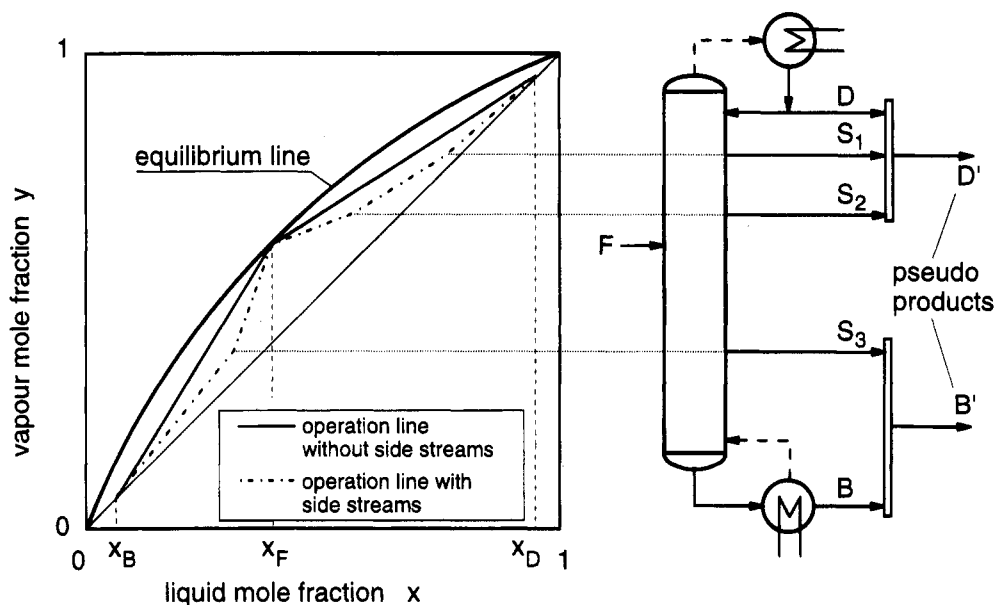**Figure 8.** Underwood's method and its offspring.

Figure 9. Pinch situation for binary distillations with side product withdrawals.

ably more recent papers investigations of the minimum energy requirement have been undertaken which, in principle, result in the same proposal [53, 54].

3.2. The Underwood Method for Columns with Several Feeds and Side Draws. As long ago as 1932 Underwood [13] investigated the calculation of multicomponent distillations with side draws, in which he took his equations for binary mixtures and used the key components as the two components. Later the methods described in section 3.1 for multicomponent mixtures were extended several times to columns having multiple feeds and/or side draws. Also graphical solution methods and solutions of special separation cases were proposed. References 59—69 cover some of this work but probably not all of it. Of these sources Chou and Yaws [67] quote a series of further publications on the calculation—sometimes graphical—of the minimum reflux ratio for ideal binary systems.

The core of every procedure for dealing with side draws is the following consideration: if side streams are withdrawn from a column, then, as a rule, the draw will be made from the liquid phase in the rectifying section and from the vapor phase in the stripping section, so as to guarantee the highest possible purity. For the binary case Figure 9 illustrates that for side draws the lowest reflux ratio (definition: $r = L/(D + \Sigma S_j)$) always

lies in the feed region (balance line is chain dotted). Thus, also for this type of column both pinch points have the same composition as the feed. If we form a pseudoproduct (D') from all the products of the rectifying section and the same for the stripping section (B'), then the minimum reflux ratio can be calculated again by solving the system of pinch equations for the feed composition. Sugie and Benjamin [60] had the same idea for multicomponent distillations and prove that here the controlling pinch points in both halves of the column must lie between the feed point and the first side draw. We can thus use the simple Underwood relations for multicomponent columns with side draws, provided that we also form pseudoproducts.

However, the approaches mentioned are only suitable for carrying out performance and rating calculations on existing columns, since several figures of interest for complex columns—the flow quantities and the compositions of the side draws—cannot be determined a priori and must be estimated for the summation to pseudoproducts [117]. Particular notice must be taken here, since there are maximum values for the mole fractions of the intermediate boilers in side draw products. The exact data for the side draw products will not be known until simulation calculations with a concrete number of stages and a reflux ratio above the minimum have been carried
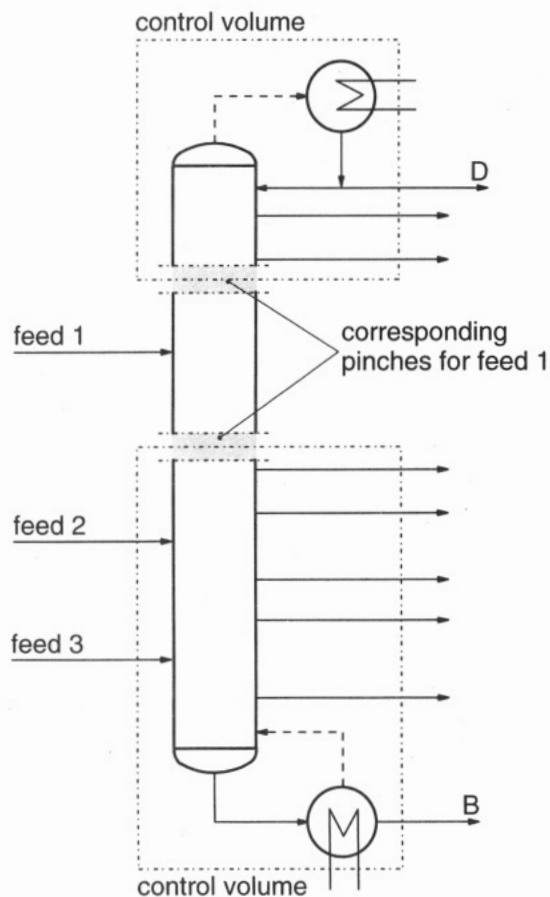
Figure 10. A column with multiple feeds and side products.

side stripper and equivalent arrangement

side rectifier and equivalent arrangement

Figure 11. Side stream stripper and side stream enricher.

out. That is why iteration is necessary for the computer-based column design.

