Multicomponent Thermally Coupled Systems of Distillation Columns at Minimum Reflux

Zbigniew T. Fidkowski and Rakesh Agrawal
Air Products and Chemicals, Inc., Allentown, PA 18195

A method for calculating the minimum vapor flow in a ternary fully thermally coupled system of distillation columns was developed earlier by Fidkowski and Krolikowski. This method was developed further for fully thermally coupled systems separating four or more components. For multicomponent mixtures having constant relative volatilities and equal latent heats, the method leads to the identification of all of the minimum vapor flow rates in each distillation column that provide the same overall minimum heat duty in the reboiler. The quaternary fully coupled system of columns requires less heat energy than conventional configurations. These savings are often on the order of 20−50%.

Introduction

A simple distillation column separates a feed mixture into two products—a more volatile distillate and a less volatile bottom product. If the feed mixture consists of more than two components and more than two products are desired, then the continuous separation is usually accomplished by using multiple distillation columns in series. Several combinatorial possibilities for separating ternary mixtures into three products by distillation have been discussed in the literature (King, 1980). They include a direct sequence (two columns in series, where the most volatile product is removed from the first column), an indirect sequence (two columns in series, where the least volatile product is removed from the first column), a single column with a side stream to remove (impure) intermediate product, a column with a prefractionator (where the feed is initially prefractionated to form two feeds of different compositions passed to the second column), and three thermally coupled systems: a column with a side rectifier, a column with a side stripper, and a fully thermally coupled system (FC). More combinations of thermally coupled column arrangements for ternary separations are possible (Agrawal and Fidkowski, 1999). Other examples of column configurations for ternary distillations were given by Glinos (1985).

Thermally coupled distillation columns have been known and studied for many years, but their industrial application is still limited. A column with dividing wall, shown in Figure 1a, was patented for its ability to make all three products of any purity from one column (Wright, 1949). This could not have been achieved in previously known columns; for example, a side product from a simple column without the dividing wall is always contaminated with either the heavy or the light component. An equivalent FC system for ternary mixtures (also known as a Petlyuk column (Petlyuk et al., 1965)) is shown in Figure 1b. In this figure *A,B,C* are the components of the feed mixture listed in the order of decreasing volatilities. The same convention is used throughout this article.

Petlyuk et al. (1965) analyzed the FC system and found it thermodynamically attractive due to the reversible mixing of feeds with internal column streams. Petlyuk and his coauthors, Platonov and Slavinskii, also defined the features characterizing a general fully coupled distillation system for any number of components. These features are: $n(n\text{-}1)$ sections for an n-component mixture, only one condenser and one reboiler for the entire system, all the components of each feed (except the most and the least volatile) distribute between the top and the bottom product of each column, and all of the n products are obtained from a product column that is composed of $(n\text{-}1)$ binary separation columns built on top of each other.

Multiple studies of the FC system confirmed its attractiveness for ternary mixtures. Stupin and Lockhart (1972) found it insensitive to changes in design parameters (number of stages and flow rates). Kaibel (1987, 1988) studied thermally coupled systems and especially distillation columns with vertical partitions. Fidkowski and Krolikowski (1987) proved that for the separation of an ideal ternary mixture into pure com-

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Correspondence concerning this article should be addressed to Z. T. Fidkowski.

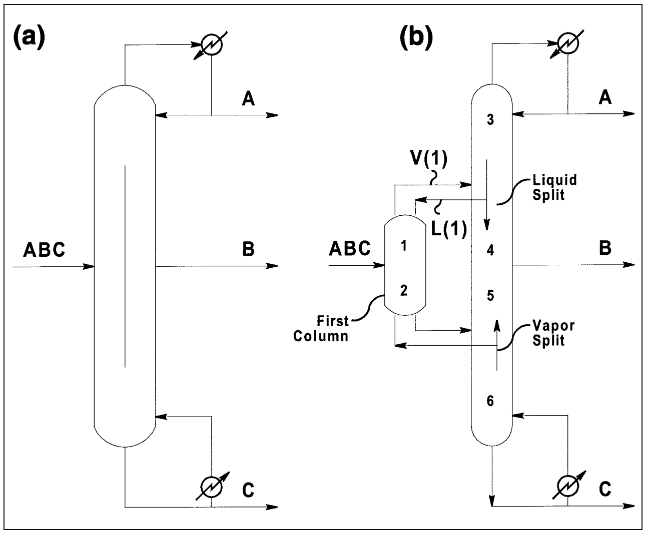

Figure 1. (a) Column with dividing wall; (b) fully coupled system for ternary mixtures (1,2,...6—column sections).

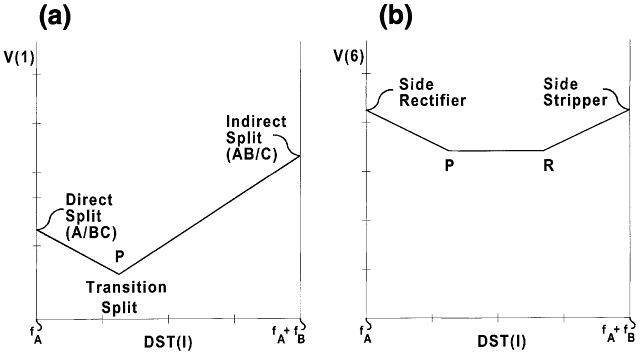

Figure 2. (a) Minimum vapor flow in the first column—V(1); (b) total minimum vapor flow—V(6) in the ternary FC system.

Both as functions of net distillate flow from the first column —DST(I).

ponents the minimum vapor flow in the FC configuration is smaller than in any other configuration of columns for ternary distillation. Vu et al. (1987) compared the cost of several column configurations for ternary feed mixtures, including the FC system. Glinos and Malone (1988) compared the minimum vapor flows and identified optimality regions in feed composition space for complex ternary column systems. They found that the FC system (when compared to other systems) can provide a considerable reduction of a minimum vapor flow. Carlberg and Westerberg (1989), and, more recently, Halvorsen and Skogestad (1999), used Underwood's method for the ternary FC system separating a mixture containing more than three components into three products only (some of the products were not pure). Chavez et al. (1986) dealt with the problem of multiple steady states in the FC system. Triantafyllou and Smith (1992) presented a design method for the FC system based on analysis of simpler column structures. Wolff et al. (1993) analyzed operation and control of the FC system. Christiansen (1997) studied optimal design and operation of thermally coupled distillation arrangements.

The low heat energy requirements of the FC system have sometimes been confused with high thermodynamic efficiency. Agrawal and Fidkowski (1998a) presented a method for calculating the thermodynamic efficiencies of various ternary systems of columns and compared efficiencies of these systems. They concluded that the FC system is not always the most efficient.

Fidkowski and Krolikowski (1986) developed analytical equations for the minimum vapor flow rates in a ternary FC system. Mixtures of components with constant relative volatilities and constant molar overflow in columns were assumed. The vapor flow rate from the reboiler was represented as a function of β where β is the fraction of component B leaving the first column (prefractionator) in the distillate ($\beta = d_B/f_B$). Their results are re-plotted in Figure 2 as a function of the net distillate flow from the first column. This net distillate flow rate is a linear function of β [$DST(\mathrm{I}) = V(1) - L(1) = f_A + \beta f_B$].

Figure 2a shows the minimum vapor flow in the first column only $V(1)$. The separation in the first column, where the distillate [$DST(\mathrm{I})$] is rich in component A and bottoms contains B and C ($\beta \to 0$), is the same as for the *direct split* configuration. Conversely, when $\beta \to 1$ (the distillate contains component A and B and bottoms contains C only), we have a separation like in an *indirect split*. Point P corresponds to the minimum value of the minimum reflux in the first column. This is referred to as *the transition split* (Fidkowski et al., 1993), and is also called the *preferred split* by Christiansen and Skogestad (1997). In the transition split component B is divided between the distillate and the bottom product.

