Minimum Reflux Behavior of Complex Distillation Columns

A continuum model for multicomponent distillation in the minimum reflux limit, first proposed by Nandakumar and Andres, is refined for the special case of constant relative volatility (CRV) and constant molar overflow (CMO) and is extended to columns with multiple feeds and multiple products. A relaxation algorithm for calculating steady-state conditins in any minimum reflux CRV, CMO column is established. This generalization of Underwood's classic treatment of single-feed columns is used to explore the characteristics of several single-feed and multiple-feed distillation systems. Critical operating points at which the steady-state composition profile in a minimum reflux column is indeterminate are identified and analytical expressions predicting the location of these points are established.

John A. Wachter, Terry K. T. Ko,
Ronald P. Andres
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

Introduction

This paper presents a generalization of Underwood's (1946, 1948) minimum reflux description of multicomponent distillation columns. The new description is applicable to distillation columns and coupled distillation networks with any number of multicomponent feeds and any number of intermediate product streams as long as the relative volatilities of all species are constant and there is constant molar overflow.

The approach taken in deriving this generalized minimum reflux description differs from previous efforts in that it is based on a dynamic model (Nandakumar and Andres, 1981). Criteria are established for testing the stability of composition profiles that satisfy the steady-state mass balance equations for minimum reflux columns. The proposed algorithm for calculating steady-state operating conditions starts with an arbitrary initial composition profile and follows the transient evolution of the column as it relaxes to its unique steady state. An important benefit of this approach is that unlike previous treatments (Barnes et al., 1972) it assures that the true steady-state solution is obtained.

The numerical properties of the algorithm are excellent. It is robust and requires modest computational effort. The minimum reflux description that is obtained is exact. However, it is based on assumptions of constant relative volatility (CRV) and constant molar overflow (CMO). If these assumptions or the assumption of infinite equilibrium stages are not justified, the resulting composition profile can be employed as the initial guess in an equilibrium stage simulation of the column.

An additional benefit of the continuum model developed in this work is analytical prediction of operating conditions at which the steady-state composition profile in a distillation column becomes indeterminate and of the dynamic evolution of composition waves in distillation networks. In particular it is possible to analytically predict the "trapped composition waves" described by Rosenbrock (1960) in his classic paper on dynamic conservation in distillation.

In what follows, the mathematical model is first developed. Then the algorithm for calculating the steady-state conditions in a complex column is described. Several examples of the use of this algorithm and the stability criteria on which it is based are presented. The dynamics and steady-state characteristics of binary and ternary separations in single-feed (simple) columns are explored. Finally, binary separation in a two-feed column without intermediate product withdrawal and in a single-feed column with intermediate product withdrawal, and ternary separation in the coupled distillation network proposed by Petlyuk (Petlyuk et al., 1965; Fidkowski and Krolikowski, 1986), are examined.

Continuum Model for Minimum Reflux Columns

Modular breakdown of distillation systems

All continuous distillation columns or coupled distillation networks, no matter how complex, can be constructed from two basic elements: countercurrent sections and feed/product

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Correspondence concerning this paper should be addressed to R. P. Andres.

stages. A countercurrent section is a linear array of countercurrent stages bounded on each end by a product or feed stage. A feed stage is the position in the column where a feed stream of known composition, quality, and flow rate is introduced; a product stage is the position in the column where a product of known quality and flow rate is withdrawn.

In the notation that follows, each of the feed/product stages and each of the countercurrent sections will be indexed sequentially, starting from the top of the column. All flows and compositions identified with a specific feed/product stage or a specific countercurrent section will be designated by a superscript consisting of this index. The simplest subcase of the generalized system is the simple column shown in Figure 1a, which contains a feed stage bounded from above and below by a countercurrent section and a product stage. Applying the notation just described, the countercurrent sections above and below the feed are indexed *1* and *2,* respectively, while the distillate product, feed and bottoms product stages are indexed *1, 2,* and *3,* respectively.

The considerably more complex system involving two thermally coupled columns shown in Figure 1b serves to illustrate indexing for multiple feed and product columns. In this case, the product stages *1* and *3* from the first column are linked by internal flows to the feed stages *2* and *4* in the second column. The second column in Figure 1b is the most general form of a two-feed column. The situation in which the intermediate product stream is absent is obtained from this more general case by setting the flow from the intermediate product stage equal to zero. The situation in which there is an intermediate product stream but only one feed stream is obtained by setting the flow of one of the feed streams equal to zero.

Premises

The continuum model, which will be derived below, is predicated on four assumptions:

1. Minimum reflux design. Each countercurrent section must contain a sufficient number of stages to produce at steady state a pinch region where composition does not change from stage to stage.

2. Negligible mass transfer resistance and vapor holdup. On each stage or at each point in a countercurrent section, the vapor and liquid are in equilibrium and the amount of material in the vapor phase is negligible when compared to the material in the liquid phase. This double assumption does not affect the column's steady-state behavior but permits important simplifications of the dynamic model.

3. Constant relative volatility (CRV). The vapor-liquid equilibrium can be modeled as:

$$Y_i = K\alpha_i X_i \quad i = 1, M \tag{1}$$

where Y_i is the mole fraction of species *i* in vapor phase, *K* is the reference equilibrium coefficient, α_i is the relative volatility of species *i*, X_i is the mole fraction of species *i* in liquid phase, and all of the α_i ($i = 1, M$) are constant. Since the vapor mole fractions sum to unity, *K* may be expressed as

$$K = \frac{Y_i}{\alpha_i X_i} = \frac{1}{\sum_{i=1}^{M} \alpha_i X_i} \tag{2}$$

In the notation that follows, the chemical species will be sequenced in ascending order from least volatile to most volatile.

$$\alpha_1 < \alpha_2 < \alpha_3 \cdots < \alpha_M \tag{3}$$

Partial molar flows and species mole fractions will be designated by a subscript consisting of this species index.

4. Constant molar flow (CMO). The total molar flow of vapor and liquid are constant throughout each countercurrent section. These flows may of course change across a feed/product stage.

Distillation columns usually are modeled as a series of equilibrium stages. While such equilibrium stage models are mathematically simpler than a continuum model, they have two serious drawbacks. First, practical distillation columns are designed to operate near their minimum reflux or infinite plate limit.

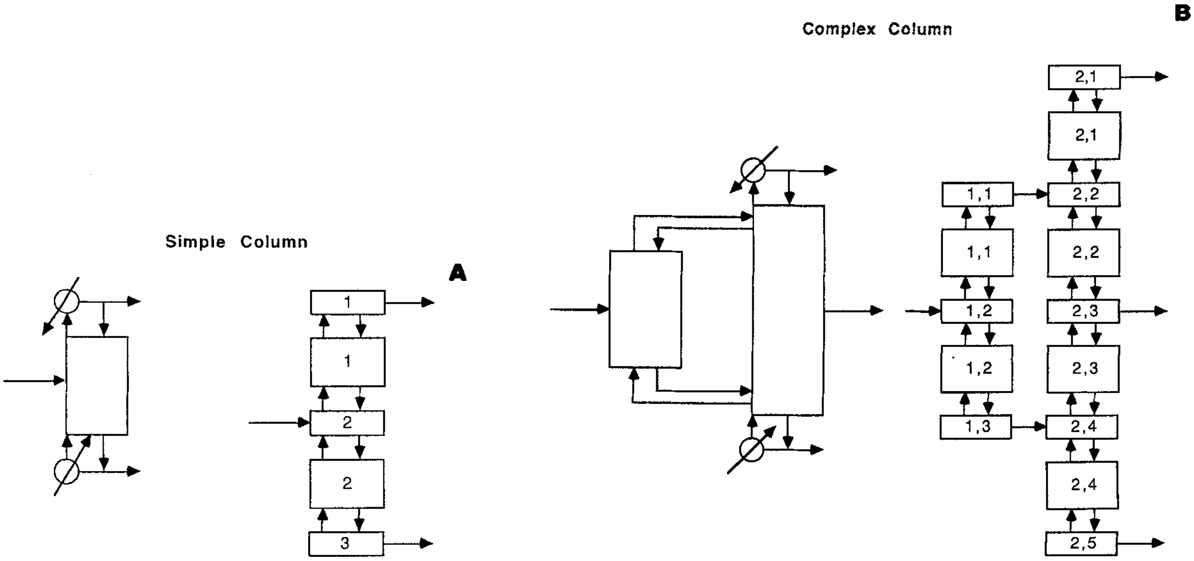

Figure 1. Representation of distillation column in terms of countercurrent sections and feed/product stages.

Thus, the number of equations involved in an equilibrium stage model often becomes too large to handle, especially when multicomponent mixtures and dynamic behavior are considered. Second, equilibrium stage models provide little insight into the physical phenomena occurring in the column, again because they consist of too many equations. Both of these limitations are overcome by transforming the large set of ordinary differential equations of the staged model into a smaller set of partial differential equations representing each countercurrent section.

The key properties of a countercurrent section that must be modeled are:

1. The partial molar flows within the section of each species. These f_i are calculated from the relation

$$f_i = VY_i - LX_i \quad i = 1, M \tag{4}$$

where V is the total molar vapor flow, L is the total molar liquid flow, and Y_i and X_i are evaluated in the pinch region

2. The magnitude and velocity of transient composition waves, which are produced by composition changes in the adjacent feed and product stages or by changes in L/V

Both of these are often well predicted by the continuum model developed below, which becomes an exact representation in the limit as the number of stages in each countercurrent section tends to infinity.

Figure 2 compares composition profiles calculated using the equilibrium stage model with profiles calculated using the continuum model for the rectifying section of a minimum reflux design column. The steady-state solutions shown in Figure 2a are for the case of a ternary mixture ($\alpha_1 = 0.5$, $\alpha_2 = 6$, $\alpha_3 = 8$, and feed composition $Z_1 = 0.1$, $Z_2 = 0.18$, $Z_3 = 0.72$). The internal reflux ratio ($L/V = 0.4$) is sufficient to eliminate component 1 from the distillate product.

The equilibrium stage model ($N = 50$) predicts that the liquid composition changes rapidly in the regions adjacent to the feed stage and the product stage, but is constant in the remainder of the section. The continuum model ($N = \infty$) predicts that the liquid composition changes discontinuously at the feed and the product stages to establish a steady-state pinch composition that is constant across the entire section. The key point is that for this minimum reflux design column the continuum model predicts the same steady-state pinch composition as the equilibrium stage model.

Figure 2b shows the result of a step change in the feed composition to $Z_1 = 0.1$, $Z_2 = 0.41$, $Z_3 = 0.49$. This change gives rise to a composition wave that moves through the rectifying section of the column. The continuum model accurately predicts the size and mean velocity of this wave.

Continuum model for countercurrent section

The differential material balance equations for a countercurrent section, assuming negligible mass transfer resistance, negligible vapor holdup, and large N, are (Nandakumar and Andres, 1981; Ko 1985)

$$\frac{\partial}{\partial \tau}(X_i) + \frac{\partial}{\partial z}\left(\frac{V}{|\Delta|}Y_i - \frac{L}{|\Delta|}X_i\right) = 0 \quad i = 1, M \tag{5}$$

where

$\tau = |\Delta| t/Nh$ = dimensionless time
$|\Delta| = |V - L|$ = absolute value of net molar flow through section
t = time
N = total number of stages in section
h = liquid holdup on a single stage
X_i = mole fraction of species i in liquid
$z = n/N$ = dimensionless distance
n = stage number ascending in direction of vapor flow
V = total molar flow of vapor
Y_i = mole fraction of species i in vapor
L = total molar flow of liquid

Introducing the simplifications inherent in the CRV and CMO assumptions, the system of equations introduced in Eq. 5 becomes

$$\frac{\partial}{\partial \tau}(X_i) + \frac{L}{|\Delta|}\frac{\partial}{\partial z}\left[X_i\left(\frac{\alpha_i}{w} - 1\right)\right] = 0 \quad i = 1, M \tag{6}$$

where $w = (L/V)\sum_{i=1}^{M} \alpha_i X_i$ = mean rectifying factor.

It is this set of coupled, first-order partial differential equations that must be solved.

