Shortcut Methods for Nonideal Multicomponent Distillation: 2. Complex Columns

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In an earlier article of the authors, the rectification body method was introduced for rapidly calculating the minimum reflux of nonideal and azeotropic multicomponent separations. Here, the RBM is generalized to two important classes of complex columns: (1) columns having sidestreams, and (2) columns with one or several side-enricher and/or side-stripper columns. As in the case of simple columns, the method is entirely general and does not require any a priori information on the limiting pinches prevailing in the various column sections.

Introduction

It is well established that the employment of complex columns, such as thermally coupled columns or columns with sidestreams, can frequently result in significant savings of both capital and energy costs. The benefits of complex distillation arrangements have been demonstrated in a number of case studies over the years (Tedder and Rudd, 1978; Doukas and Luyben, 1978; Glinos and Malone, 1988). However, there are two major difficulties associated with the design of complex distillation columns. First, the number of design variables is augmented by additional degrees of freedom such as, for example, the location of the withdrawal, the number of stages, and the reboiler study of a side-stripper column. Due to a lack of experience and intuition the proper selection and specification of these design variables is significantly more difficult, as in the case of simple columns. Second, the number of design alternatives for the separation of a multicomponent mixture increases tremendously when complex columns are to be considered, and it is by no means an easy task to decide upon the most favorable structure.

Frequently, the use of heuristic rules has been advocated for the sequencing of distillation columns (such as Nishida et al., 1981; Nadgir and Liu, 1983; Malone et al., 1985; Liu and Xu, 1995). Even though these rules are sometimes contradictory, they can help to reduce the number of design alternatives to be studied in case of simple columns. Occassionally, the formulation of similar heuristics for the selection of appropriate complex column arrangements has been attempted (Glinos et al., 1986; Tedder and Rudd, 1978; Glinos and Malone, 1988). It turns out, however, that even for ideal separations the appropriate selection of a complex column is highly dependent on the particular separation problem as characterized by the relative volatilities of the various components, the feed composition, and product specifications (Glinos et al., 1986). Consequently, no general, reliable heuristics can be formulated for the selection of complex columns, and numerous design alternatives have to be studied instead.

In principle, mixed-integer nonlinear-programming (MINLP) techniques allow us to address the two problems of finding an optimal column configuration and the optimal design of the individual equipment items in a simultaneous way. In fact, in recent years efforts have been directed toward the treatment of the design of column sequences as a MINLP problem using rigorous distillation models as constraints (such as Aggarwal and Floudas, 1990; Floudas and Anastasiadis, 1985; Bauer and Stichlmair, 1996). While this approach seems to be feasible for flowsheets of simple columns, the computational effort increases tremendously in the case of consideration of complex column arrangements due to the size and complexity of the required superstructure. Using eight different column types, 110,415 different flowsheet alternatives can be distinguished for the separation of a five-component mixture. This number reduces to merely 14 if only simple columns are considered (Glinos and Malone, 1988).

In light of these two difficulties related to the design of complex columns, shortcut methods for the calculation of the

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minimum reflux are of tremendous value. First, the design of a complex fractionator is effectively segregated into two subsequent steps. For minimum reflux calculations an infinite fractionator comprising an infinite number of stages in each section is considered. Consequently, the specification of the number of stages of the various sections and the location of interconnecting or sidestream streams is no longer required. Rather, these quantities can be determined in a second design step subsequent to the calculation of the minimum reflux. Second, minimum reflux constitutes a purely thermodynamically defined quantity providing an effective indicator of both the relative capital and operating costs of different distillation arrangements (Glinos and Malone, 1985a; Glinos and Malone, 1988). Due to their low computational complexity, minimum-energy shortcut calculations allow for a fast screening of a large number of design alternatives and a preselection of the most favorable candidate structures. In addition, shortcut calculations provide knowledge on the limiting values of internal streams that is useful for the initialization of rigorous simulation methods. When simulating complex columns with many stages and components, this information may become absolutely necessary for achieving convergence.

In the following, the rectification body method (RBM), introduced in the first part (Bausa et al., 1998) of this series of articles, is generalized to two important classes of complex columns: columns with sidestreams, and columns comprising one or several side columns. As is the case for the RBM, the methods proposed are entirely general and applicable to nonideal and azeotropic mixtures. Illustrative examples highlight the underlying concepts and the reliability of the new shortcut techniques.

The shortcut procedures presented rely on the concepts of the RBM. In order to avoid repetition, these concepts are not discussed in this article. Instead, the reader is advised to use Bausa et al. (1998) as a reference.

Columns with a Sidestream

Sidestream distillation columns are frequently encountered in industrial practice. Common examples for the employment of sidestream columns include:

1. The elimination of traces of middle boiling impurities from an essentially binary feed.
2. The withdrawal of a high-purity product as a sidestream when light or heavy boiling impurities are formed in the column (such as due to thermal decomposition or polymerization).
3. The production of a product stream of low purity requirements (such as for recycling as a reactor feed).

Extensive work was performed on the development of shortcut procedures for distillation columns having one (Short and Erbar, 1963; Glinos and Malone, 1985a) or several side draws and feed locations (such as Sugie and Lu, 1970; Nikolaides and Malone, 1987; Wachter et al., 1988; Cho and Yaws, 1988; Youssef et al., 1989). With the exception of two articles published recently by Köhler et al. (1994) and Rooks et al. (1996), which we will discuss in some more detail below, all the techniques proposed previously constitute generalizations of the classic Underwood equations (Underwood, 1948), and are thus limited to ideal separations. Their underlying, common idea is to decompose the column into simple separator sections, each involving only one feedstream, and to lump all product streams above and below the selected separator section to net streams. Subsequently, the Underwood equations can be applied to each simple column section separately. In the case of several feedstreams, the column section with the highest individual minimum reflux ratio determines the overall minimum energy demand. This column section will be pinched, while all other column sections will operate above their minimum reflux and no additional pinches will occur.

In the following we restrict ourselves to a single feed location and a single sidestream per column section, as this case is still analytically tractable and does not require any iterations. Given a single feed and a single sidestream, the column can be decomposed into a *primary separation* performed in the two-column sections adjacent to the feed stage, with a *secondary separation* taking place in the remaining column section. The decomposition of a column involving a single sidestream is shown in Figure 1.

The main restriction of the preceding approach for minimum reflux calculation is twofold. First some estimate of the sidestream composition has to be provided, at least in terms

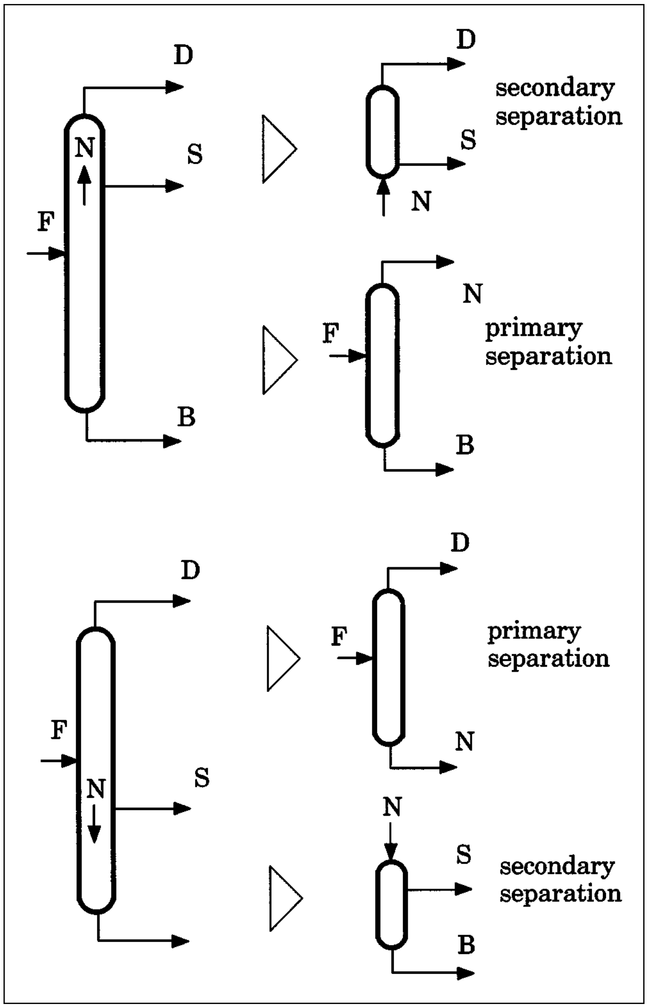

Figure 1. Decomposition of sidestream column into primary and secondary separation.

of the key component concentrations. Frequently, the sidestream composition is simply specified regardless of whether the specified purities can be achieved or not (Short and Erbar, 1963; Cho and Yaws, 1988; Youssef et al., 1989). In order to overcome this problem, Solari et al. (1981) proposed deriving the sidestream composition estimate from the composition profile under total reflux. As is discussed below, however, the sidestream purities are dependent on the internal column flows, and no arbitrary values can be assigned to the sidestream products. Second, it is assumed that limiting pinch conditions prevail in the primary separation adjacent to the feed tray. In case of multicomponent separations, however, this is generally only true if all components distribute, that is, if all components are present in all products in nonvanishing quantities. Otherwise, if some components are depleted in some products, certain restrictions apply to the purity of the sidestream products, as pointed out by Glinos and Malone (1985a). If these restrictions are not accounted for, additional reflux will be required in order to meet the sidestream product specifications. Hence, the secondary separation will be limiting and the primary separation will be overrefluxed (Rooks et al., 1996; Glinos and Malone, 1985a).