Figure 2b shows the minimum vapor flow for the entire FC system [$V(6)$] as a function of $DST(\mathrm{I})$. Note that, at $DST(\mathrm{I}) \to f_A (\beta \to 0)$, a fully coupled system can be reduced to a side rectifier and, at $DST(\mathrm{I}) \to f_A + f_B (\beta \to 1)$, it becomes a side stripper. The horizontal section PR in Figure 2b represents the minimum value of the minimum vapor flow from the reboiler. Point P corresponds to transition split in the first column. Point R corresponds to the second column being pinched at both feed locations (AB and BC) simultaneously. The value of $DST(\mathrm{I})$ (or β) is not an independent control variable. It depends on the liquid and vapor flows in the first column, which are set by the vapor split and the liquid split in the product column (see Figure 1b). If these splits are not controlled to place $DST(\mathrm{I})$ inside the PR range, the FC system will not be at its optimum. Consequently, the expected heat energy savings will not be achieved. In the worst case, the minimum vapor flow of a nonoptimal FC system will be close to the minimum vapor flow of a side stripper or a side rectifier. This penalty may or may not be substantial, depending on relative volatilities and feed composition.

The length of the PR section in Figure 2b is also a function of the feed's composition and relative volatilities. If the PR section is long enough, then the column may be very insensitive to its operating parameters (liquid and vapor split). For example, in a dividing wall column (Figure 1a), where the liquid split and the vapor split are not controlled and occur naturally (Abdul Mutalib and Smith, 1998), the column may still be able to work at its optimal conditions. If, however, the PR section is short, then the FC system is more sensitive to the operating parameters. In this case "natural operation" at optimum conditions is less likely. Certain changes in the structure of the FC system can make it more operable (Agrawal and Fidkowski, 1998b; Agrawal, 1999). These operability improvements remove a big obstacle in the industrial implementations of fully thermally coupled systems for three or more components.

Ternary FC systems have been very well studied, but not much attention has been devoted to multicomponent thermally coupled systems, where a mixture containing more than three species is separated into almost pure components. These systems of columns may also be attractive, by analogy to the ternary systems.

For four or more component feed mixtures, there are several possible ways to draw FC systems, containing $n(n\text{-}1)$ sections (Agrawal, 2000). For example, there are 32 possible configurations of FC separating a four-component feed mixture. This includes the earlier proposed sequential configuration of Sargent and Gaminibandara (1976) and the satellite columns configuration of Agrawal (1996). All the 32 configurations are expected to have identical vapor flows in corresponding sections at minimum reflux conditions.

However, some of the substructures obtained from the satellite arrangements are not contained in the sequential arrangement of Sargent and Gaminibandara. For a four-component feed, Christiansen (1997) performed simulations of a substructure derived from the satellite configuration containing ten sections ($4n\text{-}6$) and the sequential configuration containing twelve sections [$n(n\text{-}1)$]. He also performed calculations of minimum vapor flow for a quaternary FC system, by using an optimizer with the column simulator to minimize the reboiler vapor flow. These calculations were carried out for an FC system, where columns had a fixed number of stages. The number of stages was then increased and the system was reoptimized. This procedure was repeated until the resulting vapor flow (for sufficiently large number of stages) did not change appreciably. This iterative procedure suggests that there is a need for a simple, direct method to calculate the minimum vapor flow for a multicomponent FC system (that is, the vapor flow in FC columns with an infinite number of stages operating at pinched conditions).

The primary objective of the present work is to further develop the Fidkowski and Krolikowski's (1986) optimization method for ternary FC system to FC systems for the separation of mixtures with four or more components. This method will then be used to compare the fully coupled system with the other well-known column arrangements for the separation of multicomponent mixtures.

A FC system for four components is shown in Figure 3. It contains only one reboiler and one condenser and has twelve sections [$n(n\text{-}1)$]. Comparison of minimum vapor flows in the FC system with partially thermally coupled systems, with fewer connections between the columns [from ($4n\text{-}6$) to less than $n(n\text{-}1)$], will not be done in this article.

We assume mixtures with constant relative volatilities of components, constant molar overflow and unit feed flow rate (for example 1 kmol/s). Feed and products are boiling liquids. The mixture is to be separated into pure components.

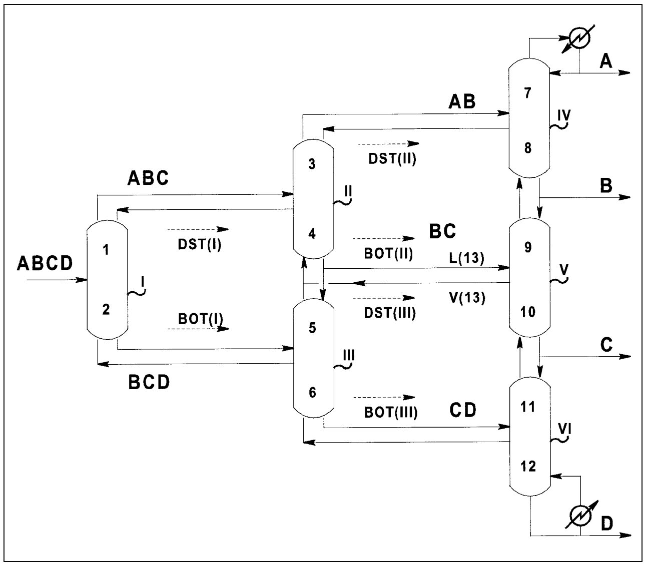

Figure 3. Fully coupled system for quaternary mixtures.

Multicomponent Mixtures

We will use Underwood's (1948) method described also by Shiras et al. (1950) to calculate the minimum vapor flow for a multicomponent system.

First, the roots ϕ of the following equation are calculated

$$\sum_{i=1}^{n} \frac{\alpha_i z_i^F}{\alpha_i - \phi} = 1 - q^F \tag{1}$$

For a mixture containing n components, there are $n-1$ roots ϕ_j ($j = 1,2,\ n-1$) with values between those of the relative volatilities of the components

$$\alpha_1 > \phi_1 > \alpha_2 > \phi_2 > \ldots > \alpha_{n-1} > \phi_{n-1} > \alpha_n \tag{2}$$

It is convenient to categorize the components as follows:

- *Light* component(s) appear only in the distillate.
- *Light key* component is the most volatile component present in the bottom product.
- *Distributing* component(s), nonkey component(s), present in both the distillate and bottom products.
- *Heavy key* component is the least volatile component present in the distillate.
- *Heavy* components appear only in the bottom product.

Usually, compositions or recoveries of the key components are specified.

It is worth noting that the definition of component presence in a given product is not clear. For example, a printout of a distillation column concentration profile (from a computer simulation) shows that all of the components are present in all of the products, although their concentrations may sometimes be extremely low.

The minimum vapor flow in the rectifying section is determined (together with distillate flow rates for the distributing components) by solving the following system of equations

$$V = \sum_{i=1}^{n} \frac{\alpha_i d_i}{\alpha_i - \phi_j} \tag{3}$$

where j is the index of the Underwood's root of the value contained between the relative volatilities of the key components. The number of equations in the system of Eq. 3 depends on the number of distributing components, for example:

- *If there are no distributing components, there is only one equation (Eq. 3) with one unknown:* the minimum vapor flow V; all the distillate flow rates are specified; the value of Underwood's root ϕ used in Eq. 3 is contained between the values of relative volatilities of the light key and the heavy key component;
- *If there is one distributing component (for example component k), there are two equations (Eq. 3) with two unknowns:* the minimum vapor flow V, and the distillate flow of the distributing component (d_k); all the distillate flow rates (except d_k) are known as specified; the two values of ϕ that are used in Eq. 3 are contained between the relative volatilities of the light key and the heavy key component;
- *Similarly, for two distributing components, there will be three equations (Eq. 3) where unknowns are:* the minimum vapor flow V, and the distillate flows of the two distributing components and so on. In general, the number of Underwood's equations in the system of Eq. 3 is equal to the number of the distributing components plus one, and the unknowns are the distillate flow rates of the distributing components and the minimum vapor flow.