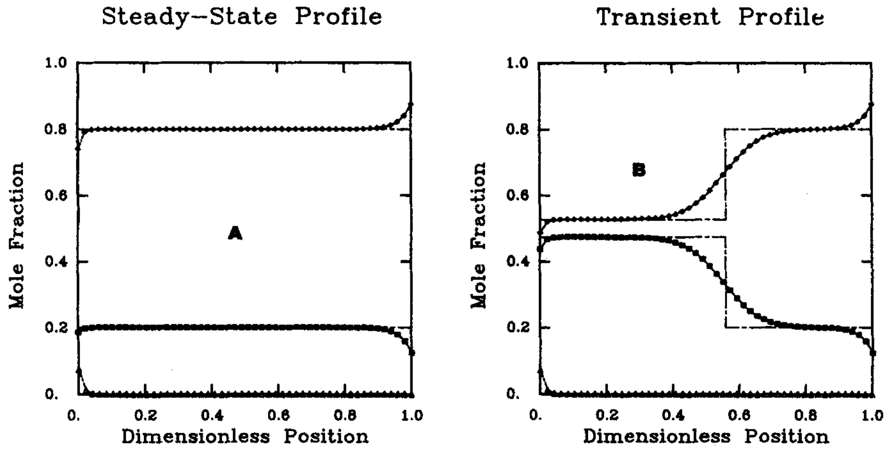

Figure 2. Composition profiles in rectifying section of ternary column.
Equilibrium stage model: △ X_1^l; □ X_2^l; ◊ X_3^l
--- Continuum model

The ideal way to solve such a set of equations is by using the method of characteristics (Courant and Hilbert, 1962; Aris and Amundson, 1973). The solution is greatly simplified in the case of the system described in Eq. 6 if the representation in terms of liquid mole fractions, X_i: $i = 1, M$, is transformed into a representation in terms of eigencompositions, ϕ_k: $k = 1, M - 1$, which are defined by the relations

$$\sum_{i=1}^{M} \frac{\alpha_i X_i}{\alpha_i - \phi_k} = 0 \quad k = 1, M - 1 \tag{7}$$

where

$$\alpha_1 \leq \phi_1 \leq \alpha_2 \leq \phi_2 \cdots \leq \phi_{M-1} \leq \alpha_M \tag{8}$$

The system of equations represented by Eq. 7 is often referred to as Underwood's minimum reflux equations; they have been derived in a number of different contexts for CRV, CMO distillation problems (Underwood, 1946, 1948; Acrivos and Amundson, 1955; Ramkrishna and Amundson, 1973; Nandakumar and Andres, 1981). These equations also define the *h*-transformation introduced by Helfferich and Klein (1970) to simplify the treatment of multicomponent chromatographic columns. In the present situation, representing the multicomponent composition in a continuous countercurrent section by the eigencompositions, ϕ_k, yields

$$\frac{\partial}{\partial \tau}(\phi_k) + \sigma_k \frac{\partial}{\partial z}(\phi_k) = 0 \quad k = 1, M - 1 \tag{9}$$

where

$$\sigma_k = \frac{L}{|\Delta|}\left(\frac{\phi_k}{w} - 1\right) \quad k = 1, M - 1 \tag{10}$$

and

$$w = \frac{L}{V} \frac{\prod_{j=1}^{M} \alpha_j}{\prod_{k=1}^{M-1} \phi_k} \tag{11}$$

The details of this derivation are provided in the appendix.

The continuum model defined by Eqs. 9, 10, and 11 offers a concise mathematical description of the behavior of a countercurrent section in the infinite plate limit. This model is closely analogous to the models established by Rhee and Amundson (1970, 1972) and Rhee et al. (1970, 1972) for physical adsorption and by Helfferich and Klein (1970) for multicomponent chromatography. A good discussion of the wavelike behavior of solutions to these equations can be obtained from these references. At steady state, the only possible solution is for all ϕ_k to be constant throughout the entire section from $z = 0$ to $z = 1$, Figure 2a.

Once the ϕ_k in the pinch region of a countercurrent section are known, the X_i can be calculated from the expressions

$$X_i = \frac{\prod_{k=1}^{M-1}\left(\frac{1}{\phi_k} - \frac{1}{\alpha_i}\right)}{\prod_{\substack{j=1 \\ j \neq i}}^{M}\left(\frac{1}{\alpha_j} - \frac{1}{\alpha_i}\right)} \quad i = 1, M \tag{12}$$

and the f_i can be calculated from the equations

$$\sum_{i=1}^{M} \frac{\alpha_i f_i}{\alpha_i - \phi_k} = V \quad k = 1, M - 1 \tag{13}$$

and

$$\sum_{i=1}^{M} f_i = V - L \tag{14}$$

A derivation of these equations is provided in the appendix.

Perturbation of the steady-state conditions in a section can occur either by a change in the eigencompositions on an adjacent feed or product stage (Φ_k) or by a change in L/V, which alters the mean rectifying factor, w. Consider the transient situation that results when there is a step change both in the set of Φ_k on the feed/product stage at $z = 0[\Phi_k(z = 0)]$ and in the set of Φ_k on the feed/product stage at $z = 1[\Phi_k(z = 1)]$ and L/V remains constant. Representing the initial steady-state condition in the section by ϕ'_k: $k = 1, M - 1$, a set of new eigencompositions, $\phi''_k = \Phi_k(z = 0)$, will move into the section if $\sigma_k^{\prime,\prime\prime} > 0$ and $\phi''_k = \Phi_k(z = 1)$ if $\sigma_k^{\prime,\prime\prime} < 0$. Here $\sigma_k^{\prime,\prime\prime}$ is the mean velocity of a wave corresponding to the change from ϕ'_k to ϕ''_k,

$$\sigma_k^{\prime,\prime\prime} = \frac{L}{|\Delta|}\left(\frac{\phi'_k \phi''_k}{\Lambda_k} - 1\right) \tag{15}$$

where

$$\Lambda_k = \frac{L}{V} \frac{\prod_{j=1}^{M} \alpha_j}{\prod_{\substack{l=1 \\ l \neq k}}^{M-1} \phi_l} \tag{16}$$

Each $\phi'_k \rightarrow \phi''_k$ transition corresponds to a coherent change involving all chemical species, Figure 2b. The change in X_i across such a wave can be calculated from Eqs. 12.

Because of the ordering imposed by Eq. 8,

$$\sigma_{k+1}^{\prime,\prime\prime} > \sigma_k^{\prime,\prime\prime} \tag{17}$$

Thus, the first (fastest) wave to travel from $z = 0$ is indexed with $k = M - 1$, the second with $k = M - 2$, etc., while the first (fastest) wave to travel from $z = 1$ is indexed with $k = 1$, the next with $k = 2$, etc. As each new wave travels into the section, it alters the value of the mean rectifying factor, w. Eventually a situation is reached for which the next fastest wave from $z = 0$ will have $\sigma_k^{\prime,\prime\prime} \leq 0$ and the next fastest from $z = 1$ will have $\sigma_k^{\prime,\prime\prime} \geq 0$. Obviously, such transitions are dynamically forbidden and as long as $\Phi_k(z = 0)$, $\Phi_k(z = 1)$, and L/V all remain constant a new steady-state condition is established.

The relationship at steady state between the ϕ_k in a countercurrent section and $\Phi_k(z = 0)$ and $\Phi_k(z = 1)$ can be succinctly expressed in terms of a stability index I:

$$\begin{aligned} \phi_k &= \Phi_k(z = 1) \quad k = 1, I \\ \phi_k &= \Phi_k(z = 0) \quad k = I + 1, M - 1 \end{aligned} \tag{18}$$

These relations are established by the following argument. If $\Phi_m(z = 1) < w$ and $\phi_m \neq \Phi_m(z = 1)$, a wave in which $\Phi_m(z = 1)$ replaces ϕ_m will travel into the section from $z = 1$. If $\Phi_m(z = 0) > w$ and $\phi_m \neq \Phi_m(z = 0)$, a wave in which Φ_m $(z = 0)$ replaces ϕ_m will travel into the section from $z = 0$.

Now consider the transient situation when there is a step change in L/V and $\Phi_k(z = 0)$ and $\Phi_k(z = 1)$ remain constant. It is apparent from Eqs. 18 that the ϕ_k will change only if the stability index, I, changes. As I switches between m and $m - 1$, ϕ_m will switch between $\Phi_m(z = 1)$ and $\Phi_m(z = 0)$ producing a relatively large change in the composition in the pinch region. Such transitions occur at discrete values of L/V defined by the equation

$$\left[\frac{L}{V}\right]_m = \Phi_m(z = 0)\Phi_m(z = 1)\frac{\prod_{\substack{k=1\\k\neq m}}^{M-1}\phi_k}{\prod_{i=1}^{M}\alpha_i} \qquad m = 1, M - 1 \tag{19}$$

At each of the stability boundaries defined by Eq. 19, I becomes indeterminant. Whenever L/V crosses one of these boundaries, the composition profile in the column is altered. In single-feed (simple) columns at each $[L/V]_m$ defined by Eq. 19 one of the partial molar product flows from the column becomes identically equal to zero.

The mean velocity of the transition between $\Phi_m(z = 1)$ and $\Phi_m(z = 0)$ is identically zero at the critical operating condition defined by Eq. 19 (see Eq. 15). Thus, a change in the stability index within a section of a column is usually accompanied by an extremely slow-moving composition wave and a relatively large change in the steady-state composition in the pinch region.

The stability index I also specifies the direction of all but one of the partial molar flows in a section. At steady state the partial molar flows, f_i, satisfy the equation

$$f_i = VY_i\left(1 - \frac{w}{\alpha_i}\right) \tag{20}$$

A derivation of this expression is provided in the appendix. If $\phi_k < w$, then $\alpha_k < w$. If $\phi_k > w$, then $\alpha_{k+1} > w$. Therefore,

$$\begin{aligned} f_i &\leq 0 \quad i = 1, I \\ f_i &\geq 0 \quad i = I + 2, M \end{aligned} \tag{21}$$

The index I is related to the concept of a key component. In a single-feed (simple) column the heavy key (i.e., the least volatile species in the distillate product) is the $I^1 + 1$ species. The light key (i.e., the most volatile species in the bottoms product) is the $I^2 + 1$ species.

Model for feed/product stage

The differential material balance equations for a well-mixed feed/product stage are

$$h\frac{d\chi_i^{j+1}}{dt} = F^{j+1}Z_i^{j+1} + f_i^{j+1} - f_i^j \quad i = 1, M \tag{22}$$

where the superscripts follow the conventions introduced in Figure 1 and h = liquid holdup on a stage; χ_i^{j+1} = mole fraction of species i in liquid on $j + 1$ stage; F^{j+1} = total molar flow into column at $j + 1$ stage ($F^{j+1} > 0$: feed stage, $F^{j+1} < 0$: product stage); Z_i^{j+1} = mole fraction of species i in feed/product flow; f_i^{j+1} = partial molar flow of species i in countercurrent section $j + 1$ at $z = 1$; f_i^j = partial molar flow of species i in countercurrent section j at $z = 0$.

At steady state Eq. 22 becomes

$$F^{j+1}Z_i^{j+1} = f_i^j - f_i^{j+1} \quad i = 1, M \tag{23}$$

Also at steady state Eqs. 18 require that

$$\begin{aligned} \phi_k^j &= \Phi_k^{j+1} \quad k = I^j + 1, M - 1 \\ \phi_k^{j+1} &= \Phi_k^{j+1} \quad k = 1, I^{j+1} \end{aligned} \tag{24}$$

where

$$\sum_{i=1}^{M}\frac{\alpha_i\chi_i^{j+1}}{\alpha_i - \Phi_k^{j+1}} = 0 \quad k = 1, M - 1 \tag{25}$$

For a feed stage, $f_i^{j+1} \leq f_i^j$ at steady state, Eq. 23, and from Eq. 21

$$I^{j+1} \geq I^j - 1 \tag{26}$$

Thus, at steady state

$$\phi_k^j = \Phi_k^{j+1} = \phi_k^{j+1} \quad k = I^j + 1, I^{j+1} \tag{27}$$

if the $j + 1$ stage is a feed stage.

For a product stage, $f_i^{j+1} \geq f_i^j$ at steady state, Eq. 23, and from Eq. 21

$$I^{j+1} \leq I^j + 1 \tag{28}$$

Thus, at steady state

$$\phi_k^j = \phi_k^{j+1} \quad k = 1, I^{j+1} \text{ and } I^j + 1, M - 1 \tag{29}$$

if the $j + 1$ stage is a product stage.

When an eigencomposition is constant across a feed stage (i.e., $\phi_k^j = \Phi_k^{j+1} = \phi_k^{j+1} \equiv \phi_k^{j,j+1}$), Eqs 13 and 23 can be combined to yield

$$\sum_{i=1}^{M}\frac{\alpha_i F^{j+1}Z_i^{j+1}}{\alpha_i - \phi_k^{j,j+1}} = V^j - V^{j+1} \quad k = I^j + 1, I^{j+1} \tag{30}$$

This equation establishes a relationship between the feed flows and the eigencomposition profile in the column.

Steady-state description of a complex column

Multiple-feed/multiple-product distillation columns can be constructed of segments, consisting of a feed stage, two adjoining countercurrent sections, and two product stages, as shown in Figure 3. A simple column may be thought of as a column with only one segment. The most general $N/2$ feed column can be represented as $N/2$ such segments with shared immediate product stages (e.g., the two-feed column in Figure 1b). Reflux boundary conditions are imposed at the top and bottom of the column by introducing fictitious countercurrent sections defined by the relations

$$\begin{aligned} f_i^0 &= f_i^{N+1} = 0 \quad i = 1, M \\ \Phi_k^0 &= \alpha_k \quad k = 1, M - 1 \\ \Phi_k^{N+2} &= \alpha_{k+1} \quad k = 1, M - 1 \end{aligned} \tag{31}$$

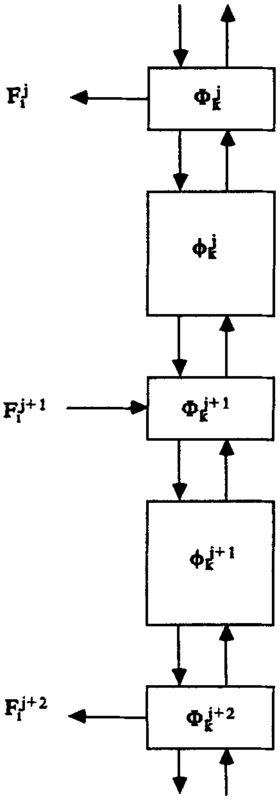

Figure 3. Segment of complex column.

