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A Globally-Convergent Flash Calculation for Constant K-Values Based on a Parameterization of the Tie-Line Field

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Abstract

We propose a novel approach to flash calculation, with particular application to negative flash. The ability to compute a negative flash for any composition state is important in practice, as the construction of analytical solutions for multicomponent systems by the method of characteristics (MOC) relies heavily on the identification of tie lines and tie-line extensions. MOC solutions are at the heart of some techniques for the calculation of the minimum miscibility pressure, and are the key building blocks for fast simulation of multidimensional reservoir flows by the front-tracking / streamline method.

The basis of the proposed negative-flash method is a parameterization of the tie-line field. Rather than solving the Rachford–Rice equation (or any of its variants) we solve directly for the parameters defining the tie line. For an N-component system, our approach leads to a system of $N - 2$ *quadratic* equations, which we solve efficiently using a Newton method. The iterative method is very robust: unlike other negative flash procedures, the solution displays continuous dependence on the overall composition, even in the transition to negative concentrations. We illustrate the properties and behavior of the proposed approach on three-component and four-component systems, and we then generalize the method to systems of N components. From the global triangular structure of the system with constant K-values, it follows that the system of $N-2$ quadratic equations can only have two roots. For the important case of three components, the flash calculation is explicit.

Introduction

A flash calculation consists in determining the amount of gas and liquid (and their composition) of a mixture with a known overall composition. It is an integral part of computational models in both the upstream and downstream oil industry. Flash calculations can be responsible for a significant fraction of the computational time in compositional reservoir simulation models (Gerritsen and Durlofsky, 2005).

At equilibrium, a two-phase mixture will satisfy

$$K_i = \frac{y_i}{x_i}, \tag{1}$$

for all of its chemical components $i = 1, \ldots, N$. In Equation (1), y_i and x_i are the mass fraction of component i in the vapor and liquid phases, respectively, and K_i is the equilibrium ratio (also known as K-value) for that component. In general, the K-values depend on pressure, temperature and overall composition. In this paper, we shall assume that K-values are constant. This is often a good approximation for many hydrocarbon systems at moderate pressures and temperatures (Orr, 2007). When this is not the case, the methodology presented here must be understood as the building block for an overall flash calculation in which an outer iteration is performed to determine the K-values (Michelsen, 1982; Whitson and Michelsen, 1989; Wang and Orr, 1997; Orr, 2007).

The flash problem can be expressed as follows: given a set of positive K-values, K_i, and nonnegative overall concentrations C_i satisfying $\sum_{j=1}^{N} C_j = 1$, find the gas saturation S and the concentrations in the liquid and vapor, x_i and y_i, respectively, such that

$$C_i = (1 - S)x_i + Sy_i \quad \text{for all } i = 1, \ldots, N \tag{2}$$

with the restrictions

$$\sum_{j=1}^{N} x_j = 1, \quad \sum_{j=1}^{N} y_j = 1, \quad y_i = K_i x_i \quad \text{for all } i = 1, \ldots, N. \tag{3}$$

The standard procedure for solving the flash problem is to note that

$$\sum_{j=1}^{N} y_j - \sum_{j=1}^{N} x_j = 0. \tag{4}$$

Several variants of this equation exist. The original method proposed by Rachford and Rice (1952) expressed it as a function of the vapor saturation S. Whitson and Michelsen (1989) showed that this procedure will converge even if the mixture is in the single-phase region (a calculation known as negative flash), as long as

$$\frac{1}{1 - K_{\text{max}}} < S < \frac{1}{1 - K_{\text{min}}}. \tag{5}$$

If the overall composition is far away from the two-phase region—in particular, if it is outside the region of positive overall compositions—Wang (1998), and Wang and Orr (1997), proposed to solve Equation (4) in terms of a liquid composition x_l for some component $l \in \{1, \ldots, N\}$—in fact, they assumed that $l \equiv 1$ in all cases. As we show in the next section, this procedure may diverge or converge to a spurious root even if the initial guess is arbitrarily close to the root.

The ability to compute a negative flash for *any* composition state is important in practice. The construction of analytical solutions for multicomponent systems relies heavily on the identification of tie lines (for states in the two-phase region) and tie-line extensions (for states in the single-phase regions) (Isaacson, 1980; Johansen and Winther, 1988; Johns et al., 1993; Johns and Orr, 1996; Jessen et al., 2001; Johansen et al., 2005; Wang et al., 2005; Orr, 2007; Seto, 2007; Seto and Orr, 2007). Analytical solutions to oil/gas displacements by the method of characteristics are at the heart of some techniques for the calculation of the minimum miscibility pressure (Wang and Orr, 1997; Jessen et al., 1998), and are the key building blocks for fast simulation of multidimensional reservoir flows by the front-tracking / streamline method (Seto et al., 2007; Juanes and Lie, 2007, 2008).

A tie line is a straight line in composition space that connects a liquid composition to a gas composition, both states being at thermodynamic equilibrium. Therefore, the flash problem is solved if, for a given overall composition state, the tie line passing through that state is identified. Jessen et al. (1998) presented an approach to the calculation of minimum miscibility pressure in which tie-line intersections were computed using a novel co-linearity condition that avoided convergence problems of the negative flash approaches of Whitson and Michelsen (1989), and Wang and Orr (1997). It is in this context—tie line identification in the single-phase region through a negative flash—that the developments presented here are relevant.

We propose a new approach for the (negative) flash problem. We use the three-component system to illustrate the shortcomings of existing negative flash procedures, and to develop the rationale for the new method. In this important case, the flash problem reduces to the solution of a quadratic equation. Next, we extend our analysis to the four-component system, where we show that our parameterization of the tie-line field leads to a system of two *quadratic* equations. We provide a geometric interpretation of the solution as the intersection of two conics. Newton iteration leads to quadratic convergence to the physical solution in all cases. We then generalize the framework to the N-component system. In the last section, we give some concluding remarks.

Three-Component System

Without loss of generality, we shall assume that the K-values satisfy the following ordering relations:

$$K_1 > K_2 > K_3, \quad K_1 > 1, \quad K_3 < 1. \tag{6}$$

Two cases are possible: a high-volatility intermediate component ($K_2 > 1$), and a low-volatility intermediate component ($K_2 < 1$). Typical phase diagrams for these two cases are shown in Figure 1. Compositions close to the C_1-vertex are in vapor phase, and compositions close the the C_3-vertex (the origin) are in liquid phase. For constant K-values, the vapor and liquid loci (the curves separating the single-phase regions from the two-phase region) are straight lines. We denote by $\hat{x}_i$ and $\hat{y}_i$ the intersections of the liquid and gas loci, respectively, with the C_i-axis:

$$\hat{\boldsymbol{x}}_1 = \begin{bmatrix} \hat{x}_1 \\ 0 \end{bmatrix}, \quad \hat{x}_1 = \frac{1 - K_3}{K_1 - K_3}, \quad \hat{\boldsymbol{y}}_1 = \begin{bmatrix} \hat{y}_1 \\ 0 \end{bmatrix}, \quad \hat{y}_1 = K_1 \frac{1 - K_3}{K_1 - K_3}, \tag{7}$$

$$\hat{\boldsymbol{x}}_2 = \begin{bmatrix} 0 \\ \hat{x}_2 \end{bmatrix}, \quad \hat{x}_2 = \frac{1 - K_3}{K_2 - K_3}, \quad \hat{\boldsymbol{y}}_2 = \begin{bmatrix} 0 \\ \hat{y}_2 \end{bmatrix}, \quad \hat{y}_2 = K_2 \frac{1 - K_3}{K_2 - K_3}. \tag{8}$$

If $K_2 > 1$, the C_2-component is a gas and the numeric values of $\hat{x}_2$ and $\hat{y}_2$ are less than 1. In this case, the two-phase region extends to the C_2-axis. In contrast, if $K_2 < 1$, the C_2-component is a liquid and $\hat{x}_2 > \hat{y}_2 > 1$. This means that the liquid and vapor lines intersect the diagonal edge of the triangle corresponding to $C_3 = 0$.