The calculation of the minimum energy requirement for columns with several feeds and side draws proceeds in an analogous way (Figure 10). In principle any feed stream can determine the minimum energy requirement, and the two pinch zones are once again to be found between the feed point in question and the first side draw. The question to be answered is which of the feeds is the controlling one? In other words, we are looking for the feed whose pinch points occur first when we continuously reduce the reflux, starting with a high initial value. Hence, the minimum energy values must be evaluated for all feeds, and the highest value is the governing one. The control volume in Figure 10 (drawn chain dotted for the pinch combination of feed 1) should illustrate that, when making a component balance during pinch calculations, we must take into account that several feed and product streams enter and leave the respective control volume. Nikolaides and Malone [66] also use the method just described without further explanation and derive the relations for the column design. They also give approximation criteria for esti-mating the side stream compositions.

3.3. The Underwood Method for Side Stream Columns and for the Petlyuk Configuration. In addition to the two clear and instructive publications of Carlberg and Westerberg [70], references 71–74 are also devoted to side stream columns and to the Petlyuk configuration.

In the calculation of the minimum reflux ratio for columns having side stream rectifiers and strippers, thermodynamically equivalent column arrangements are considered (Figure 11). A net product stream can
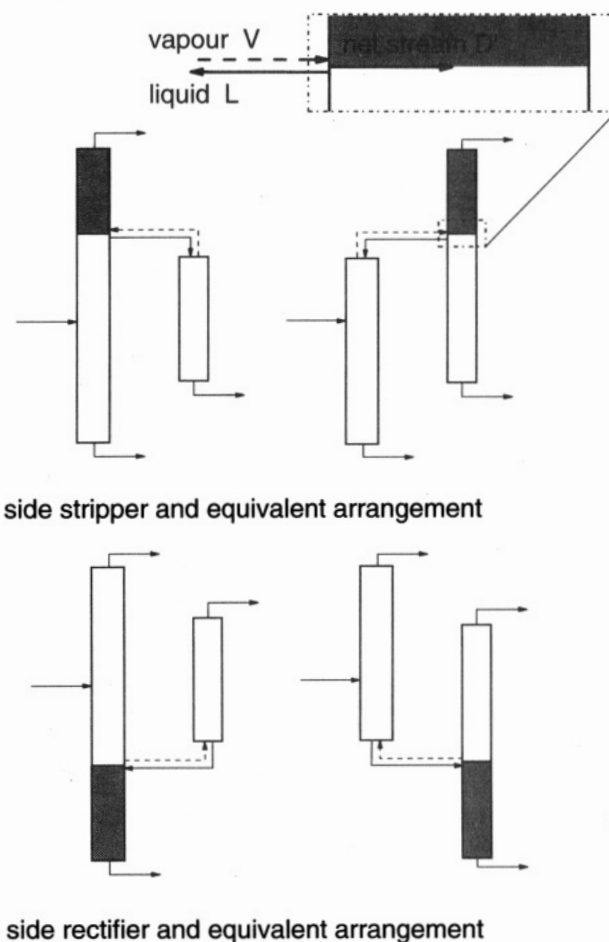
then be allotted to the first column of the equivalent sequence. This stream consists of the difference be-tween the streams entering and leaving the end of the column under consideration (e.g., $D' = V - L$). Then the minimum energy requirement can be calculated using the Underwood equations. The key idea of this approach via equivalent column arrangements is that the Underwood relations are derived from material balances. Product compositions do not have to be given explicitly. In the Underwood equations there is also no assumption that the reflux (or vapor return) must be generated by a heat exchanger installed at the ap-propriate column end. One is free to use external reflux or vapor as in the equivalent schemes.

The second columns of the equivalent arrangements can be calculated using the same Underwood relations, if the appropriate value of q for the vapor fraction of the "net" feed is used in eq 15:

$$q = \frac{L}{L + V} \tag{17}$$

where streams entering the column have positive signs. One can easily convince oneself that, in the equivalent sequence for a side stream rectifier, the q value is larger than 1 and in the case of a side stream stripper it is less than 0. In the one case the feed can be regarded as subcooled liquid and in the other as superheated vapor.

Extensions of this approach to sequences with several side stream columns and to the so-called thermally coupled Petlyuk scheme (Figure 12) have also been discussed [70]. In this latter case the first column
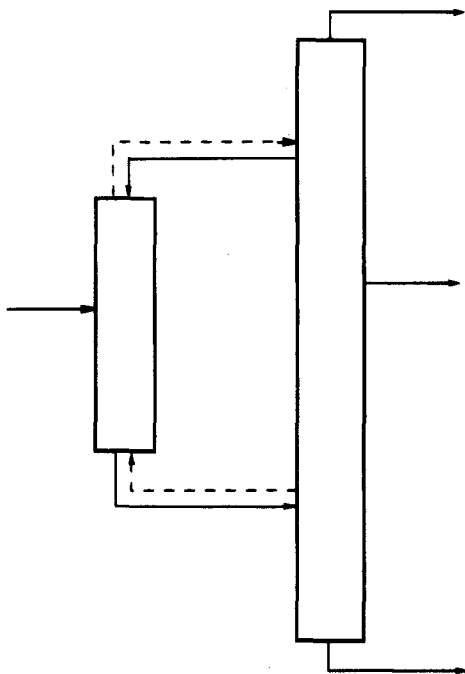
Figure 12. Thermally coupled Petlyuk scheme.

carries out only a prefractionation. This column has no heat exchangers of its own; its reflux and also its vapor come from the columns downstream. In the equations given by Petlyuk [75], there is the important restriction that they apply only for the special case of the lightest possible cut in the first column, i.e., for the potentially reversible cut for which the pinch points lie exactly at the feed stage (cf. section 2.1).

4. Nonideal Mixtures

4.1. Binary Nonideal Mixtures. Featherstone [55] and Vogelpohl [56] have introduced approaches to treat binary azeotropic mixtures. While Featherstone obtains relatively inaccurate results, Vogelpohl reports good agreement between rigorous and shortcut results. In order to apply the equations of Underwood, he performs a coordinate transformation for the mole fractions by dividing the system into two subsystems, each of which contains the azeotrope as one pseudocomponent and one of the two pure compounds as the other component. Seen graphically, the McCabe–Thiele diagram for the azeotropic mixture is split at the azeotropic composition into two diagrams for ideal mixtures. In both subsystems the transformed relative volatilities are assumed to be constant again. This coordinate transformation can also be performed for multicomponent systems. Anderson and Doherty [57] make use of the same model and also report good results. Of course, solutions can as well be obtained purely graphically via the McCabe–Thiele plot or, if the assumption of constant molal overflow is not justified, via the Ponchon–Savarit diagram [120].

