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Part II: Numerical Solution

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Two new algorithms for calculating minimum reflux conditions in multicomponent distillation columns are described. Both algorithms are based on the continuum model for an infinite stage column proposed by Nandakumar and Andres. Several example problems demonstrate the accuracy and computational efficiency of the new algorithms.

SCOPE

It has been shown (Nandakumar and Andres, 1981) that modeling the rectifying and stripping sections of a distillation column as continuous countercurrent exchangers leads to a particularly simple mathematical description of minimum reflux behavior. This approach not only guarantees the exact infinite plate limit but also substantially decreases the number of equations necessary to define a minimum reflux solution. Two calculation methods have been proposed based on this model. The first is a short-cut method which extends Underwood's classic minimum reflux treatment to variable molar overflow situations. The second is a rigorous method which incorporates nonideal equilibrium and enthalpy behavior.

The objective in this investigation is to apply these new equations in an algorithmic form to calculate minimum reflux conditions for adiabatic, multicomponent distillation columns. Two algorithms are described. The accuracy of the new algorithms is established by comparing their solution with Underwood solutions and with plate-by-plate simulations of large finite columns. The computational efficiency of the algorithms is also demonstrated by means of examples.

CONCLUSIONS AND SIGNIFICANCE

The first algorithm that is described parallels Underwood's classic minimum reflux algorithm and is similar in both speed and accuracy. This algorithm represents a short cut method for use when accurate thermodynamic data are not available or when a rigorous calculation is not warranted. It assumes that constant relative volatilities and constant molar heats of vaporization are known for all components. Although formally identical to the Underwood algorithm and as fast computationally, the new algorithm incorporates the important effects of variable molar overflows.

The second algorithm represents a rigorous minimum reflux method and can incorporate most non ideal equilibrium and enthalpy behavior. This algorithm is in the form of a double iteration. The inner iteration involves simultaneous solution of a set of algebraic equations whose dimension equals the number of chemical species in the feed plus twice the number of nondistributed species in the column plus five. These equations completely define minimum reflux conditions for the ideal solution case, and this portion of the algorithm can be used alone in such situations. The outer iteration accounts for the composition dependence of the temperature dependent equilibrium constants and partial molar enthalpies that are used in the inner iteration.

The numerical algorithm representing the inner iteration is shown to be rapidly convergent, and the outer iteration representing as it does a relatively small correction to the system equations also converges rapidly. This calculation is more analogous to a multicomponent flash calculation than a multistage, multicomponent distillation calculation. It requires much less computer time than does conventional plate-by-plate simulation of a large column.

Two calculation methods developed by Nandakumar and Andres (1981) are presented here in algorithmic form. The first is a short cut method for use when accurate thermodynamic information is not available. This method assumes ideal solution behavior, constant relative volatilities, and temperature independent partial molar enthalpies. This calculation is based on the constancy of the enthalpy flux in each section of an adiabatic column and incorporates the effects of variable molar overflows.

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The numerical algorithm is almost identical to Underwood's minimum reflux algorithm and is as simple to use.

The second method is rigorous. It assumes only that there is invariant relative volatility ordering among the components and that the "shock model" developed by Nandakumar and Andres is valid. The vapor-liquid equilibrium relationship may be represented by an nonideal model, any nonideal enthalpy model may be assumed for the vapor or liquid phases, and any number of species may be nondistributed. The exact infinite plate limit is obtained.

The first two sections present the two calculation methods in algorithmic form and discuss various numerical methods for solving these equations. The last section presents sample results and discusses the accuracy and convergence properties of both algorithms.

SHORT CUT (Generalized Underwood) ALGORITHM

This calculation assumes ideal solution behavior, constant relative volatilities, and temperature independent molar enthalpies. The algorithm developed below assumes that the feed is completely specified and that relative volatilities and molar heats of vaporization are known for all components. It also assumes that split specifications for two components, HS and LS, are given.

Given:

(i) $\{Z_i^o \mid i = 1,2, \ldots C\}$, molar component feed rates.
(ii) $Z\Delta H^o$, difference between total enthalpy feed rate and that of a saturated liquid feed.
(iii) $\{\alpha_i \mid i = 1,2, \ldots C\}$, relative volatility of each component.

$$\alpha_1 > \alpha_2 > \ldots . \alpha_C \tag{1}$$

(iv) $\{\Delta H_i \mid i = 1,2, \ldots C\}$, molar heat of vaporization of each component.
(v) $\{ZD_{LS} = Z_{LS}^D/Z_{LS}^B$ and $ZD_{HS} = Z_{HS}^D/Z_{HS}^B\}$, splits between distillate and bottom products.