For any composition state on the unit triangle there exist liquid and vapor compositions that are in thermodynamic equilibrium. The straight line connecting such two compositions is called a *tie line*. Figure 1 shows the tie-line field for the cases $K_2 > 1$ (left) and $K_2 < 1$ (right).
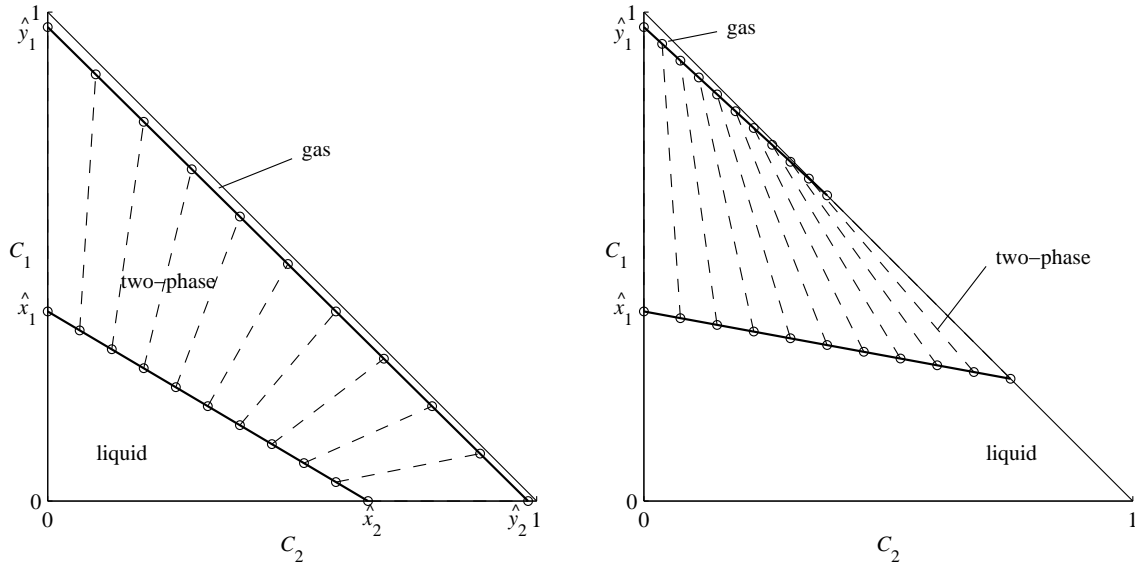
Figure 1: Ternary diagram and tie-line field for $K_2 > 1$ (left) and $K_2 < 1$ (right).
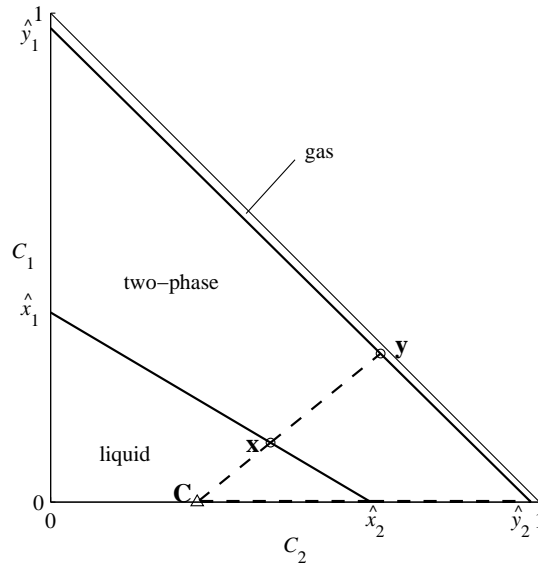

Figure 2: Ternary diagram showing the two tie lines passing through overall composition $C = (0, 0.3)$. The tie line coinciding with the axis $C_1 = 0$ would lead to analytical solutions to gas/oil displacements that do not depend continuously on the initial data, and must therefore be discarded.

Whitson and Michelsen Negative Flash. Combining Equations (1)–(4), the Rachford–Rice equation may be written in the following residual form as a function of gas saturation:

$$R(S) = \sum_{j=1}^{N} \frac{(K_j - 1)C_j}{1 + (K_j - 1)S} = 0. \tag{9}$$

This is the form employed by Whitson and Michelsen (1989). They showed that a Newton iteration will converge provided that: (1) The resulting saturation is in the range $(1 - K_{\max})^{-1} < S < (1 - K_{\min})^{-1}$; (2) The initial guess is sufficiently close to the root. This is the case as long as the overall composition is *inside* the composition triangle, that is, if all the overall concentrations are strictly positive (see, for example, Table 1 in Whitson and Michelsen (1989)). In this case, a combination of the bisection method and Newton iteration is a robust iterative technique for finding the root. As noted by Wang and Orr (1997), the procedure faces difficulties for compositions outside the range of positive concentrations. We illustrate this behavior next.

In Figure 2 we plot the tie lines passing through a reference overall concentration $C = [C_1, C_2]^t = [0, 0.3]^t$, for a system with the following K-values: $K_1 = 2.5$, $K_2 = 1.5$ and $K_3 = 0.05$. Two tie lines pass through that state: one in the interior of
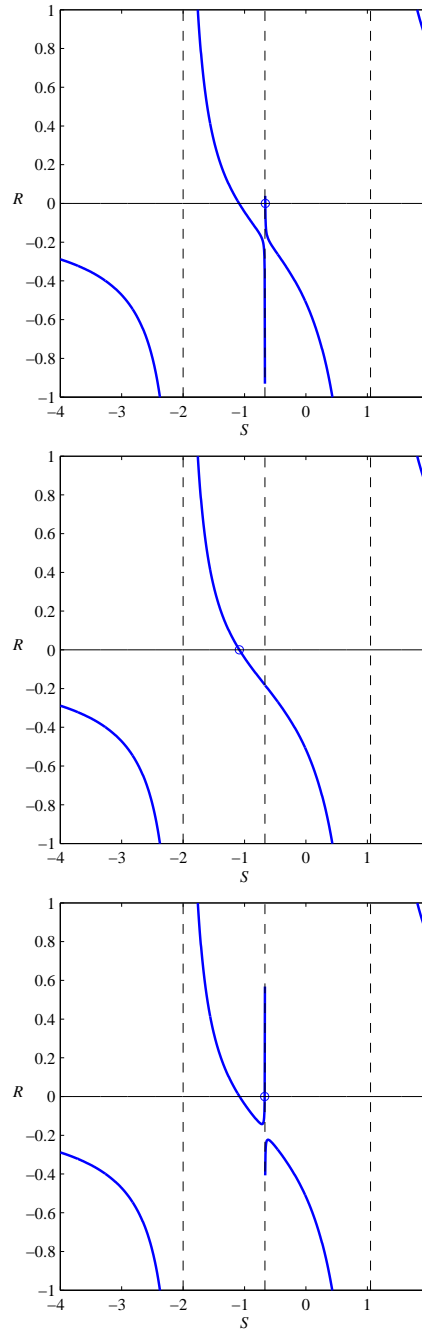
Figure 3: Residual of the Whitson–Michelsen negative flash equation (as a function of gas saturation S) for overall compositions $C = [0.001, 0.3]^t$ (top), $C = [0, 0.3]^t$ (middle), and $C = [-0.001, 0.3]^t$ (bottom).

the phase diagram, and one that coincides with the axis $C_1 = 0$. For displacements by gas of an oil with the overall composition chosen for the example, the tie line in the interior of the phase diagram is the correct tie line. The reason is that this tie line is stable under perturbation of the composition state. This is essential in the construction of analytical solutions to compositional flows (Wang and Orr, 1997; Wang et al., 2005; Orr, 2007). The existence, multiplicity, and selection of tie lines for general composition states is discussed at length later in this section, under the heading *Existence of Solutions*. Here we simply illustrate the behavior that may arise for a state near the edge $C_1 = 0$.

In Figure 3 we plot the residual $R(S)$ of Equation (9) as a function of the gas saturation for three different (but very close) compositions: one inside, one at the edge, and one outside the composition triangle. The function $R(S)$ displays a vertical asymptote at $S = \frac{1}{1-K_1} = -\frac{2}{3}$. It is the solution near the asymptote that corresponds to the physical tie line. We make two observations: (1) Convergence to this solution is not favored in any tangent-based iteration. (2) More importantly, the transition between the compositions inside and outside the ternary diagram is such that the vertical asymptote disappears, and the physical

solution is missing altogether. Any iteration will necessarily converge to the spurious solution.