Köhler et al. (1994) proposed a minimum reflux method for sidestream columns and nonideal or azeotropic mixtures based on the minimum-angle criterion (MAC). As for ideal mixtures, however, the location of the pinch is assumed to be in the primary separation, and the method cannot be applied if the secondary separation is limiting. Further, as discussed in detail in the first part of this series of articles, application of the MAC is limited to ternary mixtures (Bausa et al., 1998).

In a recent publication Rooks et al. (1996) extended the boundary-value method (BVM) to sidestream columns. The BVM requires tray-to-tray calculations to be performed repeatedly under a variation of the reboiler duty until the column profiles calculated from the top and from the bottom of the column intersect. The BVM has the advantage that the sidestream composition need not to be specified. Merely the vapor flow (in the case of a vapor sidestream) or the liquid flow (in the case of a liquid sidestream) is reduced by a predefined value when the sidestream stage is reached and the tray-to-tray calculation is further advanced toward the feed tray. As pointed out by Bausa et al. (1998), however, the composition profile as calculated by the tray-to-tray algorithm depends not only on the heat duty but also on the precise specification of the impurities. Hence, the BVM requires many tedious manual iterations in order to achieve intersection of the column profiles.

In order to properly understand the thermodynamics of sidestream columns an analysis of the location of pinch zones prevailing in the column under minimum reflux is essential. Two different design cases can be distinguished. In the first case, the column is fully specified in terms of mass balances. The minimum energy demand of the primary and the secondary separation required to meet the respective product specifications is determined separately. The larger value of the two defines the overall minimum energy demand. As a consequence, only one of the two separations will be pinched, while the other will operate above minimum reflux. Alternatively, the difference in heat duty can be provided by intermediate heat exchange in order to realize energy savings or to facilitate heat integration.

In the second case, minimum reflux is requested in all column sections simultaneously, and both the heat duty and the sidestream flow rate have to be adjusted in such a way that a pinch zone prevails in each column section. Consequently, the sidestream flow rate cannot be fixed arbitrarily and the sidestream composition cannot be determined merely from mass balances prior to the minimum energy calculation. Rather, it is the task of the shortcut calculation to determine both the heat duty and the corresponding optimal sidestream flow rate. Once this particular value of the sidestream flow rate is known, the maximum obtainable sidestream purity can be calculated from mass balances and all three column sections will be pinched.

The conceptual idea of a sidestream column is generally to satisfy high-purity requirements for the bottom and distillate product and to perform an additional, loosely defined separation via the sidestream without additional costs. Hence we will usually first determine the maximum purity that can be achieved at the sidestream *without extra reflux* by means of the second design case. If the purity of the side product fails to meet our requirements, we might explore the amount of extra reflux necessary to achieve the desired side product by means of the first design case.

For a single sidestream, both design cases can be tackled sequentially without iterations. In case of several sidestreams per column section only, the first design approach is tractable and an *a-priori* decision concerning the sidestream compositions has to be made. Subsequently, using an iterative approach, the sidestream flow rates can be readjusted in such a way that the discrepancies between the individual minimum energy demands of the different simple separator sections are minimized. In the following, the calculation procedure is outlined in detail for the two different design cases. As an illustrative example, we consider the ternary azeotropic mixture acetone/chloroform/benzene and a saturated vapor feed with

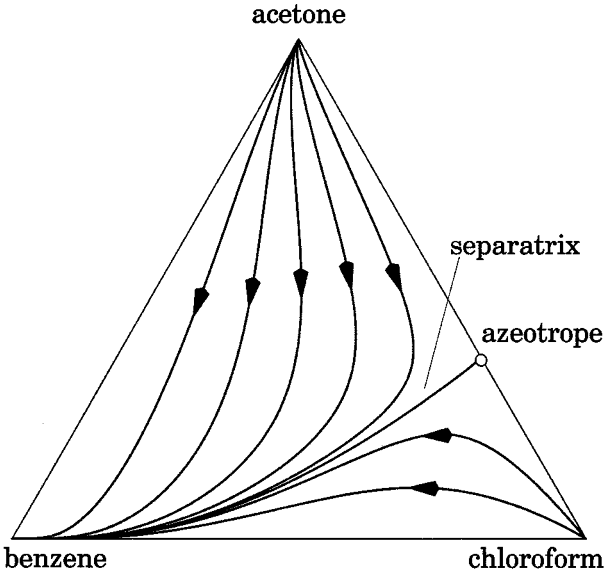

Figure 2. Residue curve map for the acetone/chloroform/benzene system at $p = 1.013$ bar.

The arrows indicate the direction of increasing time and temperature.

Table 1. Columns with Sidestream: Results of ASPEN PLUS vs. RBM ($p = 1.013$ bar)

	Specification					Q_B [mJ/kmol]		
	x_F x_B	x_D x_S	q_F q_S	D/F	S/F			
Figures						ASPEN	BVM	RBM
3,4,5	0.2/0.2/0.6 0/0.1/0.9	1/0/0 0.3798/0.5087/0.1116	0 1	0.098	0.269	28.4	32.4	32.8
6	0.2/0.2/0.6 0/0.1/0.9	1/0/0 0.3854/0.5049/0.1108*	0 1	0.0957*	0.271*	26.8	27.4	26.1
7	0.2/0.2/0.6 0/0.1/0.9	1/0/0 0.3377/0.5431/0.1192	0 1	0.115	0.252	—** —**	27.7 221.0	26.1 229.2
8,9	0.4/0.1/0.1/0.4 0/0/0.005/0.995	0.993/0/0.007/0 0.013/0.435/0.415/0.138*	1 0	0.4*	0.23*	42.40	—	42.25

*Values calculated by the shortcut procedure, not specified.
**Convergence was not achieved.

the composition $x_F = (0.2/0.2/0.6)$. Figure 2 depicts the residue curve map of the mixture. A concise summary of the examples that are presented below is given in Table 1.

Fully specified column with a single sidestream

For the first design case the column is fully specified in terms of mass balances. For the specified products, only the usual constraints for azeotropic mixtures have to be considered (such as Wahnschafft et al., 1992).

Degrees of Freedom. Given the feed composition, the thermal state of the feed, the column pressure, and the thermal state of the sidestream, $C+3$ equations are obtained by formulating mass balances and the summation conditions for each product stream. The $3C+3$ unknowns are the product compositions and flows, leaving $2C$ unknowns. In the case of a sidestream above the feed tray, specification of the bottom product (composition and flow) and the distillate composition leaves one unknown (note that the specification of the composition removes only $C-1$ degrees of freedom, as the summation condition is counted as one equation). If a sidestream below the feed tray is considered, the corresponding specifications will be the distillate product (composition and flow) and the bottoms composition.

In order to satisfy all degrees of freedom, one additional specification is required. Because the composition of the sidestream is restricted by the balance line of the secondary separation, it is most convenient to specify one additional product flow rate. This fully specifies the column in terms of mass balances and both the sidestream purity and the remaining product flow rate can be calculated.

Calculation Procedure. Using mass balances for the primary separation, the net product N leaving the primary separation is calculated by

$$N = F - B \tag{1}$$

$$Nx_N = Fx_F - Bx_B \tag{2}$$

for a sidestream in the rectifying section, or by

$$N = F - D \tag{3}$$

$$Nx_N = Fx_F + Dx_D \tag{4}$$

for a sidestream in the stripping section. Using the net product and the specified bottom product (sidestream above the feed tray) or the specified distillate product (sidestream below the feed tray), the RBM (Bausa et al., 1998) for simple columns can be applied in order to determine the minimum energy demand of the primary separation.

Subsequent to the calculation of the minimum energy demand for the primary separation, the secondary separation is considered. The secondary separation is fully specified in terms of mass balances. It is the task of the second step of the shortcut procedure to determine the minimum energy demand for the secondary separation.

The necessary criterion for feasibility of the secondary separation is that a plate-to-plate profile calculated from the known product (either distillate or bottom, depending on the location of the sidestream) exists, which reaches the liquid-phase state of the sidestream tray in the composition space (Rooks et al., 1996). In the case of a vapor side product, the liquid-phase composition corresponding to the specified vapor side-product is determined by an equilibrium calculation.

As discussed in conjunction with the BVM for simple columns, the plate-to-plate column profile is highly sensitive against the precise specification of impurities (Figure 3, bottom). Testing the plate-to-plate profiles for intersection with the sidestream state, as calculated from mass balances, requires a nested iteration modifying the heat duty in one iteration loop, and the concentration of product impurities in the other iteration loop.

