

# A Robust Method To Solve Mass Balances in Reversible Column Sections

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Reversible composition profiles in azeotropic and reactive distillation were used as pieces of new methods for the prediction of product composition regions and minimum reflux in single- and multiple-feed columns. A simple and robust algorithm to solve the nonlinear equation system corresponding to mass and energy balances in a reversible distillation column section for highly nonideal mixtures is proposed. If a distillate (bottom) is specified, one additional variable has to be set to calculate a cross section in the rectifying (stripping) part. We initially use the concentration of the component to be eliminated in the section as the variable to be fixed. A former direct successive substitution (DSS) procedure used in a previous paper is here analyzed, and the conditions for convergence are discussed. A damped Newton–Raphson method (DNR) is an alternative also presented. The new algorithm involves an improved direct successive substitution (IDSS) outer loop and a bubble point temperature (BUTE) loop included. By assuming the liquid phase composition at the reversible section, solving BUTE, and using geometric considerations, a related “hypothetical” product composition can be calculated. The difference between the real and the “hypothetical” product composition is used to recompute the liquid phase. This method can be considered robust in view that it does not use derivative calculations that cause numerical drawbacks in cases that maxima, minima, or turning points are reached. The initialization variables are the liquid mole fractions instead of temperatures and component flow rates, resulting in a more general case-independent method. The geometrical characteristics allow that the algorithm can be initialized in any arbitrary region of the concentration simplex. For constant relative volatility (CRV) mixtures, a small number of iterations are needed despite the start point selected. The convergence was found always satisfactory independently of the start point, even when inversions in volatility order of some components take place. Finally, a variant (secant) of imbedding homotopy continuation is proposed to efficiently trace the complete path of the reversible profile, using the IDSS algorithm as the corrector. This combination becomes necessary when multiple disjoint branches of a product pinch point curve must be computed in highly nonideal mixtures. Other approaches to the problem are mentioned and their results compared.

## 1. Introduction

The design and evaluation of distillation sequences are commonly carried out to obtain optimal structures and operating conditions which satisfy some economical criteria. Many methods to support the selection of distillation sequences have been developed, but most of these are based on heuristics and shortcuts; otherwise, they require difficult and time-consuming optimization procedures. The fundamental literature can be found in several review articles (Nishida et al., 1981; Westberg, 1985; Floquet, 1988). Among the most important diagnosis variables, the minimum reflux of a definite separation plays the central role in determining optimal alternatives. Normally, the trade-off between energy and investment costs operates as the decision factor for single columns. Both the energy consumption and the tower diameter increase while the number of trays decreases as functions of the reflux value. Today the tendency is to select a reflux value as close as possible to the minimum.

The minimum reflux prediction can be tackled either via rigorous or shortcut methods. In synthesis and optimization problems shortcut methods are preferable due to their lower computation effort. At least two such procedures are successful in working with highly nonideal mixtures: the “zero volume criterion (ZVC)” (Julka and Doherty, 1990, 1993) and the “minimum angle criterion (MAC)” (Koehler et al., 1991). The first of

these was developed from the computation of all the pinch compositions which could appear in column sections operating at minimum reflux conditions.

A pinch in a distillation column section is characterized by the equilibrium conditions between the vapor and liquid streams which come into contact in the same plate. Such a situation takes place at each position in the reversible rectification (Fonyo, 1974; Petlyuk et al., 1981), and because of this, reversible profiles are associated with pinch calculations. The pinch compositions corresponding both to the stripping and to the rectifying sides determine characteristic hyperplanes in the concentration simplex (Franklin and Forsyth, 1953). The minimum reflux corresponds just with the “contact” of one of the hyperplanes of the stripping with one of the hyperplanes of the rectifying section. This “contact” generally occurs with an hyperplane containing the feed composition (Franklin and Forsyth, 1953); we refer to this case as “feed pinch case”. For quaternary mixtures and direct separation, one pinch of the stripping side “contacts” the hyperplane conformed with three pinches of the rectifying side. This “contact” can be mathematically determined by the zero volume criterion in the concentration simplex. For systems showing tangent pinches, the design method proposed by Fidkowski et al. (1991) can be used. The mentioned contributions (Julka and Doherty, 1990, 1993; Fidkowski et al., 1991) must determine the location of all the pinch points of the distillation map for distinct values of the reflux ratio.

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An alternative to the design was proposed through the minimum angle criterion (Koehler et al., 1991): only one characteristic pinch at each side of a column is selected; the stripping pinch is associated with the rectifying pinch by means of the energy balance. Finally, the minimum reflux condition is given when the angle between the two composition vectors connecting the pinch points on the reversible rectifying and stripping profiles to the feed point is a minimum. Newly, the complete reversible path must be obtained, but for different values of the key component mole fraction.

By computing reversible profiles, one can evaluate not only minimum reflux requirements but also heat demand profiles along column sections, which can be used in the design of distillation sequences and heat integration (Terranova and Westerberg, 1989; Koehler et al., 1992). Furthermore, these heat profiles allow us to identify tangent pinches showing a greater minimum energy demand than the energy demand of the "conventional" saddle or end pinch (Koehler et al., 1991). Another important aspect involving the use of this method is that related to the computation of the complete reversible profiles to determine the feasible product regions for a given feed composition (Wahnschafft et al., 1992; Fidkowski et al., 1993; Poellmann and Blass, 1994; Espinosa et al., 1995).

This work proposes the analysis of the equation system of the reversible mass and energy balances. We will also show that the method used in a previous paper, from now on called the DSS method (Koehler et al., 1991), always converges for constant relative volatility (CRV) mixtures. As we will show later, if a distillate (bottom) is specified, one additional variable has to be set to calculate a cross section in the rectifying (stripping) part. We initially use the concentration of the component to be eliminated in the section as the variable to be fixed. Since this algorithm is part of others even more complex, the robustness is almost a necessary condition. The DSS algorithm fails in problems involving highly nonideal mixtures; then, we propose an improved method (IDSS method) which allows us to deal with such systems. In design, the complete reversible profile is of interest; then, imbedding homotopy (Rion and Van Brunt, 1990) using internal variables as parameters is an appropriated method to track the path when multiple disjoint branches of a product pinch point curve must be computed in highly nonideal mixtures. Fidkowski et al. (1991) propose the use of pseudo-arc-length continuation to resolve the difficulties presented when parametric continuation with  $\lambda = 1/r$  is used for finding pinch points. The continuation method recommended by Fidkowski et al. (1991) is the pseudo-arc-length, predictor-corrector algorithm of Keller (1987). [Fidkowski et al. (1991) refer back to Keller (1977).] Our approach to the corrector (the new IDSS) requires no derivative calculations; therefore, we will develop an imbedding homotopy algorithm without derivatives, too. In our case the path is followed approximating the augmented Jacobian of the solution curve with the secant in two consecutive points. Moreover, we consider the original problem variables (component mole fractions) as homotopy parameters.

The algorithm and equations developed in the paper are related to conventional distillation, but it should be noted that, using the transformed composition presented in a previous paper (Espinosa et al., 1995), the same applies to reactive distillation as well.

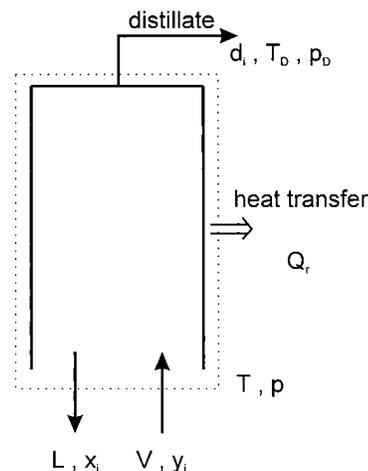


Figure 1. Reversible column: control volume in the rectifying section.

## 2. Model for Reversible Rectification and Problem Characteristics

The conditions for a reversible distillation column are the following:

- (1) Heat to and from the column has to be transferred at zero temperature difference.
- (2) Without any device for a reversible pressure adjustment no pressure drop along the column owing to hydrodynamic resistance (friction) is allowed. The column commonly is assumed to operate at constant pressure.
- (3) No contact of nonequilibrium liquid and vapor streams is allowed at any point in the column, including at the column's top and bottom, and—above all—at the feed point.

As opposed to requirements 1 and 2, which are common assumptions in all approximate rectification calculations, requirement 3 defines the inherent differences between the adiabatic and reversible rectification models and imposes severe restrictions. The reversible separation must go from equilibrium state to equilibrium state in infinitesimally small concentration steps. Consequently, reversible rectification columns would be infinitely high. It must be emphasized that this model should not be confounded with the idea of equilibrium stages, where *stage-leaving* streams are assumed to be in equilibrium.

The enriching section of a multicomponent rectification column is depicted in Figure 1. Note that in a completely general case the locations of heat transfer are not yet fixed. Considering that the countercurrent liquid and vapor streams are in equilibrium, the mathematical formulation for isobaric operation is

$$\begin{aligned}
 Vy_i - Lx_i - d_i &= 0 \\
 \sum x_i - 1 &= 0; \quad \sum y_i - 1 = 0 \\
 y_i - K_i x_i &= 0 \\
 Vh^V - Lh^L - h^P \sum d_i - Q_r &= 0 \\
 p - p_D &= 0 \\
 K_i - K_i(\mathbf{x}, \mathbf{y}, T, p) &= 0 \\
 h - h(\mathbf{x}, \mathbf{y}, T, p) &= 0 \quad (1)
 \end{aligned}$$

with  $i = 1, \dots, n_C$ ,  $n_C$  being the number of components.