Basically, however, there is no need to use approximation methods to calculate the minimum energy requirement of nonideal and azeotropic binary distillations. The reversible rectification model (cf. section 4.4) represents an absolutely exact and almost equally fast calculation method, which furthermore gives the optimum energy profile along a distillation column [58]. The reversible distillation model also applies to complex column schemes with multiple feeds and products or with side stream columns, and it also covers the special case of a tangent pinch; see section 4.5.

4.2. Rigorous Column Simulations. If we deal with nonideal multicomponent mixtures and approximation methods for the calculation of the minimum energy requirement are to be rejected because of poor accuracy, then exact column simulation programs must be used. Unfortunately this is laborious, since to date these programs are intended for carrying out performance and rating calculations of existing columns. It is not possible to exploit a priori the pinch characteristic that vapor and liquid at certain points in the column are in equilibrium with each other. It is necessary to allow for repeated time-consuming calculations of columns having large numbers of stages. One possibility, for example, is to start with a column having a small number of stages and, by gradually reducing the energy input, to build the column up in small steps—the results of one calculation being used as the initial values for the next one. Another strategy is to choose a very large number of stages to start with and to vary the reflux ratio. Then each value of the reflux ratio produces a pinch point pair and the reflux ratio corresponds to the minimum value for the combination of distillate and bottoms product which the calculation produces. Furthermore, product concentrations, product flows, or yields could be specified directly, together with the large number of stages, and the reflux could be minimized using an optimization routine. In the authors' experience this numerically difficult approach leads to success only if a realistic estimate of the column's vapor and liquid profiles for the chosen specification is already available.

Since the methods just mentioned for the evaluation of the minimum energy consumption are very time-consuming and therefore cost-intensive, several tailor-made calculation algorithms have been proposed [5, 6, 76–82, 123]. They all have one factor in common, however, in that a complete tray-to-tray simulation of the column or at least of column sections (column partitioning methods) is necessary. As an example the calculation model of Tavana and Hanson [81] will be considered, since it explicitly allows the input of product flows of the key components. Only that part of the column between the pinch points including the feed tray is modeled stagewise, and the common material and energy balance equations are used. The "pinch trays" which lie at the top and at the bottom of this part of the column are described by special equations which express the pinch condition, i.e., that the compositions of the phases do not change from tray to tray. The solution of the system of equations is carried out using an adaptation of the Newton–Raphson method. The portions of the column between the pinch zones and the product exits do not have to be calculated. The approach to the minimum energy requirement will be achieved here as in most other cases by gradual increases in the number of stages between the pinch zones. Unfortunately, example calculations with these column partitioning methods are scarce and are given mostly for ideal mixtures; such examples are of limited worth in evaluating the methods.

Another calculation procedure is presented by Nandakumar and Andres [53], who investigated the dynamic behavior of distillation columns. They model the columns using a nonsteady system of partial differential equations. Since the authors specify column sections with large numbers of stages, they are virtually describing columns at minimum reflux. The high computation effort for this deviation via the dynamic model means
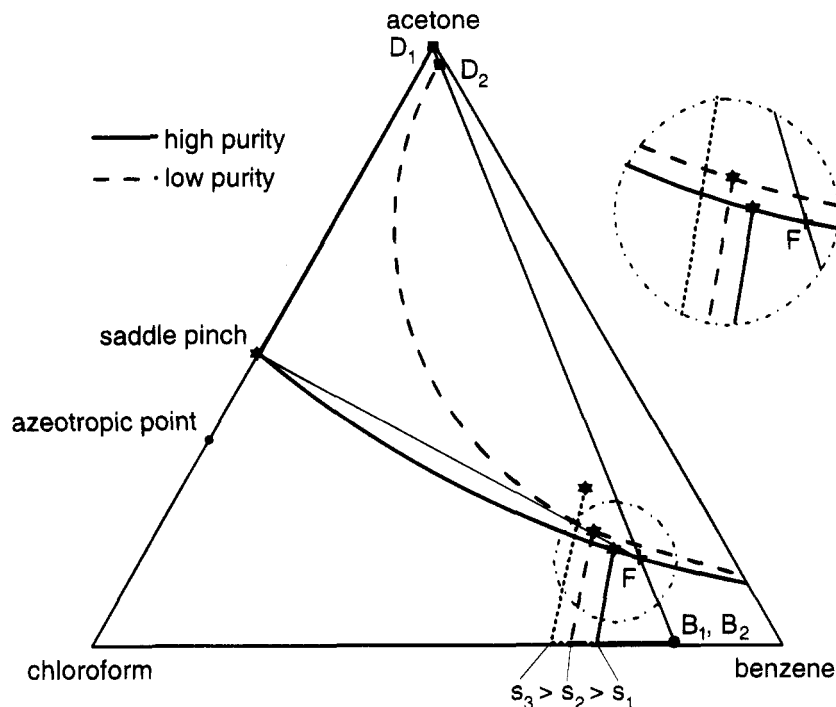
Figure 13. Minimum energy interpretation according to Doherty et al.

that their method must be rejected for all practical purposes. It is nevertheless very interesting that with this method the movement of the pinch points away from the feed tray with increasing reflux can be directly followed, since fewer components are distributed in both products as the reflux increases.

Some Soviet [83–87] and some Japanese papers [112–114] have a certain similarity of topic. In these papers the change of the product compositions and the location of the pinch points is investigated for azeotropic ternary systems under varying reflux conditions in columns having an infinite number of stages.

4.3. The Approaches of Doherty and Co-workers. Mainly in the middle of the 1980s, Doherty and his co-workers published several papers on the modeling of distillation processes and on approximation calculations of the minimum energy requirements, in particular for nonideal and azeotropic mixtures. All of their models assume steady-state operation, theoretical trays, and constant column pressure. They always require the multiple calculation of concentration, temperature, and possibly flow profiles in parts of the column, with the goal of attaining a correct material balance over the whole column. The separation profiles can be calculated either using a tray-to-tray process (favored recently by the group [90]) or using a differential equation, which is discussed briefly below.