A similar set of equations can, of course, be written for the stripping section.

Optimization of a Quaternary System

We will first consider the separation of a quaternary mixture $ABCD$, where components are ordered according to decreasing volatility. An FC system for the separation of quaternary mixtures into four products is shown in Figure 3. This system can be arbitrarily divided into six distillation columns. First, there is a distillation column separating a quaternary mixture $ABCD$ into ABC on the top and BCD in the bottom (split ABC/BCD). This is column I that contains sections 1 and 2. Then, there are two ternary columns (that could be built in the same shell): column II (sections 3 and 4) separating AB from BC (AB/BC) and column III (sections 5 and 6) separating BC from CD (BC/CD). Finally, there are three binary columns (IV, V and VI) (that could also be built in the same shell) separating A from B (A/B), B from C (B/C) and C from D (C/D), respectively. These columns contain sections numbered from 7 to 12. Flows in a given section are denoted using this section number, for example, $L(11)$ and $V(11)$ denote the liquid and vapor flows in section 11. Finally, liquid and vapor flows BC between sections 4,5 and 9,10 are denoted as $L(13)$ and $V(13)$. Direction of streams $L(13)$ and $V(13)$ has been chosen arbitrarily. Calculated values of any of these two flow rates may be negative, which means that the direction of this stream is opposite to the one shown in Figure 3.

The division of the system into columns I, II, …, VI is purely hypothetical and made only for convenience. This numbering system is not essential for the given calculation method, but it makes the description easier and precise.

Columns, sections, or parts of sections can be moved between various shells (without changing their connectivity) giving various combinatorial possibilities of equivalent structures that may turn out to be more operable (Agrawal, 1999). All these equivalent structures of columns require the same overall minimum vapor flow from the reboiler (same heat duty) at pinched conditions. At unpinched conditions (above the minimum reflux), and, with a similar total number of theoretical stages, the vapor flow rate requirements could vary significantly between these possible structures.

In addition to constant relative volatilities of components and constant molar overflows, we assume liquid products withdrawn as almost pure components. A full procedure is described below for calculating the minimum vapor flow required for this separation.

Four component column

In the first column of the FC structure shown in Figure 3 the quaternary mixture $ABCD$ is separated to give the distillate containing all the components except the least volatile component D, and to give the bottom product containing all the components except the most volatile component A. Therefore, components A and D are fully separated, but the separation of the intermediate components (B and C) is not known. Their compositions in the distillate and in the bottom product may either be specified (if B and C are the key components) or they must be calculated. The well-known classic procedure of determining the separation of components B and C is based on trial-and-error calculations (Shiras et al., 1950), where a possible assignment of the key components is first assumed. All the combinatorial possibilities for these assignments (or splits) are presented in Table 1. Then, the corresponding set of Underwood's equations (Eq. 3) is created and solved for the minimum vapor flow rate and the distillate flow rates of the distributing components. If a component is presumed to distribute at minimum reflux, but in fact it does

Table 1. Possible Combinations of Key Components and Corresponding Roots of Underwood's Equation for a Four-Component Mixture*

Case	Lights	Light Key	Distributing	Heavy Key	Heavies	Split	Underwood Roots
1		A		B	C, D	A/BCD	ϕ_1
2		A	B	C	D	AB/BCD	ϕ_1,ϕ_2
3		A	B, C	D		ABC/BCD	ϕ_1,ϕ_2,ϕ_3
4	A	B		C	D	AB/CD	ϕ_2
5	A	B	C	D		ABC/CD	ϕ_2,ϕ_3
6	A, B	C		D		ABC/D	ϕ_3

*Note: $\alpha_A > \phi_1 > \alpha_B > \phi_2 > \alpha_C > \phi_3 > \alpha_D$.

not, then the solution of the set of Eq. 3 will give rise to an impossible value of distillate flow rate for this component (negative—for heavy components or larger than the feed flow rate for light components). If either of these results occurs, a different assignment of the key components is made and the procedure is repeated.

An equivalent, but less tedious, method has been used by Tedder and Rudd (1978) and Fidkowski and Krolikowski (1986). In this direct method, the minimum vapor flows for all the possible splits are calculated and then the maximum value of these minimum vapor flows is accepted as the minimum vapor flow in the rectifying section of the column

$$V = \max_{j} \sum_{i=1}^{n} \frac{\alpha_i d_i}{\alpha_i - \phi_j} \tag{4}$$

In column I we have $d_A^{\mathrm{I}} = f_A^{\mathrm{I}}$ and $d_D^{\mathrm{I}} = 0$. Therefore, the minimum vapor flow in section 1 is a function of the two remaining component flow rates in the distillate: d_B^{I} and d_C^{I}

$$V(I) = \max_{j} \left\{ \frac{\alpha_A f_A^{\mathrm{I}}}{\alpha_A - \phi_j^{\mathrm{I}}} + \frac{\alpha_B d_B^{\mathrm{I}}}{\alpha_B - \phi_j^{\mathrm{I}}} + \frac{\alpha_C d_C^{\mathrm{I}}}{\alpha_C - \phi_j^{\mathrm{I}}} \right\} \tag{5}$$

where (from Eq. 2) the Underwood roots satisfy the following inequalities

$$\alpha_A > \phi_1^{\mathrm{I}} > \alpha_B > \phi_2^{\mathrm{I}} > \alpha_C > \phi_3^{\mathrm{I}} > \alpha_D \tag{6}$$

Since only column I is discussed in the current section, we will omit superscript "I" in all symbols below.

For a given ϕ_j, when the vapor flow rate as calculated from Eq. 5 is plotted as a function of d_B and d_C, the resulting figure is a plane. Equation 5 can be depicted as three intersecting planes inclined toward the common minimum. The upper portions of these planes (above their intersections) are shown in Figure 4. Each of the planes corresponds to minimum vapor flow in the first column calculated using one of the Underwood roots: ϕ_1, ϕ_2 or ϕ_3. Because of the inequalities in Eq. 6, the plane denoted as ϕ_1 has negative slopes in both independent directions d_B and d_C (the coefficients of d_B and d_C in the resulting Eq. 5 for this case are both negative). Plane ϕ_2 rises along d_B, but descends along d_C and plane ϕ_3 has positive slopes in both directions. It is more convenient to discuss the projection of the minimum vapor flow on the plane (d_B, d_C), shown in Figure 5.

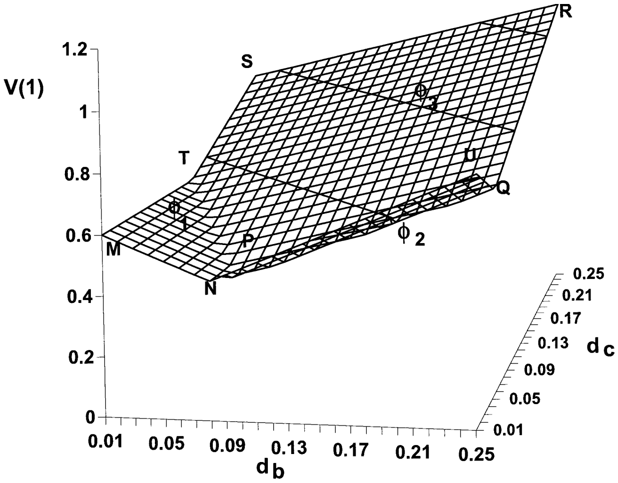

Figure 4. Minimum vapor flow in the rectifying section of quaternary column as a function of the distillate flows of components *B* and *C*.

Data are given in the description of Table 2.