It can be shown (Kaibel, 1987; Koehler et al., 1991) that  $3n_C + 7$  equations are connecting any arbitrary column cross section to the distillate. An analogous system of equations can be derived for the stripping section. The degree of freedom of the system is  $n_C + 3$ ; consequently  $n_C + 3$  variables have to be set to completely describe the system of Figure 1. If a distillate is specified, which requires assignment of  $n_C + 2$  variables of the product stream ( $n_C$  product component flows  $d_i$  and the condenser temperature and pressure), one additional variable has to be set to calculate a cross section in the rectifying part. Choose, e.g.,  $Q_r$  as this free variable. For any value we select, at least one physically meaningful solution of the system of equations exists. If we wish to "move along" the column,  $Q_r$  must be varied. The column cannot operate adiabatically, even if it were infinitely high. Vapor and liquid flows have to be adjusted continuously by condensation and vaporization to maintain phase equilibrium. Among others, Fitzmorris and Mah (1980), Flower and Jackson (1964), and Naka et al., (1980) devised column schemes for which heat distribution curves could be realized.

In our previous paper (Koehler et al., 1991) we have concluded that any approach that relies on solving the algebraic system of equations for a given value of the external reflux ratio or the equivalent  $Q_r$  suffers from numerical drawbacks. Julka and Doherty (1992) obtained similar results. In order to produce a reliable algorithm, our suggestion was do not use the reflux ratio as the variable to be fixed because multiple solutions can exist and the iterative procedure could oscillate between distinct points and therefore it becomes more unstable. Instead use a variable that increases/decreases monotonically between the column end and the respective pinch. We resorted to the concentration of the component to be eliminated in the section. An additional advantage with this selection is preserved: the material and energy balances can be decoupled and hence, enthalpy calculations can be ignored until convergence of the reduced system of eq 1 has been achieved. We will return later to this topic.

For constant volatility order mixtures (CVOM) containing  $n_C$  components from which only  $n_D$  components are present in the distillate, it can be seen from Franklin and Forsyth (1953) and Nandakumar and Andres (1981) papers that there exist at least  $n_C - (n_D - 1)$  solutions for the equations system at a given external reflux ratio and for all these solutions it is satisfied  $x_i \geq 0$  and  $y_i \geq 0$ . Furthermore, these solutions are characterized by

$$S[1]: x_i > 0 \{i \leq n_D\}; \text{ otherwise } x_i = 0$$

$$S[2]: x_i > 0 \{i \leq n_D \text{ and } i = n_D + 1\}; \\ \text{ otherwise } x_i = 0$$

$$S[3]: x_i > 0 \{i \leq n_D \text{ and } i = n_D + 2\}; \\ \text{ otherwise } x_i = 0$$

⋮

$$S[j]: x_i > 0 \{i \leq n_D \text{ and } i = n_D + (j - 1)\}; \\ \text{ otherwise } x_i = 0$$

⋮

$$S[n_C - (n_D - 1)]: x_i > 0 \{i \leq n_D \text{ and } i = n_C\}; \\ \text{ otherwise } x_i = 0$$

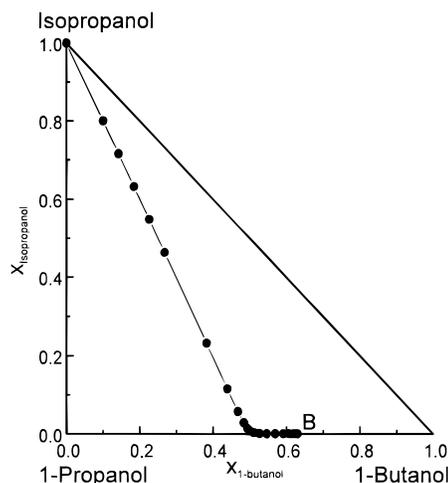
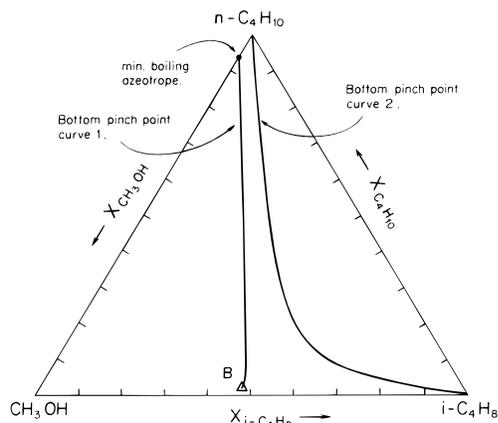


Figure 2. Reversible path for a bottom: distillative alcoholic mixture.

where  $n_C$  and  $n_D$  represent the number of components in the feed and in the distillate, respectively. In line with this assertion, near ideal ternary distillative mixtures will give two reversible paths if the distillate contains only the two most volatile components (Koehler et al., 1991). These curves can be plotted in the concentration simplex by joining the solutions for different values of the reflux ratio. One of them follows the triangle edge corresponding to the most volatile components while the other completely lies within the triangular diagram, i.e.  $x_i \neq 0$  for all the species. Alternatively, if the residue curve maps are calculated (Doherty and Perkins, 1978), the thermodynamically optimum separation path (pinch point curve) for the given distillate can be graphically constructed by finding the points on the residue curves with their tangents passing through the distillate (Wahnschafft et al., 1992). In an analogous manner, the same occurs for near-ideal quaternary reactive systems when a set of transformed compositions are defined (Espinosa et al., 1995).

As we quoted above, the reversible path that completely lies within the triangular diagram can be more easily obtained if the composition of the component to be eliminated in the section is selected as the fixed parameter instead of the reflux ratio (or  $Q_r$ ). The pinch point curve lying in the triangle edge corresponds to a binary system, and therefore, no iterations in concentrations are needed. Figure 2 shows the reversible path (pinch point curve) in the triangular diagram for a bottom containing 62.97% 1-butanol, 36.98% 1-propanol, and 0.05% 2-propanol. In obtaining this curve, a method developed in Koehler et al., (1991) was applied.

On the other hand, if the condition of CVOM is not valid, which is the case for azeotropic and reacting mixtures, multiple stationary points can be found. For highly nonideal ternary distillative and quaternary reactive mixtures (Wahnschafft et al., 1992; Espinosa et al., 1995) geometric explanations can be given. Assuming a product containing all the components present in the feed stream, then there exists at least one pinch point curve (a branch) for a given distillate that represents the thermodynamically optimum separation. However, an additional pinch point curve (another branch) can appear when the highly nonideal behavior of the mixture gives rise to inflections in the residue curves, and therefore, a new solution to the reversible model equations there exists. For CVOM no inflections in the residue curves appear and, hence, only



**Figure 3.** Multiple branches of a bottom pinch point curve: reactive mixture containing  $\text{CH}_3\text{OH}$ ,  $i\text{-C}_4\text{H}_8$ , MTBE, and  $n\text{-C}_4\text{H}_{10}$  (inert).

one pinch point curve corresponds to a given distillate. Figure 3 shows two pinch point curves for a given bottom composition in a quaternary reactive mixture for which a new set of transformed compositions were defined (Espinosa et al., 1995) in order to apply the well-known geometrical properties of distillative mixtures to reactive ones.

As can be seen in Figure 3, multiple solutions can also appear for a given inert transformed composition (i.e., for any line parallel to the  $\text{CH}_3\text{OH}/i\text{-C}_4\text{H}_8$  axis above the bottom composition) due to the disjoint branches of the pinch curve. Hence, for these difficult cases a homotopy continuation method must be used to reach the desired solution. Since the complete path must be obtained, an imbedding continuation method is also desirable. Despite the concepts above, the selection of the mole fraction of the component to be eliminated as the parameter is again an option better than the reflux ratio. In fact, at each of the branches of the pinch point curve multiple solutions can exist for a given value of the reflux ratio. This behavior typically appears in columns operating at minimum reflux conditions showing tangential pinches (Koehler et al., 1991). In addition, describing the complete path by varying  $r$  (i.e., from 0 to  $1.2r_{\min}$ ) is also inconvenient because a small change in the reflux ratio causes a jump of the pinch concentration at the tangential pinch location. For this reason, the algorithm proposed by Terranova and Westerberg (1989) that uses the reflux ratio as the fixed variable can only be applied for near-ideal mixtures. Fidkowski et al. (1991) recommend a pseudo-arc-length continuation algorithm.

The approach presented here is to solve the equation system given by eq 1 only when the concentration of a pivot component in a section is the fixed parameter. As we mentioned above, with this concentration selection, the energy balance and the enthalpy calculations are dropped from the system of eq 1. This problem appears to be similar to a flash calculation of types I and IV according to the classification given by Boston and Britt (1978) in which that problem can be solved either by the theta method or by the method proposed in that paper. However, these procedures cannot be satisfactorily extended to solve eq 1. In fact, we have found that for cases including inversion in the volatility order between any nonkey species and one key component, adapted theta methods must be controlled and modified during the same iteration which leads to oscillating behavior of the system. The structural difference causing this is clearly due to the sign change in the first

equation of the system of eq 1 (Terranova and Westerberg, 1989). Furthermore, for CVOM, any adaptation of the theta method is not satisfactory because of the great number of equilibrium calculations needed for the system given by eq 1.