For constant molal overflow in simple columns, the method is described first in ref 88 and is derived in detail in ref 89. It approximates the difference of the liquid mole fractions between two neighboring trays, which is obtained from a material balance around one end of the column, via the first differential of an imaginary, continuous profile of the liquid mole fraction over the trays. The result for the stripping section is

$$\frac{dx_{i,n}}{dn} \approx x_{i,n+1} - x_{i,n} = \frac{s}{s+1}y_{i,n} - x_{i,n} + \frac{x_{i,B}}{s+1}$$

$$(i = 1, ..., C - 1) \quad (18)$$

and the equation for the rectifying section is similar.

The less the concentrations change along the column trays, the more accurate will be the resulting differential approximation of the discrete balance. At minimum reflux the composition changes at pinch points and the differential quotient disappear completely $(dx_{i,n}/dn = 0)$. The result can be interpreted as a system of equations for calculating pinch points (cf. section 2.2).

The procedure for the approximation calculation of the minimum energy requirement according to Doherty will now be described with the help of the separation of the low boiler acetone from the azeotropic acetone/chloroform/benzene mixture. Starting with specified products (given a correct mass balance) and with an estimate for the reflux ratio, the separation profiles of the rectifying and stripping sections are calculated. Because the differentials appear explicitly in the balances (eq 18), they can be integrated by single-step or multiple-step procedures for ordinary differential equations. The separation is achieved with minimum energy consumption if the pinch at the end of the stripping profile lies exactly on the concentration profile of the rectifying section. If the profiles miss each other, then the separation is not possible with the estimated reflux ratio. If one profile penetrates the other, then the reflux is higher than the minimum. This interplay can easily be followed graphically.

In Figure 13 the dashed curve starting at D_2 shows the concentration profile in the rectifying section of a column. This profile, which ends on the acetone/benzene side of the triangle, is virtually insensitive to small variations in the reflux ratio and therefore in the energy throughput. The three concentration profiles in the stripping section starting at bottoms product B show the situation at varying vapor rates $s = V_s/B$ (reboiler loads). The vapor flow s_1 is not sufficient for the required separation, since the separation profile of the stripping section (bold) ends before it reaches the rectifying section profile. If the reboiler load is s_2 (dashed line), then the stripping profile just reaches the rectifying profile and at s_3 (chain dotted line) it penetrates it. With this sharpness of separation the distil-

late contains all three components in noticeable quantities, and thus only one pinch occurs at the feed point.

If we sharpen the separation by reducing the mole fraction of benzene in the distillate (D_1, bold profile in the rectifying section), then the second pinch appears in the column—in the middle of the rectifying section. In the figure it is found at the now abrupt change of direction in the rectifying section concentration profile on the acetone/chloroform side. Doherty denotes this as a "saddle pinch" and has recognized that this pinch, together with the feed (assumed as boiling liquid) and the end pinch of the stripping section (feed pinch), must lie on an approximately straight line (thin line in Figure 13). Doherty uses this as the basis of his "algebraic method" to calculate the minimum energy requirement: now, the specific reflux ratio is to be found, which leads to the colinearity just mentioned. (Note that, since only pinch points and the feed composition are involved in fulfilling the minimum reflux criterion, column simulations are not required but only a pinch point search, cf. section 2.2.) This criterion applies only to ternary mixtures. Here, a close relationship to the Underwood method becomes clear, which looks for that reflux ratio for which the feed pinch lies in between the saddle pinch and the end pinch in the other section of the column (cf. section 3.1). Because of the curvature of the separation profiles which occurs in real systems, Doherty's criterion gives more accurate results, since it requires colinearity in a narrower range of mole fractions. The "tangent criterion" further developed by Doherty is less suitable for a rapid evaluation of the minimum energy requirement because, to use it, the tangent to a concentration profile must be calculated and therefore at least column section simulations are necessary.

As indicated, the bold curve in Figure 13 corresponds to a lower minimum energy throughput but to a better sharpness of separation than the dashed curve. How can this apparent contradiction be explained? In the case of the low separation sharpness (dashed line) only one pinch occurs, viz. at the feed point in the stripping section. Thus separation stages can be added to the rectifying section—at constant energy input—to improve the separation until a pinch appears there (saddle pinch, bold line).

In the algorithm of his algebraic method Doherty proposes determining the relevant pinch points via the system of pinch equations derived from the differential balances (eq 18 with $dx_{i,n}/dn = 0$), but he provides no method of doing so. Recently, the group has addressed the problem of the direct pinch point calculation [90].

In the approaches by Doherty and co-workers concerning the calculation of the minimum energy requirement (exact method: separation profile for one half of the column ends on the profile for the other half; approximating method: colinearity), it is very important to recognize that the authors assume that there is always one of the two pinch zones at the feed point. These approaches can therefore only handle those splits where only the most or only the least volatile component is separated from the remaining components or the even more restricted case where both pinch points are at the feed point [91].

The methods described were first published by Levy et al. [10], then extended to columns with several feeds [92], and—still using the assumption of constant molal overflow—to the distillation of heteroazeotropes [93]. More recent publications have generalized the colinear-

ity criterion to coplanarity of the feed composition and appropriate pinch points for quaternary mixtures, and given us a glimpse of mixtures with even more components [94]. However, to our knowledge, Doherty and co-workers have not yet relaxed their assumption of a feed pinch and are thus still only addressing the special types of splits mentioned in the preceding paragraph.

The authors have programmed and thoroughly analyzed the column model of Doherty and co-workers in its most general form, leaving the assumption of constant molal overflow behind [95]: a differential energy balance has been added to the differential mass balance of a column section. The results can be roughly summarized as follows:

1. The calculation of the separation profile via the differential approximation produces no saving of time, but it certainly produces a loss of accuracy compared with a direct solution of the discrete, exact balance equations. The differential equations were integrated with two of the usual procedures, the Runge–Kutta–Fehlberg single-step procedure and the Adams–Bashforth–Moulton multiple-step procedure, both being of the fourth order with step-size control. These procedures frequently posed the additional problem of having to correct negative mole fractions which occurred in the calculation of intermediate values in the numerical procedures.

2. The repeated separation profile calculation—with iteration of the reflux ratio and visual and numerical judgment of the separation profiles in the triangular diagram—is, for ternary mixtures, an effective and accurate method of calculating the minimum energy requirement and is not least a valuable instructional aid, when one is trying to "get a feel for" the behavior of strongly nonideal and azeotropic distillations. For quaternary mixtures, however, the quasi-graphical method requires a considerable ability to think in three dimensions, and for higher numbers of components it is no longer practicable.

