



A robust negative flash 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 basis of the 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.

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1. 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 [1].

At equilibrium, a two-phase mixture will satisfy

$$K_i = \frac{y_i}{x_i}, \quad (1)$$

for all of its chemical components $i = 1, \dots, N$. In Eq. (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 [13]. 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 [12,13,20,21].

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The flash problem can be expressed as follows: given a set of positive K -values, K_i , and non-negative 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

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

with the restrictions

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

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

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

Several variants of this equation exist. The original method proposed by Rachford and Rice [14] expressed it as a function of the vapor saturation S . Whitson and Michelsen [21] 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

$$\frac{1}{1 - K_{\max}} < S < \frac{1}{1 - K_{\min}}. \quad (5)$$

If the overall composition is far away from the two-phase region – in particular, if it is outside the region of positive overall com-

positions – Wang [18], and Wang and Orr [20], proposed to solve Eq. (4) in terms of a liquid composition x_l for some component $l \in \{1, \dots, N\}$ —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) [2,4–8,13,15,17,19]. 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 [3,20], and are the key building blocks for fast simulation of multidimensional reservoir flows by the front-tracking/streamline method [9,10,16].

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. [3] 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 Refs. [21,20]. 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. In Section 2, 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. We extend our analysis to the four-component system in Section 3, 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. In Section 4 we generalize the framework to the N -component system. In Section 5 we give some concluding remarks.

2. Three-component system

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

$$K_1 > K_2 > K_3, \quad K_1 > 1, \quad K_3 < 1. \quad (6)$$

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 Figs. 1 and 2, respectively. Compositions close to the C_1 -vertex are in vapor phase, and compositions close 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:

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

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

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

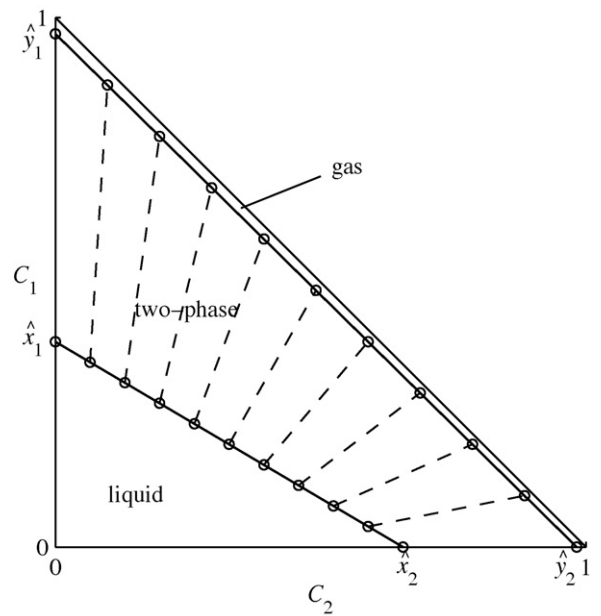


Fig. 1. Ternary diagram and tie-line field for $K_2 > 1$.

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*. Figs. 1 and 2 show the tie-line field for the cases $K_2 > 1$ and $K_2 < 1$, respectively.

2.1. Whitson and Michelsen negative flash

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

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

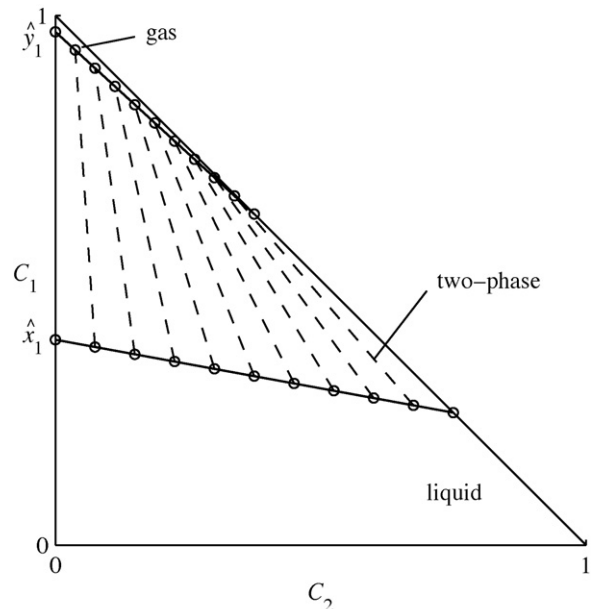


Fig. 2. Ternary diagram and tie-line field for $K_2 < 1$.