As in the case of simple columns, however, the envelope of all plate-to-plate profiles can be approximated by the rectification body, that is, the polyhedron spanned by the specified product (distillate in the case of a sidestream above the feed tray; bottom in the case of a sidestream below the feed tray) and the pinch points calculated by a variation of the heat duty. Consequently, as illustrated by Figure 3, minimum reflux for the secondary separation is determined by the particular value of heat duty (of the condenser in the case of a sidestream above the feed tray or of the reboiler otherwise), where the sidestream composition *rests on a surface of the polyhedron* in composition space. Hence, the new shortcut method merely requires the selection of a set of corresponding pinch points, constructing the rectification body, and checking its surface for intersection with the specified liquid

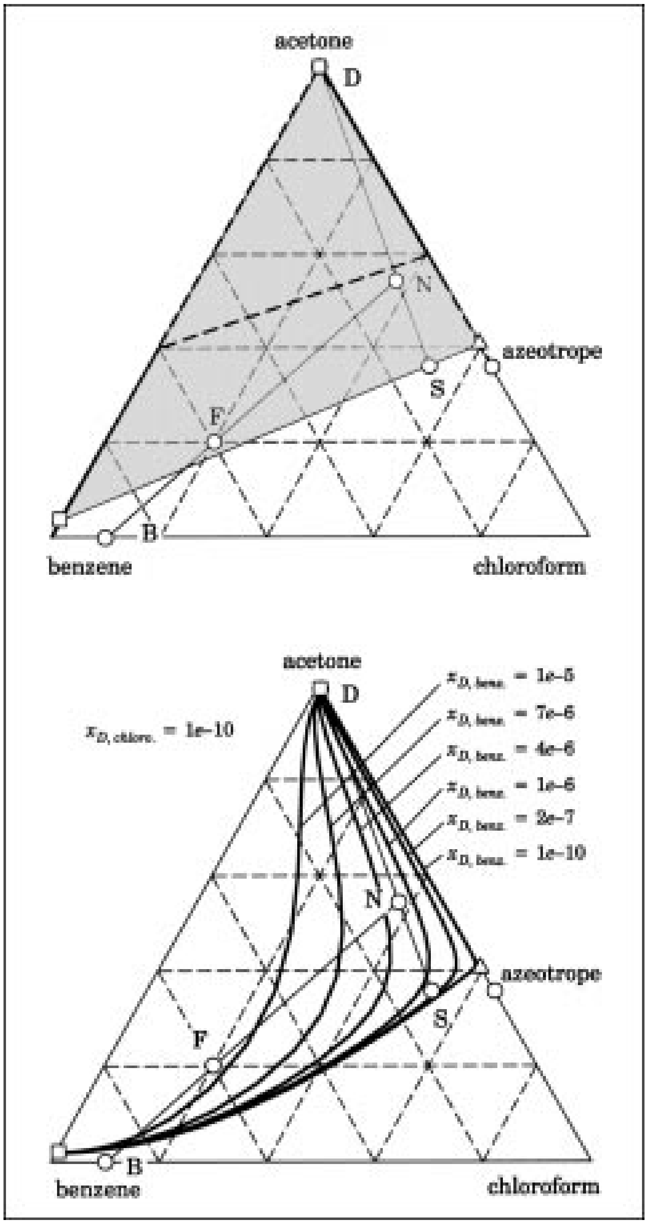

Figure 3. Sidestream column with nonoptimal sidestream flow rate.

Pinch lines, rectification body (top), and adiabatic composition profiles calculated with variation of impurity concentration in the distillate (bottom) for the secondary separation at minimum reflux.

state on the sidedraw tray. As in the case of simple columns, this criterion is entirely general and not restricted to certain separations or to a limited number of species.

In general, the energy demand of the secondary separation required to meet the chosen specifications will be different from that of the primary separation, and a condenser load (in the case of a sidestream above the feed tray) will be required, which is inconsistent with the reboiler duty with respect to the overall energy balance. Thus, the maximum of the energy demands of the primary and the secondary separation will be controlling and determines the minimum energy demand of the complex column. Consequently, only one set of pinch points, either in the primary or in the secondary separation, will prevail, and the other separation will operate at a reflux higher than the minimum.

Illustrative Example. Consider a column with a liquid sidestream above the feed tray. The bottom and distillate products are specified as $x_B = (0/0.1/0.9)$ and $x_D = (1/0/0)$, respectively. The recovery of benzene in the bottom product shall be $\sigma_B = 0.9$ and the distillate flow rate is specified as $D/F = 0.098$ [note that a higher recovery of benzene (such as $\sigma_B = 1$) is possible; the value is chosen arbitrarily to improve the graphical presentation].

Using mass balances the net product N of the primary separation is determined. Figure 4 depicts the application of the shortcut method for the primary separation. The top figure depicts the pinch equation solution branches [see Eqs. B1 and B2 in Bausa et al. (1998)] in conjunction with the rectification bodies for the primary separation. In contrast to the case of a simple column described in Bausa et al. (1998), the product of the rectifying section N is only a net stream and not a physical product that is withdrawn at some stage. Thus, x_N cannot be used as the starting point of the tray-to-tray recurrence for the calculation of the column composition profile. However, due to the specified sidedraw purity, the liquid composition x_S on the sidedraw tray is known. Hence, as depicted in Figure 4, the composition x_S rather than x_N is used for both the construction of the rectification body and as the starting point of the column composition profile of the rectifying section. However, the second point of the rectification body of the rectifying section, the pinch rn1, depends only on the net product and not on the composition of the sidestream [see Eqs. B1, B2 in Bausa et al. (1998)].

Under minimum reflux the stable pinch rn1 calculated with the net product of the primary separation touches the rectification body of the stripping section defined by the bottom product B and the pinches s1 and s2. Note, that the intersection of both rectification bodies is not affected by the sidestream composition.

The bottom figure shows the adiabatic plate-to-plate column profiles as obtained for the primary separation. As required for a minimum reflux condition, the column profiles of the two sections just touch each other.

Figure 3 shows the rectification body D-r1-r2 of the secondary separation. As a particularity of the azeotropic mixture considered, the type of pinch curve alternates. In the upper region close to the acetone vertex, the stable branch follows the acetone/chloroform edge. In the lower part of the composition space, the stable pinch branch coincides with the binary acetone/benzene edge. This is due to the fact that in the vicinity of the acetone vertex chloroform constitutes the heavy key, while for lower acetone concentrations benzene is the least volatile component.

As can be seen in Figure 3, the minimum energy demand of the secondary separation is determined from the set of pinch points for which the sidestream composition resides on the edge of the rectification body. The bottom presentation in Figure 3 shows that the rectification body is an approximation of the manifold of adiabatic column profiles calculated with different concentrations of impurities. Note that for an unfortunate choice of the impurity concentration in the distillate the BVM will indicate that the desired sidestream purity cannot be achieved at the true minimum reflux.

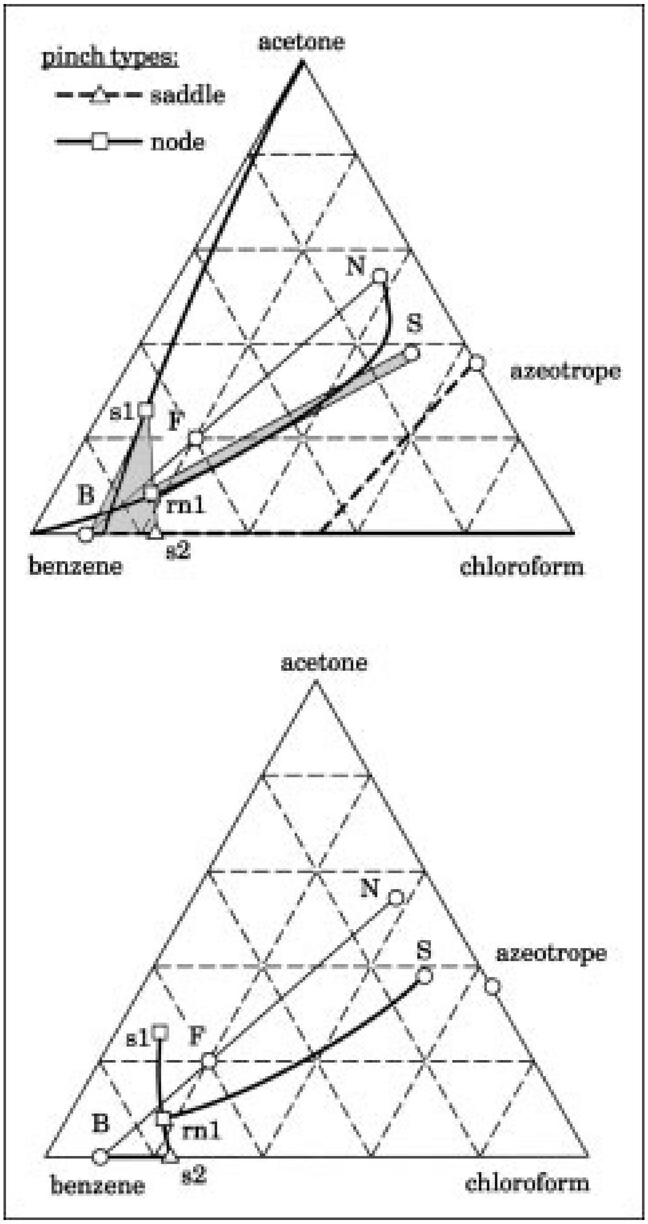

Figure 4. Sidestream column with nonoptimal sidestream flow rate.

Pinch lines, rectification bodies (top), and adiabatic composition profiles (bottom) for the primary separation at minimum reflux.

Figure 5 depicts the adiabatic composition profile of the sidestream column for the specified value of the distillate flow rate $D/F = 0.098$. As can be seen, the secondary separation is controlling. The primary separation operates above minimum reflux, and the adiabatic composition profiles obtained from plate-to-plate calculation intersect. Hence, the specified value of the distillate flow rate is thermodynamically nonoptimal in the sense that additional reflux beyond the minimum reflux of the primary separation is required in order to achieve the sidestream purity corresponding to the specified distillate flow rate. In the next subsection we will show how to determine the thermodynamically optimal distillate flow rate such that the minimum energy demand of the primary separation exactly matches that of the secondary separation. Note that for the example considered, application of the MAC will give an overall minimum reflux that is too low, as only the primary separation is considered.

The specified bottom composition requires the profile to cross the separatrix connecting the binary azeotrope with the benzene vertex in Figure 2. For the given separation, crossing of the separation is feasible because of its strong curvature and the location of the bottom product in its direct vicinity (Wahnschafft et al., 1992).

Single sidestream with optimal sidestream flow rate

If all column sections are at minimum reflux, the sidestream flow rate is related to the minimum energy demand and cannot be arbitrarily specified. However, in the case of a single sidestream, the calculation can be performed in a two-step manner.