In the following sections we will expose two methodologies based on direct successive substitution. The first direct successive substitution (DSS) method (Koehler et al., 1991) was generated by rearranging the reduced equation system given by eq 1 in such a way to obtain a set of recursive formulas. The coefficients of these formulas must be corrected in each iteration (solving a bubble point temperature subroutine BUTE), and they contain the prefixed values of the problem and the relative volatilities of all the components. This method was employed for most cases including mixtures showing inversion in the volatility order. However, convergence to negative concentrations or even no convergence after 2000 iterations in some special difficult cases was found. In this paper we demonstrate that under constant relative volatility (CRV) assumptions, the algorithm proposed in Koehler et al. (1991) converges for all initial liquid concentration values selected to start the calculation.

Also a damped Newton–Raphson (DNR) method is presented for this special equation system and the characteristics of this method are analyzed.

In addition, an improved direct successive substitution (IDSS) method is developed on the basis of the geometrical conditions that must be fulfilled by the compositions of the liquid and vapor phases at a given cross section and by the product composition. By assuming the liquid phase composition at the reversible section and solving the bubble point temperature subroutine (BUTE), a hypothetical product composition can be calculated. The concentration errors between the hypothetical product composition and the real product composition are used to recompute the liquid phase and, after normalization, to return to the first step.

Finally, when the goal is to find the complete reversible path, the IDSS method is used in combination with (secant) imbedding homotopy continuation. The results of several recent contributions (Terranova and Westerberg, 1989; Fidkowski et al., 1991; Poellmann and Blass, 1994) are mentioned.

### 3. Direct Successive Substitution Procedure

In a previous paper (Koehler et al., 1991), a direct successive substitution procedure generated to solve the equations system given in eq 1 was presented. The eq 1 system was rearranged to satisfy the following requirements:

(i) For any given initial value of the liquid phase composition used to start the calculation, the convergence must be assured. In other words, global convergence should be guaranteed.

(ii) The number of equilibrium calculations should be the minimum into each iteration.

For this method we will demonstrate that, for CRV mixtures, condition i is asserted, needing for ii only one equilibrium calculation for all the procedure. For mixtures showing either inversion in the volatility order or great changes in the values of the volatilities, neither condition i nor condition ii can be demonstrated; the success for convergence depends strongly upon the start point. Furthermore, it has been found that multiple solutions can occur, some of these with negative con

centrations; in most of such cases the algorithm converges to the nonphysical solution.

In order to show how the system is rearranged and conditions i and ii are satisfied, consider the following mass balances for the rectifying section,

$$Vy_i - Lx_i = d_i \quad (2)$$

$$V = L + D \quad (3)$$

and the equilibrium relationship,

$$y_i = \frac{\alpha_i x_i}{\sum x_j \alpha_j} \quad (4)$$

where  $\alpha_i$  is the relative volatility of component  $i$ . Rewriting eq 2 for the two most and least volatile components lc and hc that do appear in the column section, eliminating the liquid flow  $L$ , and using eqs 3 and eq 4, leads to

$$L = \frac{\alpha_{lc}}{\alpha_{lc} - \alpha_{hc}} \left( \frac{\alpha_{hc} d_{lc}}{\alpha_{lc} x_{lc}} - \frac{d_{hc}}{x_{hc}} \right) \quad (5)$$

$$V = \frac{\sum x_j \alpha_j}{\alpha_{lc} - \alpha_{hc}} \left( \frac{d_{lc}}{x_{lc}} - \frac{d_{hc}}{x_{hc}} \right) \quad (6)$$

If  $x_{hc}$  is the prefixed variable, and the mixture shows constant relative volatility for all the components, eq 6 has the form

$$V = (\psi/x_{lc}) + \varphi \quad (7)$$

where  $\psi$  and  $\varphi$  are constant values for all the problems:

$$\psi = \frac{\alpha_{hc} d_{lc}}{\alpha_{lc} - \alpha_{hc}}$$

$$\varphi = d_{hc} \left[ \frac{1}{y_{Dhc}} - \frac{\alpha_{lc}}{x_{hc}(\alpha_{lc} - \alpha_{hc})} \right] \quad (8)$$

It is important to note that once we have fixed the heavy key component composition, the vapor flow rate  $V$  depends only of the light key component mole fraction. This occurs due to the severe restriction imposed by the thermodynamical equilibrium over the liquid and vapor compositions at any point of the reversible enriching section.

The concentration  $x_j$  for the remaining species can be expressed from eqs 2 and 3 as

$$x_i = \frac{d_i}{V[(y_i/x_i) - 1] + D} \quad i \neq hc, \quad i \neq lc \quad (9)$$

By using the nonkey component balance and the heavy component balance, a more convenient expression for  $x_i$  can be obtained:

$$x_i = \frac{1}{V\eta_i - \mu_i} \quad (10)$$

$$\eta_i = \frac{\alpha_i - \alpha_{hc}}{\alpha_{hc} d_i}; \quad \mu_i = \frac{d_{hc}}{\alpha_{hc} d_i} \left( \frac{\alpha_i - \alpha_{hc}}{y_{Dhc}} - \frac{\alpha_i}{x_{hc}} \right)$$

where again the coefficients  $\eta_i$  and  $\mu_i$  are constant for the problem if the mixture shows constant relative

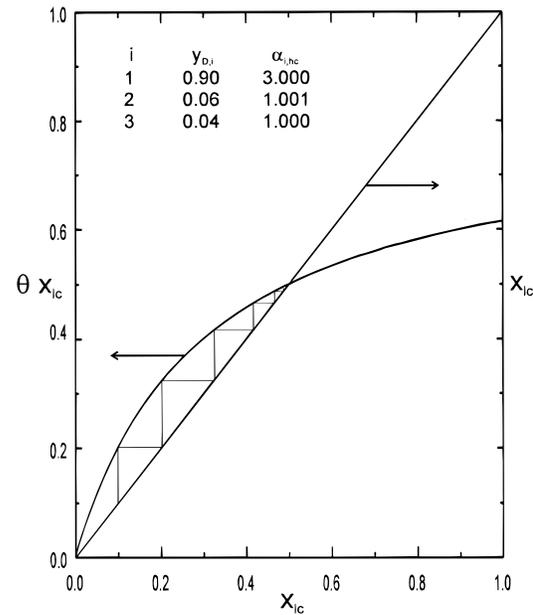


Figure 4. DSS method for a CRV mixture.

volatility. From eqs 7 and 10, the summation of mole fractions for the nonkey components results:

$$\sum_{\substack{i \neq hc \\ i \neq lc}} x_i = \sum \frac{1}{[(\psi/x_{lc}) + \varphi]\eta_i - \mu_i} \quad (11)$$

In addition, the mole fraction summation over all the components must be equal 1; therefore, the following relationship must be obeyed at convergence:

$$x_{lc} + \sum_{\substack{i \neq hc \\ i \neq lc}} x_i = 1 - x_{hc} \quad (12)$$

Into the iterative procedure we define

$$\Theta = \frac{1 - x_{hc}}{x_{lc} + \sum_{\substack{i \neq hc \\ i \neq lc}} x_i} \quad (13)$$

with  $\Theta = 1$  holding at the solution. From eq 11 we have an expression of  $\Theta$  as a function of  $x_{lc}$ :

$$\Theta = \frac{1 - x_{hc}}{x_{lc}[1 + g(x_{lc})]} \quad (14)$$

$$g(x_{lc}) = \sum_{\substack{i \neq hc \\ i \neq lc}} \frac{1}{[\eta_i \psi + x_{lc}(\varphi \eta_i - \mu_i)]}$$

Let us examine the function defined as

$$\Theta x_{lc} \equiv \frac{1 - x_{hc}}{1 + g(x_{lc})} \quad (15)$$

This function plotted against  $x_{lc}$ , the iterative variable, is shown in Figure 4 for a ternary mixture showing CRV behavior ( $x_{hc} = 0.20$ ). The coefficients of eq 10, from which this function is derived, are fixed values only under the two following conditions: constant relative volatility and fixed  $x_{hc}$ . In Figure 4, the function  $x_{lc}$  is also depicted. From this figure it is easy to recognize

that the successive substitution procedure, also sketched in Figure 4, based on the following recursive calculation,

$$x_{lc}^{new} = \frac{1 - x_{hc}}{1 + g(x_{lc}^{old})} \quad (16)$$

will result convergent assuming only nonnegative concentrations at the start point. It can be shown that eq 15 has only nonnegative coefficients and, hence, the first and second derivative show constant signs for  $x_{lc} \geq 0$ . In fact, introducing eqs 8 and eq 10 into eq 15 we get

$$\Theta_{x_{lc}} = \frac{1 - x_{hc}}{1 + \sum_{\substack{i \neq hc \\ i \neq lc}} \left[ \frac{\alpha_i - \alpha_{hc}}{\alpha_{lc} - \alpha_{hc}} \frac{d_{lc}}{d_i} + x_{lc} \frac{d_{hc}}{x_{hc} d_i} \frac{\alpha_{lc} - \alpha_i}{\alpha_{lc} - \alpha_{hc}} \right]^{-1}} \quad (17)$$

which under the assumptions:  $\alpha_{lc} > \alpha_i > \alpha_{hc}$  results in an expression in  $x_{lc}$  with strictly positive first and strictly negative second derivatives (see the Appendix).

In addition,  $\Theta_{x_{lc}}$  tends to values greater than zero when  $x_{lc}$  tends to zero and asymptotically to  $1 - x_{hc}$  when the iterative variable tends to infinity. Because of this, the iterative function is a strictly monotonically increasing function of the light key mole fraction defined between 0 and  $1 - x_{hc}$ . From these characteristics, it follows that  $|(\Theta_{x_{lc}})'| < 1$  at the solution. Therefore, the direct substitution procedure will be convergent for any starting value  $x_{lc}^0$  greater or less than the value of the  $x_{lc}$  corresponding to the solution.