Situations in which one or more intermediate product streams or feed streams are absent are handled by setting the corresponding F^j to zero and setting $\phi_k^{j-1} = \phi_k^j$: $k = 1, M - 1$.

Two steady-state descriptions of multiple-feed/multiple-product columns will be presented. In both cases it is assumed that the total liquid and total vapor flows in the column are all known. In the first approach it is assumed that the Φ_i^{j+1} on each feed stage are known. In the second, it is assumed that the Z_i^{j+1} for each feed stream are known.

The first step in describing a column is to establish the stability index profile. When the Φ_k^{j+1} are known, this is straightforward. For each segment ($j + 1 = 2, 4, \ldots, N$) in the column:

1. Set $I^j = I^{j+1} = 0$
2. Set $w^j = \dfrac{L^j}{V^j} \dfrac{\prod_{i=1}^{M} \alpha_i}{\prod_{k=1}^{M-1} \Phi_k^{j+1}}$ and $w^{j+1} = \dfrac{L^{j+1}}{V^{j+1}} \dfrac{\prod_{i=1}^{M} \alpha_i}{\prod_{k=1}^{M-1} \Phi_k^{j+3}}$
3. If $\Phi_{I^j+1}^{j-1} < w^j$, set $I^j = I^j + 1$ and then $w^j = w^j \dfrac{\Phi_{I^j}^{j+1}}{\Phi_{I^j}^{j-1}}$ and repeat until $\Phi_{I^j+1}^{j-1} > w^j$ or $I^j = M - 1$
4. If $\Phi_{I^j+1}^{j+1} < w^{j+1}$, set $I^{j+1} = I^{j+1} + 1$ and then $w^{j+1} = w^{j+1} \dfrac{\Phi_{I^j+1}^{j+3}}{\Phi_{I^j+1}^{j+1}}$ and repeat until

   $\Phi_{I^j+1}^{j+1} > w^{j+1}$ or $I^{j+1} = M - 1$

The eigencompositions in each countercurrent section of the column segment are then:

$$\begin{aligned} \phi_k^j &= \Phi_k^{j-1} \quad k = 1, I^j \\ \phi_k^j &= \Phi_k^{j+1} \quad k = I^j + 1, M - 1 \\ \phi_k^{j+1} &= \Phi_k^{j+1} \quad k = 1, I^{j+1} \\ \phi_k^{j+1} &= \Phi_k^{j+3} \quad k = I^{j+1} + 1, M - 1 \end{aligned} \tag{32}$$

Once the eigencompositions are known, the partial molar flows in each countercurrent section can be calculated using Eqs. 13 and 14. The partial molar feed and product flows are calculated using Eq. 23.

Obtaining the correct steady-state description of a complex column when the Z_i^{j+1} are known requires an iterative calculation (Wachter, 1988). First, the Z_i^{j+1}'s are used to calculate $\phi_k^{j,j+1}$'s ($k = 1, M - 1$) for each feed stream and the Φ_k^{j+1} on each feed stage are set equal to the $\phi_k^{j,j+1}$. Next, a stability index profile is assumed. Starting with the segment at the top of the column ($j + 1 = 2$) and proceeding down and then up the column ($j + 1 = 2, 4, \ldots, N, N - 2, N - 4, \ldots, 2$), the following calculations are performed until the Φ_k^{j+1} on each feed stage remain constant:

1. Solve for $f_i^j \quad i = 1, M$:

$$\sum_{i=1}^{M} \frac{\alpha_i f_i^j}{\alpha_i - \Phi_k^{j-1}} = V^j \quad k = 1, I^j$$

$$(\text{If } \Phi_k^{j-1} = \alpha_k, \text{ substitute } f_k^j = 0) \tag{33}$$

$$\sum_{i=1}^{M} \frac{\alpha_i f_i^j}{\alpha_i - \phi_k^{j,j+1}} = V^j \quad k = I^j + 1, I^{j+1} \tag{34}$$

$$\sum_{i=1}^{M} \frac{\alpha_i (f_i^j - F^{j+1} Z_i^{j+1})}{\alpha_i - \Phi_k^{j+3}} = V^{j+1} \quad k = I^{j+1} + 1, M - 1$$

$$(\text{If } \Phi_k^{j+3} = \alpha_{k+1}, \text{ substitute } f_{k+1}^j = F^{j+1} Z_{k+1}^{j+1}) \tag{35}$$

$$\sum_{i=1}^{M} f_i^j = V^j - L^j \tag{36}$$

2. Solve for $f_i^{j+1} \quad i = 1, M$:

$$f_i^{j+1} = f_i^j - F^{j+1} Z_i^{j+1} \tag{37}$$

3. Solve for $\Phi_k^{j+1} \quad k = 1, I^j$ and $I^{j+1} + 1, M - 1$:

$$\sum_{i=1}^{M} \frac{\alpha_i f_i^j}{\alpha_i - \Phi_k^{j+1}} = V^j \quad k = I^{j+1} + 1, M - 1 \tag{38}$$

$$\sum_{i=1}^{M} \frac{\alpha_i f_i^{j+1}}{\alpha_i - \Phi_k^{j+1}} = V^{j+1} \quad k = 1, I^j \tag{39}$$

4. Solve for $\Phi_k^{j+1} \quad k = I^j + 1, I^{j+1}$:

$$\Phi_k^{j+1} = \phi_k^{j,j+1} \quad k = I^j + 1, I^{j+1} \tag{40}$$

This calculation yields a self-consistent set of partial molar flows in each countercurrent section and eigencompositions on each feed stage. The stability index profile must now be checked. If it is correct, the partial molar product flows are calculated as before using Eq. 23.

General Relaxation Algorithm

Having derived a continuum description for a complex column, we describe a computational algorithm for determining the steady-state behavior of any multiple-feed/multiple-product, minimum reflux CRV, CMO, distillation column. The algorithm outlined below assumes that all liquid flows, vapor flows, and feed compositions are given as inputs. The partial molar flows in each countercurrent section, the eigencomposition profile, and the partial molar product flows are determined as outputs.

The algorithm makes use of the iterative calculation outlined previously, Eqs. 33–40. The stability index profile is established by assigning arbitrary initial compositions to each feed stage in the column and allowing the χ_i^{j+1}'s to relax toward their steady-state values as predicted by Eq. 22.

The following calculations are performed (a Fortran program embodying this algorithm is available in Wachter and Andres, 1988):

1. Calculate eigencompositions, $\phi_k^{j,j+1}$, and establish reflux boundary conditions at the top and bottom of the column.
   a. Using Eq. 30 calculate $\phi_k^{j,j+1} k = 1, M - 1$ and $j + 1 = 2, 4, \ldots, N$
   b. Set $\Phi_k^0 = \alpha_k$ and $\Phi_k^{N+2} = \alpha_{k+1} \quad k = 1, M - 1$
   c. Set $f_i^0 = f_i^{N+1} = 0 \quad i = 1, M$
2. Estimate I^j $j = 1, N$.
   a. Set $\Phi_k^{j+1} = \phi_k^{j,j+1} \quad k = 1, M - 1$ and $j + 1 = 2, 4, \ldots, N$
   b. Solve Eq. 25 for $\chi_i^{j+1} \quad i = 1, M$ and $j + 1 = 2, 4, \ldots, N$
   c. Given Φ_k^{j+1}, determine the stability index profile, the eigencompositions in each column segment, Eqs. 32, and the partial molar flows in each section, Eqs. 13 and 14
   d. Recalculate $\chi_i^{j+1} \quad i = 1, M$ and $j + 1 = 2, 4, \ldots, N$:

$$\chi_i^{j+1} = \chi_i^{j+1} + \delta\left[Z_i^{j+1} + \frac{(f_i^{j+1} - f_i^j)}{F^{j+1}}\right] \tag{41}$$

where $\delta = 0.05$ and $\chi_i^{j+1} \geq 0$

   e. Normalize $\chi_i^{j+1} \quad i = 1, M$ and $j + 1 = 2, 4, \ldots, N$:

$$\chi_i^{j+1} = \chi_i^{j+1} \Big/ \sum_{i=1}^{M} \chi_i^{j+1} \tag{42}$$

   f. Solve Eq. 25 for $\Phi_k^{j+1} \quad k = 1, M - 1$ and $j + 1 = 2, 4, \ldots, N$
   g. Repeat steps c–f until each χ_i^{j+1} exhibits a fractional change less than some arbitrary small number.
3. Given I^j, make use of the interactive calculation described in the previous section to solve for the steady-state eigencompositions and partial molar flows in each countercurrent section. Finally, use Eq. 23 to calculate the partial molar product flows.

In order to illustrate this calculation, consider a two-feed column such as the second column in Figure 1b, but with no intermediate product. The column is fed with two liquid streams containing butane, propane, and ethane; specifications are given in Table 1a. The steady-state I^j are found to be $I^1 = 0$, $I^2 = 1$, $I^3 =$

Table 1a. Two-Feed Column without Intermediate Product Stream

Input Data: $\alpha = 0.52, 1.0, 2.47$		
Section	L	V
1	30	130
2	130	130
3	130	130
4	230	130
Liquid Feed Streams	$\phi_k^{j-1,j}$	$Z_1^j F^j$
2	0.6347	30
	1.401	30
		40
4	0.6188	30
	1.805	50
		20

Table 1b. Two-Feed Column without Intermediate Product Stream

Steady-State Conditions				
Section	w	ϕ_k^j	f_1^j	I^j
1	0.282	0.6347	8.29	0
		1.656	31.71	
			60.00	
2	0.976	0.6347	−21.71	1
		2.073	1.71	
			20.00	
3	0.976	0.6347	−21.71	1
		2.073	1.71	
			20.00	
4	1.474	0.6240	−51.71	1
		2.470	−48.29	
			0.00	

Table 2a. Two-Feed Column with Intermediate Product Stream

Input Data: $\alpha = 0.52, 1.0, 2.47$		
Section	L	V
1	70	130
2	170	130
3	80	130
4	180	130
Liquid Feed Stream	$\phi_k^{j-1,j}$	$Z_1^j F^j$
2	0.6347	30
	1.401	30
		40
4	0.6188	30
	1.805	50
		20

Table 2b. Two-Feed Column with Intermediate Product Stream

Steady-State Conditions				
Section	w	ϕ_k^j	f_1^j	I^j
1	0.853	0.5200 1.558	0.00 7.22 52.78	1
2	1.275	0.6109 2.156	−30.00 −22.78 12.78	1
3	0.592	0.6188 2.156	−3.12 33.12 20.00	0
4	1.164	0.6188 2.470	−33.12 −16.88 0.00	1

1, $I^4 = 1$. Applying the calculation sequence, Eqs. 33–40, to the upper segment ($j + 1 = 2$), the following results are obtained:

$$f^1 = 6.33, 23.44, 70.23$$

$$f^2 = -23.67, -6.56, 30.23$$

$$\Phi^2 = 0.6347, 1.505$$

When these calculations are next applied to the lower segment ($j + 1 = 4$), the following values are obtained:

$$f^3 = -21.71, 1.71, 20.0$$

$$f^4 = -51.71, -48.29, 0.0$$

$$\Phi^4 = 0.6247, 2.073$$

Returning to the upper segment, the updated estimates are:

$$f^1 = 8.29, 31.71, 60.0$$

$$f^2 = -21.71, 1.71, 20.0$$

$$\Phi^2 = 0.6347, 1.556$$

Convergence of the calculation is confirmed by a check of the I^j. A check of the intermediate product flows also confirms that $F_i^3 Z_i^3 = 0$: $i = 1, 3$.

A two-feed column with no intermediate product has the inherent simplification that the set of eigencompositions below the upper feed and above the lower feed must be identical at steady state. This is not necessarily true when an intermediate product stream is withdrawn. The column specified in Table 2a has the same feed streams and vapor flows as the previous example, but has substantial intermediate product withdrawal. Comparing the two steady-state profiles, Tables 1b and 2b, it can be seen that in this case withdrawal of intermediate product causes

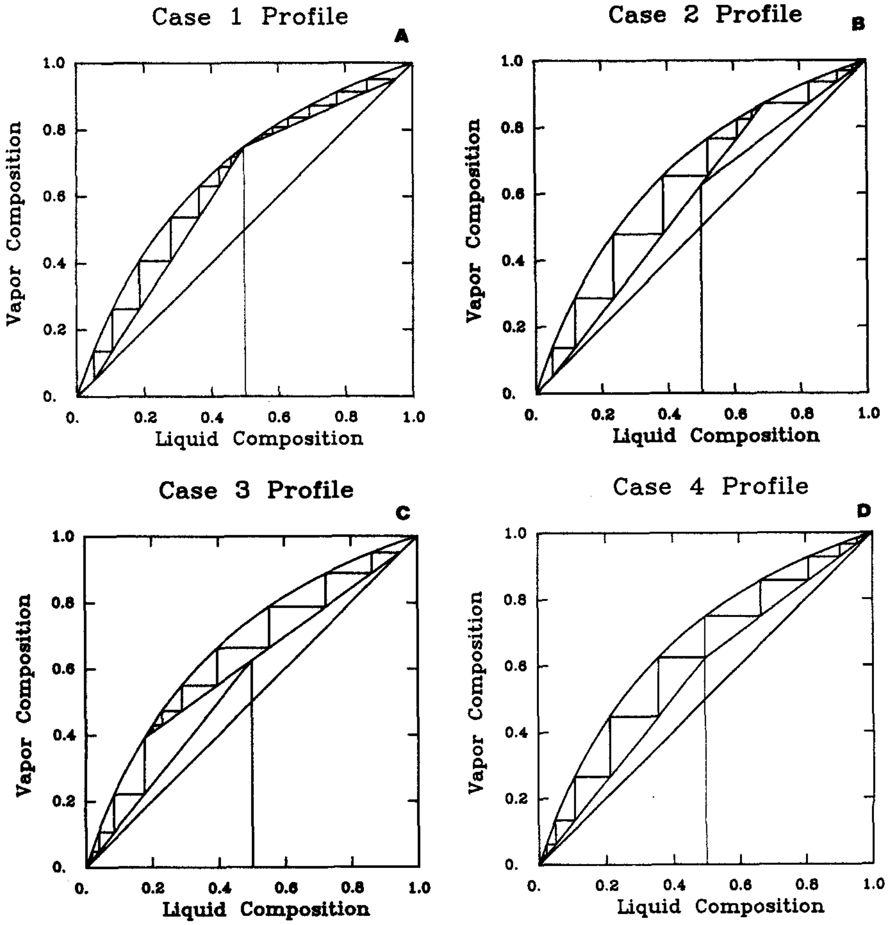

Figure 4. McCabe-Thiele diagrams for simple binary columns.