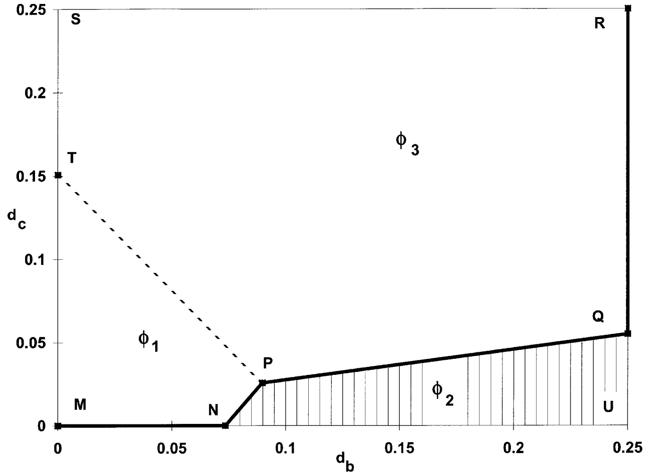

Figure 5. Projection of the minimum vapor flow in the rectifying section of quaternary column on the plane (d_B^I,d_C^I).

Data are given in the description of Table 2. Dashed region NPQU, together with line MNPQR represent feasible distillate compositions.

Not all pairs of (d_B,d_C) are feasible. For example, it is well known that it is not possible to concentrate component *C* in the distillate more than (more volatile) component *B*. The feasibility of each region in Figure 5 can be determined by checking to see if the compositions in this region correspond to the appropriate case listed in Table 1.

In particular, when we consider plane ϕ_1 (or the quadrilateral MNPT in Figure 5), we conclude that the interior of MNPT is infeasible. As listed in Table 1, case 1, plane ϕ_1 corresponds to split *A/BCD*, and in this split component *C* does not appear in the distillate. Inside the quadrilateral MNPT $d_C > 0$, which is not possible for this split.

The edge MN of this quadrilateral, however, where $d_C = 0$, is feasible.

The section NP is also feasible, because it belongs to two planes simultaneously: ϕ_1 and ϕ_2, which corresponds to case 2 in Table 1—split *AB/BCD*.

Similarly, the section *PQ* is also feasible, because it belongs to two planes simultaneously: ϕ_2 and ϕ_3, which corresponds to case 5 in Table 1—split *ABC/CD*. The interior of pentagon *PQRST* (plane ϕ_3) is again infeasible, because here $d_B < f_B$. Since only *ABC/D* split is allowed on this plane, B, as a light component, must all be present in the distillate. The edge QR of this pentagon, where $d_B = f_B$, is feasible (case 6 in Table 1, split *ABC/D*).

Finally, the dashed quadrilateral *NPQU* (plane ϕ_2) is feasible, and it corresponds to case 4 in Table 1 (split *AB/CD*).

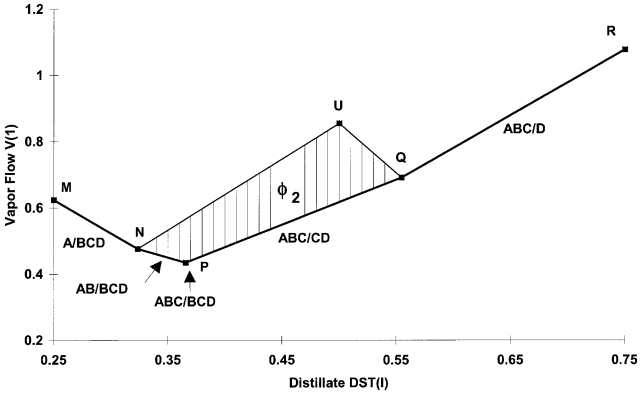

Figure 6. Minimum vapor flow in the rectifying section of quaternary column as a function of its distillate flow rate.

Data are given in the description of Table 2. In the dashed region NPQU there are multiple values of minimum vapor flow for a given distillate flow.

Interestingly, point P in Figure 5 belongs to three planes simultaneously (ϕ_1, ϕ_2 and ϕ_3) which corresponds to case 3 in Table 1—split *ABC/BCD* with two distributing components: *B* and *C*. Point *P* also corresponds to the minimum value of the minimum vapor flow in Figure 4 and is analogous to the transition split in ternary mixtures shown in Figure 2a.

Variables d_B and d_C can be used as independent variables in the computational search for the overall minimum vapor flow. In the operation of a real column, however, the distillate flow rates for components *B* and *C* are not the independent control variables. Two variables that could be independently set for the first column might be the vapor flow and the liquid flow, or the vapor flow and the distillate flow. The line of minimum vapor flow (*MNPQR* in Figure 5) can also be drawn as a function of the total distillate flow [calculated as $DST(\mathrm{I}) = d_A + d_B + d_C$ for all the points on this line] as shown in Figure 6. This can be compared to the analogous relation for ternary mixtures shown in Figure 2a. Unlike for ternary mixtures, in addition to line *MNPQR*, we also have the feasible region ϕ_2 shown as dashed quadrilateral *NPQU*. In this region, depending on the composition of distillate $DST(\mathrm{I})$, there are multiple values of the minimum vapor flow for a given value of the distillate flow.

In summary, the feasible region of distillate flow rates in Figure 5 consists of the region ϕ_2 and line *MNPQR*. However, the minimum vapor flow rate for the first column is smaller along the line *NPQ* than inside the region ϕ_2, at any given flow rate of distillate $DST(\mathrm{I})$. As shown in Figure 6, the distillate flow rate from the first column varies over quite a wide range $[A \le DST(\mathrm{I}) \le A + B + C]$. We want to ensure that all of the components, except *D*, are present in this distillate and that all of the components, except *A*, are present in the bottom product from this column. Otherwise, certain sections or columns of the *FC* system will become unnecessary. For example, if the distillate from the first column contains only component *A*, there is no need for columns II and IV in Figure 3. Therefore, we will exclude from the feasible region section *MN* (no component *C* in the distillate) and section *QR* (no component *B* in the bottom product). This restricts our range of possible operation in Figures 5 or 6 to the quadrilateral *NPQU* (plane ϕ_2). Along the sections *NP* and *PQ*, the distillate flows d_B and d_C are linearly dependent and can easily be calculated for any given distillate rate $DST(\mathrm{I})$ (see Appendix). Inside the region *NPQU* we may set d_B and d_C independently and calculate $DST(\mathrm{I})$. Boundaries *NU* and *QU* (similarly to *MN* and *QR*) are excluded from the search space.

Knowing d_B and d_C, one can calculate $V(1)$ from Eq. 5; the remaining flows in column I can be determined as

$$L(1) = V(1) - DST(\mathrm{I}) \tag{7a}$$

$$V(2) = V(1) - (1 - q^{F(\mathrm{I})}) \tag{7b}$$

$$L(2) = L(1) + q^{F(I)} \tag{7c}$$

Three-component separations

Ternary separations are carried out in columns II and III.

Distillate from the first column forms the feed to column II, where the separation *AB/BC* is performed

$$F(\mathrm{II}) = DST(\mathrm{I}) = V(1) - L(1) \tag{8a}$$

$$f_A^{\mathrm{II}} = d_A^{\mathrm{I}} = f_A^{\mathrm{I}} \tag{8b}$$

$$f_B^{\mathrm{II}} = d_B^{\mathrm{I}} \tag{8c}$$

$$f_C^{\mathrm{II}} = d_C^{\mathrm{I}} \tag{8d}$$

$$f_C^{\mathrm{II}} = d_D^{\mathrm{I}} = 0 \tag{8e}$$

The mol fractions of all the components are easily calculated as

$$z_i^{F(\mathrm{II})} = \frac{f_i^{\mathrm{II}}}{F(\mathrm{II})}, \quad i = A, B, C, D \tag{9}$$

The thermodynamic quality of this feed, defined as the fraction of liquid present in the feed is

$$q^{F(\mathrm{II})} = -\frac{L(1)}{F(\mathrm{II})} \tag{10}$$

where the negative sign in Eq. 10 accounts for the direction of stream $L(1)$ which is leaving column II instead of coming in with the feed; vapor $V(1)$ is fed to column II at the same place. Note that the value of the $q^{F(\mathrm{II})}$ of this feed is negative as if it were superheated.