3. The method should in principle be classed with the tray-to-tray methods, and consequently also suffers from the well-known shortcomings of such methods. The extreme sensitivity of separation profiles to changes in the product compositions—the starting values of the numerical integration—should be regarded as the most serious. This problem can mostly be observed at the edges of the triangular diagram and in the neighborhood of product region boundaries. One advantage of the tray-to-tray method is, however, that each tray cascade calculated alone gives correct mass and energy balances, even though the combination of two such cascades does not necessarily result in a correct column.

4.4. The Significance of Pinch Point Curves. A new approximation method developed by the authors for the evaluation of the minimum energy requirement for ideal, nonideal, and azeotropic distillations manages without simulating columns or parts of columns. The basis of the method is the previously mentioned pinch point curves in both halves of the column (section 2.2), which are linked via the energy balance and which are calculated in the first step. A one-dimensional search algorithm then identifies the specific pinch point pair which determines the minimum energy requirement from the multiplicity of solutions via a novel geometric criterion. The criterion is exactly valid for ideal three-component separations and states that the angle between the two vectors which point from the feed to the two pinch points must be a minimum.
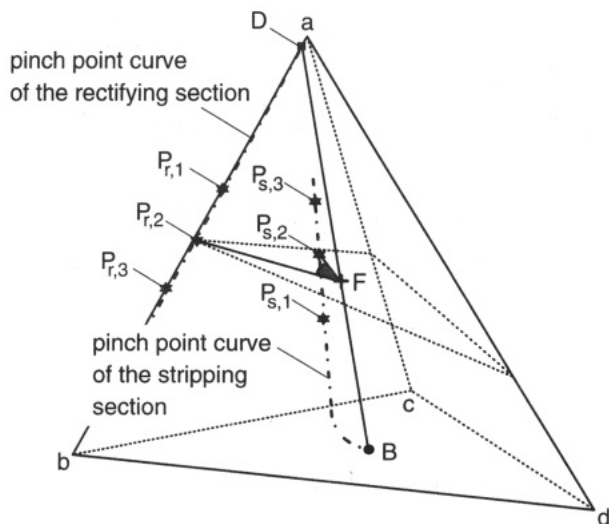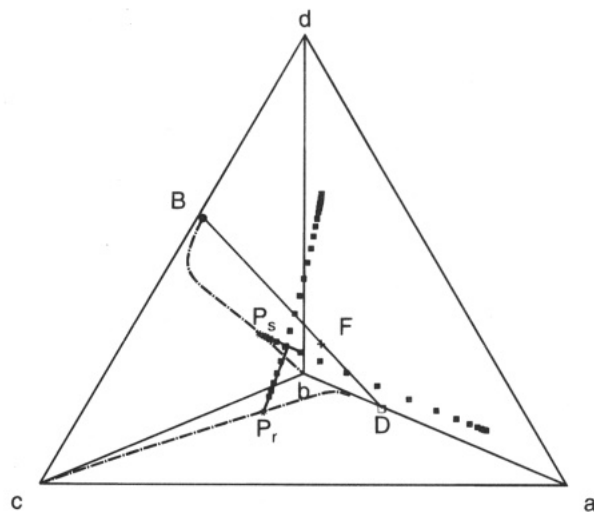
Figure 14. Minimum angle criterion for a four-component separation (a, light key; b, heavy key; P_r and P_s, pinch points).

Figure 15. Minimum energy criterion based on eigenvalue theory (b, light key; c, heavy key; P_r and P_s, pinch points with eigendirections).

Figure 14 gives a graphical explanation. The mixture of components abcd is separated into the top product a, with a small amount of component b, and the bottom product bcd, with traces of component a. The two pinch point curves originating at the two products are given as chain dotted lines. $P_{s,2}$ and $P_{r,2}$ are the two pinches under minimum reflux; the indicated angle has its minimum value. Any lower or higher reflux rate—see pinch point pairs $P_{s,1}/P_{r,1}$ and $P_{s,3}/P_{r,3}$ respectively—produces a larger angle. Additionally, the slanted dashed triangle is drawn to indicate that the concentrations of the two pinches ($P_{s,2}$ and $P_{r,2}$) and the feed are located on a plane ("coplanarity" [*94*], see section 4.3).

Many check calculations with ideal, nonideal, and azeotropic mixtures indicate that this "angle criterion" can be used safely to provide good approximate solutions for nonideal and azeotropic multicomponent distillations. There is no assumption concerning its use for certain separations only. More detailed information can be found in ref 8 and in the Ph.D. work [*58*]. Results which were obtained with this method for nonideal mixtures in columns with side products and for sloppy separations are now as well available [*117*] and extend the range of applicability of the approach.

The authors have shown [*122*] that rigorous minimum energy prediction is possible using eigenvalue theory. Again, pinch point calculation is performed prior to the evaluation of the minimum energy criterion itself. As an example, Figure 15 presents a split between the two intermediate boiling components of a non-azeotropic four-component mixture abcd. The non-key component concentrations have been set to zero in the products (a in B and d in D). Then plate-to-plate calculations starting at the products can never leave the faces of the tetraedron. The calculations approach ternary pinch points, which can be calculated directly as described above and which are situated in the figure on the pinch point curves given on the base and on the left face of the tetrahedron. If even smallest traces of non-key components would be present in the products, the separations would pass by the pinch points (here P_s and P_r) and leave the pinch point surroundings following the directions indicated by thick short lines in Figure 15. The directions are the eigendirections of the Jacobian matrixes of plate-to-plate calculation evaluated at the pinch points. The directions point into the interior of concentration space. Let us now initiate rigorous

concentration profile calculations close to the pinch points P_s and P_r on the eigendirections in the interior of concentration space: if these two concentration profiles (dotted lines) intersect, the minimum reflux ratio is found. In ideal mixtures it would, of course, be sufficient to check the intersection of the eigendirections and only minor differences would occur compared to rigorous predictions. In strongly nonideal mixtures, however, concentration profiles differ significantly from eigendirected straight lines.