$\alpha_1 = 1$; $\alpha_2 = 3$; $Z_1^2 = Z_2^2 = 0.5$

one of the eigencompositions to change across the intermediate product stage.

The eigencomposition, ϕ_k, is constant across the $j + 1$ product stage only when k does not lie within the interval spanned by I^{j+1} and I^j. When product withdrawal becomes substantial, the interval between w^{j+1} and w^j becomes large, $I^{j+1} < I^j$, and fewer eigencompositions remain constant across the $j + 1$ product stage. When no eigencomposition remains constant across an intermediate product stage, the portions of the column above and below this stage are uncoupled as far as their composition profiles are concerned and can be described separately.

Application of Continuum Model to Simple Columns

Binary separations

In the case of simple columns the general algorithm reduces to the classic Underwood solution. With a binary feed, analysis is further simplified since a single eigencomposition describes the composition profile.

There are four possible composition profiles:

1. Both species 1 and 2 are present in distillate and bottom products ($I^1 = 0, I^2 = 1$)
2. Species 1 is absent from the distillate product ($I^1 = 1, I^2 = 1$)
3. Species 2 is absent from the bottom product ($I^1 = 0, I^2 = 0$)
4. Species 1 is absent from the distillate and species 2 is absent from the bottoms ($I^1 = 1, I^2 = 0$)

These composition profiles are often classified as type I separations (case 1) in which all feed components appear in both product streams and type II separations (cases, 2, 3, and 4) which involve elimination of one or more components originally present in the feed from at least one of the product streams.

The equilibrium stage description of a binary, simple column is often presented graphically by means of a McCabe-Thiele diagram. Figure 4 contains McCabe-Thiele diagrams for each of the four cases. In case 1, Figure 4a, the pinch in the rectifying section and in the stripping section both occur at the feed stage. The composition profile for case 1, Figure 5a, is characterized by a constant composition across the feed stage ($\phi_1^1 = \phi_1^2 = \phi_1^{1,2}$) and a rapidly changing composition at both ends of the column. In both case 2 and case 3, Figures 4b and 4c, the pinch in one section is adjacent to the feed stage, while the pinch in the other section is adjacent to the product stage. This behavior is seen in the corresponding composition profiles, Figures 5b and 5c. In case 4, Figure 4d, both pinches are adjacent to the product stages. This is also seen in the composition profile, Figure 5d.

An eigencomposition can be constant across the feed stage only when $\phi_k^{1,2}$ lies within the interval spanned by w^1 and w^2. When the feed rate is relatively large compared to internal liq-

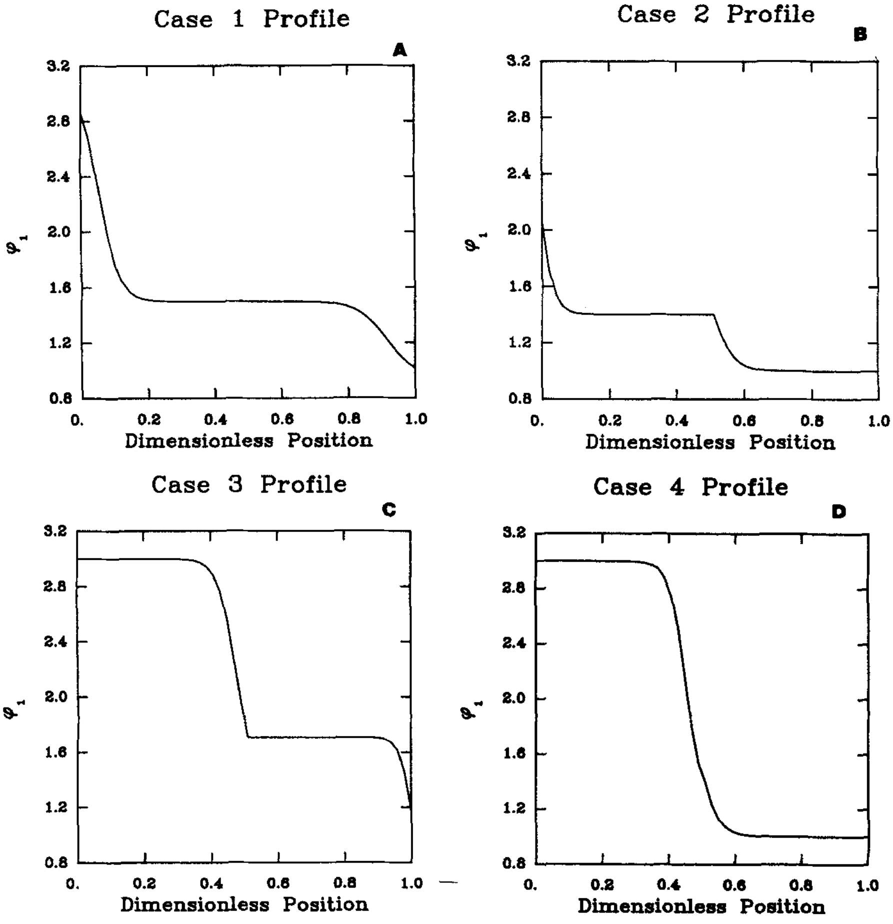

Figure 5. Composition profiles in simple binary columns.

$\alpha_1 = 1$; $\alpha_2 = 3$; $Z_1^2 = Z_2^2 = 0.5$

uid and vapor flows, w^1 and w^2 are far apart and the type I profile is common. As the relative magnitude of the internal liquid and vapor flows increases, the interval between w^1 and w^2 decreases and type II profiles appear.

In the case of a binary separation, when the distillate product flow is less than the partial molar flow of the more volatile species in the feed, at each value of $\Delta^1 = V^1 - L^1$ a critical L^1/V^1 exists at which the composition profile in the column switches from case 1 to case 2 (i.e., I^1 switches from 0 to 1). This stability boundary is found from Eq. 19 to be

$$\frac{L^1}{V^1} = \frac{\phi_1^{1,2}}{\alpha_2} \tag{43}$$

Expressing this relation in terms of L^1 and Δ^1:

$$L^1 = \left(\frac{\phi_1^{1,2}}{\alpha_2 - \phi_1^{1,2}}\right)\Delta^1 \tag{44}$$

Similarly, as long as the bottoms product flow is less than the partial molar flow of the less volatile species in the feed, at each value of $\Delta^2 = V^2 - L^2$ a critical L^2/V^2 exists at which the composition profile switches from case 1 to case 3 (i.e., I^2 switches from 1 to 0). This boundary is found to be

$$\frac{L^2}{V^2} = \frac{\phi_1^{1,2}}{\alpha_1} \tag{45}$$

Assuming the feed to be a saturated liquid ($V^1 = V^2$ and $L^1 = L^2 - F^2$) and expressing Eq. 45 in terms of L^1 and Δ^1:

$$L^1 = \left(\frac{\phi_1^{1,2}}{\alpha_1 - \phi_1^{1,2}}\right)\Delta^1 - \left(\frac{\alpha_1}{\alpha_1 - \phi_1^{1,2}}\right)F^2 \tag{46}$$

For a saturated liquid feed $\phi_1^{1,2}$ is found from Eq. 30 to be

$$\phi_1^{1,2} = \frac{\alpha_1\alpha_2}{\alpha_1 Z_1^2 + \alpha_2 Z_2^2} \tag{47}$$

The stability regions delineated by these expressions are shown in Figure 6. Case 1 operation is limited to a triangular area bounded by Eqs. 44 and 46. Case 2 occurs when L^1 is greater than the value given by Eq. 44 and Δ^1 is less than $F^2Z_2^2$. Case 3 occurs when L_1 is greater than the value given by Eq. 46 and Δ^1 is greater than $F^2Z_2^2$. Case 4 occurs along a vertical line originating from the intersection of Eqs. 44 and 46.

The steady-state design equations for each of the four cases are given in Table 3. Typical steady-state conditions for a case 1 binary column separating butane and propane are given in Table 4. A plot of the boilup rate V^1 necessary for a given fractional recovery of propane in the distillate β_2 at various distillate compositions Z_2^1 for this column is presented in Figure 7.

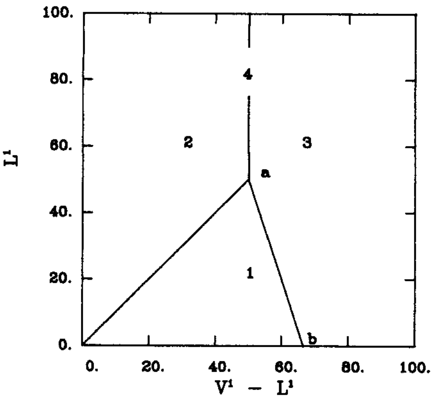

Figure 6. Stability diagram for simple binary columns with saturated liquid feed.

$\alpha_1 = 1$; $\alpha_2 = 3$; $F^2 = 100$; $Z_1^2 = Z_2^2 = 0.5$

a:$\Delta^1 = F^2Z_2^2$; b:$\Delta^1 = \dfrac{\alpha_1 F^2}{\phi_1^{1,2}}$

The steady-state predictions of the continuum model for a simple column are identical to Underwood's classic results. The continuum model, however, also provides important new insight into the dynamic behavior of a minimum reflux design column. Consider a perturbation in the feed composition for a case 1 column. This disturbance will change the eigencomposition $\phi_1^{1,2}$ from $(\phi_1^{1,2})' \rightarrow (\phi_1^{1,2})''$, which in turn introduces a composition wave $[(\phi_1^1)' \rightarrow (\phi_1^1)'']$ in the rectifying section traveling from the feed stage with a positive eigenvelocity

$$\sigma_1^{\prime,\prime\prime} = \left(\frac{L^1}{|\Delta^1|}\right)\left[\frac{V^1}{L^1}\frac{(\phi_1^1)'(\phi_1^1)''}{\alpha_1\alpha_2} - 1\right] \tag{48}$$

where $(\phi_1^1)' = (\phi_1^{1,2})'$ and $(\phi_1^1)'' = (\phi_1^{1,2})''$ and a complementary composition wave $[(\phi_1^2)' \rightarrow (\phi_1^2)'']$ in the stripping section traveling with a negative eigenvelocity

$$\sigma_1^{\prime,\prime\prime} = \left(\frac{L^2}{|\Delta^2|}\right)\left[\frac{V^2}{L^2}\frac{(\phi_1^2)'(\phi_1^2)''}{\alpha_1\alpha_2} - 1\right] \tag{49}$$

where $(\phi_1^2)' = (\phi_1^{1,2})'$ and $(\phi_1^2)'' = (\phi_1^{1,2})''$. A perturbation in the

Table 3. Binary Single-Feed Column (Saturated Liquid Feed)

Case 1 (given $F_1^3 = Z_1^3F^3$ and $F_2^1 = Z_2^1F^1$)

$$L^1 = \frac{\phi_1^{1,2}(F^2Z_1^2 + F_1^3)}{\alpha_1 - \phi_1^{1,2}} + \frac{-\phi_1^{1,2}(F_2^1)}{\alpha_2 - \phi_1^{1,2}}$$

$$\Delta^1 = F^2Z_1^2 + F_1^3 - F_2^1$$

Case 2 (given F_2^1)

$$L^1 > \frac{-\phi_1^{1,2}F_2^1}{\alpha_2 - \phi_1^{1,2}}$$

$$\Delta^1 = -F_2^1$$

Case 3 (given F_1^3)

$$L^1 > \frac{\phi_1^{1,2}(F_1^3)}{\alpha_1 - \phi_1^{1,2}} - F^2$$

$$\Delta^1 = F^2 + F_1^3$$

Case 4

$$L^1 > \frac{\phi_1^{1,2}(F_2Z_2^2)}{\alpha_2 - \phi_1^{1,2}} = \frac{\alpha_1 F_2}{\alpha_2 - \alpha_1}$$

$$\Delta^1 = F^2Z_2^2$$

Table 4a. Binary Single-Feed Column

Input Data: $\alpha = 0.52, 1.0$		
Section	L	V
1	150	250
2	350	250
Liquid Feed Stream	$\phi_k^{j-1,j}$	$Z_i^j F^j$
2	0.6842	100.0 100.0

internal liquid or vapor flows, due to changes in the reflux ratio or vapor boilup, has no effect on ϕ_1^1 or ϕ_1^2 as long as L^1 and Δ^1 remain in the case 1 stability region. Thus, the pinch composition on the feed stage and throughout both countercurrent sections is *unchanged*.