All of component *A* leaves column II in the distillate and the entire flow rate of component *C* leaves in the bottom product (*AB/BC* split). Therefore, for a given value of distillate flow rate $[DST(\mathrm{II})]$, the distillate composition and the bottom flow rate and composition are determined

$$d_A^{\mathrm{II}} = f_A^{\mathrm{II}} \tag{11a}$$

$$d_B^{\mathrm{II}} = DST(\mathrm{II}) - f_A^{\mathrm{II}} \tag{11b}$$

$$d_C^{\mathrm{II}} = d_D^{\mathrm{II}} = 0 \tag{11c}$$

$$BOT(\mathrm{II}) = F(\mathrm{II}) - DST(\mathrm{II}) \tag{12a}$$

$$b_A^{\mathrm{II}} = 0 \tag{12b}$$

$$b_B^{\mathrm{II}} = f_B^{\mathrm{II}} - d_B^{\mathrm{II}} \tag{12c}$$

$$b_C^{\mathrm{II}} = f_C^{\mathrm{II}} \tag{12d}$$

$$b_D^{\mathrm{II}} = f_D^{\mathrm{II}} = 0 \tag{12e}$$

Mol fractions calculated from Eq. 9, together with the thermodynamic state of the second feed (Eq. 10) may now be substituted into the Underwood equation (Eq. 1) to calculate roots ϕ_1^{II} and ϕ_2^{II}. For a given $DST(\mathrm{II})$(or d_B^{II}), the minimum vapor flow in section 3 is

$$V(3) = \max_j \left\{ \frac{\alpha_A f_A^{\mathrm{II}}}{\alpha_A - \phi_j^{\mathrm{II}}} + \frac{\alpha_B d_B^{\mathrm{II}}}{\alpha_B - \phi_j^{\mathrm{II}}} \right\}, \quad j = 1, 2 \tag{13a}$$

The remaining flows in column II may be calculated from the following balances

$$L(3) = V(3) - DST(\mathrm{II}) \tag{13b}$$

$$V(4) = V(3) - V(1) \tag{13c}$$

$$L(4) = L(3) - L(1) \tag{13d}$$

The bottom product from the first column forms the feed to column III, where the separation *BC/CD* is performed.

$$F(\mathrm{III}) = BOT(\mathrm{I}) = \boldsymbol{L}(2) - \boldsymbol{V}(2) \tag{14a}$$

$$f_A^{\mathrm{III}} = b_A^{\mathrm{I}} = 0 \tag{14b}$$

$$f_B^{\mathrm{III}} = b_B^{\mathrm{I}} \tag{14c}$$

$$f_C^{\mathrm{III}} = b_C^{\mathrm{I}} \tag{14d}$$

$$f_D^{\mathrm{III}} = b_D^{\mathrm{I}} = f_D^{\mathrm{I}} \tag{14e}$$

and mol fractions of all the components in feed III are easily calculated as

$$z_i^{F(\mathrm{III})} = \frac{f_i^{\mathrm{III}}}{F(\mathrm{III})}, \quad i = A, B, C, D \tag{15}$$

The thermodynamic quality of this feed, defined as a fraction of liquid coming in the feed, is

$$q^{F(\mathrm{III})} = \frac{L(2)}{F(\mathrm{III})} \tag{16}$$

Note that the value $q^{F(\mathrm{III})}$ of this feed is greater than 1, as if it were subcooled (because liquid $L(2)$ is fed to column III and vapor $V(2)$ is withdrawn from the same place).

For a given value of distillate flow rate $DST(\mathrm{III})$, the distillate composition and the bottom flow rate and composition are determined

$$d_A^{\mathrm{III}} = f_A^{\mathrm{III}} = 0 \tag{17a}$$

$$d_B^{\mathrm{III}} = f_B^{\mathrm{III}} \tag{17b}$$

$$d_C^{\mathrm{III}} = DST(\mathrm{III}) - d_B^{\mathrm{III}} \tag{17c}$$

$$d_D^{\mathrm{III}} = 0 \tag{17d}$$

$$BOT(\mathrm{III}) = F(\mathrm{III}) - DST(\mathrm{III}) \tag{18a}$$

$$b_A^{\mathrm{III}} = b_B^{\mathrm{III}} = 0 \tag{18b}$$

$$b_C^{\mathrm{III}} = f_C^{\mathrm{III}} - d_C^{\mathrm{III}} \tag{18c}$$

$$b_D^{\mathrm{III}} = f_D^{\mathrm{III}} \tag{18d}$$

Mol fractions calculated from Eq. 15, together with thermodynamic state of the feed (Eq. 16), are then substituted into Underwood's equation (Eq. 1) to calculate roots ϕ_2^{III} and ϕ_3^{III}. For a given $DST(\mathrm{III})$ (or d_C^{III}), the minimum vapor flow in section 5 is

$$V(5) = \max_j \left\{ \frac{\alpha_B f_B^{\mathrm{III}}}{\alpha_B - \phi_j^{\mathrm{III}}} + \frac{\alpha_C d_c^{\mathrm{III}}}{\alpha_C - \phi_j^{\mathrm{III}}} \right\}, \; j = 2,3 \tag{19a}$$

The remaining flows in column III are calculated from the following balances

$$L(5) = V(5) - DST(\mathrm{III}) \tag{19b}$$

$$V(6) = V(5) + V(2) \tag{19c}$$

$$L(6) = L(5) + L(2) \tag{19d}$$

and

$$V(13) = V(4) - V(5) \tag{20a}$$

$$L(13) = L(4) - L(5) \tag{20b}$$

Binary separations

There are three distillation columns performing the binary separations *A/B*, *B/C*, and *C/D*. We calculate the minimum vapor flows from the reboiler that are necessary for each of these three separations and then we choose the largest of these as a controlling minimum vapor flow rate

$$V(12) = \max\{VAB, VBC, VCD\} \tag{21}$$

The distillate from column II constitutes the feed to column IV

$$F(\mathrm{IV}) = DST(\mathrm{II}) = V(3) - L(3) \tag{22a}$$

$$f_A^{\mathrm{IV}} = d_A^{\mathrm{II}} = f_A^{\mathrm{I}} \tag{22b}$$

$$f_B^{\mathrm{IV}} = d_B^{\mathrm{II}} \tag{22c}$$

$$f_C^{\mathrm{IV}} = f_D^{\mathrm{IV}} = 0 \tag{22d}$$

The mol fractions of A and B in this feed are

$$z_i^{F(\mathrm{IV})}=\frac{f_i^{\mathrm{IV}}}{F(\mathrm{IV})},\ i=A,\ B \tag{23}$$

The thermodynamic state of this feed is

$$q^{F(\mathrm{\ IV})}=-\frac{L(3)}{F(\mathrm{IV})} \tag{24}$$

We use these calculated mol fractions and thermodynamic state of feed IV to compute the root of Underwood's Equation ϕ_1^{IV} $(\alpha_B<\phi_1^{\mathrm{IV}}<\alpha_A)$ from Eq. 1. This root is then used to calculate the minimum vapor flow in column IV, assuming a pinch at AB feed

$$V(7)=\frac{\alpha_A f_A^{\mathrm{IV}}}{\alpha_A-\phi_1^{\mathrm{IV}}} \tag{25}$$