The installation of intermediate reboilers and condensers has no influence on the minimum energy requirement for a given distillative separation. In the total of all the heat exchangers there must be so much energy input and output that in terms of the concentration profile the pinch points, which control the minimum energy requirement, are at least reached. If, for example, in the distillation in Figure 5, only the energy quantity $Q_{B,4}$ is supplied to begin with, then the adiabatic separation takes place along the corresponding composition profile (which would end in pinch $P_{s,4}$). If we were then to add the heat flow $\Delta Q_B = Q_{B,2} - Q_{B,4}$ in a second reboiler, the separation would be continued from the new reboiler along the profile belonging to $Q_{B,2}$. The pinch which would be reached in an infinitely long stripping section would be $P_{s,2}$. The extreme case is when the quantity Q_B is introduced "so late" that a second pinch ($P_{s,4}$) occurs in the stripping section. In this way intermediate reboilers and condensers can generate further pinch points, which, of course, must all lie on the pinch point curves—this underlines their importance.

In recent papers Doherty and co-workers use pinch point curves, which they call "fixed-point branches", for the design of distillation columns. With these curves they evaluate the number of stages and the distribution of the components in the bottoms product and in the distillate [*90*] or calculate minimum entrainer flows for extractive distillations [*124*]. Wahnschafft et al. [*96, 121*] also use pinch point curves for the determination of product regions for the separation of azeotropic mixtures by simple and extractive distillation.

Also recently, Stichlmair et al. [*119*] report a novel shortcut method to estimate the minimum reflux and reboil ratios for nonideal and azeotropic ternary separations, provided that tangent pinches do not appear. Apart from "preferred separations" (cf. section 2.1),
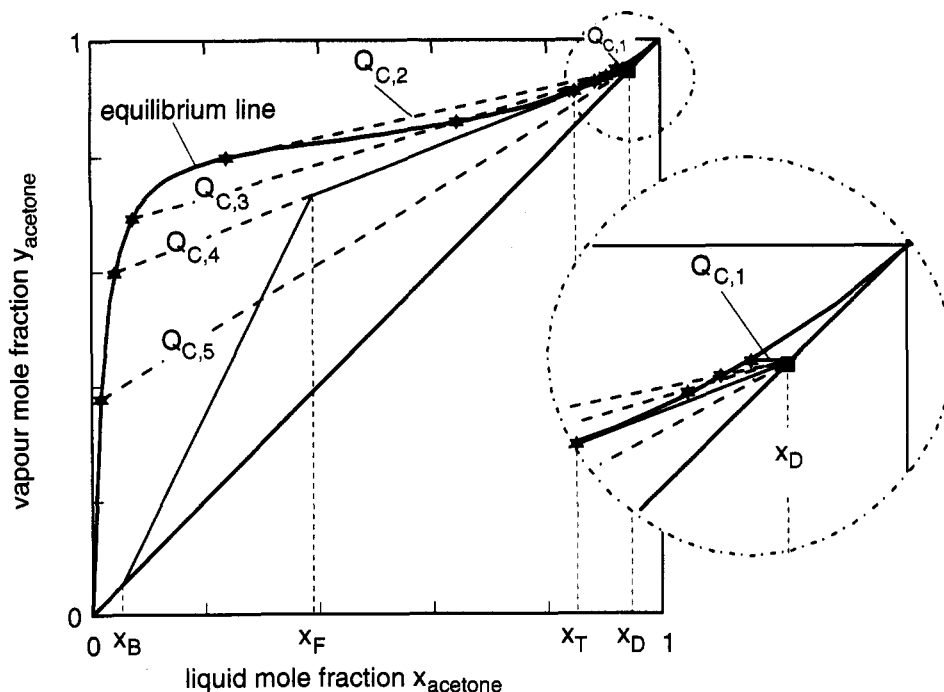
Figure 16. Tangent pinch for a binary separation (x_T mole fraction of the liquid phase at the tangent pinch).

ternary distillation at minimum reflux exhibits one pinch adjacent to the feed plate in one section of the column and a second pinch in the interior of the other section. However, their method dispenses with the calculation of the second pinch point, but rather makes use of the fact mentioned already that in ideal mixtures the feed pinch, feed, and second pinch points as well as the liquid concentration profile between the feed and second pinch must lie on a straight line. If constant molar overflow is valid, this profile is parallel with the vapor concentration profile. From the parallelism, in turn, the direction of the profiles can be calculated. Thus, on a straight line through the feed composition with direction found by the parallelism criterion, the feed pinch can be located via the system of pinch equations: if a straight line through an estimated feed pinch composition and its equilibrium vapor composition contains the product of the feed pinch column section, the minimum reflux criterion is fulfilled. This approach is fast but restricted to splits with a pinch at the feed plate. In the multicomponent case ($C > 3$) this is rather the exception than the rule (see, e.g., Figure 4). Furthermore the method is likely to suffer from not including the enthalpy balance if the mixture exhibits substantial heat effects.

4.5. Minimum Energy Requirement with a Tangent Pinch. There is one important special case, in which the occurrence of the pinch points does not satisfy the conditions described up to now. Figure 16 shows the strongly nonideal acetone/water system, where the equilibrium line has a point of inflection. Besides the equilibrium line the diagram displays the operating lines for the two column halves at minimum reflux (solid line) for the separation of a liquid feed x_F at its boiling point. Here, a so-called tangent pinch controls the minimum energy requirement: The operating line of the rectifying section is tangent to the equilibrium curve at concentration x_T when the condenser load is $Q_{C,4}$. The operating lines of the stripping and rectifying sections do not touch the equilibrium line where they meet. The
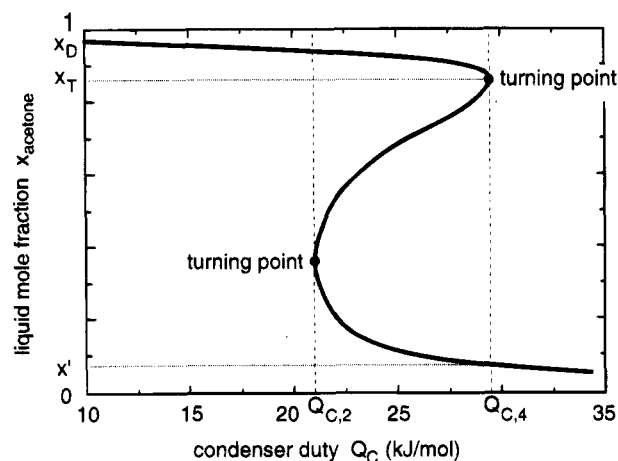

Figure 17. Tangent pinch point in the concentration vs energy plot.

concentration profile in the stripping section is thus, in spite of the minimum reflux condition, not ended by a pinch.