Unlike the situation for a case 1 column, perturbations in the internal flows cause composition waves in case 2 and case 3 columns. For case 2 a composition wave $(\phi_1^2)' \rightarrow (\phi_1^2)''$ travels from the feed stage into the stripping section with a negative eigenvelocity, which is given by Eq. 49. For case 3, a $(\phi_1^1)' \rightarrow (\phi_1^1)''$ wave travels from the feed stage into the rectifying section with a positive eigenvelocity, which is given by Eq. 48. The dynamic consequences of crossing a stability boundary at which either I^1 or I^2 changes are discussed in the next section.

Ternary separations

The addition of a third component to the feed introduces a second eigencomposition in the column. The steady-state stability criteria can now be satisfied in eight different ways:

1. All three species present in both distillate and bottom products ($I_1 = 0, I^2 = 2$)

2a. Species 1 absent from distillate product ($I^1 = 1, I^2 = 2$)

2. Species 1 and 2 absent from distillate product ($I^1 = 2, I^2 = 2$)

3a. Species 3 absent from bottoms product ($I^1 = 0, I^2 = 1$)

3. Species 2 and 3 absent from bottoms product ($I^1 = 0, I^2 = 0$)

4. Species 1 absent from distillate product and species 3 absent from bottoms product ($I^1 = 1, I^2 = 1$)

4a. Species 1 and 2 absent from distillate product and species 3 absent from bottoms product ($I^1 = 2, I^2 = 1$)

4b. Species 1 absent from distillate product and species 2 and 3 absent from bottoms product ($I^1 = 1, I^2 = 0$).

Again, these profiles are classified as type I separations (case 1) and Type II separations (Cases 2a–4b).

Table 4b. Binary Single-Feed Column

Steady-State Conditions				
Section	w	ϕ_k^j	f_i^j	I^j
1	0.456	0.6842	10.53 89.47	0
2	1.064	0.6842	−89.47 −10.53	1

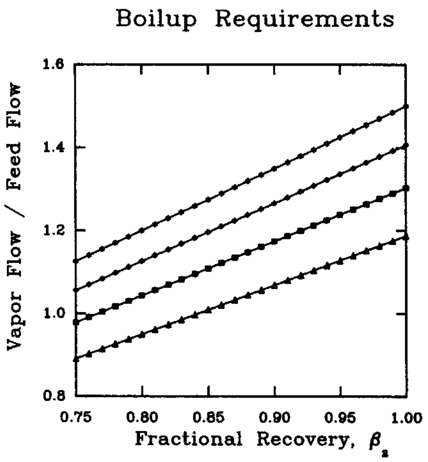

Figure 7. Boilup rate necessary for various values of Z_2^1 and β_2.
$\alpha_1 = 0.52$; $\alpha_2 = 1.0$; $Z_1^2 = Z_2^2 = 0.5$
△ $Z_2^1 = 0.80$; □ $Z_2^1 = 0.85$; ◇ $Z_2^1 = 0.90$; + $Z_2^1 = 0.95$

The stability diagram for a ternary separation assuming a saturated liquid feed is presented in Figure 8. The boundary between case 1 and case 2a is found from Eq. 19 to be

$$\frac{L^1}{V^1} = \frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_2\alpha_3} \tag{50}$$

The boundary between case 2a and case 2 is

$$\frac{L^1}{V^1} = \frac{\phi_2^{1,2}}{\alpha_3} \tag{51}$$

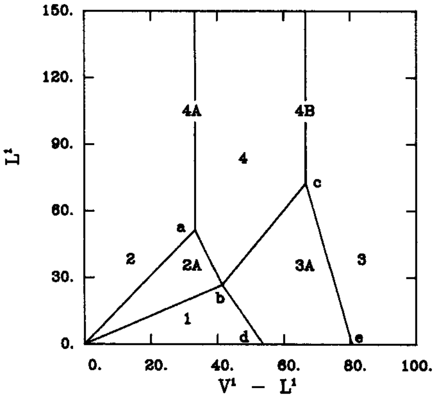

Figure 8. Stability diagram for simple ternary column with saturated liquid feed.
$\alpha_1 = 0.52$; $\alpha_2 = 1.0$; $\alpha_3 = 2.47$; $F^2 = 100$;
$Z_1^2 = Z_2^2 = Z_3^2 = 0.33$

a: $\Delta^1 = F^2 Z_3^2$; b: $\Delta^1 = \dfrac{F^2\left(\sum_{i=1}^{3} \alpha_i Z_i^2\right) - \alpha_1}{\alpha_3 - \alpha_1}$

c: $\Delta^1 = F^2(Z_2^2 + Z_3^2)$; d: $\Delta^1 = \left(\dfrac{\alpha_1\alpha_2}{\phi_1^{1,2}\phi_2^{1,2}}\right)F^2$

e: $\Delta^1 = \left(\dfrac{\alpha_1}{\phi_1^{1,2}} F^2\right)$

Similarly, the transition from case 1 to case 3a occurs at

$$\frac{L^2}{V^2} = \frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_1\alpha_2} \tag{52}$$

while the boundary between case 3a and case 3 is

$$\frac{L^2}{V^2} = \frac{\phi_1^{1,2}}{\alpha_1} \tag{53}$$

Expressing these relations in terms of L^1 and Δ^1:

$$L^1 = \left(\frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_2\alpha_3 - \phi_1^{1,2}\phi_2^{1,2}}\right)\Delta^1 \tag{54}$$

$$L^1 = \left(\frac{\phi_2^{1,2}}{\alpha_3 - \phi_2^{1,2}}\right)\Delta^1 \tag{55}$$

$$L^1 = \left(\frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_1\alpha_2 - \phi_1^{1,2}\phi_2^{1,2}}\right)\Delta^1 - \left(\frac{\alpha_1\alpha_2}{\alpha_1\alpha_2 - \phi_1^{1,2}\phi_2^{1,2}}\right)F^2 \tag{56}$$

and

$$L^1 = \left(\frac{\phi_1^{1,2}}{\alpha_1 - \phi_1^{1,2}}\right)\Delta^1 - \left(\frac{\alpha_1}{\alpha_1 - \phi_1^{1,2}}\right)F^2 \tag{57}$$

The stability boundary between case 2a and case 4 is

$$\frac{L^2}{V^2} = \frac{\Phi_1^2\phi_2^{1,2}}{\alpha_1\alpha_2} \tag{58}$$

or

$$L^1 = \frac{\phi_2^{1,2}(\beta_2 F^2 Z_2^2)}{\alpha_2 - \phi_2^{1,2}} + \frac{\phi_2^{1,2}(F^2 Z_3^2)}{\alpha_3 - \phi_2^{1,2}} \tag{59}$$

while the stability boundary between case 3a and case 4 is

$$\frac{L^2}{V^1} = \frac{\phi_1^{1,2}\Phi_2^2}{\alpha_2\alpha_3} \tag{60}$$

or

$$L^1 = \frac{\phi_1^{1,2}(\beta_2 F^2 Z_2^2)}{\alpha_2 - \phi_1^{1,2}} + \frac{\phi_1^{1,2}(F^2 Z_3^2)}{\alpha_3 - \phi_1^{1,2}} \tag{61}$$

Steady-state design equations for each of the eight cases are given in Table 5.

The dynamic behavior of a type I ternary column is similar to the behavior already established for a type I binary column. A perturbation in the feed composition will change the set of eigencompositions on the feed stage from $(\phi_k^{1,2})' \rightarrow (\phi_k^{1,2})''$: $k = 1, 2$. This in turn introduces a pair of composition waves that propagate from the feed stage into each of the two adjoining countercurrent sections. In the rectifying section, where both waves have positive eigenvelocities, the wave associated with $\phi_2^{1,2}$ will propagate ahead of the wave associated with $\phi_1^{1,2}$. In the stripping section, the wave associated with $\phi_2^{1,2}$ will travel fastest. A perturbation of the internal liquid or vapor flows has no effect on either $\phi_1^{1,2}$ or $\phi_2^{1,2}$. In the face of such a change in operating conditions the pinch composition within the column is unchanged as long as the case 1 profile remains stable.

The above results are generally applicable to any simple multicomponent column with a type I profile. Of course, as the number of species present in the column increases so does the number of eigencompositions needed to describe the column's behavior.

The dynamic behavior of the countercurrent section of a case 2a or case 3a ternary column that contains only two species closely resembles that of a section of a type I binary column. A perturbation in the composition of the feed will alter the eigencompositions $\phi_1^{1,2}$ and $\phi_2^{1,2}$ in a manner that may be predicted from Eq. 30. As long as the stability index profile in the column remains unchanged, one composition wave will enter the section containing two species and two composition waves will enter the section containing all three species. Altering the internal flows, while maintaining the feed composition constant, has no effect on the eigencomposition in the section containing only two species, but will result in a single composition wave traveling into the section containing all three species.

Let us now investigate the situation that arises when a perturbation in operating conditions converts a type I column into a type II column or vice versa. Consider the rectifying section of a column operating with a type I profile (case 1) and with $\Delta^1 < F^2\alpha_1(\alpha_2\alpha_3 - \phi_1^{1,2}\phi_2^{1,2})/(\alpha_3 - \alpha_1)\phi_1^{1,2}\phi_2^{1,2}$. With increasing internal reflux ratio L^1/V^1 the case 1 profile will remain stable only up to the point where

$$\frac{L^1}{V^1} = \frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_2\alpha_3} \tag{50}$$

Beyond this point, I^1 switches from 0 to 1, and a composition wave $(\phi_1^{1,2} \longrightarrow \alpha_1)$ will enter the rectifying section from the distillate product stage. If this critical value of L^1/V^1 is approached from the other side, the case 2A profile remains stable as L^1/V^1 decreases up to the critical point. Beyond this point, I^1 switches from 1 to 0, and a composition wave $(\alpha_1 \longrightarrow \phi_1^{1,2})$ enters the rectifying section from the feed stage.

At the boundary defined by Eq. 50, $\sigma_1^{\prime,\prime\prime}$ is zero whether it is calculated for the $\phi_1^{1,2} \longrightarrow \alpha_1$ transition or for the $\alpha_1 \longrightarrow \phi_1^{1,2}$ transition. Thus, as L^1/V^1 crosses this critical value not only does the pinch condition in the rectifying section make a discontinuous jump between $(\phi_1^{1,2}, \phi_2^{1,2})$ and $(\alpha_1, \phi_2^{1,2})$, (i.e., species 1 appears or disappears in the rectifying section) but the velocity at which the resulting wave travels through the column is vanishingly small.

Several authors (Jackson and Pigford, 1956; Rosenbrock, 1960, 1962) have modeled the dynamics of simple distillation columns in terms of diffusion-type equations and composition waves. These formulations predict "trapped waves" analogous to the zero-velocity waves discussed here. The presence of extremely slow transient waves led Magnussen et al. (1979) to hypothesize the existence of multiple steady-state profiles in distillation. These authors reported three steady-state solutions at the same operating condition for an azeotropic column separating ethanol from water using benzene as the entrainer. Prokapakis et al. (1983) simulated the transient behavior of this column. They confirmed the three regimes of operation reported by Magnussen et al. The first steady-state solution corresponded to

Table 5. Ternary Single-Feed Column (Saturated Liquid Feed)

Case 1 (given $F_1^3 = Z_1^3F^3$ and $F_3^1 = Z_3^1F^1$)

$$L^1 = \frac{\phi_1^{1,2}(F^2Z_1^2 + F_1^3)}{\alpha_1 - \phi_1^{1,2}} + \frac{\phi_1^{1,2}(\beta_2F^2Z_2^2)}{\alpha_2 - \phi_1^{1,2}} + \frac{-\phi_1^{1,2}(F_3^1)}{\alpha_3 - \phi_1^{1,2}}$$

$$\Delta^1 = F^2Z_1^2 + F_1^3 + \beta_2F^2Z_2^2 - F_3^1$$

where

$$\beta_2 = \frac{(\alpha_2 - \phi_1^{1,2})(\phi_2^{1,2} - \alpha_2)}{\alpha_2F^2Z_2^2}\left[\frac{\alpha_1(F^2Z_1^2 + F_1^3)}{(\alpha_1 - \phi_1^{1,2})(\alpha_1 - \phi_2^{1,2})} + \frac{\alpha_3(-F_3^1)}{(\alpha_3 - \phi_1^{1,2})(\alpha_3 - \phi_2^{1,2})}\right]$$