The minimum vapor flow from the reboiler, if the AB separation controls, is then determined as

$$VAB=\mathrm{V}(7)-\mathrm{V}(3)+\mathrm{V}(13)+\mathrm{V}(6) \tag{26}$$

Similarly for column V (B/C): the bottoms from column II, together with the distillate from column III, form the feed to column V

$$F(\mathrm{V})=BOT(\mathrm{II})+\mathrm{DST(III)}=L(13)-V(13) \tag{27a}$$

$$f_A^{\mathrm{V}}=0 \tag{27b}$$

$$f_B^{\mathrm{V}}=b_B^{\mathrm{II}}+d_B^{\mathrm{III}} \tag{27c}$$

$$f_C^{\mathrm{V}}=b_C^{\mathrm{II}}+d_C^{\mathrm{III}} \tag{27d}$$

$$f_D^{\mathrm{V}}=0 \tag{27e}$$

The mol fractions of B and C in this feed are

$$z_i^{F(\mathrm{V})}=\frac{f_i^V}{F(\mathrm{V})},\quad i=B,C \tag{28}$$

The thermodynamic state of this feed is

$$q^{F(\mathrm{V})}=\frac{L(13)}{F(\mathrm{V})} \tag{29}$$

We use these calculated mol fractions and thermodynamic state of the feed to column V to compute the root of Underwood's Equation $\phi_2^V(\alpha_C<\phi_2^{\mathrm{V}}<\alpha_B)$ from Eq. 1. This root is then used to calculate the minimum vapor flow in column V, assuming a pinch at BC feed

$$V(9)=\frac{\alpha_B f_B^V}{\alpha_B-\phi_2^V} \tag{30}$$

The minimum vapor flow from the reboiler, if the BC separation controls, is then determined as

$$VBC=V(9)+V(13)+V(6) \tag{31}$$

Finally, for the C/D separation, the bottoms from column III forms the feed to column VI

$$F(\mathrm{VI})=BOT(\mathrm{\ III})=L(6)-V(6) \tag{32a}$$

$$f_A^{\mathrm{VI}}=f_B^{\mathrm{VI}}=0 \tag{32b}$$

$$f_C^{\mathrm{VI}}=b_C^{\mathrm{III}} \tag{32c}$$

$$f_D^{\mathrm{VI}}=b_D^{\mathrm{III}}=f_D^{\mathrm{I}} \tag{32d}$$

The mol fractions of C and D in this feed are

$$z_i^{F(\mathrm{VI})}=\frac{f_i^{\mathrm{VI}}}{F(\mathrm{VI})},\quad i=C,D \tag{33}$$

The thermodynamic state of this feed is

$$q^{F(\mathrm{\ VI})}=\frac{L(6)}{F(\mathrm{VI})} \tag{34}$$

We use these calculated mol fractions and thermodynamic state of feed V to compute the root of Underwood's Equation ϕ_3^{VI} $(\alpha_D<\phi_3^{\mathrm{VI}}<\alpha_C)$ from Eq. 1. This root is used then to calculate the minimum vapor flow in column VI, assuming a pinch at CD feed

$$V(11)=\frac{\alpha_C f_C^{\mathrm{VI}}}{\alpha_C-\phi_3^{\mathrm{VI}}} \tag{35}$$

The minimum vapor flow from the reboiler, when a CD separation controls, is then determined as

$$VCD=V(11)+V(6) \tag{36}$$

Usually, only one of the binary columns is pinched (either column IV or column V or column VI). The remaining two columns operate at above minimum reflux. Operation of this part of the FC system can be made more efficient by introducing two additional reboiler condensers at the places where the intermediate components (C and D) are withdrawn. This would provide the additional degrees of freedom that would allow reducing the flow rates in the unpinched binary columns down to the pinched conditions.

Optimization procedure

For quaternary mixtures (unlike Fidkowski and Krolikowski's (1986) method for ternary mixtures), we did not develop explicit analytical equations. It seemed less tedious just to write a computer program, using all the equations discussed above. The objective of the calculations is to find the composition of DST(I) and the distillate flow rates [DST(I), DST(II), DST(III)] that minimize reboiler vapor flow V(12).

Although we chose distillates as independent variables, other choices (bottom products, or some distillates some bottom products) are also possible. The algorithm that we developed is a simple search throughout all the possible values of these distillate flow rates and the compositions of $DST(\mathrm{I})$. This optimization algorithm can be briefly summarized as follows:

(1) Calculate the Underwood roots for the given quaternary feed to column I (Eq. 1).

(2) Assume feasible d_B^{I} and d_C^{I} from NPQU region (Figure 5). Calculate the flow rate of distillate from the first column: $DST(\mathrm{I}) = f_A^{\mathrm{I}} + d_B^{\mathrm{I}} + d_C^{\mathrm{I}}$ (see the Appendix for the equations of lines *NP* and *PQ*).

(3) Calculate the liquid and vapor flows in the quaternary column at minimum reflux conditions (Eqs. 5 and 7).

(4) Calculate the Underwood roots for the ternary feed to column II, *ABC* (Eqs. 8, 9, 10 and 1).

(5) Assume a feasible distillate flow rate from column II (column separating *AB/BC*) - $DST(\mathrm{II})$ and calculate its composition (Eq. 11).

(6) Calculate the liquid and vapor flows in column II at minimum reflux conditions (Eqs. 13).

(7) Calculate the Underwood roots for the ternary feed to column III, *BCD* (Eqs. 14, 15, 16 and 1).

(8) Assume a feasible distillate flow rate from column III (column separating *BC/CD*), $DST(\mathrm{III})$, and calculate its composition (Eq. 17).

(9) Calculate the liquid and vapor flows in column III at minimum reflux conditions (Eqs. 19).

(10) Both ternary columns, column II and column III, operate at minimum reflux (pinched) conditions. The difference between their liquid and vapor flows is balanced by the supply or withdrawal of the liquid and vapor intermediate streams 13. The necessary flow rates of these streams are calculated from Eq. 20.

(11) Calculate the minimum vapor flow from the reboiler assuming *AB* pinch in column IV (Eq. 26, together with Eqs. 22–25 and 1).

(12) Calculate the minimum vapor flow from the reboiler assuming *BC* pinch in column V (Eq. 31, together with Eqs. 27–30 and 1).

(13) Calculate the minimum vapor flow from the reboiler assuming *CD* pinch in column VI (Eq. 36, together with Eqs. 32–35 and 1).

(14) Calculate the minimum vapor flow from the reboiler (Eq. 21). If it is the smallest minimum vapor flow so far, store this solution.

(15) If it is still possible to change the value of $DST(\mathrm{III})$, go to step 8.

(16) If it is still possible to change the value of $DST(\mathrm{II})$, go to step 5.

(17) If it is still possible to change the value of d_B^{I} and d_C^{I} go to step 2.

Note that it is not necessary to calculate the compositions of the liquids and vapors for the interconnecting streams in order to determine the minimum vapor flows. To find these compositions, one would have to solve, for each interconnecting stream, a system of n (linear) equations containing material balances and n (nonlinear) equilibrium relations for n components. Instead of solving these systems of equations, we use the net flows of distillates and bottom products [for example, $DST(\mathrm{I}) = V(1) - L(1)$], the compositions of which are much easier to determine. The only nonlinear equation that we solve is Underwood's equation (Eq. 1) with one unknown ϕ and well-defined ranges for all the roots.

Results and Comparison of Thermally Coupled System with Classic Distillation Configurations for Quaternary Mixtures

It is well known (Fidkowski and Krolikowski, 1986) that the optimum value of minimum vapor flow for a ternary FC system is usually constant (flat) over a certain range of independent variable [β or $DST(\mathrm{I})$]. This range is shown in Figure 2b as section *PR*. Similar ranges of independent variables for quaternary mixtures also exist, where the minimum vapor flow has a constant, lowest value.

In general, the multiple optimal solutions lie along boundary *NPQ* (see Figure 5 or Figure 6), and for only a few cases are optimal solutions also found inside the feasible NPQU region.

In such cases there are three independent variables: $DST(\mathrm{I})$, $DST(\mathrm{II})$, and $DST(\mathrm{III})$. An example of all possible optimal values of all distillate flows, for an equimolar feed mixture with the unit flow rate [$F(\mathrm{I}) = 1$] and for relative volatilities between any adjacent components of 2.5, is shown in Figure 7. The optimum values of $DST(\mathrm{I})$ and the corresponding vapor flow rates in the quaternary column are located in this case within the PQ section of Figure 6. The optimal distillate flow rates vary in this example in the following ranges: $0.37 \leq DST(\mathrm{I}) \leq 0.54$, $0.32 \leq DST(\mathrm{II}) \leq 0.48$ and $0.02 \leq DST(\mathrm{III}) \leq 0.22$.