Degrees of Freedom. As in the previous section, the bottom and distillate compositions are specified. For a column with a sidestream above the feed tray, the bottom flow rate is also specified. Otherwise, the distillate flow rate is specified. Using these specifications of the mass balances, one degree of freedom is left. In this case, the energy balance is used to satisfy the remaining degree of freedom. Note that the sidestream composition is not yet specified, whereas the net stream of the rectifying section (for a sidestream above the feed tray) is readily defined.

Calculation Procedure. First, the net product of the primary separation is calculated from mass balances, and the minimum energy demand of the primary separation is determined as in the last section.

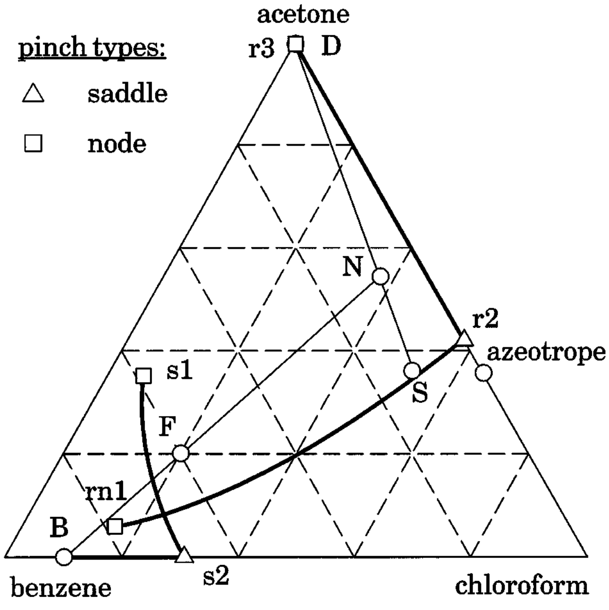

Figure 5. Sidestream column with nonoptimal sidestream flow rate: adiabatic composition profile.

Given the minimum energy demand of the primary separation, the minimum energy calculation for the secondary separation requires that the particular value of the sidestream flow rate for which a third pinch point arises is determined. In contrast to the design case studied in the previous subsection, the pinch points are not calculated with the heat exchanger duty function as the free parameter [see appendix B in Bausa et al. (1998)], but rather with the side product flow rate.

Consider a column with a liquid sidestream above the feed tray. The reboiler duty is known from the minimum energy shortcut for the primary separation. For the particular choice of the sidestream flow rate, the sidestream composition and the distillate flow rate are calculated from mass balances. The molar enthalpy of the sidestream can be determined using the sidestream composition. The overall energy balance yields the condenser duty for the known reboiler duty and the particular choice of sidestream flow rate. The solution of the pinch equations [see Eqs. B1 and B2 in Bausa et al. (1998)] with the specified distillate composition gives a set of pinch points corresponding to the selected sidestream flow rate. In this way, the pinch lines are calculated with the sidestream flow rate as the continuation parameter.

Subsequently, a particular value of the sidestream flow rate is selected and the corresponding pinch points are looked up. Using mass balances, the sidestream composition corresponding to the selected sidestream flow rate is calculated. According to the new shortcut criterion, whether or not the sidestream composition rests on the surface of the rectification body spanned by these pinch points is checked. If no agreement is found, a new value of the sidestream flow rate is selected and the next set of pinch points is tested.

In the case of a sidestream below the feed tray the calculation is performed analogously. Since the liquid composition on the sidestream tray is checked to see if it's lying inside the rectification body, for vapor sidestreams, the corresponding liquid composition has to be determined by means of an equilibrium calculation upon each iteration.

Illustrative Example. Consider the separation example in the last section. The pinch points and the rectification body obtained for the primary separation are equal to those shown in Figure 4. Accordingly, the same value of the minimum energy demand for the primary separation is determined. However, in this case the composition of the sidestream that was used to construct the rectifying section's rectification body is not yet known. However, Figure 4 shows that the intersection of the rectification bodies is not affected by the actual sidestream composition, but only by the pinch points and thus the net product. It is this property that allows the segregation of the calculation procedure for sidestream columns and columns with sidecolumns (see below) into two subsequent and independent steps; building the rectification body of the rectifying section utilizes the composition of the net stream x_N instead of the sidestream composition x_S, although there is no tray with the liquid composition x_N.

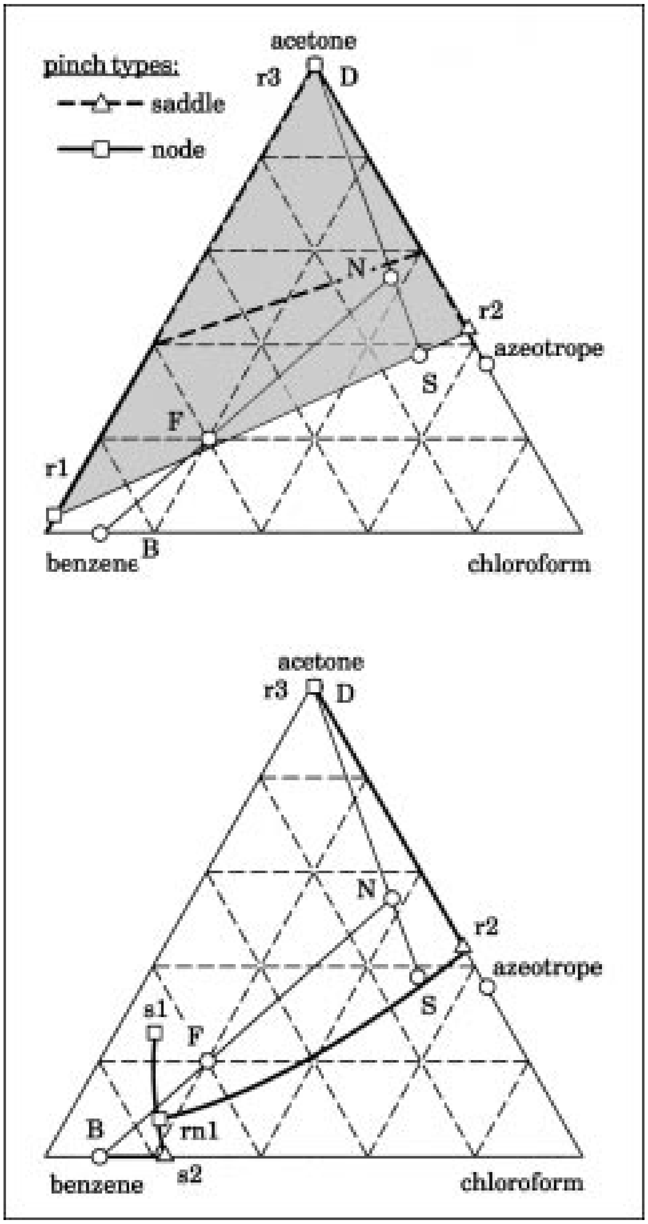

Figure 6. Sidestream column with optimal sidestream flow rate.

Pinch lines, rectification bodies for the secondary separation (top), and adiabatic composition profiles (bottom).

Calculation of the pinch curves of the secondary separation with the sidestream flow rate as independent parameter yields the rectification body D-r1-r2 depicted in Figure 6. As can be seen in Figure 6, the sidestream composition as obtained from mass balances lies on the connection of the corresponding pinch points for a particular distillate flow rate $D/F = 0.0957$. Assigning a larger value to the sidestream flow rate moves the sidestream state (point S in Figure 6) on the balance line closer to the net product (point N in Figure 6). At the same time, the saddle pinch point r2 moves closer to the azeotrope and the end pinch r1 moves closer to the benzene vertex. Similarly, assigning a smaller value to the sidestream flow rate moves S further toward the benzene/chloroform edge, while pinches r1 and r2 move toward the acetone vertex. Hence, there is a unique value of S/F where x_S intersects the surface of the rectification body.

Comparison of the rectification body with the adiabatic composition profile (Figure 6) shows that the straight line connecting the pinch points is only an approximation, and a slightly higher purity of the sidestream is encountered due to the slope of the adiabatic profile. In contrast to the example in the last section, minimum reflux conditions equally prevail in the primary separation, as can be seen by the adiabatic composition profile, which no longer intersects. Hence, for a thermodynamically optimal choice of the sidestream flow rate, three pinches are encountered in the column, one in each section: the saddle pinch s2 below the feed tray, the node pinch rn1 directly adjacent to the feed tray, and the saddle pinch r2 above the sidestream.

Sidestream column with intermediate heat exchanger

The intermediate heat exchange introduces additional degrees of freedom that allow us to enforce minimum reflux conditions in *all simple separator sections* despite a thermodynamically nonoptimal specification of the sidestream flow rate. The second design case, as discussed in the previous subsection, is merely the limiting case of an operation with vanishing intermediate heat-exchanger function.

Degrees of Freedom. The additional intermediate heat exchanger introduces two degrees of freedom, the location of the heat exchanger, and its heat function.

Calculation Procedure. As in the previous subsection and for the first design case, the minimum reflux of the primary and secondary separations are determined separately. The heat function of the intermediate heat exchanger is readily obtained as the difference of these two values. The intermediate heat exchanger should be located on the sidestream tray. Consider a column with a single sidestream above the feed tray. The following two cases are possible.

- The minimum energy demand of the primary separation is *larger* than that of the secondary. In this case, an intermediate condenser has to be installed and the condenser load is reduced to the minimum energy value of the secondary separation. Because the intermediate condenser operates at an elevated temperature compared to the main condenser, this configuration may be advantageous for low-temperature applications when refrigeration costs can be reduced.
- The minimum energy demand of the primary separation is *lower* than that of the secondary. In this case, an intermediate reboiler can be installed and the heat duty of the main reboiler is reduced to the minimum value of the primary separation. Note that this configuration involves heating *above the feed tray* at a temperature lower than in the reboiler.