Equations:

$$\sum_{i=1}^{C} \frac{\alpha_i\, \Delta H_i\, Z_i^o}{\alpha_i - \phi_k} = Z\Delta H^o \qquad (k = lk, \ldots, hk - 1) \tag{2}$$

$$\sum_{i=1}^{C} \frac{\alpha_i\, \Delta H_i\, x_i^o}{\alpha_i - \phi_k} = 0 \qquad (k = 1, \ldots, C - 1) \tag{3}$$

$$\sum_{i=1}^{hk} \frac{\alpha_i\, \Delta H_i\, Z_i^D}{\alpha_i - \phi_k} = V\Delta H^d \qquad (k = 1, \ldots hk - 1) \tag{4}$$

$$\sum_{i=1}^{hk} \frac{\alpha_i\, \Delta H_i\, x_i^d}{\alpha_i - \phi_k} = 0 \qquad (k = 1, \ldots hk - 1) \tag{5}$$

$$\sum_{i=lk}^{C} \frac{\alpha_i\, \Delta H_i\, Z_i^B}{\alpha_i - \phi_k} = -V\Delta H^b \qquad (k = lk, \ldots . C - 1) \tag{6}$$

$$\sum_{i=lk}^{C} \frac{\alpha_i\, \Delta H_i\, x_i^b}{\alpha_i - \phi_k} = 0 \qquad (k = lk, \ldots C - 1) \tag{7}$$

Algorithm:

(1) Solve Eq. 2 for $\{\phi_k \mid k = 1, \ldots C - 1\}$.
(2) Estimate lk and hk and solve Eq. 4 for

$$\{Z_i^D \mid i = lk, \ldots . hk\ (i \neq LS, HS)\} \text{ and } V\,\Delta H^d$$

Note: $Z_{LS}^D = Z_{LS}^o\left(\dfrac{ZD_{LS}}{ZD_{LS} + 1}\right)$ and $Z_{HS}^D = Z_{HS}^o\left(\dfrac{ZD_{HS}}{ZD_{HS} + 1}\right)$

$$Z_i^D = 0\ (i > hk) \text{ and } Z_i^D = Z_i^o (i < lk)$$

If the distillate product flows are negative or greater than Z_i^o, adjust lk and hk and repeat the solution of Eq. 4. If $Z_i^D < 0$, set $hk = i - 1$ and $Z_i^D = 0$. If $Z_i^D > Z_i^o$, set $lk = i + 1$ and $Z_i^D = Z_i^o$. Let the default estimate for lk and hk be: $lk = 1$ and $hk = C$.

In many practical applications $lk = LS$ and $hk = HS$. If this is known *a priori*, only ϕ_k for $k = lk, \ldots hk - 1$ need be calculated in Step (1).

Alternate column specifications such as total distillate rate, $\sum_{i=1}^{hk} Z_i^D$, or condenser duty, $V\,\Delta H^d$, can be substituted for ZD_{LS} and/or ZD_{HS}.

(3) Solve for the bottom product flows

$$Z_i^B = Z_i^o - Z_i^D \quad (i = 1, \ldots C) \tag{8}$$

$$V\,\Delta H^b = V\,\Delta H^d - Z\Delta H^o \tag{9}$$

(4) Solve Eq. 4 for $\phi_{hk} < \alpha_{hk}$; $\phi_{hk} = L^d/K^dV^d$. Then solve

$$Z_i^d = L^d x_i^d(\phi_{hk}^{-1}\alpha_i - 1) \quad (i = 1, \ldots, hk)$$

and

$$\sum_{i=1}^{hk} x_i^d = 1$$

for

$$\{x_i^d \mid i = 1, \ldots, hk\} \text{ and } L^d$$

(5) Solve Eq. 6 for $\phi_{lk-1} > \alpha_{lk}$; $\phi_{lk-1} = L^b/K^bV^b$. Then, solve

$$Z_i^b = L^b x_i^b(1 - \phi_{lk-1}^{-1}\alpha_i) \quad (i = lk, \ldots, C)$$

and

$$\sum_{i=lk}^{C} x_i^b = 1$$

for

$$\{x_i^b \mid i = lk, \ldots, C\} \text{ and } L^b.$$

(6) Solve Eq. 4 for $\phi_k (k = 1, \ldots, lk - 1)$ and Eq. 6 for $\phi_k (k = hk, \ldots, C - 1)$. Then solve Eq. 3 and $\sum_{i=1}^{C} x_i^o$ for

$$\{x_i^o \mid i = 1, \ldots, C\}.$$

This algorithm is a generalization of Underwood's classic minimum reflux algorithm. The two are identical whenever the molar heats of vaporization of all components are set equal to one.