It must be kept in mind that Figure 4 shows the solution process based on the rearranged equations obtained from eq 1 and assuming constant relative volatility. The analysis for the CRV mixtures will be also applicable to situations in which relative volatilities change but only if those changes are small. On the other hand, convergence cannot be assured for highly nonideal systems. For these mixtures, the iterative function is not necessarily a strictly monotonically increasing function with strictly positive first and strictly negative second derivatives because the coefficients of eq 17 (or  $a_i$  and  $b_i$  of eq A1 in the Appendix) are now composition and temperature dependent. As a result of this, new terms must be considered in the calculation of the first derivative of eq 17 and  $|(\Theta_{x_{lc}})'| < 1$  at the solution is not guaranteed.

The algorithm proposed in our earlier paper for both ideal and nonideal mixtures will be here summarized:

Vapor and liquid flows and their compositions for any cross section in a reversible rectifying section (i.e., under assumption of vapor–liquid equilibrium) can be calculated according the following algorithm, if distillate concentrations are given:

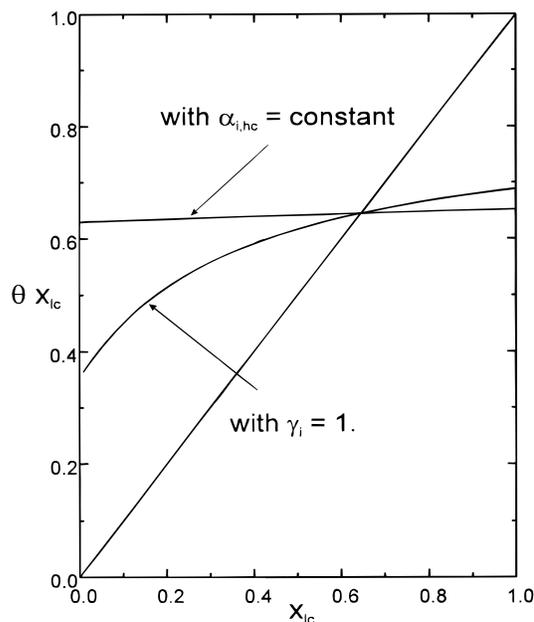
(1) Since the degree of freedom is 1, the concentration of the least volatile component  $x_{hc}$  is selected as the parameter.

(2) Estimate the concentrations for the liquid phase:  $x_{i, i \neq hc}$ .

(3) Compute the vapor–liquid equilibrium by means of a bubble point temperature routine, the  $k_i$  values, and consequently  $\alpha_i = k_i/k_{hc}$  values.

(4) Calculate  $V$  from the following equation which is equivalent to eqs 7 and 8:

$$V = \left( \frac{d_{hc}}{x_{hc}} - \frac{d_{lc}}{x_{lc}} \right) \left/ \left( \frac{y_{hc}}{x_{hc}} - \frac{y_{lc}}{x_{lc}} \right) \right. \quad (18)$$



**Figure 5.** DSS method for a ternary alcoholic mixture: comparison between the algorithms with  $\alpha_i$  constant and with correction in the relative volatilities ( $\gamma_i = 1$ ) (see Table 1).

**Table 1. Data and Results Corresponding to the Graphics of Figure 5**

1. components	ethanol (lc)	1-propanol	1-butanol (hc)
2. relative volatility at solution, $\alpha_i$	4.7750	2.2003	1.0000
3. $(\alpha_i)_{x_{lc} \sim 1} - (\alpha_i)_{x_{lc} \sim 0}$ , %	12.91	5.01	0.00
4. distillate component flow rate, $d_i$	0.905 33	0.077 92	0.016 75
5. start point for iterative calculations	0.10	0.70	0.20
6. solution point	0.645 18	0.154 82	0.200 00
7. number of iterations			
DSS, $\alpha_i = \text{constant}$	DSS, $\gamma_i = 1$	IDSS	DNR
4	8	7	5 <sup>a</sup>

<sup>a</sup> With  $V_{\text{initial}} = 1$ ,  $T_{\text{initial}} = 352.8$  K,  $T_{\text{sol}} = 358.3$  K,  $V_{\text{sol}} = 1.13$ .

(5) Calculate the new compositions  $x_{i, i \neq hc}$  using eq 9.

(6) Compare the new liquid compositions to the old ones, and if convergence is not yet achieved, normalize all  $x_{i, i \neq hc}$  with the following expression and return to 3).

$$x_i^{new} = x_i^{old} \frac{1 - x_{hc}}{x_{lc}^{old} + \sum_{\substack{i \neq hc \\ i \neq lc}} x_i^{old}} \quad (19)$$

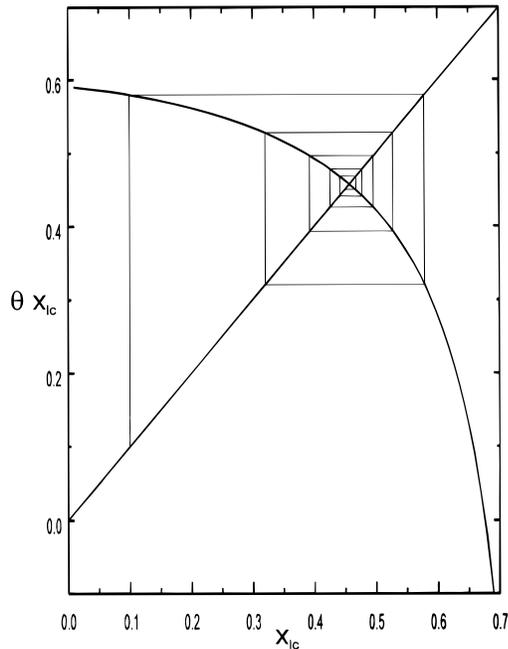
(7) Otherwise, solve the energy balance for  $Q_r$ .

The bubble point temperature routine is a direct successive substitutions calculation in the temperature, based on the approximations given by Holland (1963):

$$\ln \sum_{i=1}^{nc} y_i = \frac{K_1}{T} + K_2 \quad (20)$$

The expression used in step 6 to normalize the new concentrations, agrees with eq 15 for  $i = lc$ . In CRV mixtures concentrations other than  $x_{lc}$  and vapor–liquid equilibrium recalculations are not required. CRV assumption converts the above-stated algorithm in the procedure depicted in Figure 4.

In Figure 5 and in Table 1, a ternary system of alcohols is used to show the results of the above-



**Figure 6.** DSS method for the highly nonideal mixture: acetone–chloroform–benzene, lc = acetone (see Table 2).

**Table 2. Data and Results Corresponding to the Graphics of Figure 6**

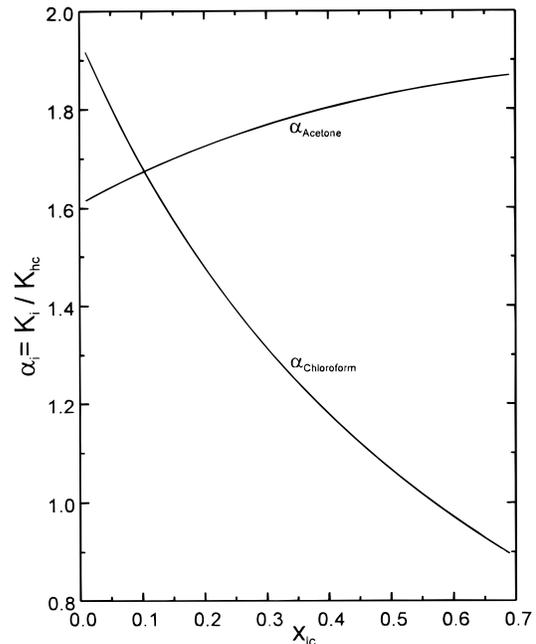
1. components	acetone (lc)	chloroform	benzene (hc)
2. distillate component flow rate	0.905 33	0.077 92	0.016 75
3. start point for iterative calculations	0.1	0.6	0.3
4. solution point	0.455 83	0.244 17	0.300 00
	5. number of iterations		
DSS	IDSS	DNR	
35	8	7 <sup>a</sup>	

<sup>a</sup> With  $V_{\text{initial}} = 1$ ,  $T_{\text{initial}} = 330.67$  K,  $T_{\text{sol}} = 337.45$  K,  $V_{\text{sol}} = 2.99$ .

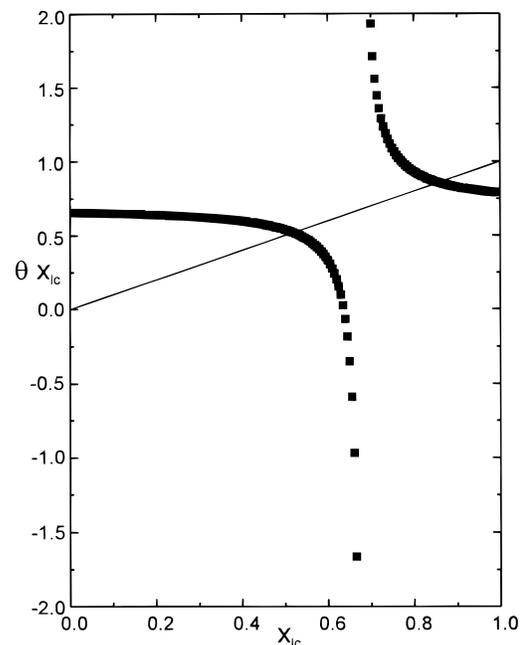
described procedures. The algorithm given through eqs 18, 9 and 19 with correction in the relative volatilities ( $\gamma_i = 1$ ) generates a curved trajectory requiring a total of eight iterations to reach the solution. On the other hand, the DSS with constant volatilities needs only four iterations to converge and the trajectory is almost flat. Both methods merge to the same solution because the volatility values for the CRV case were chosen with this purpose. Note that even in this “good system” a poor estimation of the relative volatilities could give a wrong solution if the algorithm with CRV is used.