Wang and Orr Negative Flash. Wang and Orr (1997) observed that "for an arbitrary overall composition, the vapor satura-tion S can vary in an unrestricted way" and they suggested to use the phase compositions instead of the phase saturations as the primary variables. Let l be an index between 1 and the number of components N. Then, for any l, the gas saturation satisfies:

$$S = \frac{C_l - x_l}{(K_l - 1)x_l}. \tag{10}$$

Substituting this expression in the Rachford–Rice equation, one obtains the following residual equation (Wang, 1998; Orr, 2007):

$$R(x_l) = \sum_{j=1}^{N} \frac{(K_j - 1)C_j(K_l - 1)x_l}{(K_j - 1)C_l + (K_l - K_j)x_l}. \tag{11}$$

Wang and Orr (1997) and Orr (2007) suggested a negative flash based on solving Equation (11) using a Newton method. This procedure, however, suffers from the same type of problem as the Whitson–Michelsen negative flash. In Figure 4 we plot the residual in Equation (11) as a function of the liquid composition x_2 (left column) for the same three overall saturations as in the previous section. The convergence behavior degrades when the composition state is near the edge—unless *a priori* knowledge of the solution is provided, Newton iteration will likely converge to the spurious root. Moreover, the physical root is, again, missing from the nonlinear equation when the composition is on the edge of the composition triangle. The behavior of the residual as a function of x_3 (Figure 4, right column) is analogous. For the choice x_1, the residual for a composition on the axis $C_1 = 0$ is singular, and no iteration can be defined.

Proposed Flash. The proposed approach to solving the flash problem relies heavily on geometrical properties of the phase diagram. The flash problem is solved if the tie line passing through the overall composition state is identified. The following observation is the key element of our approach:

Proposition. Tie lines intersect the liquid and vapor loci, and divide them into segments. The ratio of the length of these segments is constant.

Proof. Let α be a parameterization of the tie-line field, based on the liquid composition $\boldsymbol{x} = [x_1, x_2]^t$:

$$\boldsymbol{x} = \alpha\hat{\boldsymbol{x}}_1 + (1 - \alpha)\hat{\boldsymbol{x}}_2, \tag{12}$$

that is, α is a weighting parameter that interpolates (linearly) the two bounding tie lines that coincide with the C_1- and C_2-axis. Let β be an analogous parameterization based on the vapor composition $\boldsymbol{y} = [y_1, y_2]^t$:

$$\boldsymbol{y} = \beta\hat{\boldsymbol{y}}_1 + (1 - \beta)\hat{\boldsymbol{y}}_2. \tag{13}$$

To prove the proposition, it is sufficient to show that $\alpha = \beta$. Indeed, since the liquid and vapor loci intersection satisfy that $\hat{y}_i = K_i\hat{x}_i$, Equation (13) reads:

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \beta \begin{bmatrix} K_1\hat{x}_1 \\ 0 \end{bmatrix} + (1 - \beta) \begin{bmatrix} 0 \\ K_2\hat{x}_2 \end{bmatrix}. \tag{14}$$

Since the equilibrium liquid and gas compositions must satisfy $y_i = K_i x_i$, direct comparison of Equations (12) and (14) yield that α and β must be identically equal. $\square$

Remark 1. The proposition is a statement that the liquid locus is a straight line, and the vapor locus is another straight line for which the fraction of each component can be obtained by multiplying the component fraction on the liquid locus by the respective K-value.

Remark 2. The parameter α uniquely defines a tie line. For an overall composition inside the ternary diagram, it may take values in the range $[0, 1]$ if $K_2 > 1$ (Figure 5) or in the range $[\alpha_{\min}, 1]$ if $K_2 < 1$ (Figure 6). The flash problem then reduces to: given an overall composition state $\boldsymbol{C} = [C_1, C_2]^t$, find α corresponding to the tie line that passes through it.

In the remainder of this section we solve the flash problem. We start by noting that any state on the liquid locus may be expressed as:

$$\boldsymbol{x} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} \alpha\hat{x}_1 \\ (1 - \alpha)\hat{x}_2 \end{bmatrix} \tag{15}$$

and, analogously, any state on the vapor locus:

$$\boldsymbol{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \alpha\hat{y}_1 \\ (1 - \alpha)\hat{y}_2 \end{bmatrix}. \tag{16}$$
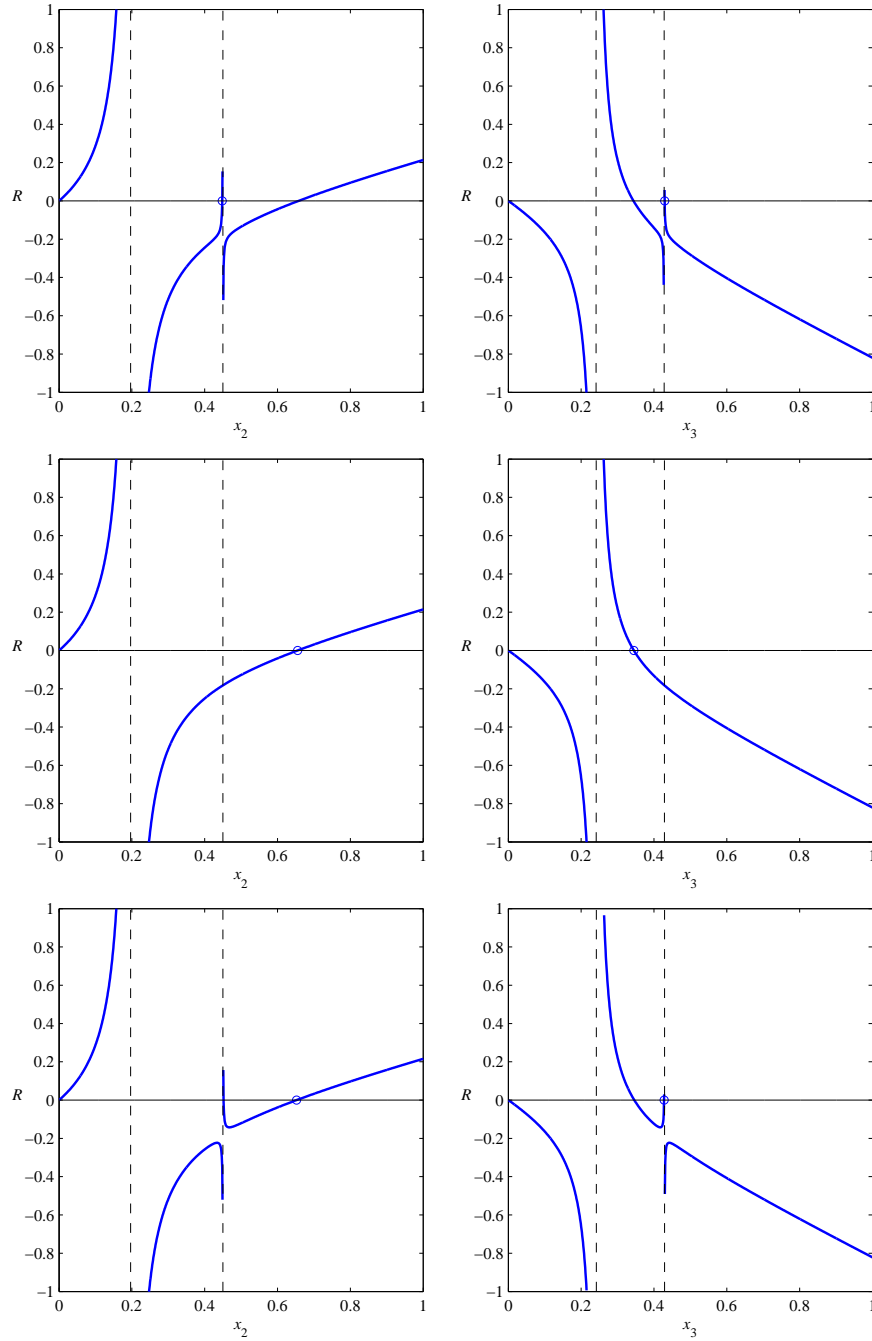
Figure 4: Residual of the Wang–Orr negative flash equation as a function of the liquid composition x_2 (left column) and x_3 (right column) for overall compositions $C = [0.001, 0.3]^t$ (top), $C = [0, 0.3]^t$ (middle), and $C = [-0.001, 0.3]^t$ (bottom).