For a column with a sidestream below the feed tray or columns with multiple sidestreams corresponding cases arise. In particular, condensing *below the feed tray* has to be accomplished if the secondary separation is controlling.

Illustrative Example. Consider the separation as stated earlier. Instead of choosing the thermodynamically optimal distillate flow rate, a larger value of $D/F = 0.115$ is specified. As before, pure acetone is specified as the distillate composition. Mass balances give the corresponding sidestream purity, as $x_S = (0.3377/0.5430/0.1192)$. Thus, the recovery of acetone in the distillate is increased compared to the case of an optimal selection of the sidestream flow rate (note that this value of the distillate flow rate is close to the maximum value feasible, as the sidestream composition gets close to the separatrix, which cannot be crossed from the convex side). Increasing the distillate flow rate increases the required condenser load of the secondary separation from $Q_{\text{opt}}/F = 56.4$ MJ/kmol to $Q/F = 285.6$ MJ/kmol. For this value the sidestream composition as calculated by mass balances rests on the edge of the distillation polyhedron D-r1-r2 (shaded area in Figure 7).

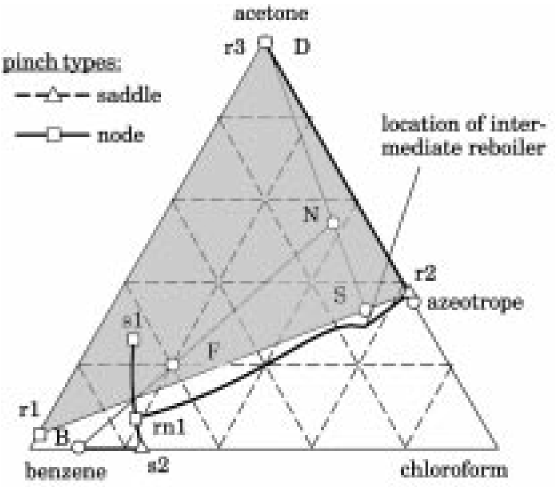

Figure 7. Sidestream column with nonoptimal sidestream flow rate and intermediate heat exchanger: rectification body for the secondary separation and adiabatic composition profile.

A plate-to-plate calculation (solid line in Figure 7) initiated from the distillate composition x_D with the minimum energy demand of the secondary separation shows that the adiabatic composition profile slopes toward a slightly higher purity of the sidestream product. Thus, a slightly greater increase in the distillate flow rate, yielding a corresponding increase in the recovery of acetone, is possible.

In order to satisfy the overall column energy balance, additional heat has to be supplied to the column. As discussed earlier, the additional heat is introduced by means of an intermediate heat exchanger rather than by increasing the bottom reboiler capacity. The composition profile in Figure 7 corresponds to an intermediate reboiler on the sidestream tray. The intermediate heat exchanger supplies exactly the difference in the minimum energy requirements of the secondary and primary separations. As can be seen in Figure 7, the composition profile and the pinch points of the primary separation remain unchanged from those obtained for a minimum refluxed primary separation (cf. Figure 6). Close to the sidestream at the location of the intermediate reboiler, the composition profile bends toward that of the *secondary separation* of increased purity. As can be seen, there are three active pinch points, s2, rn1, and r2—one in each section—encountered in the column.

Quarternary Example. In the following, the quaternary acetone/chloroform/benzene/toluene system, exhibiting a binary maximum boiling azeotrope, is studied. The specifica-

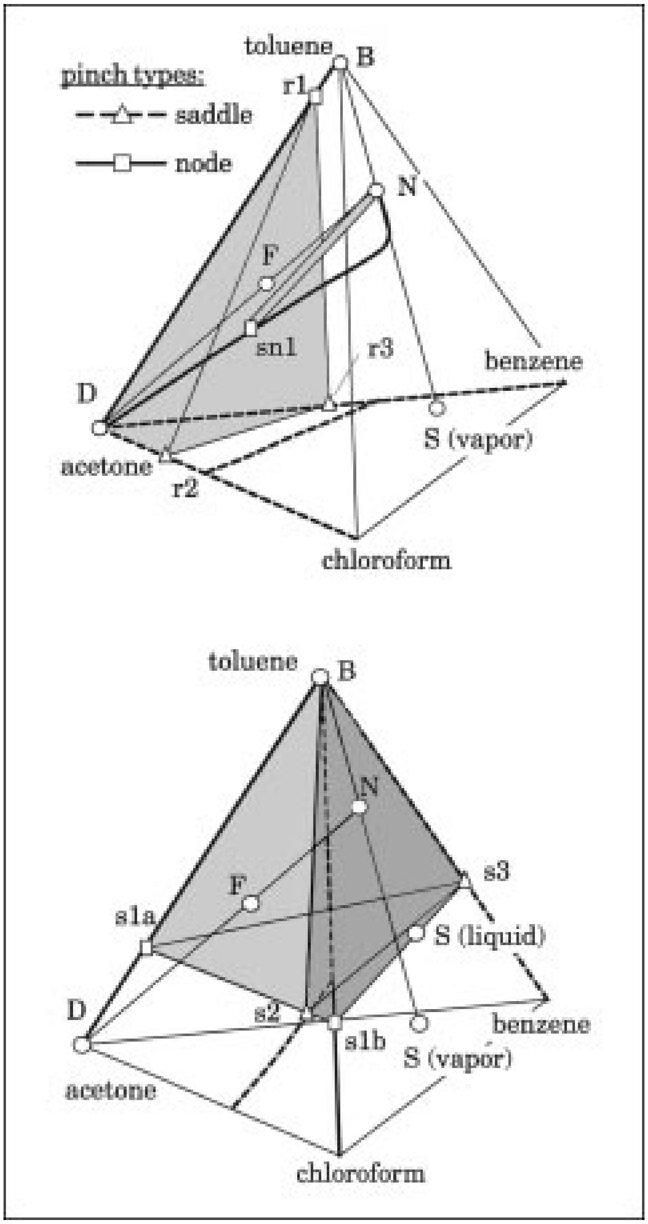

Figure 8. Quaternary example: sidestream column with optimal sidestream flow rate.

Pinch lines and rectification bodies for primary (top) and secondary separation (bottom).

tions of the separation considered are given in Table 1. A thermodynamically optimal value of the sidestream flow rate is determined.

The top part of Figure 8 shows the rectification bodies of the primary separation. Next to the acetone vertex, benzene is the second lightest component. Thus, the impurities in the distillate are essentially benzene. Three pinch points can be calculated spanning the tetrahedron plotted in gray. The net product of the primary separation contains all components in nonvanishing quantities, and only one stable pinch line is obtained. Under minimum reflux, the pinch sn1 on this pinch line touches the surface of the tetrahedron D-r1-r2-r3 spanned by the corresponding pinch points of the rectifying section.

The rectification bodies of the secondary separation are depicted in the bottom part of Figure 8. An essentially pure bottom product is specified and four pinch lines can be calculated. As the vapor sidestream is withdrawn from the column, the bottom product, the net product of the primary separation, and the *vapor* sidestream composition are situated on the balance line. The *liquid* state prevailing on the sidestream tray and corresponding to the vapor sidestream composition is indicated as *S* (liquid).

The application of the minimum-energy shortcut is entirely analogous to the ternary case. Under minimum reflux of the secondary separation, the liquid composition on the sidestream tray must be situated on the surface of one of the stripping section's rectification bodies. The column profile as calculated with ASPEN PLUS for a very large number of trays is depicted in Figure 9 in conjunction with the corresponding pinch points. Starting from the distillate *D*, the profile first follows the binary acetone/benzene edge (recall that benzene is the more volatile component in the vicinity of the acetone vertex). Subsequently, it bends toward the acetone/chloroform edge, but still rests on the lower surface of the composition tetrahedron. Because only a limited number of trays is considered in the simulation, the adiabatic profile passes through neither the unstable pinch point r2 nor r3. Instead, the adiabatic profile bends toward the interior of the tetrahedron somewhere between these two pinch points.

The profile passes through the stable pinch sn1, at the feed tray as calculated from the net product *N* of the primary separation. Subsequently, the profile bends toward the state of the liquid on the sidestream tray *S* (liquid). As enforced by the minimum-energy shortcut, the profile passes through this state. Then, the adiabatic profile reaches the binary pinch s3 of the stripping section situated on the binary toluene/benzene edge, and finally ends at the bottom product composition. As enforced by the shortcut technique, a pinch zone is

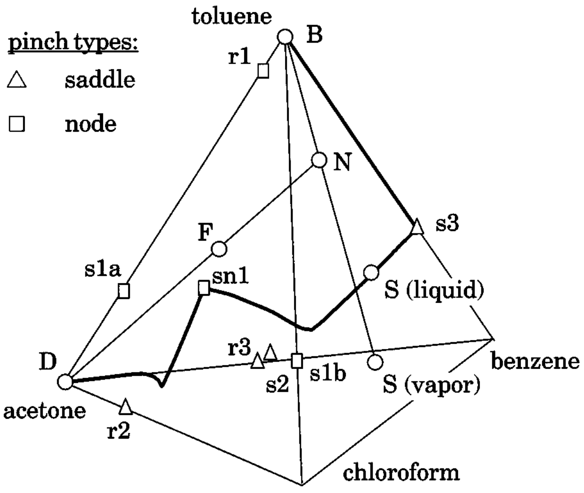

Figure 9. Quaternary example: sidestream column with optimal sidestream flow rate.