Case 2a (given β_2 and F_3^1)

$$L^1 > \left(\frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_2\alpha_3 - \phi_1^{1,2}\phi_2^{1,2}}\right)\Delta^1$$

$$L^1 < \left(\frac{\phi_2^{1,2}}{\alpha_3 - \phi_2^{1,2}}\right)\Delta^1 \quad \text{if } \Delta^1 < F^2Z_3^2$$

$$L^1 < \frac{\phi_2^{1,2}(\beta_2F^2Z_2^2)}{\alpha_2 - \phi_2^{1,2}} + \frac{\phi_2^{1,2}(F^2Z_3^2)}{\alpha_3 - \phi_2^{1,2}} \quad \text{if } \Delta^1 > F^2Z_3^2$$

$$\Delta^1 = \beta_2F^2Z_2^2 - F_3^1$$

Case 2 (given F_3^1)

$$L^1 > \frac{-\phi_2^{1,2}(F_3^1)}{\alpha_3 - \phi_2^{1,2}}$$

$$\Delta^1 = -F_3^1$$

Case 3a (given β_2 and F_1^3)

$$L^1 > \left(\frac{\phi_1^{1,2}\phi_2^{1,2}}{\alpha_1\alpha_2 - \phi_1^{1,2}\phi_2^{1,2}}\right)[(\beta_2 - 1)F^2Z_2^2 + F_1^3] - F^2$$

$$L^1 < \left(\frac{\phi_1^{1,2}}{\alpha_1 - \phi_1^{1,2}}\right)[(\beta_2 - 1)[F^2Z_2^2 + F_1^3] - F^2 \quad \text{if } \Delta^1 > F^2(Z_2^2 + Z_3^2)$$

$$L^1 < \frac{\phi_1^{1,2}(\beta_2F^2Z_2^2)}{\alpha_2 - \phi_1^{1,2}} + \frac{\phi_1^{1,2}(F^2Z_3^2)}{\alpha_3 - \phi_1^{1,2}} \quad \text{if } \Delta^1 < F^2(Z_2^2 + Z_3^2)$$

$$\Delta^1 = F^2 + (\beta_2 - 1)F^2Z_2^2 + F_1^3$$

Case 3 (given F_1^3)

$$L^1 > \frac{\phi_1^{1,2}(F_1^3)}{\alpha_1 - \phi_1^{1,2}} - F^2$$

$$\Delta^1 = F^2 + F_1^3$$

Cases 4, 4a, 4b (given β_2)

$$L^1 > \frac{\phi_2^{1,2}(\beta_2F^2Z_2^2)}{\alpha_2 - \phi_2^{1,2}} + \frac{\phi_2^{1,2}(F^2Z_3^2)}{\alpha_3 - \phi_2^{1,2}} \quad \text{if } \Delta^1 < \frac{F^2\left[\sum_{i=1}^{3}(\alpha_iZ_i^2) - \alpha_1\right]}{\alpha_3 - \alpha_1}$$

$$L^1 > \frac{\phi_1^{1,2}(\beta_2F^2Z_2^2)}{\alpha_2 - \phi_1^{1,2}} + \frac{\phi_1^{1,2}(F^2Z_3^2)}{\alpha_3 - \phi_1^{1,2}} \quad \text{if } \Delta^1 > \frac{F^2\left[\sum_{i=1}^{3}(\alpha_iZ_i^2) - \alpha_1\right]}{\alpha_3 - \alpha_1}$$

$$\Delta^1 = \beta_2F^2Z_2^2 + F^2Z_3^2$$

their initial steady state, the second solution corresponded to the state of the system 17 h after a change in operating conditions was imposed, and the third solution was the state of the system after 23 h. It is intriguing to note that these authors started with a situation in which benzene is present in the stripping section and ended with a situation in which there is negligible benzene in the stripping section, i.e., the extremely slow transient coincides with an abrupt change in the composition profile. This behavior is characteristic of a column operating at a stability boundary. Small perturbations in the operating conditions of even a CRV, CMO column containing a large number of plates can lead to discontinuous changes in the column's composition and temperature profile. The critical points at which such behavior is observed are defined by Eq. 19. In simple columns these critical points correspond to the appearance or disappearance of a species from one of the product streams (Ko, 1985). Although the partial molar product flows vary continuously across such a stability boundary, the column composition profile changes discontinuously. The wave velocity at which this change in composition travels through the column is identically zero for operating conditions on the stability boundary.

Application of Continuum Model to Complex Columns

Introducing a second feed stream or an intermediate product stream into a distillation column greatly increases the complexity of its dynamic and steady-state behavior. We consider three special cases:

1. A two-feed binary column without intermediate product withdrawal
2. A single-feed binary column with intermediate product withdrawal
3. The Petlyuk columns, Figure 1b

These illustrate the key phenomena present with complex columns.

Two-feed column with no intermediate product stream

Optimum operation of a distillation column occurs when the steady-state temperature in the column decreases in a monotonic fashion from bottom to top. For CRV separations this is equivalent to requiring that

$$\prod_{k=1}^{M-1} \phi_k^j \le \prod_{k=1}^{M-1} \phi_k^{j+1} \tag{62}$$

For a two-feed, binary column Eq. 62 is satisfied whenever $\phi_1^{1,2} < \phi_1^{3,4}$. With saturated liquid feeds this is equivalent to requiring that the bubble point temperature of the upper feed be less than that of the lower feed.

A binary column of this type can have six different composition profiles:

Case 1a. $I^1 = 0, I^2 = I^3 = 1, I^4 = 1$
Case 1b. $I^1 = 0, I^2 = I^3 = 0, I^4 = 1$
Case 2. $I^1 = 1, I^2 = I^3 = 1, I^4 = 1$
Case 3. $I^1 = 0, I^2 = I^3 = 0, I^4 = 0$
Case 4a. $I^1 = 1, I^2 = I^3 = 1, I^4 = 0$
Case 4b. $I^1 = 1, I^2 = I^3 = 0, I^4 = 0$

The stability boundary between case 1a and case 1b is

$$\frac{L^2}{V^2} = \frac{L^3}{V^3} = \frac{\phi_1^{1,2}\phi_1^{3,4}}{\alpha_1\alpha_2} \tag{63}$$

Assuming saturated liquid feeds and expressing this relation in terms of L^1 and Δ^1:

$$L^1 = \left(\frac{\phi_1^{1,2}\phi_1^{3,4}}{\alpha_1\alpha_2 - \phi_1^{1,2}\phi_1^{3,4}}\right)\Delta^1 - \left(\frac{\alpha_1\alpha_2}{\alpha_1\alpha_2 - \phi_1^{1,2}\phi_1^{3,4}}\right)F^2 \tag{64}$$

The boundaries between case 1a and case 2 and between case 1b and case 3 are, respectively,

$$L^1 = \left(\frac{\phi_1^{1,2}}{\alpha_2 - \phi_1^{1,2}}\right)\Delta^1 \tag{65}$$

and

$$L^1 = \left(\frac{\phi_1^{3,4}}{\alpha_1 - \phi_1^{3,4}}\right)\Delta^1 - \left(\frac{\alpha_1}{\alpha_1 - \phi_1^{3,4}}\right)(F^2 + F^4) \tag{66}$$

The boundaries between case 1a and case 3 and between case 1b and case 2 are, respectively,

$$L^1 = \left(\frac{\phi_1^{1,2}}{\alpha_1 - \phi_1^{1,2}}\right)(\Delta^1 - Z_2^2F^2 - Z_2^4F^4) + \left(\frac{\phi_1^{1,2}}{\alpha_2 - \phi_1^{1,2}}\right)(Z_2^2F^2 - Z_2^4F^4) \tag{67}$$

and

$$L^1 = \left(\frac{\phi_1^{3,4}}{\alpha_2 - \phi_1^{3,4}}\right)(\Delta^1 - Z_2^2F^2) + \left(\frac{\phi_1^{3,4}}{\alpha_1 - \phi_1^{3,4}}\right)(-Z_1^2F^2) - F^2 \tag{68}$$

The stability regions delineated by these expressions are illustrated in Figure 9 and steady-state design equations for cases 1a and 1b are given in Table 6.

Transition between case 1a and case 1b involves indeterminacy of the steady-state composition profile in the column and is associated with a composition wave whose velocity is zero at the stability boundary defined by Eq. 64. Unlike the situation in a simple column, however, this transition does not correspond to the condition at which one of the partial molar product flows from the column becomes equal to zero. Thus, multiple-feed columns can exhibit indeterminate composition profiles at conditions other than those associated with the appearance or disappearance of a species in a product stream. *These new critical points correspond to changes in the I^j associated with an intermediate section of the column.*

Insight into the dynamic behavior of this column can also be obtained from the continuum model. Assuming that a perturbation does not shift the column from one stability regime to

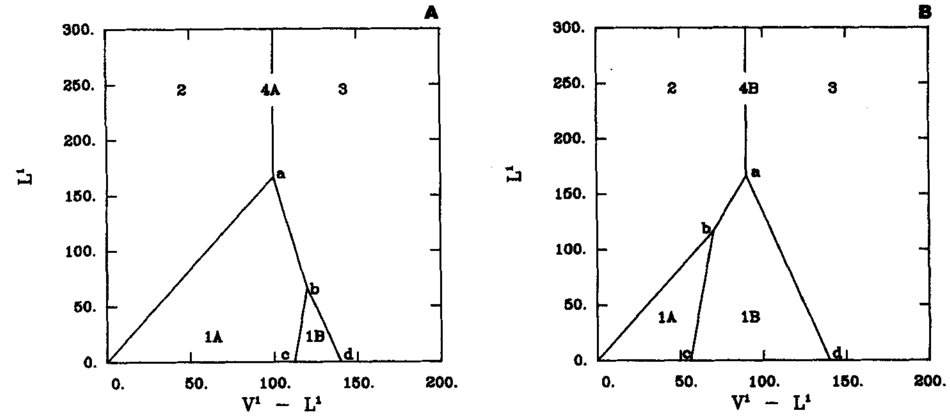

Figure 9. Stability diagrams for binary column with two feed streams.

A $\alpha_1 = 1.0;\quad \alpha_2 = 2.0;\quad Z_1^2 = Z_2^4 = 0.4;\quad Z_2^2 = Z_1^4 = 0.6$
$F^2 = 100;\quad F^2 = 100$

$$\text{a}:\Delta^1 = F^2Z_2^2 + F^4Z_2^4;\quad \text{b}:\Delta^1 = F^2 + \frac{\phi_1^{1,2}\phi_1^{3,4} - \alpha_1\alpha_2}{\phi_1^{3,4}(\phi_1^{1,2} - \alpha_2)}(F^4)$$

$$\text{c}:\Delta^1 = \frac{\alpha_1\alpha_2}{\phi_1^{1,2}\phi_1^{3,4}}(F^2);\quad \text{d}:\Delta^1 = \frac{\alpha_1}{\phi_1^{3,4}}(F^2 + F^4)$$

B $F^2 = 50;\quad F^4 = 150$

$$\text{a}:\Delta^1 = F^2Z_2^2 + F^4Z_2^4;\quad \text{b}:\Delta^1 = \frac{\alpha_1(\alpha_2 - \phi_1^{1,2})}{\phi_1^{1,2}(\phi_1^{3,4} - \alpha_1)}(F^2)$$

$$\text{c}:\Delta^1 = \frac{\alpha_1\alpha_2}{\phi_1^{1,2}\phi_1^{3,4}}(F^2);\quad \text{d}:\Delta^1 = \frac{\alpha_1}{\phi_1^{3,4}}(F^2 + F^4)$$

another, the dynamic response for a type I profile (case 1a or 1b) is similar to that of a single-feed column. For example, when the eigencomposition from the intermediate section extends across the top feed stage (case 1a), the subcolumn consisting of the rectifying section, the upper feed stage, and the intermediate section behaves as a simple type I column. A perturbation in the upper feed composition will initiate a single composition wave from this feed stage with a positive eigenvelocity above the feed and a negative eigenvelocity below the feed. The velocity of these waves is given by Eqs. 48 and 49, respectively. Perturbation of the lower feed composition or of the internal flows in the column has no effect on $\phi_1^{1,2}$ or on the pinch conditions of the upper subcolumn. However, such a change alters the eigencomposition in the stripping section below the bottom feed stage. This will change from $(\phi_1^4)' \longrightarrow (\phi_1^4)''$ and cause a wave that propagates from the bottom product stage with a velocity

$$\sigma_1'^{,''} = \left(\frac{L^4}{|\Delta^4|}\right)\left[\frac{V^4}{L^4}\frac{((\phi_1^4)'(\phi_1^4)''}{\alpha_1\alpha_2} - 1\right] \tag{69}$$

Table 6. Binary Column with Two Saturated Liquid Feed Streams and No Intermediate Product Withdrawal

Case 1a (given $F_1^5 = Z_1^5F^5$ and $F_2^1 = Z_2^1F^1$)

$$L^1 = \frac{\phi_1^{1,2}(F^2Z_1^2 + F^4Z_1^4 + F_1^5)}{\alpha_1 - \phi_1^{1,2}} + \frac{-\phi_1^{1,2}(F_2^1)}{\alpha_2 - \phi_1^{1,2}}$$

$$\Delta^1 = F^2Z_1^2 + F^4Z_1^4 + F_1^5 - F_2^1$$

Case 1b (given F_1^5 and F_2^1)

$$L^1 = \frac{\phi_1^{3,4}(F^4Z_1^4 + F_1^5)}{\alpha_1 - \phi_1^{3,4}} + \frac{-\phi_1^{3,4}(F^2Z_2^2 + F_2^1)}{\alpha_2 - \phi_1^{3,4}} - F^2$$

$$\Delta^1 = F^2Z_1^2 + F^4Z_1^4 + F_1^5 - F_2^1$$

Maximum vapor flow criterion

Barnes et al. (1972) and Yaws et al. (1981a, b) have stated that the steady-state conditions in a minimum reflux column with multiple feeds not only must satisfy the Underwood equations, Eqs. 13 and 14, and the design specifications, but also must yield the greatest internal vapor flow. In the case of a binary column with two feed streams this maximum vapor flow criterion is equivalent to the stability criteria developed in the present study. Unfortunately, this equivalence does not hold for more complex columns.