Obviously, serious convergence difficulties can take place in working with mixtures showing high deviations from the ideality. We now present some difficult cases where the DSS algorithm fails; however it must be noted that the method works well for near-ideal systems.

In Figure 6 and in Table 2 the system acetone–chloroform–benzene was selected as test case where volatility order changes do appear. The form displayed in Figure 4 is drastically altered due to the changes in the volatilities as can be recognized in Figure 7. It is important to note that eq A2 (see the Appendix) apply no longer because the terms involving the derivative of the relative volatilities with compositions were omitted. The DSS algorithm converges to the solution in oscillating form in 35 iterations. Figure 8 and Table 3 show the same system but with other distillate specifications. For this case, the iterative function presents two neighboring solutions (one of them without physical



**Figure 7.** Relative volatilities against light component mole fraction (lc = acetone): cross section corresponding to the examples of Figures 6 and 8.



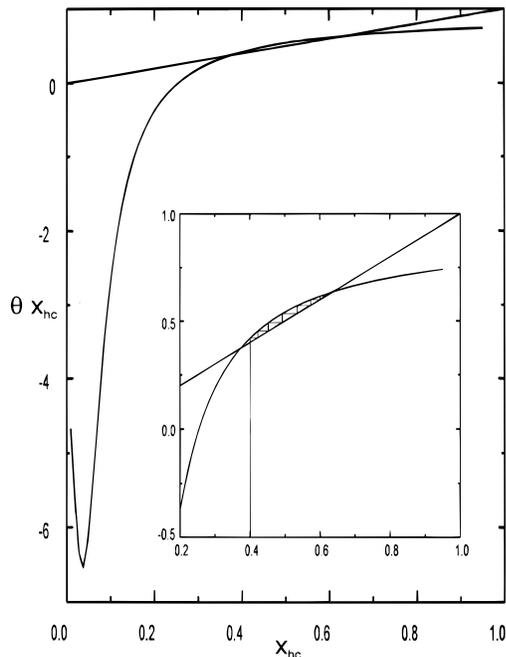
**Figure 8.** DSS method for the highly nonideal mixture: acetone–chloroform–benzene, lc = acetone (see Table 3).

**Table 3. Data and Results Corresponding to the Graphics of Figure 8**

1. components	acetone (lc)	chloroform	benzene (hc)
2. distillate component flow rate	0.95	0.03	0.02
3. start point for iterative calculations	0.1	0.6	0.3
4. solution point	0.517 476	0.182 524	0.300 000
	5. number of iterations		
DSS	IDSS	DNR	
86 (nonphysical solution)	8	7 <sup>a</sup>	

<sup>a</sup> With  $V_{\text{initial}} = 1$ ,  $T_{\text{initial}} = 329.9$  K,  $T_{\text{sol}} = 336.3$  K,  $V_{\text{sol}} = 2.75$ .

sense). The method diverges from the physical solution to converge in oscillating form to the nonphysical one in 86 iterations. Finally, Figure 9 and Table 4 cor-



**Figure 9.** DSS method for the highly nonideal mixture: acetone–chloroform–benzene, hc = benzene (see Table 4).

**Table 4. Data and Results Corresponding to the Graphics of Figure 9**

1. components	acetone (lc)	chloroform	benzene (hc)
2. bottom component flow rate	0.02	0.25	0.73
3. start point for iterative calculations	0.05	0.55	0.40
4. solution point	0.05	0.312 76	0.637 24
	5. number of iterations		
DSS	IDSS	DNR	
19	7	6 <sup>a</sup> /8 <sup>b</sup>	

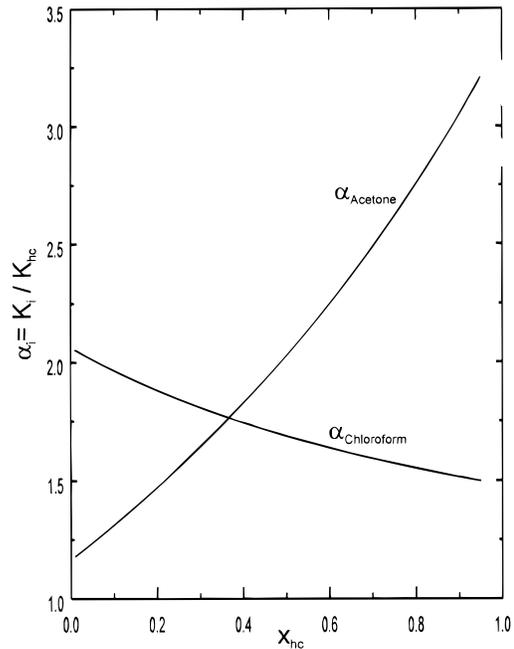
<sup>a</sup> With  $V_{\text{initial}} = 0.05B$ . <sup>b</sup> With  $V_{\text{initial}} = 0.025B$ ,  $T_{\text{initial}} = 347.8$  K,  $T_{\text{sol}} = 345.8$  K,  $V_{\text{sol}} = 0.07B$ .

respond to a reversible bottom cross section of the same system; in Figure 10 the relative volatilities are plotted against  $x_{\text{hc}}$ . Two physical solutions can be recognized, each of which corresponds to one of the branches of the pinch point curve. As pointed out in Wahnschafft et al. (1992), two branches of the pinch point curve for a given product composition are possible if the residue curves on which the product is located show an inflection. This inflection must be such that there exist other tangents to residue curves which point through the product (Figure 11). From Figure 9 it can be seen that the fixed point on the left is unstable while the one on the right is stable. Provided that the starting point for the heavy key component mole fraction is placed to the right of the unstable fixed point, the DSS will converge to the stable fixed point. Nineteen iterations were necessary to achieve the solution from  $x_{\text{hc}}^0 = 0.40$ .

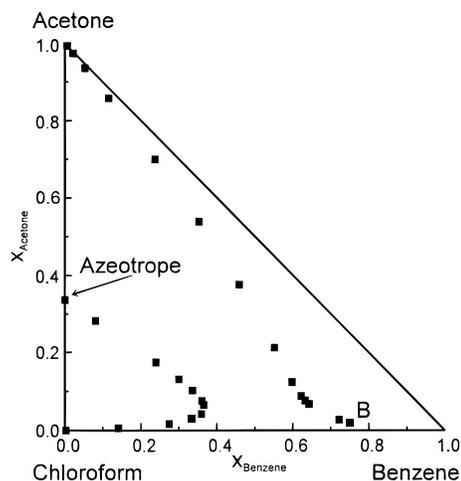
It is evident that, for these cases, the DDS iterative procedure does not guarantee the goals regarding to global convergence and minimum number of equilibrium calculations.

#### 4. Damped Newton–Raphson Algorithm for Eq 1 System

A Newton–Raphson algorithm (NR) was developed for the equations system given through eq 1. The basis equations were arranged according to the extension of



**Figure 10.** Relative volatilities against heavy component mole fraction (hc = benzene): cross section corresponding to the example of Figure 9.



**Figure 11.** Multiple branches of a bottom pinch point curve for the highly nonideal mixture: acetone–chloroform–benzene (see Table 5).

**Table 5. Reversible Stripping Path by Homotopy Continuation: Statistics**

component composition	Bottom Pinch Point Curve		
	acetone	chloroform	benzene
	0.02	0.23	0.75

statistics: total number of Euler's predictions = 18, total number of Euler's predictions discarded due to step-length control parameters = 5, total number of cross-section iterations = 34, efficiency % = useful number of cross-section iterations/total number of cross-section iterations = 68

component start point <sup>a</sup>	Disjoint Branch of the Bottom Pinch Point Curve		
	acetone	chloroform	benzene
	0.001	0.998	0.001

statistics: total number of Euler's predictions = 25, total number of Euler's predictions discarded due to secondary step-length control parameters = 11, total number of cross-section iterations = 63, efficiency % = useful number of cross-section iterations/total number of cross-section iterations = 48

<sup>a</sup> This point was corrected to achieve the initial point of the curve.

the ideas used for flash calculation. The  $n_C - 1$  liquid flow rates of components  $i$ ,  $i \neq \text{hc}$ , and the temperature were selected as iterative variables. The liquid concentration of the heavy component is the fixed parameter. The discrepancy functions  $F_i$  in terms of the iterative variables are

$$F_i = \frac{l_i + d_i}{\sum_i (l_i + d_i)} - K_i(\mathbf{x}, \mathbf{y}, T, p) \frac{l_i}{\sum_i l_i}; \quad x_i = \frac{l_i}{\sum_i l_i} \quad (21)$$

Note that the defining equation of the heavy component mole fraction in terms of the liquid flow rates is considered as an active constraint during the calculations. Numerical partial derivatives were done. A damped methodology (DNR) was also introduced by means of the step size factor  $\beta$ , with  $0 \leq \beta \leq 1$ . Numerical instabilities were found when either temperature or liquid flow rates were poorly estimated at the initialization step. As an example, in some highly nonideal systems, 5 K temperature difference between the initial value and the solution can generate a temperature correction that exceeds the limits of the vapor-pressure correlation leading to the divergence of the algorithm, even when the component liquid flow rates are assumed with the values of the solution. Other problems encountered are those related to the presence of dominant values in the Jacobian and the related errors produced. Finally near-singular and singular Jacobians were also observed in some tests for highly nonideal systems. For such difficult cases a path-following method was carried out. Moving away from an exact solution obtained by means of the DNR in an "easy to solve region" of the concentration simplex, a parametric displacement in  $x_{\text{hc}}$  is used to trace the solution path from the "easy to solve region" to the desired value of  $x_{\text{hc}}$ ,  $x_{\text{hc}}$  being the path-following parameter. The initial temperature and the liquid flow rates used in a forward point are the solutions in the actual point. The path becomes identical to the distillate pinch profile with this selection. Once an "easy" solution is obtained, the value of  $x_{\text{hc}}$  is smoothly varied from the actual toward the original value for which the problem was "difficult". This methodology is time-consuming and its success is subject to the possibility of finding points in the convergence ratio of the DNR method.