The roots of Eqs. 2-7 are bounded by the relative volatilities

$$\alpha_k > \phi_k > \alpha_{k+1} \tag{10}$$

It was found that a short Fibonacci search to reduce this interval followed by Newton-Raphson iteration gave rapid convergence. The rest of the algorithm involves linear equations which can be solved by standard matrix inversion.

RIGOROUS ALGORITHM (Steady-State Shock Model)

This calculation assumes invariant relative volatility ordering among the chemical species. A two level algorithm is proposed. The inner iteration assumes pseudo ideal solution behavior. The outer iteration accounts for nonideality.

Inner Iteration

This calculation involves solving a set of $(C + 2(d + b - 2) + 5)$

nonlinear algebraic equations for the variables:

$\{((TD^j, VD^j) \mid j = 2, \ldots d); LD^d; VD^1; TO;$

$(x_i^o \mid i = 1, \ldots . C); VB^1; LB^b; ((TB^j, VB^j))\ j = 2, \ldots b)\}$

where $d = C - hk + 1$ and $b = lk$.

Given:

(*i*) $\{Z_i^o \mid i = 1,2 \ldots C\}$, molar component feed rates.
(ii) ZH^o, total enthalpy feed rate.
(iii) $\{KD_i^j(T) \mid i = 1,2, \ldots C$ and $| = 2, \ldots d\}$,
$\{KO_i(T) \mid i = 1,2, \ldots C\}$, and
$\{KB_i^j(T) \mid i = 1,2, \ldots C$ and $j = 2, \ldots b\}$, equilibrium

constants for all components at all composition states as a function of temperature

(iv) $\{HD_i^j(T), hD_i^j(T) \mid i = 1,2, \ldots C$ and $j = 2, \ldots d\}$,
$\{HO_i^j(T), hO_i^j(T) \mid i = 1,2, \ldots C\}$, and
$\{HB_i^j(T), hB_i^j(T) \mid i = 1,2, \ldots C$ and $j = 2, \ldots b\}$,

partial molar enthalpies in vapor and in liquid for all components at all composition states as a function of temperature.

(v) $\{hk, lk, ZD_{hk}, ZD_{lk}\}$, heavy and light keys and their respective splits

Equations: Set of 2 $(d - 1)$ equations representing "bubble point" and "energy conservation" relations for the upper pinch and the virtual states that interconnect the feed stage and the upper pinch

$$\sum_{i=1}^{C+1-k} KD_i^k x_i^o \prod_{j=2}^{k} AD_i^j - 1 = 0 \quad (k = 2, \ldots d) \tag{11}$$

$$VD^k(HD^k - hD^k) + VD^{k-1}(1 - KD^{k-1}_{C+2-k})hD^k$$
$$+ VD^{k-1}(KD^{k-1}_{C+2-k}hD^{k-1} - HD^{k-1}) = 0 \quad (k = 2, \ldots d) \tag{12}$$

where

$$AD_i^j = \frac{VD^{j-1}(KD_i^{j-1} - KD^{j-1}_{C+2-j})}{VD^j(KD_i^j - 1) - VD^{j-1}(KD^{j-1}_{C+2-j} - 1)}$$

$$HD^j = \sum_{i=1}^{C+1-j} HD_i^j KD_i^j x_i^o \prod_{k=2}^{j} AD_i^k$$

and

$$hD^j = \sum_{i=1}^{C+1-j} hD_i^j x_i^o \prod_{k=2}^{j} AD_i^k$$

Set of $C + 5$ equations that couple the upper and lower sections of the column

$$(VD^d KD_i^d - LD^d) \prod_{j=2}^{d} AD_i^j x_i^o - Z_i^o = 0 \quad (i < lk) \tag{13}$$