It has been anticipated with analogy to ternary FC systems that one of the solutions exists for the system operating at the transition split in all of the pinched columns (quaternary and both ternaries) (Petlyuk et al., 1965; Westerberg, 1999). Unlike for ternary FC systems, however, no proof can easily be given that the transition split operation is optimal for qua-

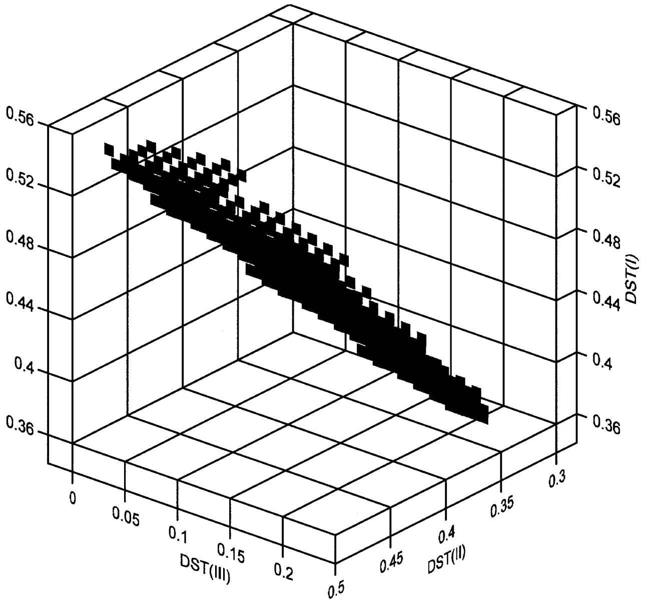

Figure 7. All optimal distillate flow rates.

Data given in the description of Table 2.

Table 2. Calculated Flow Rates in Quaternary FC System at Minimum Reflux Conditions at a Transition Split*

Section No.	Vapor Flow Rate (kmol/s)	Liquid Flow Rate (kmol/s)
1	0.4338	0.0684
2	0.4338	1.0684
3	0.4757	0.1521
4	0.0419	0.0837
5	0.2569	0.0676
6	0.6907	1.1360
7	1.0759	0.8259
8	0.6002	0.6738
9	0.6002	0.4238
10	0.3852	0.4399
11	0.3852	0.1899
12	1.0759	1.3259
13	−0.2150	0.0161

*Feed flow rate is 1.0 kmol/s. Feed contains 25 mol % of each component (A, B, C, D). Relative volatilities are: $\alpha_A = 15.625$, $\alpha_B = 6.25$, $\alpha_C = 2.5$, $\alpha_D = 1.0$. Feed is supplied as liquid at its bubble point.

Calculated distillate flow rates at transition splits are: $DST1 = 0.3654$, $DST2 = 0.3235$, $DST3 = 0.1893$.

Note that the direction of vapor stream 13 turns out to be opposite to the one shown in Figure 3. Accordingly its value is negative.

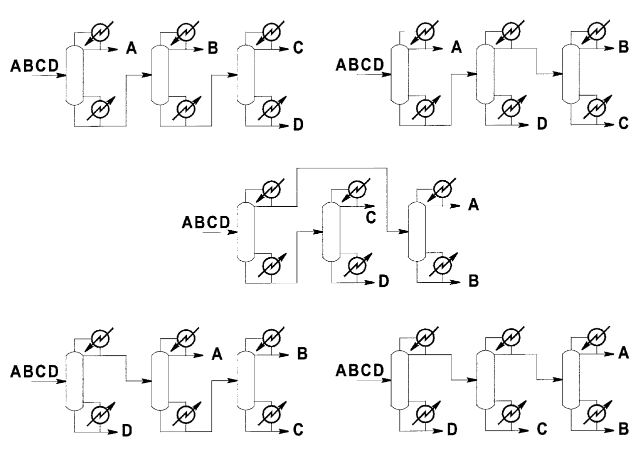

Figure 8. Conventional column configurations for quaternary distillation.

ternary FC systems. Using the optimization procedure described above, however, we were able to confirm (through extensive calculations) that this is indeed the case, that is, the transition split solution for quaternary mixtures was always contained within the set of optimal solutions. The transition split solution for the example problem of Figure 7 is given in Table 2. This one-point solution is much easier to obtain, because no exhaustive search is necessary. The quaternary column operates at the point represented by point P in Figure 6, and the corresponding distillate flow and compositions (for the transition split) can easily be calculated (see Appendix).

Similarly, both the ternary columns operate at the point represented by point P in Figure 2a; corresponding distillate flow rates in these columns can be calculated in a similar way (Fidkowski and Krolikowski, 1986). Although these one-point calculations yield the correct value of minimum vapor flow rate, they do not provide us with the optimal ranges of operation for the quaternary FC system.

With analogy to ternary systems, we may anticipate that the quaternary fully coupled system requires less heat energy than conventional column configurations. A systematic study for quaternary mixtures was performed, where the minimum vapor flow in the FC system and those for all conventional column configurations (shown in Figure 8) were calculated. The results are shown in Table 3. The calculations were performed for mixtures rich in one of the components and for a mixture containing all of the components in equal amounts. The values of relative volatilities were chosen to describe all the combinations of easily separable components ($\alpha = 2.5$) or components that are difficult to separate $\alpha = 1.1$). We see that in all cases the ratio of the minimum vapor flow in the FC system to the minimum vapor flow in the best conventional sequence is less than one. By using the FC system instead of a conventional column system, the minimum vapor flow can be reduced in 90% of cases by more than 10%; half of the cases show minimum vapor flow reduction by more than 20%. In a quarter of the cases the savings are roughly 50%.

For almost all of the cases presented in Table 3, the multiple optimal solutions lie along boundary *NPQ* (see Figure 5 or Figure 6) and there are no optimal solutions inside the feasible *NPQU* region. Only in two of the forty cases from Table 3, the multiple, optimum solutions lie not only along boundary *NPQ*, but also inside the feasible *NPQU* region shown in Figure 5 or 6. These two cases are: ede split for M mixture and edd split for B-rich mixture.

In these cases there are four independent variables: of d_B^{I} and d_C^{I}, $DST(\mathrm{II})$ and $DST(\mathrm{III})$.

The minimum value of the minimum vapor flow is determined by the optimization algorithm discussed above, where the exhaustive calculations ensure that all the optimal solutions have been found.

Extension to More than Four Components

The idea that the entire fully coupled system is optimized when each column (except the binaries) operates at the minimum value of its minimum reflux can easily be extended to

Table 3. Ratio of Minimum Vapor Flow in Quaternary FC System to the Minimum Vapor Flow for the Best of the Conventional System in Figure 8*

Split	*A*-Rich Mixture	*B*-Rich Mixture	*C*-Rich Mixture	*D*-Rich Mixture	*M* Mixture
eee	0.861	0.678	0.714	0.828	0.608
eed	0.730	0.673	0.941	0.985	0.890
ede	0.788	0.932	0.857	0.769	0.858
dee	0.977	0.853	0.496	0.648	0.821
edd	0.618	0.858	0.531	0.894	0.554
ded	0.895	0.785	0.864	0.892	0.510
dde	0.893	0.526	0.788	0.521	0.533
ddd	0.814	0.503	0.512	0.807	0.411

*e = Easy split ($\alpha = 2.5$); d = difficult split ($\alpha = 1.1$); X = rich mixture ($X = A, B, C, D$) contains 85 mol % of X and 5% of each other component.