The overall composition $\boldsymbol{C} = [C_1, C_2]^t$ is a mixture (linear combination) of the liquid and vapor compositions:

$$\begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} + S \begin{bmatrix} y_1 - x_1 \\ y_2 - x_2 \end{bmatrix}. \tag{17}$$

Solving the second equation above for the vapor saturation S,

$$S = \frac{C_2 - x_2}{y_2 - x_2}, \tag{18}$$

and substituting into the first equation:

$$(C_1 - x_1)(y_2 - x_2) = (C_2 - x_2)(y_1 - x_1). \tag{19}$$

Figure 5: Ternary diagram for $K_2 > 1$. For positive overall concentrations, the parameter α that uniquely defines the tie-line field may take values in the range $[0, 1]$.

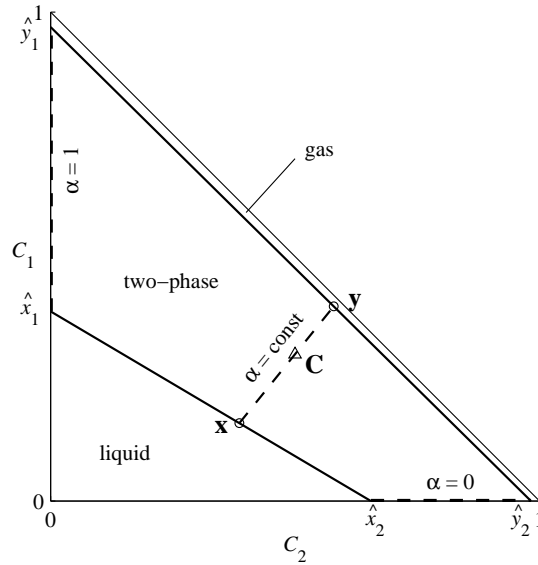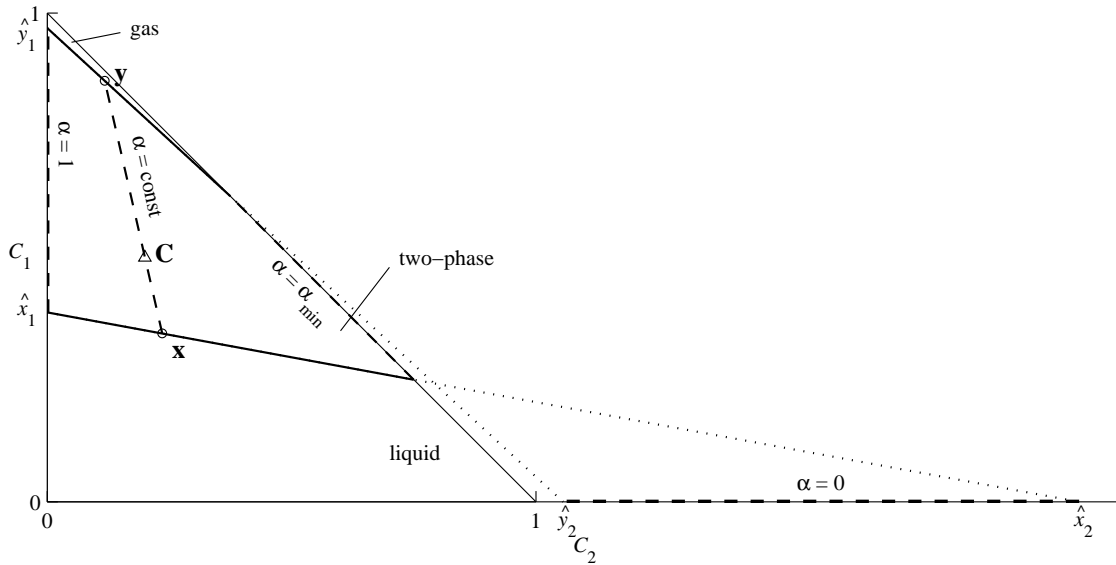**Figure 6: Ternary diagram for $K_2 < 1$. For positive overall concentrations, the parameter α that uniquely defines the tie-line field may take values in the range $[\alpha_{min}, 1]$.**

Substitution of Equations (15)–(16) and straightforward rearrangement leads to the following equation:

$$R(\alpha) \equiv [\hat{x}_2(\hat{y}_1 - \hat{x}_1) - \hat{x}_1(\hat{y}_2 - \hat{x}_2)]\,\alpha^2 + [(C_2 - \hat{x}_2)(\hat{y}_1 - \hat{x}_1) + (C_1 + \hat{x}_1)(\hat{y}_2 - \hat{x}_2)]\,\alpha - C_1(\hat{y}_2 - \hat{x}_2) = 0. \quad (20)$$

Equation (20) is a quadratic equation in α. The fact that that tie-line identification for a three-component system reduces to a quadratic equation has been pointed out previously by Whitson and Michelsen (1989) and Orr (2007, Ch. 5,Ex. 2).

It is easy to show that the coefficient of the second-order term is always positive. Let $a \equiv \hat{x}_2(\hat{y}_1 - \hat{x}_1) - \hat{x}_1(\hat{y}_2 - \hat{x}_2)$ be the coefficient of the second-degree term. Recalling that $\hat{y}_i = K_i\hat{x}_i$, we have that

$$a = \hat{x}_2(K_1 - 1)\hat{x}_1 - \hat{x}_1(K_2 - 1)\hat{x}_2 = (K_1 - K_2)\hat{x}_1\hat{x}_2.$$

Since $K_1 > K_2 > K_3$, all three factors are strictly positive and, therefore, $a > 0$. As a result, the residual R is always a convex function. In Figure 7 we show the behavior of the residual for $K_2 > 1$ (left) and $K_2 < 1$ (right), for three different overall compositions: one inside, one on the edge, and one outside of the ternary diagram. In contrast with the behavior for the Whitson–Michelsen negative flash (Figure 3) and the Wang–Orr negative flash (Figure 4), note the continuous dependence of the residual on the overall composition, and the smooth behavior at the root.
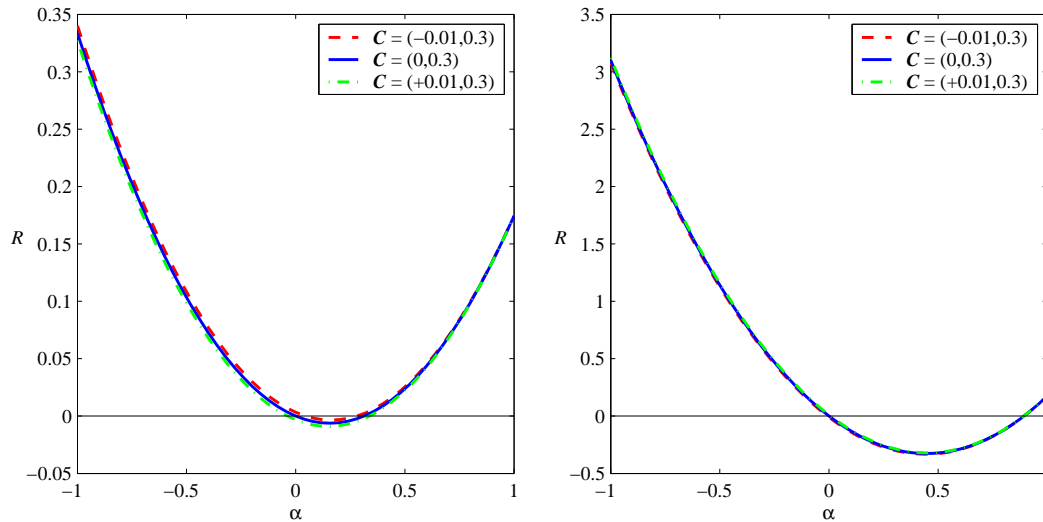
Figure 7: Plot of the residual, $R(\alpha)$, for $K_2 > 1$ (left) and $K_2 < 1$ (right), for three different overall compositions. Note the continuous dependence of the residual on the overall composition, and the smooth behavior at the root.

Once α is known, the liquid and vapor compositions are given by Equations (15)–(16), and the vapor saturation is given by Equation (18).

Existence of Solutions. The residual function has at least one root when the overall concentration state is inside the ternary diagram. More importantly, it has at least one root on the subset of the (C_1, C_2)-plane covered by tie-line extensions, that is, the region bounded by the tie-line envelope curve. This is the region of interest in the development of analytical solutions by the method of characteristics.