$$[(VD^d KD_i^d - LD^d) \prod_{j=2}^{d} AD_i^j$$
$$+ (LB^b - VB^b KB_i^b) \prod_{j=2}^{b} AB_i^j] x_i^o - Z_i^o = 0$$
$$(lk \le i \le hk) \tag{14}$$

$$(LB^b - VB^b KB_i^b) \prod_{j=2}^{b} AB_i^j x_i^o - Z_i^o = 0 \quad (i > hk) \tag{15}$$

$$\sum_{i=1}^{C} KO_i x_i^o - 1 = 0 \tag{16}$$

$$VD^d - LD^d - VB^b + LB^b - \sum_{i=1}^{C} Z_i^o = 0 \tag{17}$$

$$VD^d HD^d - LD^d hD^d - VB^b HB^b + LB^b hB^b - ZH^o = 0 \tag{18}$$

$$(VD^d KD^d_{hk} - LD^d) \prod_{j=2}^{d} AD^j_{hk}$$
$$- ZD_{hk}(LB^b - VB^b KB^b_{hk}) \prod_{j=2}^{b} AB^j_{hk} = 0 \tag{19}$$

$$(VD^d KD^d_{lk} - LD^d) \prod_{j=2}^{d} AD^j_{lk}$$
$$- ZD_{lk}(LB^b - VB^b KB^b_{lk}) \prod_{j=2}^{b} AB^j_{lk} = 0 \tag{20}$$

Set of $2(b - 1)$ equations representing "bubble point" and "energy conservation" relations for the lower pinch and the virtual states that interconnect the feed stage and the lower pinch

$$\sum_{i=k}^{C} KB_i^k x_i^o \prod_{j=2}^{k} AB_i^j - 1 = 0 \quad (k = 2, \ldots b) \tag{21}$$

$$VB^k(HB^k - hB^k) + VB^{k-1}(1 - KB^{k-1}_{k-1})hB^k$$
$$+ VB^{k-1}(KB^{k-1}_{k-1}hB^{k-1} - HB^{k-1}) = 0 \quad (k = 2, \ldots b) \tag{22}$$

where

$$AB_i^j = \frac{VB^{j-1}(KB_i^{j-1} - KB^{j-1}_{j-1})}{VB^j(KB_i^j - 1) - VB^{j-1}(KB^{j-1}_{j-1} - 1)}$$

$$HB^j = \sum_{i=j}^{C} HB_i^j KB_i^j x_i^o \prod_{k=2}^{j} AB_i^k$$

and

$$hB^j = \sum_{i=j}^{C} hB_i^j x_i^o \prod_{k=2}^{j} AB_i^k$$

Eqs. 11-22 completely determine minimum reflux conditions for the ideal solution case. This description is much simpler than that required by other approachs, e.g., Chien (1978) and Tavana and Hanson (1979), which are based on plate-by-plate simulation. The minimum reflux description has been reduced to something more analogous to a multicomponent flash calculation than to a multiplate, multicomponent, distillation calculation.

Algorithm:

(1) Obtain an initial estimate for the $C + 2(d + b - 2) + 5$ variables.

This estimate may be obtained through use of the short cut algorithm described in the previous section. The temperatures at the top pinch, feed stage, the bottom pinch can be obtained by means of a bubble point calculation. The temperatures and vapor flows at the various virtual stages can be estimated by linear interpolation between the feed stage and the pinches.

(2) Solve Eqs. 11-22 by a suitable iteration procedure.

(3) Solve for the top and bottom product flows.

$$Z_i^D = (VD^d KD_i^d - LD^d) x_i^o \prod_{j=2}^{d} AD_i^j \quad (lk \le i \le hk) \tag{23}$$

$$Z_i^D = 0 \quad (i > hk) \tag{24}$$

$$Z_i^D = Z_i^o \quad (i < lk) \tag{25}$$

and

$$Z_i^B = Z_i^o - Z_i^D \tag{26}$$

(4) Solve for the compositions at the pinches

$$x_i^d = x_i^o \prod_{j=2}^{d} AD_i^j \quad (i \le hk) \tag{27}$$

$$x_i^b = x_i^o \prod_{j=2}^{b} AB_i^j \quad (i \ge lk) \tag{28}$$

Several numerical methods for solving Eqs. 11-22 were tested. First, decomposition approaches, in which subsets of the entire equation set were solved sequentially, were tried. All these approaches exhibited convergence problems. Next, the complete set of equations were solved simultaneously using: 1) Newton-Raphson, 2) Levenberg-Marquardt, and 3) projection methods.