Application of the maximum vapor flow criterion when designing a binary, two-feed column reduces to solving Eqs. 13 for V^3 first with $\phi_1^3 = \phi_1^{1,2}$ and then with $\phi_1^3 = \phi_1^{3,4}$. If the first calculation yields the larger value for V^3, case 1a represents the stable profile in the column. If the second calculation yields the larger V^3, the correct profile is case 1b.

That the maximum vapor flow is not a valid criterion in general is easily demonstrated by a counterexample. The two-feed column defined in Table 1a exhibits the partial molar flows given in Table 1b at a vapor flow rate of 130. Applying the maximum vapor flow criterion with these same feed and product flows yields the situation defined in Tables 7a and 7b with a vapor flow rate of 145.4. Unfortunately, the column profile defined in Table 7b is unstable and does not exist at steady state. Correct steady-state conditions for the internal flows specified in Table 7a are given in Table 7c. Thus, maximum vapor flow is

Table 7a. Two-Feed, Three-Component Column without Intermediate Product Stream

Input Data: $\alpha = 0.52, 1.0, 2.47$		
Section	L	V
1	45.4	145.4
2	145.4	145.4
3	145.4	145.4
4	245.4	145.4
Liquid Feed Stream	$\phi_k^{j-1,j}$	$Z_1^j F^j$
2	0.6347	30
	1.401	30
		40
4	0.6188	30
	1.805	50
		20

not a generally valid criterion for determining the steady-state condition of a multicomponent, multiple-feed minimum reflux column.

Single-feed column with intermediate product stream

A single-feed column with an intermediate product stream can be modeled as a two-segment column for which either F^2 or F^4 is zero. We will set $F^2 = 0$.

A binary column of this type can have six different composition profiles:

Case 1. $I^1 = I^2 = 0, I^3 = 0, I^4 = 1$
Case 1a. $I^1 = I^2 = 1, I^3 = 0, I^4 = 1$
Case 2. $I^1 = I^2 = 1, I^3 = 1, I^4 = 1$
Case 3. $I^1 = I^2 = 0, I^3 = 0, I^4 = 0$
Case 3a. $I^1 = I^2 = 1, I^3 = 0, I^4 = 0$
Case 4. $I^1 = I^2 = 1, I^3 = 1, I^4 = 0$

The stability boundary between case 1 and case 1a is

$$\frac{L^1}{V^1} = \frac{L^2}{V^2} = \frac{\phi_1^{3,4}}{\alpha_2} \tag{70}$$

Table 7b. Two-Feed Column without Intermediate Product Stream

Unstable Profile Obtained by Maximum Vapor Flow Criterion				
Section	w	ϕ_k^j	f_1^j	I^j
1	0.355	0.6620	8.29	0
		1.7059	31.71	
			60.00	
2	0.981	0.6188	−21.71	1
		2.117	1.71	
			20.00	
3	0.981	0.6188	−21.71	1
		2.117	1.71	
			20.00	
4	1.418	0.6188	−51.71	1
		2.470	−48.29	
			0.00	

Table 7c. Two-Feed Column without Intermediate Product Stream

Stable Profile				
Section	w	ϕ_k^j	f_1^j	I^j
1	0.369	0.6347	6.17	0
		1.7123	33.83	
			60.00	
2	0.955	0.6347	−23.83	1
		2.120	3.83	
			20.00	
3	0.955	0.6347	−23.83	1
		2.120	3.83	
			20.00	
4	1.4058	0.6243	−53.83	1
		2.470	−46.17	
			0.00	

If it is assumed that the intermediate product is a saturated liquid, this relation can be expressed in terms of L^3 and Δ^3:

$$L^3 = \left(\frac{\phi_1^{3,4}}{\alpha_2 - \phi_1^{3,4}}\right)\Delta^3 + \left(\frac{\alpha_2}{\alpha_2 - \phi_1^{3,4}}\right)F^3 \tag{71}$$

If the feed is also a saturated liquid, the boundaries between case 1a and case 2 and between case 1 and case 3 are, respectively,

$$L^3 = \left(\frac{\phi_1^{3,4}}{\alpha_2 - \phi_1^{3,4}}\right)\Delta^3 \tag{72}$$

and

$$L^3 = \left(\frac{\phi_1^{3,4}}{\alpha_1 - \phi_1^{3,4}}\right)\Delta^3 - \left(\frac{\alpha_1}{\alpha_1 - \phi_1^{3,4}}\right)F^4 \tag{73}$$

Perhaps the most interesting case is case 3a, for which species 1 is absent from the distillate, species 3 is absent from the bottoms, and both are present in the intermediate product stream. The stability boundary between case 1a and case 3a is given by Eq. 73. The boundary between case 3 and case 3a is

$$\frac{L^1}{V^1} = \frac{L^2}{V^2} = \frac{\Phi_1^4}{\alpha_2} \tag{74}$$

or

$$L^3 = \left(\frac{\Phi_1^4}{\alpha_2 - \Phi_1^4}\right)\Delta^3 + \left(\frac{\alpha_2}{\alpha_2 - \Phi_1^4}\right)F^3 \tag{75}$$

where

$$\Phi_1^4 = \alpha_1\left[\frac{1}{1 + \left(1 - \frac{\alpha_1}{\alpha_2}\right)\left(\frac{\Delta^3 - Z_2^4 F^4}{F^3}\right)}\right] \tag{76}$$

The stability regimes delineated by these expressions are illustrated in Figure 10. Steady-state design equations for each of the six cases are given in Table 8.

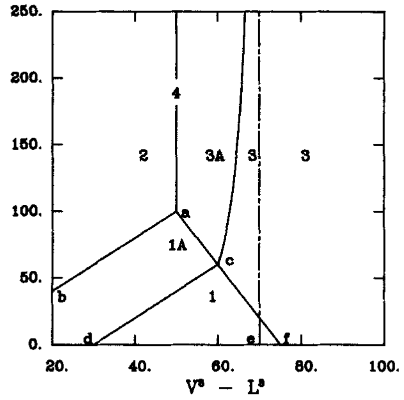

Figure 10. Stability diagram for binary column with single feed and intermediate product stream.

$\alpha_1 = 1.0$; $\alpha_2 = 2.0$; $F^4 = 100$; $F^3 = -20$; $Z_1^4 = Z_2^4 = 0.5$

a: $\Delta^3 = F^4 Z_2^4$; b: $\Delta^3 = -F^3$

c: $\Delta^3 = F^4 Z_2^4 - F^3 Z_1^4$; d: $\Delta^3 = \dfrac{\alpha_2}{\phi_1^{3,4}}(-F^3)$

e: $\Delta^3 = F^4 Z_2^4 - F^3$; f: $\Delta^3 = \dfrac{\alpha_1}{\phi_1^{3,4}}(F^4)$

The dynamic behavior of this column for cases 1, 2, and 3 is identical to that established for a simple column. Turning our attention to case 1a, consider the column to be composed of two subcolumns. The upper subcolumn consists of everything above the intermediate product stream while the lower subcolumn consists of the intermediate product stream and everything located below it. Within the lower subcolumn, the eigencomposition $\phi_1^{3,4}$ is constant across the feed stage, and thus the dynamic behavior within sections 3 and 4 is identical to the dynamic behavior of a case 1 simple column. Within the upper subcolumn, $\phi_1^1 = \phi_1^2 = \alpha_1$ as long as the case 1a profile is stable, and no composition waves will propagate between the intermediate product and the distillate product stages.

In practice, case 4 operation of a simple binary column is difficult to achieve. In order to maintain both distillate and product streams pure, the column must be operated with its disillate flow rate equal to the partial molar feed flow of the more volatile species and its bottom flow rate equal to the partial molar feed flow of the less volatile species. Any deviation in Δ^1 shifts the composition profile in the column to either case 2 or case 3. In contrast a single-feed column with intermediate product withdrawal will admit case 3a operation (i.e., pure distillate and product streams) in the range:

$$F^4 Z_2^4 < \Delta^3 < F^4 Z_2^4 - F^3$$

where F^4 and F^3 are the flow rates of the feed and intermediate product streams, respectively. As $|F^3|$ is increased, the sensitivity of the column to perturbations in internal flows is decreased.

The dynamic behavior for case 3a operation is established by again separating the column into an upper and a lower subcolumn. The lower subcolumn behaves similarly to a case 3 simple column. The dynamic behavior of the upper subcolumn is similar to that of the rectifying section of a case 2 simple column. Perturbations in either the feed composition or the internal flows will introduce a $(\phi_1^3)' \longrightarrow (\phi_1^3)''$ wave that travels from the feed stage through section 3 to the intermediate product stage with a positive eigenvelocity. As long as the case 3a profile is stable, however, no composition waves propagate between the intermediate product and the distillate product stages or between the feed stage and the bottom product stage.

Table 8. Binary Column with Saturated Liquid Feed and Intermediate Product

Case 1 or 1a (given $F_1^5 = Z_1^5 F^5$, $F_2^5 = Z_2^5 F^5$, and F^3)

$$L^3 = \frac{\phi_1^{3,4}(F^4 Z_1^4 + F_1^5)}{\alpha_1 - \phi_1^{3,4}} + \frac{\phi_1^{3,4}(F^4 Z_2^4 + F_2^5)}{\alpha_2 - \phi_1^{3,4}}$$

$$\Delta^3 = F^4 + F_1^5 + F_2^5$$

Case 1a (given F_1^5, F_2^5, and F^3)

$$F^3 < \left(\frac{\alpha_2 - \phi_1^{3,4}}{\alpha_2}\right) L^3 - \left(\frac{\phi_1^{3,4}}{\alpha_2}\right) \Delta^3$$

and

$$L^3 < \frac{\phi_1^{3,4}(\Delta^3)}{\alpha_2 - \phi_1^{3,4}} \quad \text{if } \Delta^3 < F^4 Z_2^4$$

or

$$L^3 < \frac{\phi_1^{3,4}(\Delta^3)}{\alpha_1 - \phi_1^{3,4}} - \frac{\alpha_1(F^4)}{\alpha - \phi_1^{3,4}} \quad \text{if } \Delta^3 > F^4 Z_2^4$$

Case 2 (given F_2^1 and F^3)

$$L^3 > \frac{\phi_1^{3,4}(\Delta^3)}{\alpha_2 - \phi_1^{3,4}}, \quad \Delta^3 = -F_2^1 - F^3$$

Case 3 or 3a (given F_1^5 and F^3)

$$L^3 > \frac{\phi_1^{3,4}(F_1^5)}{\alpha_1 - \phi_1^{3,4}} - F^4, \quad \Delta^3 = F^4 + F_1^5$$

Case 3a (given F_1^5 and F^3)

$$L^3 > \frac{\Phi_1^4(\Delta^3)}{\alpha_2 - \Phi_1^4} + \frac{\alpha_2(F^3)}{\alpha_2 - \Phi_1^4}$$

where

$$\Phi_1^4 = \alpha_1 \left[\frac{1}{1 + \left(1 - \dfrac{\alpha_1}{\alpha_2}\right)\left(\dfrac{\Delta^3 - F^4 Z_2^4}{F^3}\right)}\right]$$

Case 4

$$L^3 > \frac{\phi_1^{3,4}(F^4 Z_2^4)}{\alpha_2 - \phi_1^{3,4}}, \quad \Delta^3 = F^4 Z_2^4$$

Petlyuk columns

An interesting example of a two-feed column with an intermediate product stream is the second column in Figure 1b. This is part of the thermally coupled distillation system first proposed by Petlyuk et al. (1965). Fidkowski and Krolikowski (1986) obtained analytical design equations for this column for the special case where $-F^{2,1} = F^{1,2} Z_3^{1,2}$ and $-F^{2,5} = F^{1,2} Z_1^{1,2}$. A more general description is developed below.