The envelope curves for low-volatility and high-volatility intermediate components are shown in Figure 8. Three overall concentration states are indicated for the case of a high-volatility intermediate component. State A is inside the unit triangle, and all the components have positive concentrations. State B is outside the unit triangle but inside the envelope curve, that is, in the region of composition space covered by tie-line extensions. State C is outside the tie-line envelope curve. The residual $R(\alpha)$ for these composition states is shown in Figure 9. It illustrates that two solutions to the quadratic equation exist inside the tie-line envelope curve (states A and B), and no solutions outside (state C). For states exactly on the envelope curve, the quadratic equation has a double root (in fact, imposing this condition is an efficient way of determining the envelope curve).

The question arises: for states inside the envelope curve, which solution is physical, and which one should be discarded? For both high-volatility and low-volatility intermediate components, the physical root is the one that is closer to $\alpha = 1$. The reason for discarding the other root is that it corresponds to a tie-line that does not play a role in the construction of solutions to oil/gas displacements. This is clear for overall composition states inside the ternary diagram (state A). The root farthest away from one is actually negative, and corresponds to a tie-line that is outside the ternary diagram (both the liquid and vapor compositions have negative C_1-concentrations).

The generalization of this argument is as follows. Consider a composition state inside the envelope curve (it may be inside or outside the unit triangle—state B). Then, two tie lines extend through that composition state, connecting the overall composition to two different pairs of liquid and vapor compositions. One of the tie lines remains strictly inside the envelope curve, while the other has a tangency point to the envelope curve. In other words, the first tie line connects the overall composition with the vapor and liquid compositions without intersecting any other tie line. In contrast, the second tie line intersects an infinite number of tie-line extensions. The latter does not lead to physically-admissible solutions of gas/oil displacements (the entropy condition is violated) and must, therefore, be discarded. With reference to the example in Figure 9, the physically-correct solution is always the root of the quadratic equation closest to $\alpha = 1$, regardless of whether the other root is negative (for states inside the ternary triangle) or positive (for states inside the envelope curve but outside the unit triangle). Therefore, we conclude that the flash calculation for the three-component problem is explicit.

In anticipation of the more general case with $N \geq 4$ components, the solution may be achieved using Newton's method. Let us first show that the value of the residual $R(\alpha)$ at $\alpha = 1$ is always non-negative. After simple algebraic manipulation,

$$R(\alpha = 1) = C_2(K_1 - 1)\hat{x}_1.$$

The term in parenthesis is always strictly positive, and so is $\hat{x}_1$. For both high-volatility and low-volatility intermediate components, the region bounded by the envelope curve satisfies that $C_2 \geq 0$ (see Figure 8). Therefore, $R(\alpha = 1) \geq 0$.

Since the residual is a convex function and its value at $\alpha = 1$ is always greater or equal than zero, Newton's method will always converge to the physically-correct root if one chooses $\alpha^{(0)} = 1$ as initial guess.
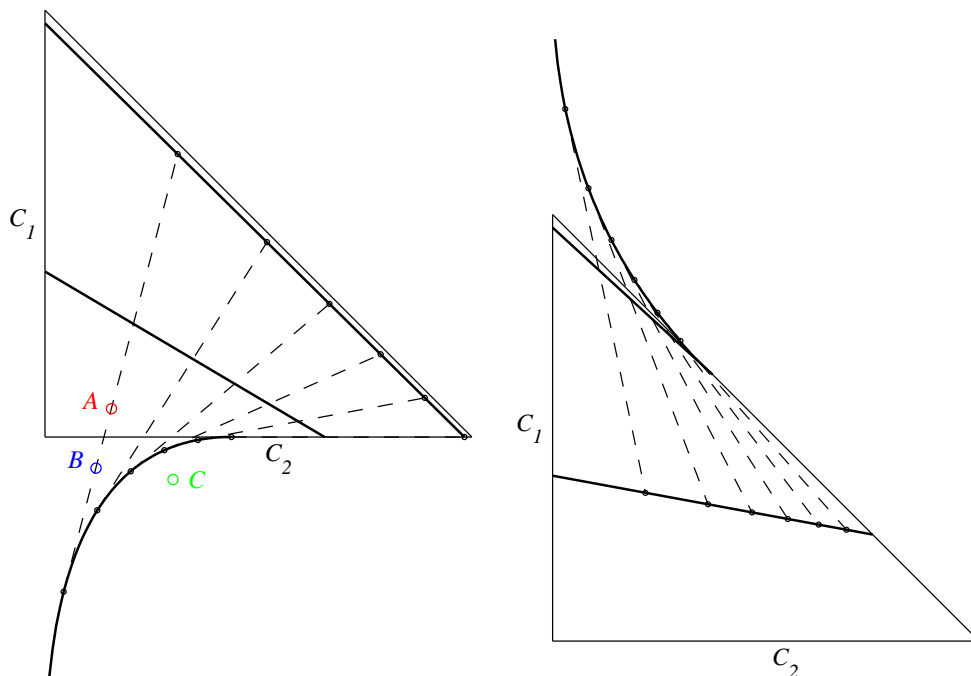
Figure 8: Tie-line envelope curves for $K_2 > 1$ (left) and $K_2 < 1$ (right). Three overall concentration states are indicated for the case of a high-volatility intermediate component. State A is inside the unit triangle, and all the components have positive concentrations. State B is outside the unit triangle but inside the envelope curve, that is, in the region of composition space covered by tie-line extensions. State C is outside the tie-line envelope curve.
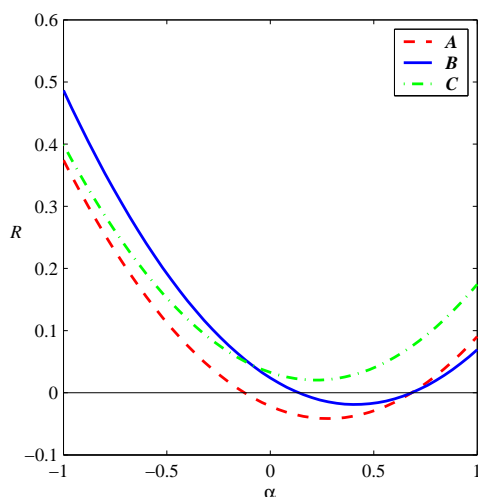

Figure 9: Residual $R(\alpha)$ for all three composition states, A, B and C, depicted on Figure 8(left). A: Two solutions exist: one positive and one negative. The negative root corresponds to a tie-line extension outside the unit triangle and is therefore unphysical. B: Two solutions exist, both of them positive. The largest root is always the physically-admissible solution (see discussion in the text). C: This state is outside the region covered by tie-line extensions and, as a result, no solutions exist.

Four-Component System

In this section, we extend the methodology to four-component systems, which are still amenable to graphical representation. Pure components are ordered according to their K-values:

$$K_1 > K_2 > K_3 > K_4, \quad K_1 > 1, \quad K_4 < 1. \tag{21}$$

In Figure 10 we show the phase diagram for a four-component system with $K_2 > 1 > K_3$. In this case, the pure components C_1 and C_2 are gases, and the pure components C_3 and C_4 are liquids. The vapor and liquid loci, separating single-phase from
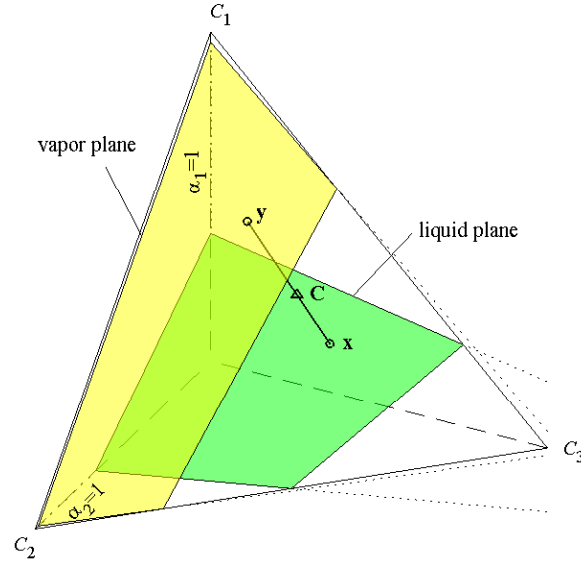
Figure 10: Quaternary diagram for $K_2 > 1 > K_3$.