Represent the nonlinear equation set as:

$$f(\underset{\sim}{x}) = 0 \tag{29}$$

with the Jacobian, $\underset{\approx}{J}(\underset{\sim}{x})$. If $\underset{\sim}{\delta}^k$ is the correction to $\underset{\sim}{x}^k$ at the k-th iteration, i.e.,

$$\underset{\sim}{x}^{k+1} = \underset{\sim}{x}^k + \underset{\sim}{\delta}^k \tag{30}$$

then $\underset{\sim}{\delta}^k$ is calculated as follows for the three methods:

1. Newton-Raphson Method

$$\sum_{j=1}^{N} J_{ij}^k \delta_j^k + f_i^k = 0 \quad (i = 1, \ldots N) \tag{31}$$

2. Levenberg-Marquardt Method (Levenberg, 1944; Marquardt, 1963)

$$\sum_{j=1}^{N} \left[\mu^k I_{ij} + \sum_{l=1}^{N} J_{li}^k J_{lj}^k\right]\delta_j^k \quad + \sum_{l=1}^{N} J_{li}^k f_l^k = 0 \quad (i = 1, \ldots N) \tag{32}$$

where μ^k is a parameter which is to be chosen in such a way that the residual decreases. Note that as $\mu^k \rightarrow 0$, the method reduces to Newton-Raphson, and as $\mu^k \rightarrow \infty$, the method reduces to steepest descent. Let

$$\begin{aligned} \mu^k &= \mu^{k-1}/C_1 \quad (k = 1,2, \ldots) \\ \mu^o &= C_o \end{aligned} \tag{33}$$

If the initial guess for $\underset{\sim}{x}$ is poor, choose C_o large and C_1 small. If the initial guess is good, make C_o small and C_1 large.

3. Projection Method (Georg and Keller, 1976)

$$\sum_{j \epsilon B_k} \left(\sum_{l=1}^{N} J_{lj}^k J_{li}^k\right)\delta_j^k + \sum_{l=1}^{N} J_{li}^k f_l^k = 0 \quad (i \epsilon B_k) \tag{34}$$

where B_k has the indices of the subset of equations to be solved at the k-th iteration. This index set is determined by a procedure outlined by Georg and Keller (1976). Note that when $B_k = [1, \ldots N]$, the method reduces to Newton-Raphson.

All of the iteration methods required evaluation of the Jacobian for Eqs. 11-22. Analytical evaluation of this Jacobian was found to be about three times faster than numerical evaluation even though the coding is much more complicated.

Outer Iteration

This calculation involves solving for the compositions at the pinches and at each virtual state interconnecting the two pinches. These compositions are then used to define new equilibrium constants and partial molar enthalpies for use in the inner iteration.

Given:

(i) $\{K_i(\{x\};T)|i = 1,2, \ldots C\}$, vapor-liquid equilibrium model.

(ii) $\{H_i(\{y\};T)|i = 1,2, \ldots C\}$, model for partial molar enthalpies of vapor.

(iii) $\{h_i(\{x\};T)|i = 1,2, \ldots C\}$, Model for partial molar enthalpies of liquid.

Equations:

$$xD_i^k = x_i^o \prod_{j=2}^{k} AD_i^j \quad \begin{matrix} (i \leq C + 1 - k) \\ (k = 2, \ldots d) \end{matrix} \tag{35}$$

$$xB_i^k = x_i^o \prod_{j=2}^{k} AB_i^j \quad \begin{matrix} (i \geq k) \\ (k = 2, \ldots b) \end{matrix} \tag{36}$$

Algorithm:

(1) Solve Eqs. 35 and 36 for xD_i^k and xB_i^k using values for AD_i^j and AB_i^j obtained from the inner iteration.