M mixture is in the middle of the composition space, containing 25 mol % of each component.

more than four components. It has been proven for three components that the transition split solution is always one of the optimal solutions (Fidkowski and Krolikowski, 1986). We observed through extensive calculations that this holds also for quaternary mixtures. We believe that this observation is true for more than four components, but have not yet developed a rigorous proof.

Note that having a transition split in a distillation column means that all of the components, other than the most and the least volatile, distribute between the top and bottom product to minimize the value of the minimum reflux. This is entirely consistent with the concept of the fully coupled column arrangement. A disadvantage of focusing only on the transition split solution is that the optimal ranges of independent variables cannot be determined by this method.

An alternative approach that would provide the optimal ranges of independent variables would be to perform exhaustive searches similar to the one described here for four components. One may note that for each column containing four or more components there are two independent search variables. For example, when a five-component mixture *ABCDE* is separated, component *E* cannot appear in the distillate and component *A* cannot be present in the bottom product. This means that *A* must be either a light or a light key component, and *E* is a heavy key or a heavy component. This narrows the possible splits to the following four combinations (where *LK* is light key component and *HK* is heavy key component and $\alpha_D > \phi_4 > \alpha_E$):

(1) $A = LK$, B, C, $D = HK$, E (use Underwood equations for ϕ_1, ϕ_2, ϕ_3)

(2) A, $B = LK$, C, $D = HK$, E (use Underwood equations for ϕ_2, ϕ_3)

(3) $A = LK$, B, C, D, $E = HK$ (use Underwood equations for $\phi_1, \phi_2, \phi_3, \phi_4$)

(4) A, $B = LK$, C, D, $E = HK$ (use Underwood equations for ϕ_2, ϕ_3, ϕ_4)

The set of Underwood equations contains four unknowns (minimum vapor flow and the distillate flow rates for components *B*, *C* and *D*). The number of equations is equal to the number of Underwood roots ϕ for each case. Therefore, there is only one independent variable in case 1 (4 variables and three equations), there are two degrees of freedom in the second case, zero degrees of freedom in the third case (transition split), and one degree of freedom in case 4. For a five-component mixture, the equations for these four cases can be solved to identify the feasible distillate flow rate region similar to the one shown for a four-component mixture in Figure 6. The maximum number of degrees of freedom is always 2, independent of the number of components. Analogous to case 2 (that is, the light key is the second most volatile component and the heavy key is the second most heavy component), for an *n*-component mixture, there will be (*n*-3) equations and (*n*-1) variables, that is, the minimum vapor flow and the distillate flow rates of each of the components ranging from the light key to the heavy key.

When performing an exhaustive search for all minimum vapor flow solutions in an FC system separating a *n*-component mixture, we encounter two independent variables in each column separating more than 3 components, 1 independent variable in each ternary column and no independent variables in binary columns. For example, for a five-component mixture there are nine degrees of freedom: two in the five-component column, two in each of the two four-component columns, and one in each of the three ternary columns.

Conclusions

A method and algorithm for calculating minimum vapor flow in quaternary fully coupled system is presented. The method is based on Underwood's minimum reflux calculations (Underwood, 1948), assuming constant relative volatilities of components and constant molar overflow. The method can also be applied for FC systems separating more than four components.

Usually, there is an infinite number of optimal solutions with the same value of minimum vapor flow from the reboiler, for various values of independent variables such as the distillate flow rates from the quaternary and ternary columns. One of these solutions is at the transition split, where each column (except the binaries) is pinched at the minimum value of the minimum vapor flow, and usually only one of the binary columns is pinched. This transition split solution is much easier to calculate, because it does not require a search over certain ranges of independent variables. It can be used to evaluate the minimum vapor flow in fully coupled systems containing three and four components. It is anticipated (without proof) that this transition split approach will quickly provide the optimized minimum vapor flow for thermally coupled configurations separating even more than four components.

The optimized quaternary fully coupled system always requires less energy than conventional systems. Various feed compositions and relative volatilities were considered. The savings in half of the calculated cases were about 20% and more. A quarter of the examples considered gave about 50% savings in the minimum vapor flow.

Acknowledgment

Thanks to Professor Art Westerberg for bringing to our attention that transition split solution was always present in the space of optimum solutions.

Notation

A, B, C, D, E = component *A, B, C, D, E*
b_i^k = bottoms flow rate of component *i* from column *k*, kmol/s
$BOT(k)$ = bottoms flow rate from column *k*, kmol/s
d_i^k = distillate flow rate of component *i* from column *k*, kmol/s
$DST(k)$ = distillate flow rate from column *k*, kmol/s
f_i^k = feed flow rate of component *i* to column *k*, kmol/s
$F(k)$ = feed flow rate to column *k*, kmol/s
HK = heavy key
$L(j)$ = liquid flow rate in section *j*, $j = 1, 2, \ldots 13$, kmol/s
LK = light key
n = number of components
$q^{F(k)}$ = thermodynamic state of feed to column *k*, defined as a mol fraction of liquid in the feed
$V(j)$ = vapor flow rate in section *j*, $j = 1, 2, \ldots 13$, kmol/s
VAB = vapor flow from reboiler of quaternary FC [$V(12)$] when binary pinch *AB* controls
VBC = vapor flow from reboiler of quaternary FC [$V(12)$] when binary pinch *BC* controls
VCD = vapor flow from reboiler of quaternary FC [$V(12)$] when binary pinch *CD* controls

$z_i^{F(k)}$ = mol fraction of component i in feed entering column k

α_i = relative volatility of component i with respect to any component in the mixture

β = fraction of component B leaving the first column of ternary FC in the distillate

ϕ_m^k = mth root of Underwood equation for feed entering column k, Eqs. 1 and 2

Superscripts

I, II, III, IV, V, VI = column number in quaternary FC, Figure 3

$F(k)$ = feed to column k

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Appendix

The coordinates (d_B^I, d_c^I) of points N, P, Q in Figures 5 and 6 can be calculated from Underwood Equations

$$V(1) = \frac{\alpha_A f_A^I}{\alpha_A - \phi_1^I} + \frac{\alpha_B d_B^I}{\alpha_B - \phi_1^I} + \frac{\alpha_C d_C^I}{\alpha_C - \phi_1^I} \tag{A1}$$

$$V(1) = \frac{\alpha_A f_A^I}{\alpha_A - \phi_2^I} + \frac{\alpha_B d_B^I}{\alpha_B - \phi_2^I} + \frac{\alpha_C d_C^I}{\alpha_C - \phi_2^I} \tag{A2}$$

$$V(1) = \frac{\alpha_A f_A^I}{\alpha_A - \phi_3^I} + \frac{\alpha_B d_B^I}{\alpha_B - \phi_3^I} + \frac{\alpha_C d_C^I}{\alpha_C - \phi_3^I} \tag{A3}$$

Point N corresponds to split *AB/BCD*. It is the common point of planes ϕ_1^I and ϕ_2^I for $d_C^I = 0$. The coordinates of point N can be calculated by substituting $d_C^I = 0$ in Eq. A1 and Eq. A2, and solving these two linear equations for $V(1)$ and d_B^I.

Point P corresponds to transition split *ABC/BCD*. It is the common point of planes ϕ_1^I, ϕ_2^I and ϕ_3^I. The coordinates of point P can be calculated by solving linear Eqs. A1, A2 and A3 for $V(1)$, d_B^I and d_C^I.

Point Q corresponds to split *ABC/CD*. It is the common point of planes ϕ_2^I,ϕ_3^I for $d_B^I = f_B^I$. The coordinates of point Q can be calculated by substituting $d_B^I = f_B^I$ in Eq. A2 and Eq. A3, and solving these two linear equations for $V(1)$ and d_C^I.

The linear relation between d_B^I and d_C^I along section NP can be obtained by substituting $V(1)$ from Eq. A1 to Eq. A2.

The linear relation between d_B^I and d_C^I along section PQ can be obtained by substituting $V(1)$ from Eq. A2 to Eq. A3.

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