The first Petlyuk column is a single-feed (simple) column operated as a case 4, ternary separation. Thus, the feed streams to the second column are:

$$\begin{aligned} F^{2,2}Z_1^{2,2} &= 0 \\ F^{2,2}Z_2^{2,2} &= F^{1,2}Z_2^{1,2}\beta_2^1 \\ F^{2,2}Z_3^{2,2} &= F^{1,2}Z_3^{1,2} \end{aligned}$$

and

$$\begin{aligned} F^{2,4}Z_1^{2,4} &= F^{1,2}Z_1^{1,2} \\ F^{2,4}Z_2^{2,4} &= F^{1,2}Z_2^{1,2}(1 - \beta_2^1) \\ F^{2,4}Z_3^{2,4} &= 0 \end{aligned}$$

For simplicity the superscript denoting the second column's index will be omitted in what follows. For this thermally coupled system, $\phi_2^{1,2}$ equals the eigencomposition in the rectifying section of the first column, and $\phi_1^{3,4}$ equals the eigencomposition in the stripping section of the first column. If the stability index profile is $I^1 = 1$, $I^2 = 2$, $I^3 = 0$, and $I^4 = 1$ each segment of the second column operates as if it were a separate type I binary column. The partial molar flows in each countercurrent section are then found from the solution of

$$\begin{aligned} \frac{\alpha_2 f_2^1}{\alpha_2 - \phi_2^{1,2}} + \frac{\alpha_3 f_3^1}{\alpha_3 - \phi_2^{1,2}} &= V^1 \\ f_2^1 + f_3^1 &= V^1 - L^1 \\ f_i^2 = f_i^1 - F^2 Z_i^2 \quad i &= 2, 3 \end{aligned} \tag{77}$$

and

$$\begin{aligned} \frac{\alpha_1 f_1^3}{\alpha_1 - \phi_1^{3,4}} + \frac{\alpha_2 f_2^3}{\alpha_2 - \phi_1^{3,4}} &= V^3 \\ f_1^3 + f_2^3 &= V^3 - L^3 \\ f_i^4 = f_i^3 - F^4 Z_i^4 \quad i &= 1, 2 \end{aligned} \tag{78}$$

In order to maintain this stability index profile, the following four conditions must be satisfied:

$$\frac{L^1}{V^1} < \frac{\phi_2^{1,2}}{\alpha_3} \tag{79}$$

$$\frac{L^2}{V^2} > \frac{\phi_2^{1,2}}{\alpha_2} \tag{80}$$

$$\frac{L^3}{V^3} < \frac{\phi_1^{3,4}}{\alpha_2} \tag{81}$$

$$\frac{L^4}{V^4} > \frac{\phi_1^{3,4}}{\alpha_1} \tag{82}$$

If species 2 is to be absent from the distillate product (Fidkowski and Krolikowski, 1986), $I^1 = 2$ and $I^2 = 2$, and

$$\frac{L^1}{V^1} > \frac{\phi_2^{1,2}}{\alpha_3} \tag{83}$$

If species 2 is to be absent from the bottoms product, $I^3 = 0$ and $I^4 = 0$, and

$$\frac{L^4}{V^4} < \frac{\phi_1^{3,4}}{\alpha_1} \tag{84}$$

The continuum model provides insight into the dynamic interaction between the two columns. A perturbation in the feed composition to the system introduces two distinct composition waves that originate from the feed stage of the first column and propagate in opposite directions. As these waves enter the second column, they propagate as if each were entering a simple binary subcolumn. A perturbation in the liquid or vapor drawoff rates from the second column leads to the same type of transient behavior, since the eigencompositions in the rectifying and stripping sections of the first column are dependent on its internal flows. Changing the internal flows in the second column will leave its composition profile unaffected if its subcolumns each exhibit a type I profile. Such changes lead to composition waves traveling from both feed stages to the intermediate product stage if the conditions indicated by Eqs. 83 and 84 are present.

Conclusions

A new description of minimum reflux CRV, CMO distillation columns is presented. This description approximates the countercurrent sections in a column by means of a continuum dynamic model. The major achievements of this approach are:

1. A general algorithm for calculating the minimum reflux operating conditions of complex columns and coupled distillation networks with any number of multicomponent feeds and any number of intermediate product streams
2. A quantitative description of the stability of the various composition profiles that can exist in such columns
3. A semiquantitative description of the dynamic behavior of minimum reflux columns in terms of interacting composition waves

Analytical expressions are derived for the steady-state and dynamic behavior of simple binary and ternary columns. A major result of this examination is the discovery of critical points at which small perturbations in the operating conditions of a minimum reflux column lead to discontinuous changes in the column's composition and temperature profile. The wave velocity at which these changes travel through the column is identically zero at the stability boundaries and is close to zero near these points. To avoid the control problems associated with slow transients and very nonlinear behavior, a column should not be operated near one of its stability boundaries.

The behavior of multiple-feed columns is briefly explored. Barnes et al. (1972) and Yaws et al. (1981a, b) have proposed a maximum vapor flow criterion for determining minimum reflux conditions in multiple-feed distillation columns. This criterion is shown to be invalid. Fidkowski and Krolikowski (1986) have derived an analytical description of the thermally coupled ternary distillation system first proposed by Petlyuk (1965). Their treatment is generalized and the dynamic behavior of this system is discussed.

The simple, nonlinear description of column dynamics provided by the model developed in this paper should prove useful in control applications. It is also expected that the continuum model will prove useful for conceiving and evaluating low-energy-use distillation networks.

Notation

f_i^j = flow of component *i* in section *j*
F_i^j = flow of component *i* in feed or product stream *j*
F^j = total flow of feed or product stream *j*
h = liquid holdup per stage
I^j = stability index in section *j*
K^j = reference equilibrium constant in section *j*
L^j = liquid flow rate in section *j*
M = number of components

n = stage number ascending in direction of vapor flow
N = number of continuous countercurrent sections in column or number of stages in countercurrent section
t = time
V^j = vapor flow rate in section j
w^j = mean rectifying factor in section j
X_i^j = liquid mole fraction of component i in section j
Y_i^j = vapor mole fraction of component i in section j
z = dimensionless distance
Z_i^j = mole fraction of component i in feed j

Greek letters

α_i = relative volatility of component i
β_i = fractional recovery of i in distillate product of single feed column
$\Delta = V^j - L^j$ = net molar flow through section j
Λ_k = characteristic wave invariant across ϕ_k transition
σ_k = characteristic of velocity of perturbation in ϕ_k
$\sigma_k^{\prime,\prime\prime}$ = mean velocity of wave corresponding to change from ϕ_k' to ϕ_k''
ϕ_k^j = eigencomposition k in section j
$\phi_k^{j,j+1}$ = eigencomposition k related to the $j + 1$ feed stream
Φ_k^j = eigencomposition k on stage j
τ = dimensionless time
χ_i^j = liquid mole fraction of component i on feed/product stage j

Appendix

Derivation of expressions for Y_i, X_i, f_i, and w in terms of ϕ_k

The ϕ_k's satisfy the relations

$$\sum_{i=1}^{M} \frac{\alpha_i X_i}{\alpha_i - \phi_k} = 0 \quad k = 1, M - 1 \tag{A1}$$

and

$$\alpha_1 \le \phi_1 \le \alpha_2 \le \phi_2 \cdots \phi_{M-1} \le \alpha_M$$

Since $Y_i = K\alpha_i X_i$, Eqs. A1 can be rewritten in terms of the Y_i's:

$$\sum_{i=1}^{M} \frac{Y_i}{\alpha_i - \phi_k} = 0 \quad k = 1, M - 1 \tag{A2}$$

Multiplying Eqs. A2 by $\Pi_{j=1}^{M} (\alpha_j - \phi_k)$ yields

$$\sum_{i=1}^{M} \left[\prod_{\substack{j=1 \\ j\neq i}}^{M} (\alpha_j - \phi_k) \right] Y_i = 0 \quad k = 1, M - 1 \tag{A3}$$

Thus,

$$\sum_{i=1}^{M} \left[\prod_{\substack{j=1 \\ j\neq i}}^{M} (\alpha_j - \phi) \right] Y_i$$

is a polynomial of degree $M - 1$ with roots ϕ_k: $k = 1, M - 1$. Since $\Sigma_{i=1}^{M} Y_i = 1$, this polynomial can be written

$$\sum_{i=1}^{M} \left[\prod_{\substack{j=1 \\ j\neq 1}}^{M} (\alpha_j - \phi) \right] Y_i = \prod_{k=1}^{M-1} (\phi_k - \phi) \tag{A4}$$

Setting $\phi = \alpha_i$ in Eq. A4 yields $Y_i(\phi_k: k = 1, M - 1)$

$$Y_i = \frac{\prod_{k=1}^{M-1} (\phi_k - \alpha_i)}{\prod_{\substack{j=1 \\ j\neq 1}}^{M} (\alpha_j - \alpha_i)} \quad i = 1, M \tag{A5}$$

$X_i(\phi_k: k = 1, M - 1)$ is obtained in a similar manner. Transforming Eqs. A1 into a form identical to Eqs. A2 yields

$$\sum_{i=1}^{M} \frac{X_i}{\dfrac{1}{\alpha_i} - \dfrac{1}{\phi_k}} = 0 \quad k = 1, M - 1 \tag{A6}$$

Following the procedure used to obtain Y_i yields

$$X_i = \frac{\prod_{k=1}^{M-1} \left(\dfrac{1}{\phi_k} - \dfrac{1}{\alpha_i} \right)}{\prod_{\substack{j=1 \\ j\neq 1}}^{M} \left(\dfrac{1}{\alpha_j} - \dfrac{1}{\alpha_i} \right)} \quad i = 1, M \tag{A7}$$

The partial molar flow of the ith component in a countercurrent section is

$$f_i = VY_i - LX; \quad i = 1, M \tag{A8}$$

Since $\Sigma_{i=1}^{M} Y_i = 1$, Eqs. A2 imply that

$$\sum_{i=1}^{M} \frac{\alpha_i Y_i}{\alpha_i - \phi_k} = 1 \quad k = 1, M - 1 \tag{A9}$$

Combining Eqs. A9, A1, and A8 yields

$$\sum_{i=1}^{M} \frac{\alpha_i f_i}{\alpha_i - \phi_k} = V \quad k = 1, M - 1 \tag{A10}$$

Equations A10 plus the relation

$$\sum_{i=1}^{M} f_i = V - L \tag{A11}$$

define a one-to-one transformation between f_i: $i = 1, M$ and ϕ_k: $k = 1, M - 1$ and $V - L$.

Finally, by definition

$$w = \frac{L}{VK} \tag{A12}$$

and making use of Eqs. A5 and A7

$$K = \frac{Y_i}{\alpha_i X_i} = \frac{\prod_{k=1}^{M-1} \phi_k}{\prod_{j=1}^{M} \alpha_j} \tag{A13}$$

Therefore,

$$w = \frac{L}{V} \frac{\prod_{j=1}^{M} \alpha_j}{\prod_{k=1}^{M-1} \phi_k} \tag{A14}$$

Derivation of the differential equations satisfied by the eigencompositions, ϕ_k

The differential material balance equations describing the behavior of a continuous section of the column are

$$\frac{\partial}{\partial \tau}(X_i) + \frac{L}{|\Delta|}\frac{\partial}{\partial z}\left(\frac{V}{L}Y_i - X_i\right) = 0 \quad i = 1, M \tag{A15}$$

Using Eqs. A5 and A7 to evaluate $\partial Y_i/\partial \phi_k$ and $\partial X_i/\partial \phi_k$, respectively, yields

$$\frac{\partial Y_i}{\partial \phi_k} = \frac{Y_i}{\phi_k - \alpha_i} \quad i = 1, M \text{ and } k = 1, M - 1 \tag{A16}$$

$$\frac{\partial X_i}{\partial \phi_k} = \frac{\alpha_i X_i}{(\phi_k - \alpha_i)\phi_k} \quad i = 1, M \text{ and } k = 1, M - 1 \tag{A17}$$

and

$$\frac{\partial}{\partial \phi_k}\left(\frac{V}{L}Y_i - X_i\right) = \frac{1}{\phi_k - \alpha_i}\left(\frac{V}{L}Y_i - \frac{\alpha_i X_i}{\phi_k}\right)$$
$$= \frac{\alpha_i X_i}{(\phi_k - \alpha_i)\phi_k}\left(\frac{\phi_k}{w} - 1\right) \quad \begin{matrix} k = 1, M - 1 \\ i = 1, M \end{matrix} \tag{A18}$$

Making use of Eqs. A17 and A18, the material balance expressions, Eqs. A15, can be transformed to yield

$$\sum_{k=1}^{M-1} \frac{\partial X_i}{\partial \phi_k}\left[\frac{\partial \phi_k}{\partial \tau} + \frac{L}{|\Delta|}\left(\frac{\phi_k}{w} - 1\right)\frac{\partial \phi_k}{\partial z}\right] = 0 \quad i = 1, M \tag{A19}$$

Equations A19 are satisfied if and only if

$$\frac{\partial \phi_k}{\partial \tau} + \sigma_k(w)\frac{\partial \phi_k}{\partial z} = 0 \quad k = 1, M - 1 \tag{A20}$$

where

$$\sigma_k(w) = \frac{L}{|\Delta|}\left(\frac{\phi_k}{w} - 1\right) \tag{A21}$$

Equations A20 imply that a disturbance in any eigencomposition, ϕ_k, introduced at $z = 0$ travels in the direction of vapor flow with an "eigenvelocity" $\sigma_k(w)$, given by Eq. A21. Equations A20 and A21 along with the Eqs. A1, A7, and A14 provide an elegant analytical description of the dynamics of each continuous countercurrent section of a minimum reflux distillation column when there is negligible mass transfer resistance and vapor holdup and the relative volatilities and total molar overflows are constant.

Derivation of explicit expression for f_i in terms of α, w, V, and Y_i

Expressing the vapor-liquid equilibrium in terms of relative volatilities,

$$\frac{Y_i}{X_i} = \alpha_i K \quad i = 1, M \tag{A22}$$

Thus,

$$\frac{LX_i}{VY_i} = \frac{L/KV}{\alpha_i} \quad i = 1, M \tag{A23}$$

Combining Eqs. A8, A23, and A12 yields

$$f_i = VY_i\left(1 - \frac{w}{\alpha_i}\right) \quad i = 1, M \tag{A24}$$

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