TABLE 1. COMPARISON OF DIFFERENT NUMERICAL METHODS FOR SOLVING RIGOROUS ALGORITHM

Components:	Ethane, Propane, N-Butane, N-Pentane, Octane
Specifications:	$Z_i^o = [0.2, 0.2, 0.2, 0.2, 0.2]$, $\Delta V = 0^*$, $ZD_4 = 0.05$, $ZD_2 = 2.5$
Initial Guesses:	$VD^1 = VD^2 = VB^1 = VB^2 = 0.43$, $LB^2 = 1.04$, $LD^2 = 0.04$, $x_i^o = [0.132, 0.249, 0.216, 0.209, 0.194]$
Case (1) . .	$TO = 354.44$, $TD^2 = 342.78$, $TB^2 = 382.78$°K
Case (2) . .	$TO = 361.11$, $TD^2 = 333.33$, $TB^2 = 388.89$°K
Case (3) . .	$TO = 333.33$, $TD^2 = 305.56$, $TB^2 = 361.11$°K

Case No.		Newton-Raphson	Levenberg-Marquardt	Projection Method $TOL = 0.25$	Projection Method $TOL = 0.05$
1.	Error	<1E-10	<1E-10	<1E-10	<1E-10
	No. Iter.	6	55	14	21
	CPU (s)	0.34	1.75	0.54	0.73
2.	Error	<1E-10	<1E-10	<1E-10	<1E-10
	No. Iter.	7	50	19	25
	CPU (s)	0.36	1.59	0.76	0.83
3.	Error	—	<1E-10	<1E-10	<1E-10
	No. Iter.	diverged	54	30	29
	CPU (s)	—	1.57	0.98	0.96

---

*$\Delta V = 0$ indicates that $VD^1 = VB^1$.

(2) Check current values of xD_i^d and xB_i^b against previous estimates. If residuals are greater than the specified tolerance level, revaluate the equilibrium constants and partial molar enthalpies to be used in the inner iteration and return to that calculation. If residuals are less than the specified tolerance, terminate the calculation.

The choice of a two level iteration was motivated by a desire to keep all Jacobian evaluations and matrix inversions small. We can combine the two levels by adding virtual state and pinch compositions to the variable set chosen for the present inner iteration. But this increases the dimension of the calculations substantially. For example, if we have a ten component feed and four nondistributed components, the present inner iteration involves 23 equations. However, if the non-ideal solution case is solved by means of a single level iteration, 53 equations must be included. In most cases, composition corrections to both equilibrium constants and partial molar enthalpies are relatively small, and in such cases the two level iteration converges rapidly.

TABLE 2. NONPHYSICAL SOLUTIONS OBTAINED WITH UNREALISTIC SPECIFICATIONS

Components:	Ethane, Propane, n-Butane, n-Pentane, Octane
Specifications:	$Z_i^o = [0.2, 0.2, 0.2, 0.2, 0.2]$, $\Delta V = 0$, $ZD_4 = 0.5$, $ZD_2 = 1.5$

	Solution 1		Solution 2	
	XD_i^d	XB_i^b	XD_i^d	XB_i^b
x_1	0.1929	0.0000	0.2318	0.0000
x_2	0.2485	0.4661	0.2522	−0.0288
x_3	0.2478	0.1915	0.2941	−0.1051
x_4	0.3108	0.1499	0.2218	0.9821
x_5	0.0000	0.1923	0.0000	0.1518
T(°K)	336.31	370.04	327.16	473.98
L	−0.1733	1.0542	−0.2770	1.6415
V	0.2842	0.5117	0.2112	1.1297

Table 3. Comparison Between Shock Model and Finite Stage Model for a Five-Component System

Components: Ethane, Propane, n-Butane, n-Pentane, Octane
Specifications: $Z_i^o = [0.1, 0.2, 0.4, 0.2, 0.1]$, $p = 300$ psia $= 2.07 \times 10^6$ Pa, $\Delta V = 0$
1. Shock Model: $ZD_4 = 0.168$, $ZD_2 = 12.8$
2. Finite Stage Model: $LD = 0.150$, $\sum_i Z_i^D = 0.3975$, 80 Plates, Feed Tray = 35

	Shock Model					Finite Stage Model				
	Z_i^D	XD_i^d	XO_i	$XB_i{}^b$	Z_i^B	Z_i^D	XD_i^d	XO_i	XB_i^b	Z_i^B
x_1	0.1000	0.0497	0.0476	0.0000	0.0000	0.1000	0.0497	0.0476	0.000	0.0000
x_2	0.1855	0.2458	0.2296	0.2543	0.0145	0.1855	0.246	0.2297	0.257	0.0145
x_3	0.1092	0.4700	0.4258	0.4440	0.2908	0.1090	0.468	0.4256	0.433	0.2910
x_4	0.0033	0.2368	0.2086	0.2130	0.1967	0.0033	0.237	0.2085	0.212	0.1967
x_5	0.0000	0.0000	0.0884	0.0887	0.1000	0.0000	0.000	0.0884	0.088	0.1000
T(°K)	—	336.43	371.99	382.81	—	—	366.40	371.97	382.79	—
L	—	0.1503	—	1.1503	0.6020	—	0.150	—	1.150	0.6025
V	0.3980	0.5484	—	0.5484	—	0.3975	0.548	—	0.548	—

RESULTS AND DISCUSSION

All the examples in this section make use of equilibrium and enthalpy data taken from Holland (1963). As these data are independent of composition, our discussion is confined to the ideal solution case.