two-phase regions, are planes. The intersection of the liquid and vapor planes with the C_i-axis, $\hat{\boldsymbol{x}}_i$ and $\hat{\boldsymbol{y}}_i$, respectively, are:

$$\hat{\boldsymbol{x}}_1 = \begin{bmatrix} \hat{x}_1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{x}_1 = \frac{1 - K_4}{K_1 - K_4}, \qquad \hat{\boldsymbol{y}}_1 = \begin{bmatrix} \hat{y}_1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{y}_1 = K_1 \frac{1 - K_4}{K_1 - K_4}, \tag{22}$$

$$\hat{\boldsymbol{x}}_2 = \begin{bmatrix} 0 \\ \hat{x}_2 \\ 0 \end{bmatrix}, \quad \hat{x}_2 = \frac{1 - K_4}{K_2 - K_4}, \qquad \hat{\boldsymbol{y}}_2 = \begin{bmatrix} 0 \\ \hat{y}_2 \\ 0 \end{bmatrix}, \quad \hat{y}_2 = K_2 \frac{1 - K_4}{K_2 - K_4}, \tag{23}$$

$$\hat{\boldsymbol{x}}_3 = \begin{bmatrix} 0 \\ 0 \\ \hat{x}_3 \end{bmatrix}, \quad \hat{x}_3 = \frac{1 - K_4}{K_3 - K_4}, \qquad \hat{\boldsymbol{y}}_3 = \begin{bmatrix} 0 \\ 0 \\ \hat{y}_3 \end{bmatrix}, \quad \hat{y}_3 = K_3 \frac{1 - K_4}{K_3 - K_4}. \tag{24}$$

In Figure 10 we also show the tie line passing through an overall composition state $\boldsymbol{C}$, defined by the equilibrium liquid and gas compositions, $\boldsymbol{x}$ and $\boldsymbol{y}$, respectively.

Proposed Approach. The essential observation leading to our computational scheme is that *the same* parameterization of the liquid and vapor planes defines the tie-line field uniquely:

$$\boldsymbol{x} = \alpha_1 \hat{\boldsymbol{x}}_1 + \alpha_2 \hat{\boldsymbol{x}}_2 + (1 - \alpha_1 - \alpha_2) \hat{\boldsymbol{x}}_3, \tag{25}$$

$$\boldsymbol{y} = \alpha_1 \hat{\boldsymbol{y}}_1 + \alpha_2 \hat{\boldsymbol{y}}_2 + (1 - \alpha_1 - \alpha_2) \hat{\boldsymbol{y}}_3. \tag{26}$$

Of course, two parameters (α_1 and α_2) are needed to parameterize a plane. The overall composition is a linear combination of the liquid and gas compositions:

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} + S \begin{bmatrix} y_1 - x_1 \\ y_2 - x_2 \\ y_3 - x_3 \end{bmatrix}. \tag{27}$$

Solving for S in the last equation,

$$S = \frac{C_3 - x_3}{y_3 - x_3}, \tag{28}$$

and substituting into the first two equations:

$$(C_1 - x_1)(y_3 - x_3) = (C_3 - x_3)(y_1 - x_1), \tag{29}$$

$$(C_2 - x_2)(y_3 - x_3) = (C_3 - x_3)(y_2 - x_2). \tag{30}$$

After substitution of (25)–(26), the equations above can be expressed as the following system:

$$R_1(\alpha_1, \alpha_2) \equiv a_1(\alpha_1^2 + \alpha_1 \alpha_2) + (b_1 + c_1)\alpha_1 + c_1 \alpha_2 - c_1 = 0, \tag{31}$$

$$R_2(\alpha_1, \alpha_2) \equiv a_2(\alpha_1 \alpha_2 + \alpha_2^2) + c_2 \alpha_1 + (b_2 + c_2)\alpha_2 - c_2 = 0. \tag{32}$$
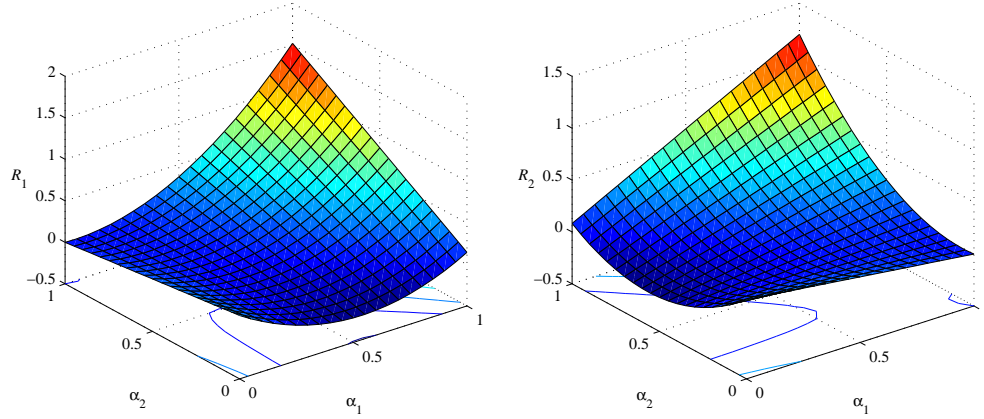
Figure 11: Surface plot of the residuals R_1 and R_2 as functions of the tie-line parameters α_1 and α_2. The case shown corresponds to the K-values $(K_1, K_2, K_3, K_4) = (2.5, 1.5, 0.5, 0.05)$ **and the overall composition** $(C_1, C_2, C_3, C_4) = (0.25, 0.25, 0.25, 0.25)$.

where the coefficients are:

$$a_i = \hat{x}_3(\hat{y}_i - \hat{x}_i) - \hat{x}_i(\hat{y}_3 - \hat{x}_3), \quad i = 1, 2, \tag{33}$$

$$b_i = (C_3 - \hat{x}_3)\hat{y}_i - (C_3 - \hat{y}_3)\hat{x}_i, \quad i = 1, 2, \tag{34}$$

$$c_i = C_i(\hat{y}_3 - \hat{x}_3), \quad i = 1, 2. \tag{35}$$

This is a system of *quadratic* equations in $[\alpha_1, \alpha_2]$. In Figure 11 we plot the residual surfaces, R_1 and R_2, for a particular choice of K-values and overall composition.

Existence of Solutions. The solution to the flash problem consists in finding the intersection of the two quadratic curves (conic sections) (31)–(32). The range of admissible values of the solution (α_1, α_2) depends on the K-values. In Figure 12 we show the liquid plane, and the associated region of admissible solutions to the negative flash problem on the (α_1, α_2) space for all three possible cases: (a) $K_2 > K_3 > 1$, (b) $K_2 > 1 > K_3$, and (c) $1 > K_2 > K_3$.

The two conic sections are in fact hyperbolas, because $a_i > 0$ for all $i = 1, 2$. Elementary analysis shows that the asymptotes of each hyperbola $R_i = 0$ are $\alpha_i = \text{const}$ and $\alpha_1 + \alpha_2 = \text{const}$. The existence of solutions to the negative flash can then be translated into the following questions: when do the two hyperbolas intersect? if so, how many times? if they intersect more than once, which one is the physical solution? While the results are general, we elaborate the argument for the case $K_2 > 1 > K_3$ only. We plot the tie-line field and observe that tie-line extensions cover part of the $C_1/C_2/C_3$-space (see Figure 13). The surface that bounds this region is called envelope surface (Orr, 2007).

As was the case for the three-component problem, the location of the overall composition state with respect to the envelope surface is essential. Shown in Figure 13 are three overall composition states: a state inside the unit tetrahedron (A), a state outside the unit tetrahedron but inside the envelope surface (B), and a state outside the envelope surface (C). In Figure 14 we plot the curves $R_1(\alpha_1, \alpha_2) = 0$ and $R_2(\alpha_1, \alpha_2) = 0$ for each of these three composition states.

The hyperbolas corresponding to state A have two intersections, one admissible and one not admissible. In this case, it is clear which one is the physical solution. For state B, there are two intersections, both in the region of admissible values of (α_1, α_2). Here, the argument for root selection is analogous to that of the three-component case. Of the two tie-lines that pass through B, one of them connects that state to the equilibrium liquid composition without intersecting any other tie line. The other tie line intersects an infinite number of tie-lines extensions along the way. This latter solution is invalid in the context of analytical solutions to gas/oil displacements, and should be discarded. For state C, the hyperbolas do not intersect, and the negative flash does not have a solution.

We conclude that the system of quadratic equations has exactly two solutions—one of which can be discarded—when the overall state is inside the region bounded by the envelope surface, and no solutions if it is outside (the system has a double root if the state is *on* the envelope surface).

These results are general. The reason is the global triangular structure of the gas/oil multicomponent system with constant K-values (Johansen et al., 2005): tie lines lie in planes. Solving the system of quadratic equations is equivalent to identifying a plane, then finding the tie-line extension within that plane. This reduces the problem (conceptually) to a three-component problem on the plane, which has *at most two roots*.