The evaluation of tangent pinch points is connected to the problem of multiple solutions of the systems of pinch equations. In Figure 16 additional balance lines are drawn (dashed lines) in the rectifying section for the given distillate and five different condenser loads Q_C. Each point where balance line and equilibrium line either intersect or touch represents a solution of the system of pinch equations. For $Q_{C,1}$ and $Q_{C,5}$ there is only one solution, for each of the limiting cases $Q_{C,2}$ and $Q_{C,4}$ there are two, and for all the energy quantities in between there are three. This is explained in more detail in Figure 17, in which the mole fraction of acetone at the points of intersection is shown as the ordinate for each energy value. The solution curve as a function of the energy has two turning points. This makes it clear why algorithms using heat exchanger loads or the reflux ratio as free variables in evaluating the minimum energy requirement must encounter greater problems with nonideal mixtures. Whether an equation solver converges, and what solution it reaches in the area of

multiple solutions, depends on the initial values at the start of the search. If every solution is to be found, then the system of pinch equations must be solved using varying start values. To overcome these problems Fidkowski et al. [115] suggested a continuation method to follow the path of pinch points.

Hence, a tangent pinch always reveals itself by a local maximum in the reversible energy profile [8, 115] (Figure 17, $Q_{C,4}$ required at x_T). This criterion is independent of the number of components and can easily be evaluated with the help of a search procedure.

Figure 17 also helps to understand the comment by Levy and Doherty [97], that tangent pinch points correspond to jumps (discontinuities) in the profile of the termination points of distillation. In the kind of tray-to-tray calculation mentioned in section 2.2—in which the number of trays is continually increased—only one pinch point can be obtained in each case, since the course of the calculation (seen from the column end) terminates at the first point of intersection of the operating line with the equilibrium line in a termination point of distillation. For each condenser load $0 < Q_C < Q_{C,4}$ there is, for the adiabatic separation profile starting from the distillate, a termination point in the range between x_D and x_T. If a reflux "slightly greater" than $Q_{C,4}$ is chosen, then the mole fraction of acetone at the pinch attained changes instantaneously to the value x'. The part of the curve between x' and x_T quasi disappears.

4.6. Minimum Energy Requirement without a Pinch: Comments on the Product Region Boundaries. A serious problem in the development of azeotropic distillation sequences is the prediction of the attainable column products for a given feed mixture. This also applies particularly for the calculation of the minimum reflux ratio, because all of the approximation and some of the exact methods (among others Tavana and Hanson [81]) assume the knowledge of physically correct column products. Tools for the rapid and reliable bracketing of the product limits for azeotropic separations have been the subject of several publications [e.g., 96, 98–100, 118, 121, 125] and are continually being researched. Still, residue curves play a most important role in this context.

An infinite reflux ratio transforms the differential balance (eq 18) formally into the differential equation of an open evaporator

$$\frac{dx_{i,n}}{dn} = y_i - x_i \quad (i = 1, ..., C) \tag{19}$$

the solution of which represents the composition changes in the residue remaining in a still during evaporation: it is known as a residue curve. Residue curves were introduced by Schreinemakers [101] as long ago as 1901 and often adopted in the literature [21, 98, 102–104]. Doherty and Perkins [88, 105–107], as well as Doherty and Caldarola [108], have supplemented and restructured this fund of knowledge for ternary mixtures, and have linked it to distillation with noninfinite reflux. Due to azeotropic points, families of residue curves, entered on triangular diagrams, often form several curve bundles (e.g., figures in ref 21), who are separated by boundary curves. It is a good approximation to say that these boundary lines must not be crossed by the concentration profiles of distillation columns. They are therefore relevant as limits of the product region for flowsheet and column design and hence also for the specification

of column products in the calculation of the minimum energy requirement.

Looking back at Figure 5, we recognize a first interesting connection between residue curves and pinch point curves. The pinch point curve leaving bottoms product B (chain dotted) marks the termination points of all possible concentration profiles in the stripping section. The residue line—drawn dotted—and also starting from the bottoms product—is the separation profile of an adiabatic distillation at total reflux. Consequently all the concentration profiles starting from a product are bounded by the pinch point curve and the residue curve [96]. A second important connection between residue curves and pinch point curves is the fact—which will not be further discussed here—that, for ternary mixtures, the latter can be generated in a very simple way from residue curve maps using a tangent construction [58].

A special case of the determination of the minimum energy requirement will now be explained with the help of the acetone/chloroform/benzene system in Figure 18. The residue curve boundary has been drawn and for a bottoms product B lying slightly below this curve, the pinch point curve, which runs in the direction of the acetone corner. The residue curve through B runs to the chloroform corner. If for product B the load on the reboiler of an adiabatic column having a stripping section of arbitrary length is varied, then the following observation is made [96]: for small loads the adiabatic separation profile of the stripping section ends at the pinch points (e.g., P_1, P_2) on the branch of the pinch point curve which leaves the bottoms product. Some of the concentration profiles cross the residue curve boundary from the convex side. This possibility has already been explained geometrically by Petlyuk [85], in which his separation profile construction corresponds to that of Kirschbaum [109]. Above a certain value of the reboiler load this is no longer possible, and the concentration profiles remain in the lower distillation region and end there in stationary points (e.g., P_3, P_4). At least two branches of the pinch point curve must therefore exist, and on each branch there must be not only a region which has a physical meaning and represents pinch points for the stripping section, but also a region which cannot be reached. The latter is shown by a dashed portion of the pinch point lines.

Consequently, in a column whose feed F lies in the lower distillation area (Figure 18), the bottoms product B can only be obtained if the boilup rate is so high that the separation profile of the stripping section does not lead into the upper distillation area, but stays in the lower one. This minimum value can already cause the concentration profiles of the rectificaton and stripping sections to cross each other, without a pinch occurring in the column. The number of separation stages does thus not become infinite—this case is shown chaindotted. This special case of a minimum energy throughput without a pinch will not be handled by any of the published approximation procedures. Exact column simulations are here unavoidable.