The rate of convergence of the rigorous algorithm is illustrated in Table 1. Each of the numerical iteration methods discussed earlier was used for comparison. Clearly Newton-Raphson is the best method when good initial guesses are available (Cases 1 and 2). This method, however, seems to be the first to diverge as the initial guesses worsen (Case 3). The Levenberg-Marquardt method converges for a wider range of initial guesses than does Newton-Raphson but at a slower rate. We found no evidence in any of our examples for the claim (Georg and Keller, 1976) that projection methods are more efficient than Newton-Raphson. However, the projection method seems to converge for a wider range of initial guesses than does Newton-Raphson as is seen in Table 1.

We have successfully used Newton-Raphson to solve the rigorous minimum reflux algorithm for a wide variety of sample problems (Nandakumar, 1979). Good initial guesses are obtained by use of the new short cut algorithm described earlier. In the examples studied, the largest being an eight component system with four nondistributed components, results accurate to about 10 significant digits were obtained on an IBM 360/91 in 2 s or less. The comparable times for plate-by-plate simulation (80 stages) were ≳20 s.

The rigorous algorithm requires specification of both light and heavy keys and their splits. In a sense this can constitute an over specification of the separation. Certain ranges of split specifications are incompatible with the requirement that the components are keys. In such cases the rigorous algorithm converges to a non-physical solution. This non-physical nature is reflected by negative flows or compositions.

Table 2 illustrates one such example. The system studied is the same as used in Table 1 but with relaxed split specifications. In this case one expects more of the components to become distributed and hence one should change the light and heavy key designations accordingly. But we have maintained the original keys, resulting in a situation in which there is no possible physical solution. Multiple solutions are often encountered in such cases. Solutions 1 and 2 were obtained by starting with the same initial guesses but using Newton-Raphson and projection methods, respectively. Multiple nonphysical solutions have also been obtained by using a single iteration method and different initial guesses.

Table 4. Comparison Between Shock Model and Finite Stage Model for a Five-Component System

Components: Ethane, Propane, n-Butane, n-Pentane, Octane
Specifications: $Z_i^o = [0.1, 0.2, 0.4, 0.2, 0.1]$, $p = 300$ psia $= 2.07 \times 10^6$ Pa, $\Delta V = 0$
1. Shock Model: $ZD_4 = 0.032$, $ZD_3 = 0.300$
2. Finite Stage Model: $Q_{\text{condenser}} = 2.5 \times 10^6$ J/s, $\sum_i Z_i^D = 0.3975$, 80 Plates, Feed Tray = 35

	Shock Model				Finite Stage Model			
No.	Z_i^D	XD_i^d	XB_i^b	Z_i^B	Z_i^D	XD_i^d	XB_i^b	Z_i^B
x_1	0.1000	0.0544	0.0000	0.0000	0.0996	0.0542	0.0000	0.0000
x_2	0.2000	0.2914	0.0000	0.0000	0.1990	0.290	0.0000	0.0000
x_3	0.0924	0.4213	0.7258	0.3076	0.0925	0.421	0.724	0.3079
x_4	0.0062	0.2329	0.2032	0.1938	0.0062	0.235	0.205	0.1943
x_5	0.0000	0.0000	0.0711	0.1000	0.0000	0.0000	0.072	0.1000
T(°K)	—	362.03	404.25	—	—	362.32	404.42	—
L	—	0.11296	1.4717	0.6014	—	0.153	1.512	0.6025
V	0.3986	0.5115	0.8703	—	0.3975	0.551	0.910	—

TABLE 5. COMPARISON OF NEW SHORT CUT ALGORITHM AND UNDERWOOD ALGORITHM

Components: Ethane, Propane, n-Butane, n-Pentane, Octane
Specifications: Z_i^o = [0.1, 0.2, 0.4, 0.2, 0.1], Liquid Feed
$ZD_4 = 0.005$, $ZD_3 = 10.0$

	New Short Cut Algorithm		Underwood Algorithm	
	Upper Pinch	Lower Pinch	Upper Pinch	Lower Pinch
L	0.4172	1.2692	0.4051	1.4051
V	1.0818	0.9338	1.0697	1.0697

In most cases a correct a priori designation of the keys is obtained from the short cut algorithm.