### 5. The New (IDSS) Algorithm for Eq 1 System

It was shown that both changes in the relative volatility order involving the extreme boiling components and strong dependence of the  $K_i$  values with the composition drastically alter the stability of the DSS method and really reduce the convergence radii of the DNR algorithm. Maxima, minima, or turning points in the error functions  $F$  were detected. The latter were noted especially in our path following with the DNR where initial temperature and liquid flow guesses must be carefully selected. In fact, the path following proposed in section 4 was applied to the same case as that depicted in Figure 11 using DNR. To initialize the path, vapor flow rates assumed between 0.1 and 0.2 times the bottom flow rate prevent convergence, while values from 0.2 to 0.7 lead to the path through the bottom composition. From the last value, the reached solution is located in the disjoint branch. Hence, there exist no numerically reliable ways, when using DNR, to find

initial values for all the disjoint branches of the product pinch point curve.

A robust method, based on geometrical characteristics of the problem, that can be easily initialized in any region of the simplex, is presented. The following main ideas are introduced in order to obtain the algorithm:

(i) The first idea is to use a modification of the DSS method. In fact, this approach will not demand derivative calculations which cause numerical drawback in cases where maxima, minima or turning points are close to the solution. An additional advantage is the fact that no matrix inversions or Jacobian approximations are required. Furthermore, all the parameters involved in the calculation of numerical derivatives, i.e., independent variable increments, are avoided, giving rise to a more general case-independent method.

(ii) The second idea is to use a criterion for adjusting the concentrations according to the most important variables detected in our experience. Corrections in all the liquid concentrations introduced into the iterative procedure should be made in a problem-independent way. The DNR is more problem-dependent since the temperature is strongly dependent on the class of mixture considered and, therefore, its initial value is difficult to estimate. To achieve these objectives, the following conditions are considered satisfied:

First, assuming the liquid phase compositions:

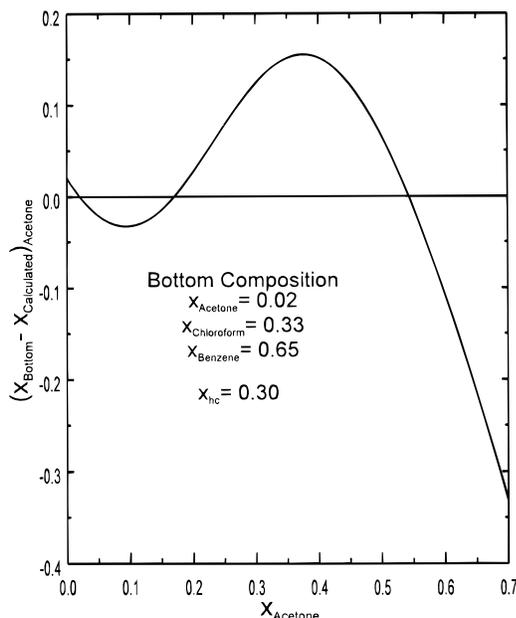
(a) The BUTE subroutine always converges and the equilibrium vapor composition can be calculated.

(b) Not only the vapor phase composition (in equilibrium with the assumed liquid) but also a set of hypothetical distillates corresponding to reversible columns can be evaluated. Only one additional variable should be fixed to completely determine one element of the hypothetical distillate composition set. The hypothetical distillate mole fraction of the heavy component hc is selected because of similar arguments as described for the selection of  $x_{\text{hc}}$  as parameter in computing reversible rectifying sections. Moreover, the hypothetical distillate composition was determined by fixing the composition of the hc component at the same value as in the real distillate.

(c) If this hypothetical distillate is just the real distillate, the solution was found; otherwise the difference between both composition vectors is a measure of how far the assumed liquid composition is from the solution.

Second, it is admitted that liquid phase concentration of component  $i$ ,  $i \neq \text{hc}$ , can be satisfactorily corrected according to the error evaluated in the distillate composition for the same component. Hence, the difference between the real and the hypothetical distillate concentration of component  $i$  gives a way to compute the new liquid concentration of component  $i$ . This decomposition, performed over the modified equation system which include the error functions with the hypothetical distillates, is appropriate for both ideal and highly nonideal mixtures. A typical error function shape calculated for such problems is depicted in Figure 12. A variant of homotopy continuation allows to assess to all these solutions when multiple solutions (multiple branches) are present. How to adapt the IDSS for the continuation algorithm will be explained later.

Vapor and liquid flows and their compositions for any cross section in a reversible rectifying section (i.e., under assumption of vapor-liquid equilibrium) can be calculated according to the following suggested algorithm, provided that distillate concentrations are given:



**Figure 12.** Typical error function in IDSS algorithm for highly nonideal mixtures.

(1) Since the degree of freedom is 1, the concentration of the least volatile component  $x_{hc}$  is selected as the parameter.

(2) As the initialization step, estimate two values for the composition vector  $\mathbf{x}^{(0)}$  and  $\mathbf{x}^{(1)}$  and calculate: the vapor–liquid equilibrium and  $\beta^{(0)}$  and  $\beta^{(1)}$  according to the general definition:

$$\beta^{(k)} = \frac{L^{(k)}}{D} = \frac{y_{D,hc} - y_{hc}^{*(k)}}{y_{hc}^{*(k)} - x_{hc}} \quad (22)$$

(3) Calculate the hypothetical distillate compositions according to the reversible mass balances and using the corresponding value of  $\beta$ . This value guarantees that the concentration of the hc component in the hypothetical distillate remains constant.

$$y_{D,i}^{(k)} = y_i^{*(k)} + \beta^{(k)}(y_i^{*(k)} - x_i^{(k)}) \quad i \neq hc \quad (23)$$

(4) From the two previously computed points, calculate the new liquid compositions:

$$x_i^{(k+1)} = x_i^{(k)} + \frac{y_{D,i} - y_{D,i}^{(k)}}{y_{D,i}^{(k-1)} - y_{D,i}^{(k)}}(x_i^{(k-1)} - x_i^{(k)}) \quad i \neq hc \quad (24)$$

and normalize.

(5) Calculate  $y_i^{*(k+1)}$ ,  $\beta^{(k+1)}$ , and  $y_{D,i}^{(k+1)}$ .

(6) If the relative error of the last hypothetical distillate becomes smaller than a prefixed  $\epsilon$ , the solution is found and go to 8; otherwise continue.

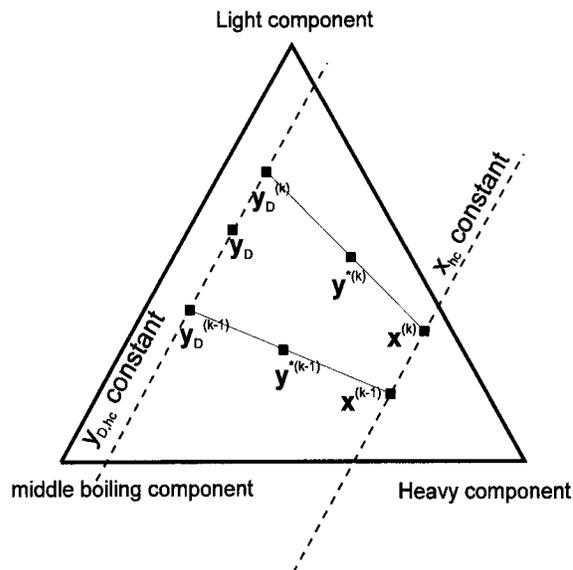
(7) Update all the variable values according to

$$\mathbf{z}^{(k+1)} \rightarrow \mathbf{z}^{(k)} \rightarrow \mathbf{z}^{(k-1)} \quad (25)$$

set  $k = k + 1$  and return to 4.

(8) Solve the energy balance for  $Q_r$ , and stop.

Figure 13 shows the geometric basis of the IDSS algorithm for a ternary system. Note that it is not necessary to initialize either the component vapor or liquid flow rates or the temperature with this method. Only two liquid composition vectors (with  $x_{hc}$  constant)



**Figure 13.** Geometric bases of the IDSS algorithm for a ternary system.

are needed for starting the IDSS algorithm. Tables 1–4 show the number of iterations necessary to achieve convergence in the previously analyzed examples. For some special difficult cases as those corresponding to Figures 11 and 12, a variant of homotopy continuation is useful to achieve all the solutions. In addition, when homotopy continuation is carried out, it is possible to trace the complete path through the product composition and all the disjoint branches of the pinch point curve. The works of Wahnschafft et al. (1992) for azeotropic mixtures and Espinosa et al. (1995) for reactive distillation clearly show the importance of obtaining these curves.