Continuing a little further with this line of thought, there must be—in nonideal systems—separations in which the minimum reflux ratio is infinite. That is, for a feed in the lower distillation area a bottoms product is specified just on the residue curve boundary. Only the separation profile for total reevaporation of the bottoms product—the residue line—will then stay in the lower region; all concentration profiles for lower reboiler
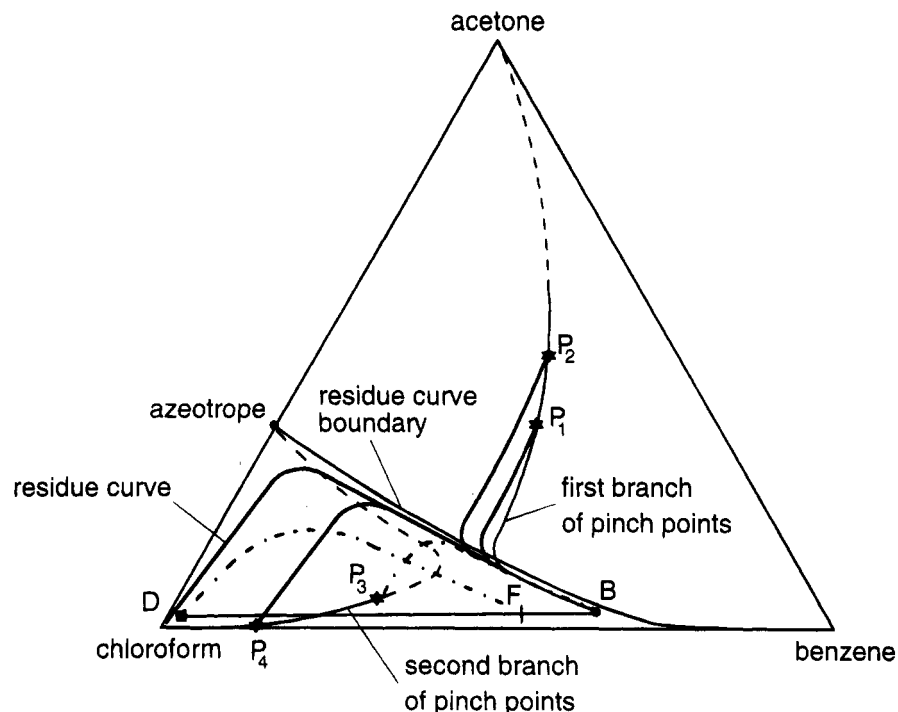
Figure 18. Pinch curve branches and minimum energy condition without a pinch.

Table 1. A Brief Extract of Methods for Calculating the Minimum Energy Demand (Methods Ranked in Order of Increasing Accuracy and Increasing Computational Effort)

	order	type of calculation	selected recommended literature examples	comments
approximation methods	1	Underwood's method for simple columns and ...	13–17, 22–26	well-suited for ideal multicomponent mixtures (constant molal overflow and constant relative volatility); dangerous with increasing nonideality of the mixture; also cover complex column sequences
		... complex columns	60, 66, 70–74	
	2	modified and extended Underwood method	52–57	allow to deal with certain nonideal cases (e.g., binary azeotropes) by formation of pseudocomponents or pseudoconcentrations; range of applicability has to be checked for each specific case
	3	pinch point criteria	8, 117	fast and (very) good approximation solutions for nonideal and azeotropic multicomponent mixtures; cover certain complex column sequences
			10, 88, 89, 92, 94	same quality, but methods are restricted to the direct and indirect splits
rigorous problem solutions	4	tangent pinch criterion	8, 97, 115	rapid exact solution for this special case (also multicomponent systems)
	5	column partitioning	79, 81, 122	more computational effort than the approximation methods, because column parts have to be simulated rigorously, but avoids entire column simulations; so far only published for simple distillation columns
	6	rigorous column simulation with a large number of stages	76, 77, 78, 82	time-consuming, but increased computer performance may facilitate this total-simulation approach

loads lead into the upper distillation region. Hence residue curve boundaries cannot be crossed by distillation mass balance lines from the convex side. Residue curve boundaries thus mark the limit of the product area in one direction.

5. Concluding Remarks

Stimuli for the development of fast procedures for the calculation of minimum energy requirements arise from the wish to appraise the operating point for the energy requirement of as many alternatives as possible during the design and analysis of distillations. In spite of numerous valuable attempts, a universal procedure, which supplies the minimum energy requirement for nonideal, multicomponent distillations at the touch of a button, has not yet been found.

Table 1 gives a brief commented selection of the most important approaches in use today. Methods are ranked in order of increasing accuracy for nonideal mixtures and increasing computational effort. Algorithms for an exact calculation suffer to some degree from considerable convergence problems, and only very few successful examples are available. The "manual" simulation-supported calculation is, in spite of vastly improved computer performance, still time-consuming and only justified if the minimum energy calculation is a seldomly required task. Approximation procedures on the basis of the idealizing Underwood equations can in many cases only be used successfully if great care is taken. Newer approaches for nonideal mixtures which strive for the exact calculation of the pinch points and the pinch point curves are—in the experience of the

authors—very promising. They must, however, first prove themselves, and require more development work. It is most important that these approaches for calculating the minimum energy requirement should cover special cases and complex column schemes also.

Acknowledgment

Nomenclature

B, D, F = bottoms, distillate, and feed flow rates, kmol/s
C = number of components
H = enthalpy flow, kW
h = molar enthalpy, kJ/kmol
Δh_V = enthalpy of vaporization, kJ/kmol
K_i = distribution coefficient ($K_i = y_i/x_i$)
L = liquid flow rate, kmol/s
n = number of stages
p = pressure, Pa
P = pinch point
q = degree of condensation of the feed ($q = L_F/F$)
Q_B = reboiler energy input, kW
Q_C = condenser energy withdrawal, kW
r = reflux ratio ($r = L/D$)
S = side stream flow rate, kmol/s
T = temperature, K
V = vapor flow rate, kmol/s
x_i, y_i = liquid or vapor mole fraction of component i, mol/mol

Greek Letters

α_i = relative volatility of component i with respect to component C
φ, ψ, Θ = Underwood's parameters

Subscripts

B = bottoms
C = component C
D = distillate
F = feed
i = component
j = counter in summations
min = minimum value
P = pinch
r = rectifying section
s = stripping section
T = tangent pinch

Superscripts

L = liquid phase
V = vapor phase

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