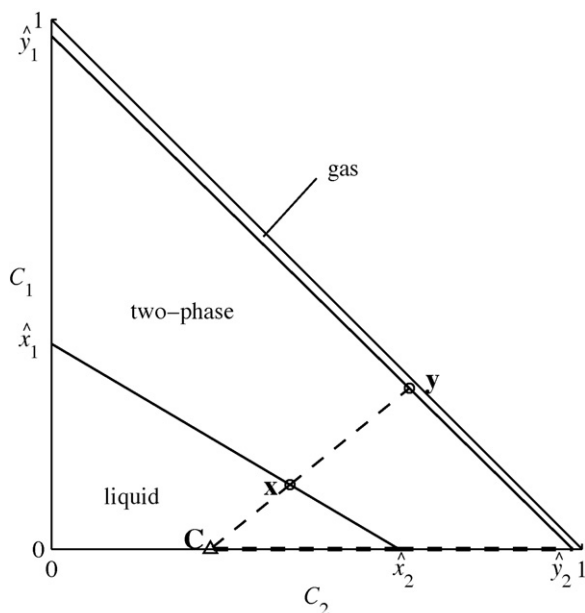


Fig. 3. Ternary diagram showing the two tie lines passing through overall composition $\mathbf{C} = (0, 0.3)$. The tie line coinciding with the axis $C_1 = 0$ would lead to analytical solutions to gas/oil displacements that do not depend continuously on the initial data, and must therefore be discarded.

This is the form employed by Whitson and Michelsen [21]. 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 [21]). 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 [20], the procedure faces difficulties for compositions outside the range of positive concentrations. We illustrate this behavior next.

In Fig. 3 we plot the tie lines passing through a reference overall concentration $\mathbf{C} = [C_1, C_2]^T = [0, 0.3]^T$, 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 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 [13,19,20]. The existence, multiplicity, and selection of tie lines for general composition states is discussed at length in Section 2.4. Here we simply illustrate the behavior that may arise for a state near the edge $C_1 = 0$.

In Fig. 4 we plot the residual $R(S)$ of Eq. (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 $S = (1/1 - K_1) = -2/3$. 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.