Adiabatic column-composition profile under minimum reflux (calculated by rigorous simulation).

encountered in each column section. As for the ternary examples, the results for both the minimum energy demand and the sidestream purity agree well with that obtained by rigorous simulation (Table 1).

Columns with Sidestream Enrichers and Strippers

Shortcut techniques for calculating the minimum reflux in sidestream columns were not developed before the early 1980s. As in the case of other complex distillation schemes, all previously proposed techniques stem from the classic Underwood method, and thus are restricted to ideal separations, where the assumptions of constant molar overflow and constant relative volatilities are justified.

Cerda and Westerberg (1981) proposed calculating the minimum-energy demand of sidestream columns in an iterative manner, using the Underwood equations to calculate the pinch-zone composition in order to readjust the estimated reflux ratio. Glinos and Malone (1985b) extended the Underwood techniques to sidestream strippers and sidestream enrichers. Besides being restricted to ideal distillation, however, their analysis is limited to the ternary case. A similar, though computationally rather involved, variation of the calculation of the minimum energy demand of sidestream strippers and enrichers was presented by Fidkowski and Królidkowski (1987), who formulated an optimization problem minimizing the vapor flow with the mass balances and pinch equations as constraints and derived its analytical solution. Again, their variation is limited to the ternary case.

Carlberg and Westerberg (1989) suggested decomposing the sidestream column into two simple thermally coupled columns. Using the decomposition, the Underwood techniques can be applied in a straightforward manner without iterations. In an entirely analogous way, application of the RBM divides the decomposition of the complex distillation column into a sequence of simple columns. The Underwood method for calculating the individual minimum-energy demands of the simple columns is simply replaced by a new, general shortcut technique, as described in the first article of this series (Bausa et al., 1998).

Decomposition of sidestream column configurations

The decomposition of the complex column for a column with one sidestream stripper and enricher is shown in Figure 10. In the first step, the complex column is decomposed into two simple columns and one prefractionator thermally coupled to the simple columns. In the second step, a virtual reboiler and condenser is added to the prefractionator, turning it into a third simple column. To account for the thermal state of the intermediate net feed N_1 and N_2, two additional heat exchangers have to be added to compensate for the heat supplied and withdrawn by the virtual prefractionator reboiler and condenser.

Using this decomposition, a sequence of three simple columns is obtained, each with the net product of the adjacent column section as feed. In a similar way, a complex column with an arbitrary number of sidestream columns can be decomposed into a sequence of simple columns. Note that in the case of a sidestream stripper column, the feed to the second column of the equivalent sequence will be superheated and in the case of a sidestream enricher subcooled, as indicated by the heat exchangers in the equivalent configuration.

Note also that the column profiles of the equivalent configuration are not identical to the profiles of the original configuration, since the net product compositions do not need to be included in the column profile of the original configuration, whereas they must be in the profile of the first column of the equivalent configuration, since the net products, N_1 and N_2, are distillate and bottom product of column I. As will be shown later, however, the energy demand of both configurations is not affected by these differences, and thus the configurations are equivalent with regard to energy demand.

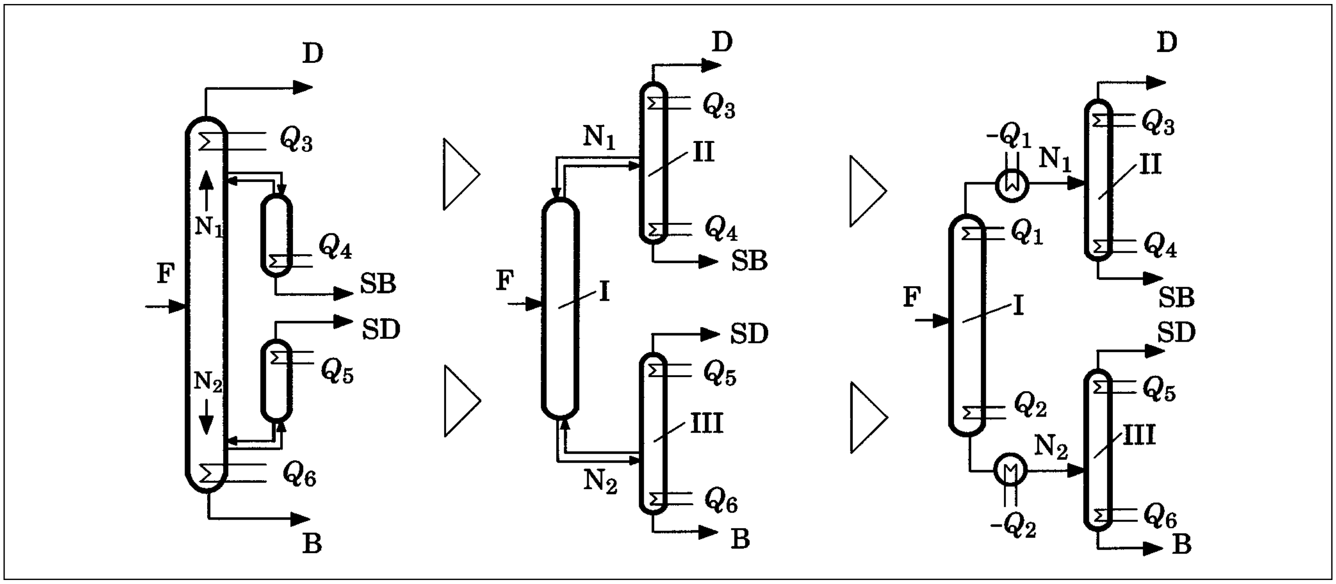

Figure 10. Decomposition of side-stripper and side-enricher columns into a sequence of simple columns.

Minimum-energy demand for sidestream column configurations

For the sake of simplicity in the following, a sidestream column configuration with a single side-stripper is considered. The application of the method to more complex configurations is straightforward.

Degrees of Freedom. In terms of mass balances, the side-stripper configuration possesses $3C+3$ unknown product compositions and flow rates, where C denotes the number of components. Mass-balance equations and summation conditions give rise to $C+3$ independent constraints, leaving $2C$ degrees of freedom. Specification of two product streams in terms of composition and flow fully specifies the side-enricher column with respect to mass balances.

Calculation Procedure. Using mass balances, the distillate composition and flow rate, as well as the composition and flow rate of the internal net product N_1, are determined from the specifications

$$N_1 = D + SB \tag{5}$$

$$N_1 x_{N_1} = D x_D + SB x_{SB}. \tag{6}$$

Applying the minimum reflux algorithm to the first column yields the reboiler function Q_2 of column I and the function of the virtual prefractionator condenser Q_1.

The shortcut algorithm is then applied to column II. First all pinch-point curves for the given products D and SB are calculated [see Eqs. B1 and B2 in Bausa et al. (1998)]. Second, corresponding pinch points (that is, pinch points that pertain to values of the reboiler and condenser duty Q_4 and Q_3 that are consistent with the energy balance for column II) are searched and used to construct the rectification bodies. Upon matching the corresponding pinch points of the upper and lower sections, the thermal state of the net feed N_1 is considered.

The shortcut method for column II yields the reboiler duty Q_4 and the condenser load Q_3 of column II. The condenser load Q_3 of column II corresponds to the condenser load of the complex column, while the reboiler duty Q_4 of column II corresponds to the duty of the side-stripper reboiler.

Illustrative Example. For an illustrative example, consider the ternary azeotropic mixture acetone/methanol/ethanol [see Figure A1 in Bausa et al. (1998) for a residue curve map of this system]. A feed of composition $x_F = (0.25/0.3/0.45)$ is separated in a sidestream-stripper column, producing a bottom product of pure ethanol, a sidestream-stripper bottom product of essentially pure methanol, and a binary methanol/acetone distillate that is nearly azeotropic.

The separation performed in the prefractionator (column I) is depicted in Figure 11. Three pinch curves are calculated for the pure-ethanol bottom product, a stable solution branch in the vicinity of the binary ethanol/methanol edge, an unstable solution branch following the binary ethanol/acetone edge, and a stable branch connecting the binary ethanol/acetone edge and the methanol/acetone azeotrope. For the binary distillate of the prefractionator, two pinch solution branches are obtained as well: a stable one and an unstable one. The bottom half of Figure 11 depicts the adiabatic plate-to-plate composition profiles as calculated for the prefractionator (column I of the simple column decomposition), indicating that the predicted value for the minimum-energy demand is an excellent approximation.