## 6. Secant Homotopy Continuation Method for Reversible Distillation

A disadvantage of Newton's method is that topological phenomena which generate singularity, or near-singularity, of the Jacobian matrix can prevent convergence. Newton's method is therefore only locally convergent and relies on initial estimates close to the solution for convergence (Rion and Van Brunt, 1990). Frequently, a large or even global convergence domain is desirable and the imbedding homotopic continuation methods allow for a greatly expanded convergence domain. In addition, multiple solutions can be easily encountered and dependence of the solution on problem parameters determined. When Newton's method is used in the correction step, the procedure to performing homotopy continuation can be summarized as follows (Rion and Van Brunt, 1990):

The path can be constructed by differentiating the equation set with respect to the arc length of the solution curve to obtain an initial value problem, using an Euler-type predictor to approximate a forward point on the path, using Newton–Raphson or DNR to correct back to the exact path, and repeating until the point of interest is reached. When the entire solution path is of interest, one of the original problem parameters can be considered as the imbedded parameter.

Because the IDSS algorithm was developed without derivative calculations, a modification of the classical homotopy continuation procedure, which uses derivative calculations in the prediction step, must be sought. It must be considered that, since the entire solution path

is of interest, we consider the original problem variables (component mole fractions) as homotopy parameters. The most important aspects included in our variant are as follows:

**Prediction Step.** The unit tangent vector obtained from the augmented Jacobian inversion at the prediction step (in the classical homotopy continuation procedure) was replaced by a secant prediction using the last two points on the homotopy path. In our method, the unit secant vector is defined on the mole fraction space. To obtain the two starting points of the continuation algorithm, the IDSS is solved for in the vicinity of pure components or azeotropes. Note that all the points belonging to the homotopy path are indeed the pinch point curve in the concentration simplex.

**Correction Step.** Once an estimate to the homotopy path is predicted using the last two points (secant prediction), the IDSS method is employed to correct back to the exact homotopy path. In order to solve the reversible equation system, one of the problem variables must be held constant. In our case, the local continuation variable (a component mole fraction) is chosen as the one whose component of the secant vector from the previous iteration has the largest absolute value (Rion and Van Brunt, 1990). This task is easily performed by changing  $x_{hc}$  in the above-stated IDSS algorithm by any of the component mole fractions (including  $x_{hc}$ ). That is, the correction step involves the possibility of selection of different component mole fractions as homotopy variables according to the topology of the product pinch curve.

**Step-Length Control.** Further improvement is achieved in continuation procedures when step-length controls are applied to the predictor. The main objectives are not to jump to other paths and not to skip portions of the solution curve. We closely follow the algorithm of Georg (1980) but adapted to our problem. This algorithm has been adopted by many researchers such as Wayburn and Seader (1987) and Frantz and Van Brunt (1987). The primary step-length control is

$$\Delta s_j = \Delta s_{j-1} \beta$$

where  $\Delta s_{j-1}$  = step length used for a previous (secant) continuation step,  $\Delta s_j$  = step length for the next (secant) continuation step, and  $\beta = \theta_{ideal}/\theta$ ,  $\theta_{ideal}$  being the ideal turning angle and  $\theta$  the local turning angle.

The local turning angle can be estimated from the last two unit secant vectors as

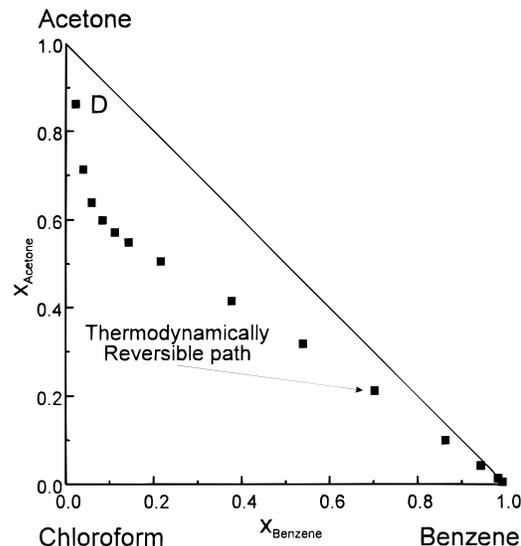
$$\theta = \cos^{-1}[\mathbf{T}_{j-1} \cdot \mathbf{T}_j]$$

with  $\mathbf{T}_j$  = unit secant vector at the current continuation step and  $\mathbf{T}_{j-1}$  = unit secant vector at the previous continuation step.

**Secondary Step-Length Control Parameters** include the number of IDSS corrections needed to converge to the exact solution from the prediction, the initial size of the corrector step, the turning angle, and the maximum and minimum step length.

The disjoint branches of the product pinch point curve can be tested by inspect all the vertices of the composition simplex. Additional information about azeotropes can be useful too. In general all the unstable (stable) nodes must be tested as probable initial points for the calculation of the pinch point curves for the bottoms (distillates).

It is important to note that the algorithm involves the possibility of selection of different homotopy variables



**Figure 14.** Thermodynamically reversible path via (secant) homotopy continuation using IDSS algorithm as the corrector (see Table 6).

according to the topology of the product pinch curve. Table 5 shows the statistics in obtaining the reversible paths corresponding to Figure 11. Figure 14 and Table 6 newly emphasize the computational economy and robustness of the method. Finally, in Figure 15 the reversible path for a nine-component mixture including hydrocarbons of very different boiling points is presented. As can be seen, our method is robust for determining all the pinch points of both the rectifying and stripping map for any specified key component mole fraction.

Other relevant contributions to solve this problem have been done. The work due to Terranova and Westerberg (1989) gives an algorithm to obtain column pinch temperatures versus reboiler and condenser duties (temperature–heat diagrams) by using the reflux ratio as fixed parameter to solve any reversible cross section. The complete rectifying path is constructed by varying the reflux ratio from 0 to  $1.2r_{min}$ . In a previous paper (Koehler et al., 1991), we have concluded that the mentioned approach fails for highly nonideal mixtures. However, the algorithm works well for near ideal systems.

Fidkowski et al. (1991) propose the use of pseudo-arc-length continuation to resolve the difficulties presented when parametric continuation with  $\lambda = 1/r$  is used for finding fixed (pinch) points. In parametric continuation, one can attempt to track all the branches of pinch points from the pure components and azeotropes ( $r \rightarrow \infty$ ,  $\lambda = 0$ ) by gradually decreasing the value of the reflux ratio and using the most recently calculated fixed points as a initial guess for a new point on a branch. The problem with this approach is that the method fails where the Jacobian becomes singular. Therefore, a simple Euler–Newton continuation is not sufficient, and an arc-length-based continuation method is required. The continuation method recommended by Fidkowski et al. (1991) is the pseudo-arc-length, predictor–corrector algorithm of Keller (1987). The algorithm is robust for determining all the fixed (pinch) points of both the rectifying and stripping map for any specified reflux ratio.

Finally, a recent paper concerning product boundaries of homogeneous azeotropic distillation (Poellmann and Blass, 1994) develops a totally different approach to solve the reversible profiles. The thermodynamically

**Table 6. Reversible Rectifying Path by Homotopy Continuation**

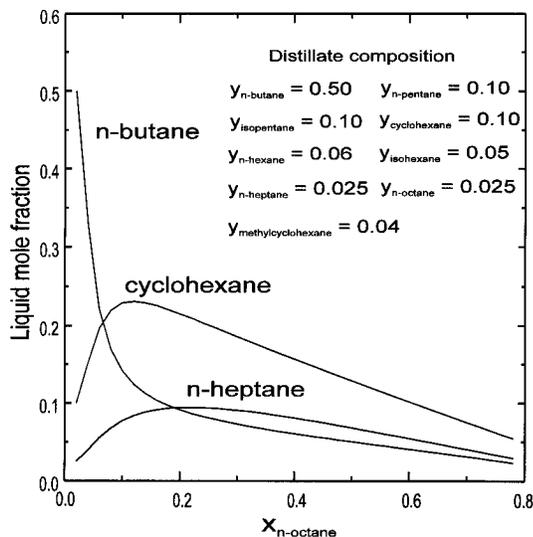
point	$x_{\text{acetone}}$	$x_{\text{chloroform}}$	$x_{\text{benzene}}$	no. of IDSS corrections (itc)
1 <sup>a</sup>	0.948 401 9	0.040 639 4	0.010 958 7	
2 <sup>b</sup>	0.905 330 0	0.077 920 0	0.016 750 0	
3	0.862 257 8	0.115 686 5	0.022 055 7	1
4	0.712 519 0	0.247 568 7	0.039 912 3	1
5	0.637 774 2	0.302 359 8	0.059 866 0	2
6	0.598 351 7	0.317 841 0	0.083 807 3	2
7	0.570 882 6	0.317 444 9	0.111 672 5	2
8	0.548 335 0	0.309 367 1	0.142 297 9	2
9	0.504 817 8	0.280 453 6	0.214 728 6	3
10	0.414 609 2	0.208 458 1	0.376 932 7	2
11	0.317 713 5	0.142 396 6	0.539 889 9	2
12	0.212 028 4	0.085 748 2	0.702 223 4	3
13	0.099 632 5	0.037 272 9	0.863 094 6	3
14	0.042 027 2	0.015 295 8	0.942 677 0	3
15	0.013 085 9	0.004 711 2	0.982 202 9	2
16	0.005 841 2	0.002 098 0	0.992 060 8	1

statistics: total number of Euler's predictions = 18, total number of Euler's predictions discarded due to step-length control parameters = 4, total number of cross-section iterations = 35

point	local continuation variable index	step-length, $\Delta s_j = \Delta s_{j-1} \theta_{\text{ideal}} / \theta$ $\Delta s_j \leq \Delta s_{\text{max}}$	turning angle, $\theta = \cos^{-1}[\mathbf{T}_{j-1} \cdot \mathbf{T}_j]$ , rad	initial length of the corrector step
1				
2				
3	1 (acetone)	0.0573	0.011 007 4	0.000 687 3
4	1	0.2000	0.003 808 3	0.000 83 2
5	1	0.1000	0.151 346 5	0.015 715 2
6	1	0.0500	0.386 136 2	0.019 414 1
7	1	0.0339	0.412 729 4	0.016 166 4
8	3 (benzene)	0.0430	0.244 892 7	0.010 437 5
9	3	0.0920	0.150 421 2	0.013 274 6
10	3	0.2000	0.051 147 3	0.009 893 5
11	3	0.2000	0.044 074 6	0.009 105 6
12	3	0.2000	0.063 853 5	0.013 635 9
13	3	0.2000	0.052 837 0	0.011 627 6
14	3	0.1000	0.027 434 3	0.002 936 2
15	3	0.0500	0.009 035 5	0.000 475 6
16	3	0.0125	0.002 908 8	0.000 037 7

step-length control:  $\theta_{\text{ideal}} = \pi/6$ ; secondary step-length control parameters:  $\Delta s_{\text{max}} = 0.2$ ,  $\text{itc}_{\text{max}} = 6$ , initial length of the IDSS correction vector  $\leq 0.05$