From a practical standpoint, the correct solution is always the one determined by the branches of the hyperbolas close to the edge $\alpha_1 + \alpha_2 = 1$, in the same way that the correct root in the three-component case was the root closer to $\alpha = 1$.

While general methods exist for the intersection of conics, here we propose to employ Newton's method to find the intersection, and exploit knowledge of the behavior of these conics. The intersection of each conic with the axes may be found directly by solving a single quadratic equation. Similarly, the extremum of each hyperbola (the point at which $\partial R_i / \partial \alpha_i = 0$)
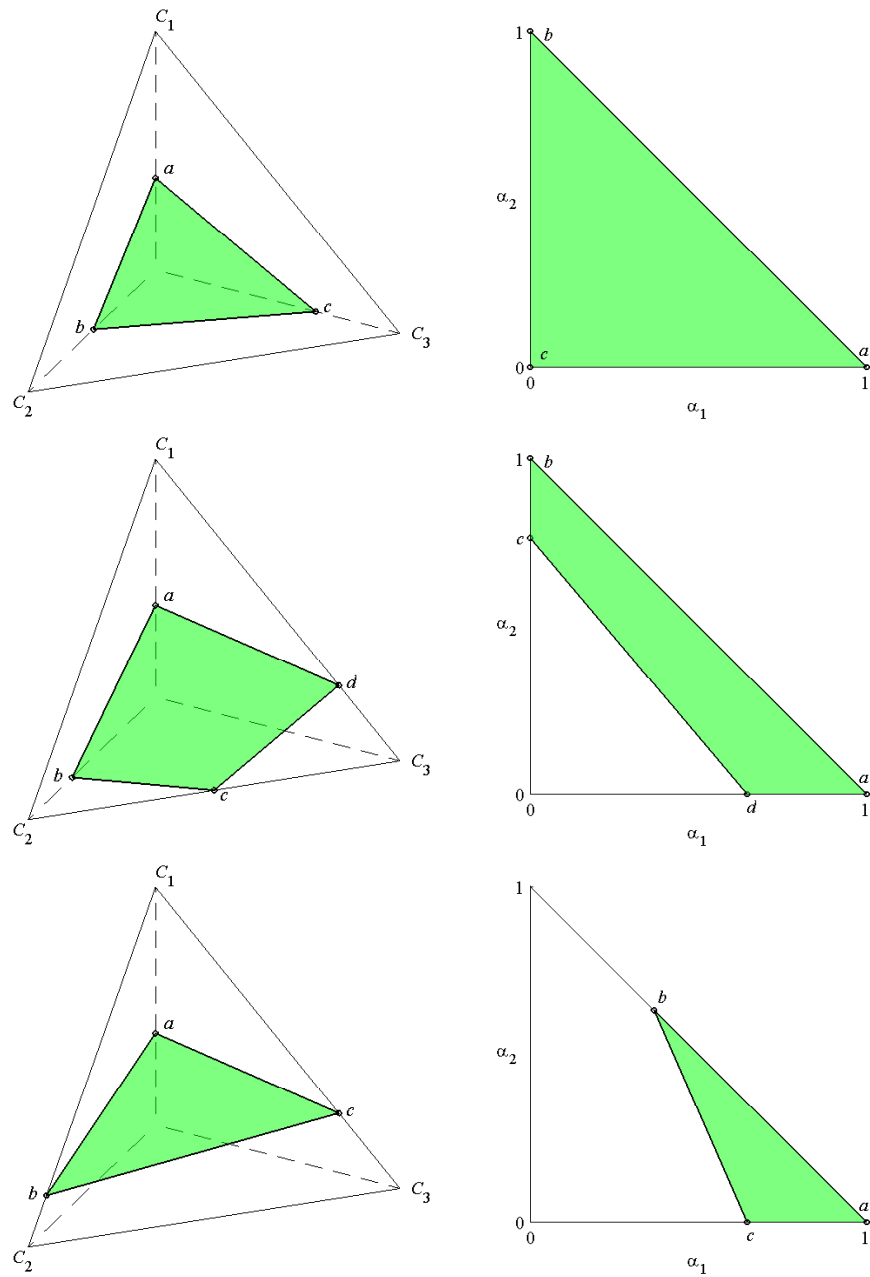
Figure 12: Plots of the liquid locus on the ternary diagram (left column) and the corresponding region of admissible solutions to the negative flash problem on the (α_1, α_2) space (right column). From top to bottom: (a) $K_2 > K_3 > 1$, (b) $K_2 > 1 > K_3$, and (c) $1 > K_2 > K_3$.
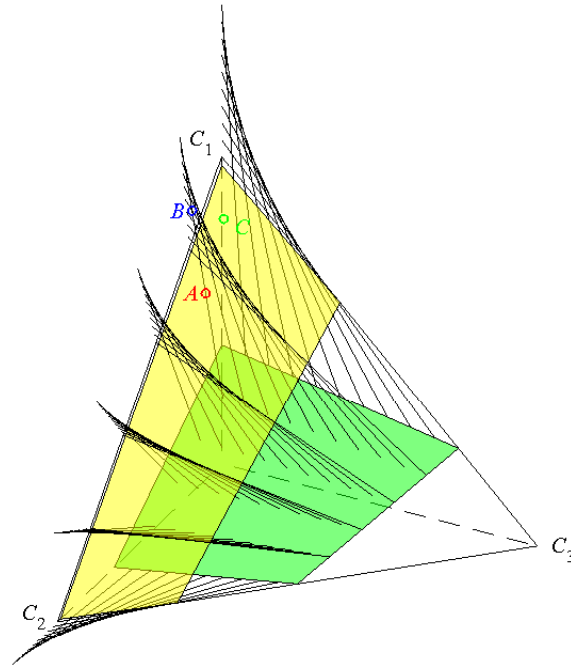
Figure 13: Plots of the tie-line field for the case $K_2 > 1 > K_3$, and its associated envelope surface. Also shown are three composition states. A: **a state inside the unit tetrahedron;** B: **a state outside the unit tetrahedron, but inside the envelope surface; and** C: **a state outside the envelope surface.**
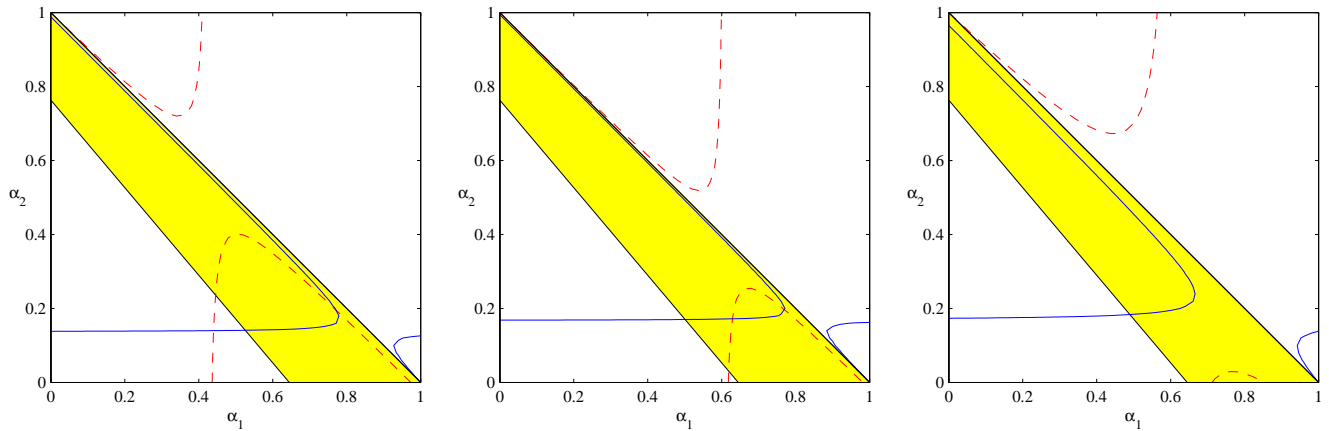

Figure 14: Plots of the curves $R_1(\alpha_1, \alpha_2) = 0$ and $R_2(\alpha_1, \alpha_2) = 0$ on the (α_1, α_2)-plane, corresponding the the K-values and composition states depicted in Figure 13. From left to right: states A, B, and C.

may also be found analytically. This information allows one to approximate (circumscribe) each hyperbola by linear segments, as shown in Figure 15. The intersection of these segmented approximations is explicit, and provides the initial guess for the Newton iteration. We have found that it is always a good approximation to the physically-correct solution, leading to quadratic convergence of the Newton iteration for all K-values and overall concentrations.