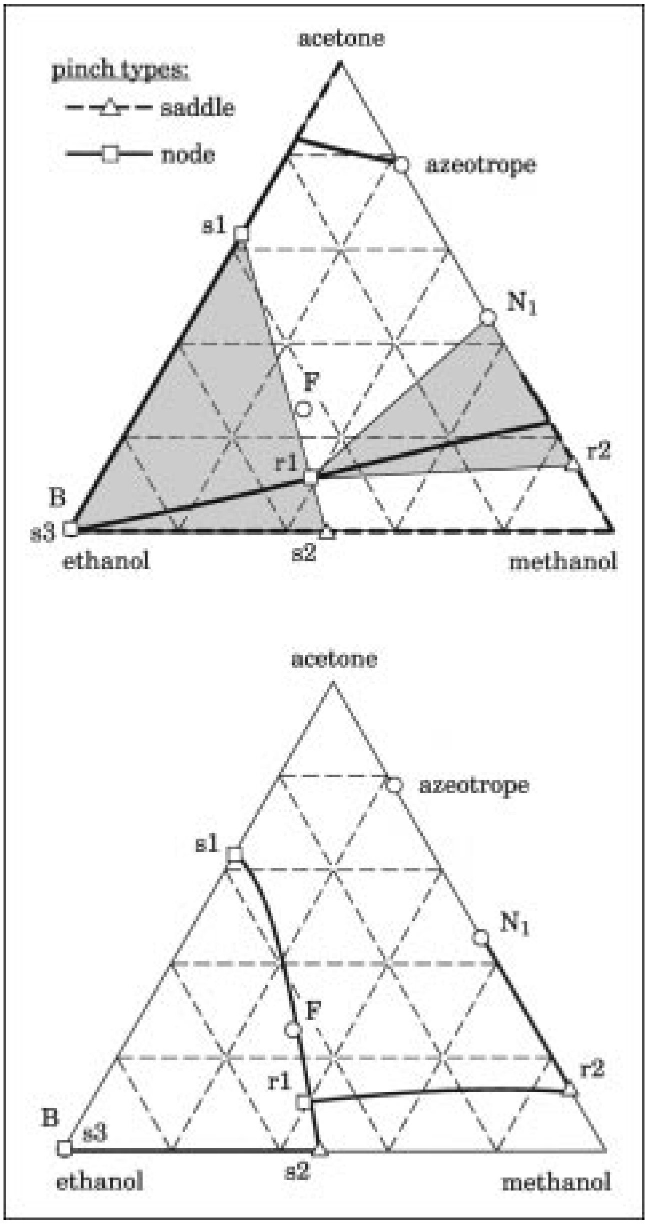

Figure 11. Sidestream stripper: separation in column I of equivalent configuration.

Pinch lines, rectification bodies (top), and adiabatic composition profiles (bottom).

Figure 12 depicts the rectification bodies for column II of the decomposition. Due to the fact that ethanol is entirely recovered in the prefractionator, the sidestream-stripper separation is essentially binary and the two active pinch points—the saddle pinch point r2 in the rectifying section and the node pinch point s1 in the stripping section—intersect in the vicinity of the feed tray. Since the intersection of

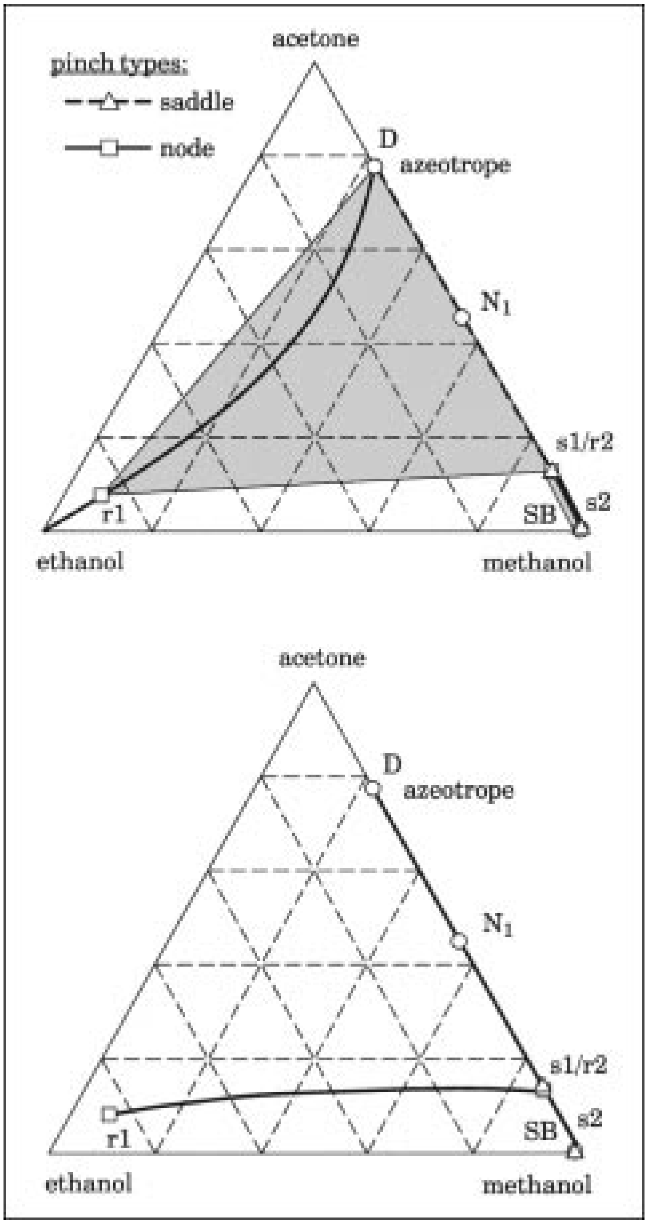

Figure 12. Sidestream stripper: separation in column II of equivalent configuration.

Rectification bodies and adiabatic composition profiles.

the column profiles is not affected by their curvature in the binary case, the minimum reflux procedure yields the exact value for the energy demand.

Note that in the original sidestripper configuration the column profile in the middle section between the connection to the sidestripper and the feed stage will extend from the *liquid composition on the feed tray of column II* (that is, pinch point s1/r2 in Figure 12) *to the liquid composition on the feed tray of column I* (that is, pinch point r1 in Figure 11). This complex-column section corresponds to the rectifying section of column I of the simple column decomposition. However, the composition profile in the rectifying section of column I extends between the state x_{N_1} of the *net product* N_1 and the pinch point r1. The minimum-energy calculation for column I is not affected by this difference, since the intersection of the rectification bodies is not influenced by the composition of N_1.

Quaternary Example. The application of the new shortcut to systems with more than three components is straightforward and is demonstrated using the example from the last section. In order to obtain 99% toluene recovery in the bottom product, a sidestream-enricher column is used. The modified product specifications are given in Figure 13 and Table 2.

The rectification bodies of the primary separation are depicted in Figure 13. Because the distillate and the net prod-

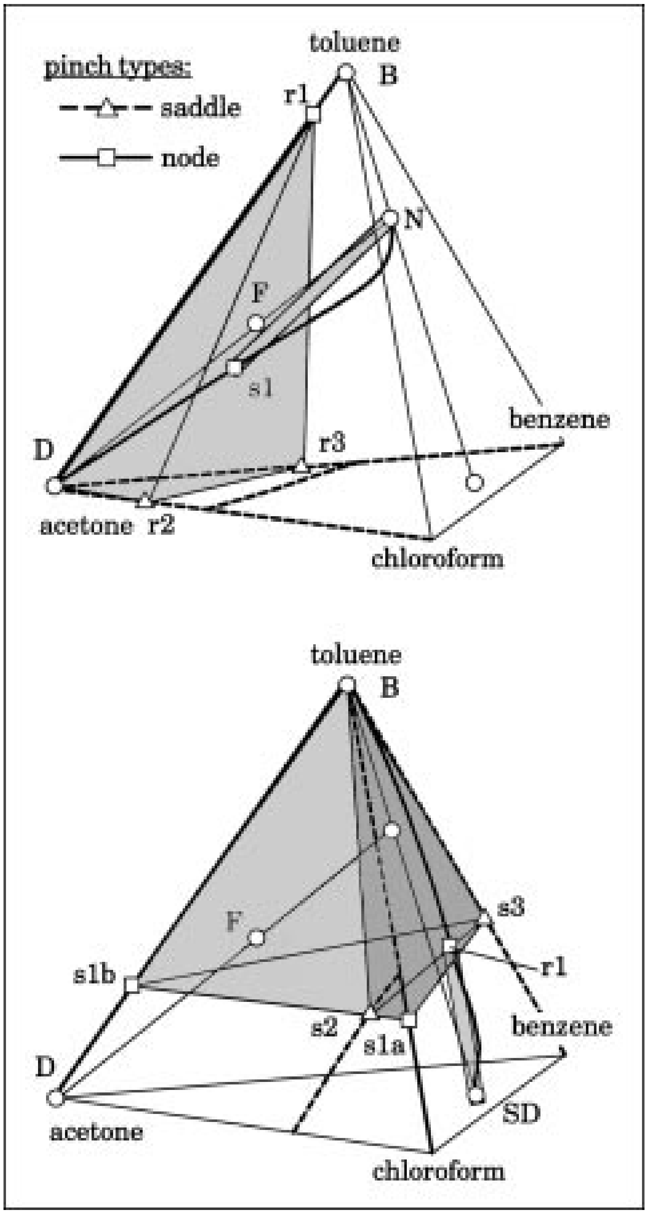

Figure 13. Quaternary example: side-enricher column.

Rectification bodies for primary (top) and secondary separation (bottom).

Table 2. Results of ASPEN PLUS vs. RBM*

	Specification				$Q_{B,1}$ [mJ/kmol]		Q_S [mJ/kmol]	
	x_F	x_D		SB/F				
Figures	x_B	x_S	D/F	SD/F	ASPEN	RBM	ASPEN	RBM
11,12	0.25/0.3/0.45	0.78/0.22/0	0.32	0.23	55.0	55.1	8.9	8.8
	0/0/1	0.0017/0.9981/0.0002						
13,14	0.4/0.1/0.1/0.4	0.993/0/0.007/0	0.4		46.8	45.3	−10.1	−10.4
	0/0/0.005/0.995	0.039/0.482/0.460/0.019		0.2072				

*$p = 1.013$ bar; $q_F = 1$.

uct of the primary separation remain the same as in the example given earlier, the rectification bodies of the primary separation are identical to those depicted in the top part of Figure 8.

For the secondary separation, three pinch lines can be calculated starting from the (essentially pure) bottom product *B*. The distillate product *SD* of the sidestream enricher comprises nonnegligible quantities of all components and gives rise to a single stable pinch line. The pinch lines for the secondary separation are depicted in Figure 13. Under minimum reflux the stable pinch node of the sidestream enricher touches the lower surface of the tetrahedron spanned by pinch points s3, s2, s1a, and the bottom product *B* in the bottom part of Figure 13.