<sup>a</sup> Vapor compositions in equilibrium with the distillate. <sup>b</sup> Distillate compositions.



**Figure 15.** Thermodynamically reversible path via (secant) homotopy continuation using IDSS algorithm as the corrector (hydrocarbon mixture).

optimum path was interpreted as a curve in mole fraction space with the temperature as parameter. A system of linear equations for the derivative of the profile with respect to the temperature was given. Numerical integration of this derivative initiated at a

point on the desired profile yields the profile quickly and accurately. To apply this method, analytical derivatives for the activity coefficient model (Taylor and Kooijman, 1991) are required during the evaluation of the differential equation. Figure 11 of that paper is very similar with Figure 11 of our paper.

## 7. Conclusions

In this paper, the equation system describing reversible sections in distillative and reactive columns was rearranged. On this basis, it was demonstrated that the direct successive substitution method (DSS) presented in a previous paper becomes globally convergent if constant relative volatility (CRV) mixtures are involved. Despite the good behavior for near-ideal mixtures, inversions in the volatility order and high cross dependence among  $K_i$  values and compositions prevent the convergence of this algorithm.

Also, multiple solutions were recognized when the mole fraction of the pivot component was fixed in order to solve the reversible model. Geometric explanations were given to demonstrate the existence of multiple branches of a product pinch point curve. This information is very important to improve the solution strategy of the problem.

Two methodologies were studied to overcome the difficulties encountered when the DSS procedure fails.

A damped Newton–Raphson (DNR) method was first developed with component liquid flow rates and temperature as iterative variables. Solving problems with nonideal mixtures, the method shows high sensitivity with the initial variable guesses. In such cases numerical unstabilities arise because of a near singular Jacobian or extreme temperatures are computed. However, when a path-following procedure was used to trace the reversible profiles, the DNR showed good behavior. Finally, the initialization of the different disjoint branches of the reversible profiles remains a difficult task for this algorithm.

A new successive substitution method (IDSS) based on the geometrical characteristics of the problem was proposed. The initialization of the algorithm can be made from any start point because of the convergence can be considered almost global. DNR is locally more efficient than the IDSS, but the worse the initialization, the better the performance of the IDSS over the DNR.

Finally, a variant of homotopy continuation was implemented using a unit secant vector in the mole fraction space as predictor and the IDSS algorithm as corrector. The computational efficiency of this combination is very adequate for finding multiple solutions corresponding to multiple branches of a product pinch point curve. The disjoint branches can be easily determined by initiating the calculation at the nodes (pure components and azeotropes) of the composition simplex.

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### Nomenclature

$B$  = bottom product flow rate, mol/s  
 $D$  = distillate flow rate, mol/s  
 $d_i$  = distillate component flow rate, mol/s  
 $h$  = molar enthalpy, J/mol  
 $K_i$  = equilibrium ratio,  $K_i = y_i/x_i$  or  $y_i^*/x_i$   
 $K_1, K_2$  = constants in the approximation given by Holand, eq 20  
 $L$  = liquid flow rate, mol/s  
 $nc$  = number of components  
 $p$  = pressure, kPa  
 $Q$  = energy, W  
 $r$  = reflux ratio  
 $\Delta s$  = step length used during continuation step  
 $T, \mathbf{T}_j$  = temperature, unit secant vector to homotopy curve at step  $j$   
 $V$  = vapor flow rate, mol/s  
 $x_i, y_i$  = phase composition, mol/mol  
 $\mathbf{Z}$  = vector of variables in IDSS algorithm

### Greek Letters

$\alpha_i$  = relative volatility,  $\alpha_i = K_i/K_{hc}$   
 $\beta$  = step-size factor in damped Newton–Raphson,  $\beta = L/D$  in the IDSS algorithm and step-length multiplier in the (secant) homotopy continuation algorithm  
 $\gamma_i$  = activity coefficient  
 $\epsilon$  = tolerance  
 $\Theta$  = function defined by eq 13 in the DSS algorithm  
 $\theta$  = local estimate of the turning angle between secant vectors to homotopy path  
 $\lambda$  = parametric continuation variable  
 $\eta_i, \mu_i$  = coefficients defined in eq 10  
 $\Psi, \varphi$  = coefficients defined in eq 8

### Subscripts

$D$  = distillate  
 $hc$  = heavy component  
 $i$  = component index  
 $ideal$  = ideal value of the turning angle, homotopy algorithm  
 $initial$  = initial value of a iterative variable  
 $j$  = iteration number in homotopy algorithm  
 $lc$  = light component  
 $min$  = minimum  
 $r$  = reversible  
 $sol$  = solution value of a iterative variable

### Superscripts

$D$  = distillate  
 $k$  = iteration number in IDSS algorithm  
 $L$  = liquid phase  
 $new$  = new value  
 $old$  = old value  
 $V$  = vapor phase

### Appendix. Characteristics of the Iterative Function Corresponding to the DSS Algorithm

The function  $x_{lc} \Theta$  is given by

$$x_{lc} \Theta = \frac{1 - x_{hc}}{1 + \sum_{\substack{i \neq hc \\ i \neq lc}} \frac{1}{a_i + b_i x_{lc}}} \quad (A1)$$

and their first derivative is

$$\frac{d\Theta x_{lc}}{dx_{lc}} = \frac{(1 - x_{hc}) \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i}{(a_i + b_i x_{lc})^2}}{\left[1 + \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{1}{(a_i + b_i x_{lc})}\right]^2} \quad (A2)$$

which results strictly positive for  $x_{lc} \geq 0$ .

The second derivative is

$$\frac{d^2\Theta x_{lc}}{dx_{lc}^2} = 2 \frac{\left[ (1 - x_{hc}) \left[ \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i}{(a_i + b_i x_{lc})^2} \right]^2 \right]}{\left[ 1 + \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{1}{(a_i + b_i x_{lc})} \right]^3 - \frac{(1 - x_{hc}) \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i^2}{(a_i + b_i x_{lc})^3}}{\left[ 1 + \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{1}{(a_i + b_i x_{lc})} \right]^2}} \quad (A3)$$

By rearranging eq A3, the sign of the second derivative becomes

$$\text{sign} \frac{d^2 \Theta_{x_{lc}}}{dx_{lc}^2} = \text{sign} \left[ \left( \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i}{(a_i + b_i x_{lc})^2} \right)^2 - \left( \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i^2}{(a_i + b_i x_{lc})^3} \right) \left( 1 + \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{1}{a_i + b_i x_{lc}} \right) \right] \quad (\text{A4})$$

Assuming  $lc = 1$ ,  $hc = nc$ , where  $nc$  is the number of component presents, we have

$$\text{sign} \frac{d^2 \Theta_{x_{lc}}}{dx_{lc}^2} = \text{sign} \left[ \sum_{i=2}^{nc-1} \frac{b_i^2}{(a_i + b_i x_{lc})^4} + 2 \sum_{i=2}^{nc-1} \sum_{j>i}^{nc-1} \frac{b_i b_j}{(a_i + b_i x_{lc})^2 (a_j + b_j x_{lc})^2} - \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i^2}{(a_i + b_i x_{lc})^3} - \sum_{i=2}^{nc-1} \frac{b_i^2}{(a_i + b_i x_{lc})^4} - \sum_{i=2}^{nc-1} \sum_{\substack{j \neq i \\ j=2}}^{nc-1} \frac{b_i^2}{(a_i + b_i x_{lc})^3 (a_j + b_j x_{lc})} \right] \quad (\text{A5})$$

and rearranging the summations we have finally

$$\text{sign} \frac{d^2 \Theta_{x_{lc}}}{dx_{lc}^2} = -\text{sign} \left[ \sum_{i=2}^{nc-1} \sum_{j>i}^{nc-1} \frac{\left( \frac{b_i}{a_i + b_i x_{lc}} - \frac{b_j}{a_j + b_j x_{lc}} \right)^2}{(a_i + b_i x_{lc})(a_j + b_j x_{lc})} + \sum_{\substack{i \neq lc \\ i \neq hc}} \frac{b_i^2}{(a_i + b_i x_{lc})^3} \right] \quad (\text{A6})$$

which is a strictly negative function for  $x_{lc} \geq 0$ .

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