Generalization to an N-Component System

The proposed methodology for flash calculation can be generalized immediately to the N-component case. Consider an ordering of the K-values: $K_1 > K_2 > \ldots > K_{N-1} > K_N$, with $K_1 > 1$ and $1 > K_N > 0$. Let the overall composition $\boldsymbol{C} = [C_1, \ldots, C_{N-1}]^t$ be given on the $(N-1)$-dimensional unit simplex, and $C_N = 1 - \sum_{j=1}^{N-1} C_j$. Now the liquid and vapor loci are $(N-2)$-dimensional hyperplanes. The intersection of the liquid and vapor hyperplanes with the C_i-axis, $\hat{\boldsymbol{x}}_i$ and $\hat{\boldsymbol{y}}_i$,
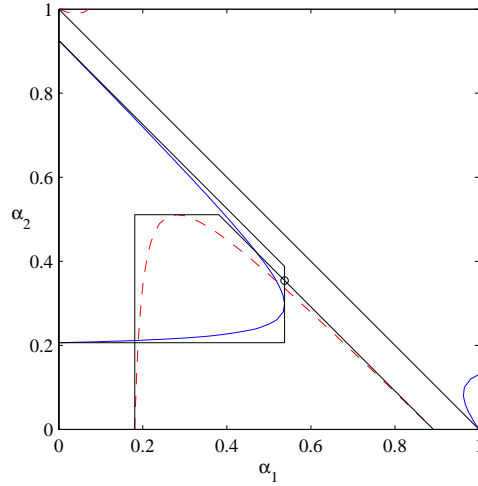
Figure 15: Intersection of the conics $R_1 = 0$ and $R_2 = 0$ defining the solution in (α_1, α_2)-space. The initial guess for Newton iteration (marked with a circle) is obtained as the intersection of a piecewise linear approximation that circumscribes the conic sections.

respectively, are:

$$\hat{\boldsymbol{x}}_i = \begin{bmatrix} 0 \\ \vdots \\ \hat{x}_i \\ \vdots \\ 0 \end{bmatrix}, \quad \hat{x}_i = \frac{1 - K_N}{K_i - K_N}, \quad \hat{\boldsymbol{y}}_i = \begin{bmatrix} 0 \\ \vdots \\ \hat{y}_i \\ \vdots \\ 0 \end{bmatrix}, \quad \hat{y}_i = K_i \hat{x}_i, \quad i = 1, \ldots, N-1. \tag{36}$$

The fundamental observation is that the same parameterization of each of these hyperplanes defines the tie-line field:

$$\boldsymbol{x} = \sum_{j=1}^{N-2} \alpha_j \hat{\boldsymbol{x}}_j + (1 - \sum_{j=1}^{N-2} \alpha_j) \hat{\boldsymbol{x}}_{N-1}, \tag{37}$$

$$\boldsymbol{y} = \sum_{j=1}^{N-2} \alpha_j \hat{\boldsymbol{y}}_j + (1 - \sum_{j=1}^{N-2} \alpha_j) \hat{\boldsymbol{y}}_{N-1}. \tag{38}$$

The tie-line field is parameterized by the vector $\boldsymbol{\alpha} = [\alpha_1, \ldots, \alpha_{N-2}]^t$. The overall composition may be expressed as a linear combination of the liquid and gas compositions:

$$C_i = x_i + S(y_i - x_i), \quad i = 1, \ldots, N-1. \tag{39}$$

Solving for S in the last equation,

$$S = \frac{C_{N-1} - x_{N-1}}{y_{N-1} - x_{N-1}}, \tag{40}$$

and substituting into the first $N - 2$ equations:

$$(C_i - x_i)(y_{N-1} - x_{N-1}) = (C_{N-1} - x_{N-1})(y_i - x_i), \quad i = 1, \ldots, N-2. \tag{41}$$

After substitution of (37)–(38), the equations above can be expressed as the following system of $N - 2$ quadratic equations:

$$R_i \equiv a_i \alpha_i (\alpha_1 + \ldots + \alpha_{N-2}) + b_i \alpha_i + c_i (\alpha_1 + \ldots + \alpha_{N-2}) - c_i = 0, \quad i = 1, \ldots, N-2, \tag{42}$$

where the coefficients are:

$$a_i = \hat{x}_{N-1}(\hat{y}_i - \hat{x}_i) - \hat{x}_i(\hat{y}_{N-1} - \hat{x}_{N-1}), \tag{43}$$
$$b_i = (C_{N-1} - \hat{x}_{N-1})\hat{y}_i - (C_{N-1} - \hat{y}_{N-1})\hat{x}_i, \tag{44}$$
$$c_i = C_i(\hat{y}_{N-1} - \hat{x}_{N-1}). \tag{45}$$

The flash problem reduces to finding the vector $\boldsymbol{\alpha} = [\alpha_1, \ldots, \alpha_{N-2}]$, solution to the $N-2$ quadratic equations (42). Once this is known, the liquid and gas compositions are immediately obtained from Equations (37)–(38).

The case of a five-component system still admits a graphical interpretation. The solution defining the tie line is a point in the unit tetrahedron, $[\alpha_1, \alpha_2, \alpha_3]$, resulting from the intersection of three quadrics (in our case, two-sheeted hyperboloids). General methods have been devised in the computer visualization community to solve this kind of problem (see, e.g. Levin (1979)). Alternatively, the equations can be solved efficiently by using Newton iteration.

Traditional negative flash procedures based on the Rachford–Rice equation result in a rational residual with N asymptotes and, often, bad behavior near the roots. In contrast, the proposed method based on tie-line identification only has *at most two roots*, even for an N-component system. This is due to the global triangular structure of the system with constant K-values (Johansen et al., 2005), by which tie lines lie in $N-2$-dimensional hyperplanes. The correct solution is the one associated with the tie line that does not intersect any other tie line as it connects the overall composition state with its vapor/liquid equilibrium concentrations.

Conclusions

We have presented a new method for flash calculation, based on a parameterization of the tie-line field. For the general N-component case, the problem reduces to the solution of $N-2$ quadratic equations. The main application of the method is the calculation of negative flash, possibly with negative overall compositions. The proposed method is very robust in the sense that the solution displays continuous dependence on the overall composition even in the region of negative concentrations, and no primary variable switching is required. This is to be contrasted with classical methods based on the solution of the Rachford–Rice equation (Rachford and Rice, 1952; Whitson and Michelsen, 1989; Wang and Orr, 1997), in which the iteration may converge to a spurious root, either due to convergence difficulties or because the nonlinear residual does not contain the physical root.

For the important case of three components ($N = 3$), our method leads to an explicit, non-iterative flash calculation. For $N = 4$, the solution is the intersection of two hyperbolas. For $N = 5$, it is the intersection of three two-sheeted hyperboloids. Even in the general N-component case, the global triangular structure of the system with constant K-values guarantees that the system of quadratic equations has at most two roots.

While the method presented in this paper is restricted to constant K-values, its relevance stems from the fact that this is often a good approximation for many hydrocarbon systems at moderate pressures and temperatures (Orr, 2007). When this is not the case, the methodology presented here must be understood as the building block for an overall flash calculation in which an outer iteration is performed to determine the K-values (Michelsen, 1982; Whitson and Michelsen, 1989; Wang and Orr, 1997; Orr, 2007). We are currently working on a direct extension of the method—based on a parameterization of the tie-line field—for nonconstant K-values.

Acknowledgments

Nomenclature

Roman symbols

$\boldsymbol{C}$	overall composition vector
C_i	overall concentration of the i-component
K_i	equilibrium ratio of the i-component
N	number of components
S	vapor saturation
$R_i(\cdot)$	residual function
$\boldsymbol{x}$	liquid composition vector
x_i	mass fraction of the i-component in the liquid phase
$\hat{\boldsymbol{x}}_i$	intersection of liquid locus with C_i-axis
$\boldsymbol{y}$	vapor composition vector
y_i	mass fraction of the i-component in the vapor phase
$\hat{\boldsymbol{y}}_i$	intersection of vapor locus with C_i-axis

Greek letters

α_i	parameter defining the tie-line field

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