The adiabatic column profile is given in Figure 14. Starting from the main-column distillate state, the adiabatic profile bends from the binary acetone/benzene edge toward the first pinch zone, passes through the stable pinch point sn1 at the feed tray, and continues across the plane spanned by pinch points s3, s2, and s1a. It finaly arrives at the binary pinch point s3 in the stripping section of the main column and follows the binary edge toward the bottom product *B*. The adiabatic profile of the side-enricher column starts at *SD* and ends at the stable pinch point sr1, located at the interconnection with the main column.

The results of the minimum-energy calculation using the new shortcut and the results obtained from the rigorous simulation of a column with a very large number of trays using ASPEN PLUS are given in Table 2 and show excellent agreement.

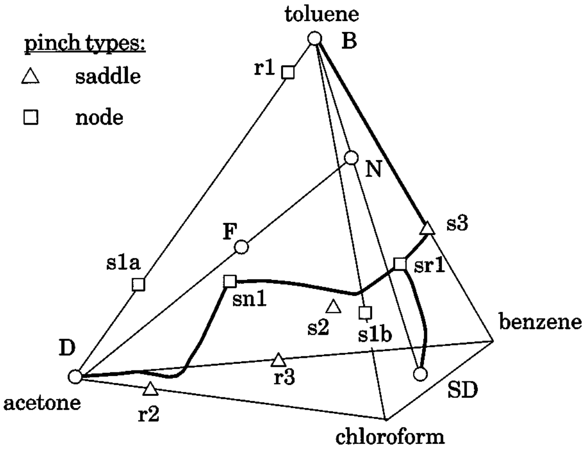

Figure 14. Quaternary example: side-enricher column.

Adiabatic column-composition profile under minimum reflux (calculated by rigorous simulation).

Conclusions

The RBM introduced in the first article of this series (Bausa et al., 1998) can readily be extended to columns with one or several sidedraws. It was shown that two different types of design problems can be identified for sidestream columns. In the first case, the column is fully specified in terms of mass balances, and the limiting energy demand (that is, the energy demand of the controlling separation) is determined. Only the column sections pertaining to this separation will be at minimum reflux, while the other column section(s) will operate above minimum reflux. Alternatively, the difference between the reboiler and the condenser heat duty can be supplied by an intermediate heat exchanger at the sidedraw tray. In the second design case, minimum reflux conditions are required in all column sections. It was shown that a particular value of the sidestream-product flow rate corresponds to this second operating condition and that sidestream purity cannot be specified *a priori*. Shortcut calculation methods for both design cases have been formulated and successfully applied to ternary and quaternary azeotropic mixture separations. As for simple columns, the shortcut method is entirely independent of the type of split and the number of components. It uses all solutions of the pinch equations, and is in excellent agreement with the rigorous simulation both in terms of the minimum-energy demand (first design case), and minimum-energy demand and side stream purity (second design case).

Further, the new shortcut method was extended to columns comprising side-strippers or -enrichers. Using the analogous separation scheme proposed by Carlberg and Westerberg (1989) for ideal separations, the problem of the minimum reflux calculation for columns with side columns is reduced to the minimum reflux calculation for *sequences* of simple columns, which can be dealt with sequentially without iterations. Again excellent agreement is obtained using the new shortcut method.

Acknowledgment

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Notation

B = bottom product flow rate, kmol/s
D = distillate flow rate, kmol/s
F = feed flow rate, kmol/s

L = liquid flow rate, kmol/s
p = pressure, bar
q = thermal state (1 = liquid; 0 = vapor)
Q = energy, W
SB = side-stripper product flow rate, kmol/s
SD = side-enricher product flow rate, kmol/s
V = vapor flow rate, kmol/s
x, y = phase composition, kmol/kmol
σ = recovery, kmol/kmol

Subscripts and superscripts

B = bottom
D = distillate
F = feed
f = feed tray
P = pinch point
N = net product
L = liquid phase
V = vapor phase
r = rectifying section
ri = pinch i in the rectifying section
s = stripping section
si = pinch i in the stripping section
sr = side rectifier
ss = side stripper

Literature Cited

Aggarwal, A., and C. A. Floudas, "Synthesis of General Distillation Sequences—Nonsharp Separations," *Comput. Chem. Eng.*, **14**, 631 (1990).

Bauer, M. H., and J. Stichlmair, "Superstructures for the Mixed Integer Optimization of Nonideal and Azeotropic Distillation Processes," *Comput. Chem. Eng.*, **20** (Suppl.), S25 (1996).

Bausa, J., R. von Watzdorf, and W. Marquardt, "Shortcut Methods for Nonideal Multicomponent Distillation: 1. Simple Columns," *AIChE J.*, **44**, 2181 (1998).

Carlberg, N. A., and A. W. Westerberg, "Temperature−Heat Diagrams for Complex Columns. 2. Underwood's Method for Side Strippers and Enrichers," *Ind. Eng. Chem. Res.*, **28**, 1379 (1989).

Cerda, J., and A. W. Westerberg, "Shortcut Methods for Complex Distillation Columns: 1. Minimum Reflux," *Ind. Eng. Chem. Process Des. Dev.*, **20**, 546 (1981).

Cho, S. M., and C. L. Yaws, "Minimum Reflux for Complex Distillation," *Chem. Eng.*, **25**, 79 (1988).

Doukas, N., and W. L. Luyben, "Economics of Alternative Distillation Configurations for the Separation of Ternary Mixtures," *Ind. Eng. Chem. Process Des. Dev.*, **17**, 272 (1978).

Fidkowski, Z., and L. Królidkowski, "Minimum Energy Requirements of Thermally Coupled Distillation Systems," *AIChE J.*, **33**, 643 (1987).

Floudas, C. A., and S. H. Anastasiadis, "Synthesis of Distillation Sequences with Several Multicomponent Feed and Product Streams," *Chem. Eng. Sci.*, **43**, 2407 (1985).

Glinos, K., and M. F. Malone, "Design of Sidestream Columns," *Ind. Eng. Chem. Process. Des. Dev.*, **24**, 822 (1985a).

Glinos, K., and M. F. Malone, "Minimum Vapor Flows in a Distillation Column with a Sidestream Stripper," *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1087 (1985b).

Glinos, K., and M. F. Malone, "Optimality Regions for Complex Column Alternatives in Distillation Systems," *Chem. Eng. Res. Des.*, **66**, 229 (1988).

Glinos, K. N., I. P. Nikolaides, and M. F. Malone, "New Complex Column Arrangements for Ideal Distillation," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 694 (1986).

Köhler, J., T. Kuen, and E. Blass, "Minimum Energy Demand for Distillations with Distributed Components and Sideproduct Withdrawals," *Chem. Eng. Sci.*, **49**, 3325 (1994).

Liu, Z. Y., and X. E. Xu, "Heuristic Procedure for the Synthesis of Distillation Sequences with Multicomponent Products," *Chem. Eng. Sci.*, **50**, 1997 (1995).

Malone, M. F., K. Glinos, F. E. Marques, and J. M. Douglas, "Simple, Analytical Criteria for the Sequencing of Distillation Columns," *AIChE J.*, **31**, 683 (1985).

Nadgir, V. M., and Y. A. Liu, "Studies in Chemical Process Design and Synthesis: V. A Simple Heuristic Method for the Systematic Synthesis of Initial Sequences of Multicomponent Separation," *AIChE J.*, **29**, 926 (1983).

Nikolaides, I., and M. F. Malone, "Approximate Design of Multiple Feed/Side Draw Distillation Systems," *Chem. Eng. Res. Des.*, **26**, 1839 (1987).

Nishida, N., G. Stephanopoulos, and A. W. Westerberg, "A Review of Process Synthesis," *AIChE J.*, **27**, 321 (1981).

Rooks, R. E., M. F. Malone, and M. F. Doherty, "A Geometric Design Method for Side-Stream Distillation Columns," *Ind. Eng. Chem. Res.*, **35**, 3653 (1996).

Short, T. E., and J. H. Erbar, "Minimum Reflux for Complex Fractionators," *Petro/Chem Eng.*, 180 (1963).

Solari, R. B., M. Carballo, R. Garaldon, and J. Estévez, "A Shortcut Method to Evaluate Minimum Reflux in Complex Fractionators," *Rev. Tech. Intevep.*, **2**, 153 (1981).

Sugie, H., and C. Y. Lu, "On the Determination of Minimum Reflux Ratio for a Multicomponent Distillation Column with Any Number of Side Cuts," *Chem. Eng. Sci.*, **25**, 1837 (1970).

Tedder, D. W., and D. F. Rudd, "Parametric Studies in Industrial Distillation: I. Design Comparisons," *AIChE J.*, **24**(2), 303 (1978).

Underwood, A. J., "Fractional Distillation of Multicomponent Mixtures," *Chem. Eng. Progr.*, **44**, 603 (1948).

Wachter, J. A., T. K. T. Ko, and R. P. Andres, "Minimum Reflux Behaviour of Complex Distillation Columns," *AIChE J.*, **34**, 1164 (1988).

Wahnschafft, O. M., J. W. Koehler, E. Blass, and A. W. Westerberg, "The Product Composition Regions of Single-Feed Azeotropic Distillation Columns," *Ind. Eng. Chem. Res.*, **31**, 2345 (1992).

Youssef, S., S. Domenech, and L. Pibouleau, "Calcul d'une Colonne de Recitification à Multiples Alimentations et Soutirages Latéraux," *Chem. Eng. J.*, **42**, 153 (1989).

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