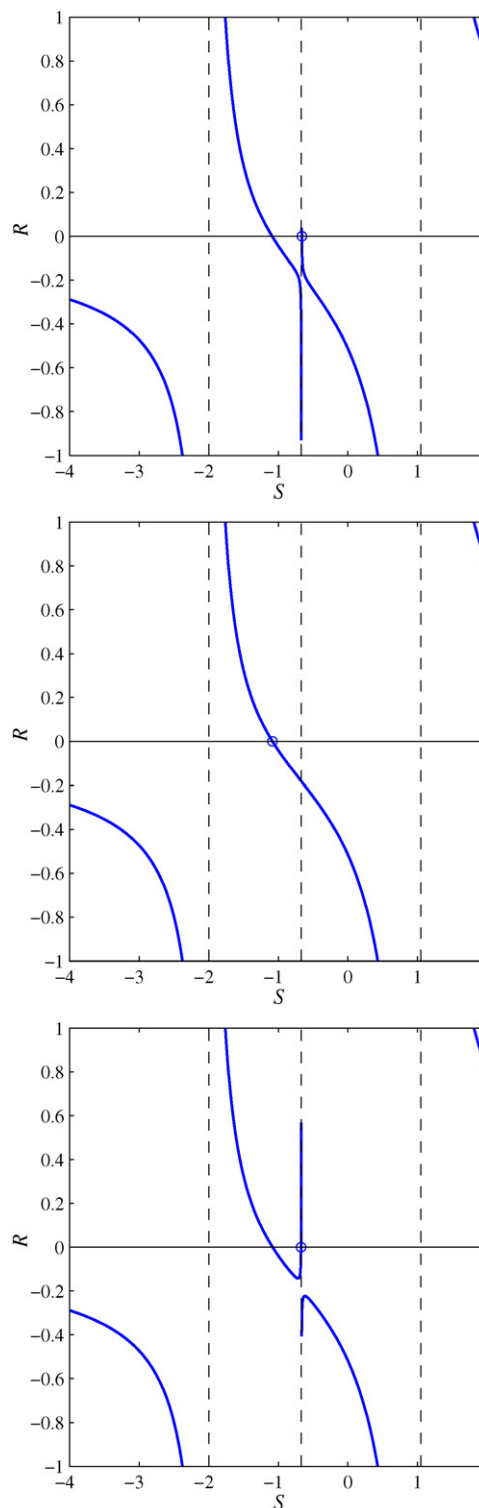


Fig. 4. Residual of the Whitson–Michelsen negative flash equation (as a function of gas saturation S) for overall compositions $\mathbf{C} = [0.001, 0.3]^T$ (top), $\mathbf{C} = [0, 0.3]^T$ (middle), and $\mathbf{C} = [-0.001, 0.3]^T$ (bottom).

2.2. Wang and Orr negative flash

Wang and Orr [20] observed that “for an arbitrary overall composition, the vapor saturation S can vary in an unrestricted way” and they suggested to use the phase saturations 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:

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

Substituting this expression in the Rachford–Rice equation, one obtains the following residual equation [13,18]:

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

Wang and Orr [13,20] suggested a negative flash based on solving Eq. (11) using a Newton method. This procedure, however, suffers from the same type of problem as the Whitson–Michelsen negative flash. In Fig. 5 we plot the residual in Eq. (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 non-linear equation when the composition is on the edge of the composition triangle. The behavior of the residual as a function of x_3 (Fig. 5, 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.

2.3. 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 $\mathbf{x} = [x_1, x_2]^T$:

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

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 $\mathbf{y} = [y_1, y_2]^T$:

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

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

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

Since the equilibrium liquid and gas compositions must satisfy $y_i = K_i x_i$, direct comparison of Eqs. (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 $K_2 > 1$ (Fig. 6) or in the range $[\alpha_{\min}, 1]$ if $K_2 < 1$ (Fig. 7). The flash problem then reduces to: given an overall composition state $\mathbf{C} = [C_1, C_2]^T$, 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:

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

and, analogously, any state on the vapor locus:

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \alpha \hat{y}_1 \\ (1 - \alpha) \hat{y}_2 \end{bmatrix}. \quad (16)$$

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

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

Solving the second equation above for the vapor saturation S ,

$$S = \frac{C_2 - x_2}{y_2 - x_2}, \quad (18)$$

and substituting into the first equation:

$$(C_1 - x_1)(y_2 - x_2) = (C_2 - x_2)(y_1 - x_1). \quad (19)$$

Substitution of Eqs. (15) and (16) and straightforward rearrangement leads to the following equation:

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

Eq. (20) is a quadratic equation in α . The fact that tie-line identification for a three-component system reduces to a quadratic equation has been pointed out previously in Refs. [21,13 (Chapter 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 Fig. 8 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 (Fig. 4) and the Wang–Orr negative flash (Fig. 5), 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 Eqs. (15) and (16), and the vapor saturation is given by Eq. (18).