A number of examples were solved using both the rigorous minimum reflux algorithm and a detailed plate-by-plate calculation [Nandakumar (1979)]. The purpose of these calculations was to empirically confirm the validity of the steady-state shock model. The plate-by-plate simulation was accomplished by sequentially: 1) assuming temperatures and flows at each stage; 2) solving the component mass balances using a tridiagonal system solver; 3) solving bubble point and energy conservation equations to get new temperature and flow estimates, etc. For the general non-constant flow case significant convergence problems were encountered with this algorithm. Thus, the results in such cases are accurate only to about 3 significant digits. Better results, good to about 4 significant digits, were obtained when the molar overflows were held constant.

Tables 3 and 4 present sample solutions of the shock model algorithm and of the finite plate algorithm. Constant molar flow conditions were assumed for the calculations underlying Table 3. Note that in this case $(d + b - 2)$ energy conservation equations in the shock model algorithm drop out and only $C + (d + b - 2) + 5$ equations must be solved. The agreement between the two calculations is essentially exact. For the non-constant flow example presented in Table 4 the agreement is again within the accuracy of the plate-by-plate simulation.

The short cut algorithm described in this work is computationally identical to Underwood's classic minimum reflux algorithm.

The new algorithm should be used in place of Underwood's algorithm whenever molar heats of vaporization are known. It is particularly useful when minimum reflux estimates for column energy flows are desired. Table 5 (see also Nandakumar and Andres, 1981) illustrates this point. The vapor flow in the bottom pinch region as calculated by the variable overflow algorithm is 13% lower than the Underwood prediction for this example. Applying an energy balance a posteriori to the Underwood solution, one finds that this method has in effect assumed a subcooled feed in order to satisfy its assumption that the vapor flow in both pinch regions of the column is the same.

NOTATION

AB_i^j = xB_i^j/xB_i^{j-1}, mole fraction ratio in stripping section
AD_i^j = xD_i^j/xD_i^{j-1}, mole fraction ratio in rectifying section
B_k = set of indices used in projection method
C = total number of components in feed
$f(\underset{\sim}{x})$ = set of nonlinear equations in $\underset{\sim}{x}$
H = enthalpy of vapor phase defined on molar basis
h = enthalpy of liquid phase defined on molar basis
H_i = partial molar enthalpy of component i in vapor
h_i = partial molar enthalpy of component i in liquid
(ΔH_i) = latent heat of vaporization of component i
hk = heavy key component (heaviest component in distillate)
J = Jacobian of $f(\underset{\sim}{x})$
K_i = vapor-liquid equilibrium constant of component i
L = liquid flow rate defined on molar basis
lk = light key component (lightest component in bottom product)
p = pressure
T = absolute temperature
V = vapor flow rate defined on molar basis
x_i = liquid mole fraction of component i
y_i = vapor mole fraction of component i
Z_i = molar rate of component i
ZH = total enthalpy rate
ZD_i = product specification defined as split of component i between distillate and bottom produce (Z_i^D/Z_i^B)
$Z\Delta H^o$ = difference between enthalpy of feed and enthalpy of a saturated liquid feed

Greek Letters

α_i = relative volatility of component i
$\underset{\sim}{\delta}$ = correction to $\underset{\sim}{x}$
ϕ_i = Underwood roots
μ = a parameter used in Levenberg-Marquardt method

Subscripts

hk = heavy key component
HS = specific heavy component
i = component identification number
lk = light key
LS = specific light component

Superscripts

B = a quantity defined for the stripping section
b = a quantity defined at the stripping pinch ($b = lk$)
D = a quantity defined for the rectifying section
d = a quantity defined at the rectifying pinch ($d = C - hk + 1$)
j, k = define virtual states (plateau compositions)
o = quantities defined for the feed zone

Note: Variables like temperature, flow rates, etc. are defined in the rectifying section, feed zone, and stripping section by appending the letters D, O, and B, respectively.

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