2.4. 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 Fig. 9. 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

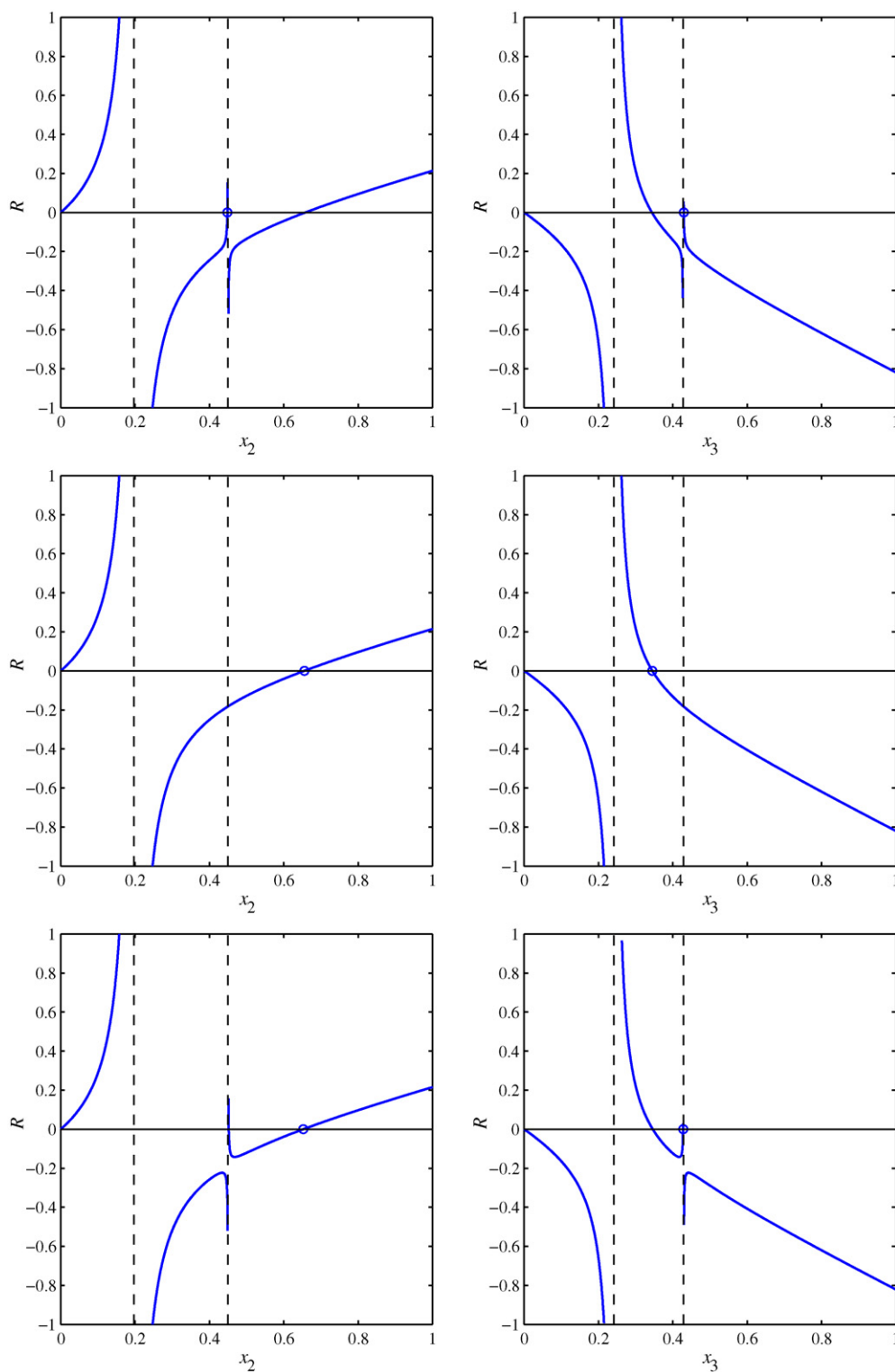


Fig. 5. Residual of the Wang–Orr negative flash equation as a function of the liquid composition x_2 (left column) and x_3 (right column) for overall compositions $\mathbf{C} = [0.001, 0.3]^t$ (top), $\mathbf{C} = [0, 0.3]^t$ (middle), and $\mathbf{C} = [-0.001, 0.3]^t$ (bottom).

the tie-line envelope curve. The residual $R(\alpha)$ for these composition states is shown in Fig. 10. 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

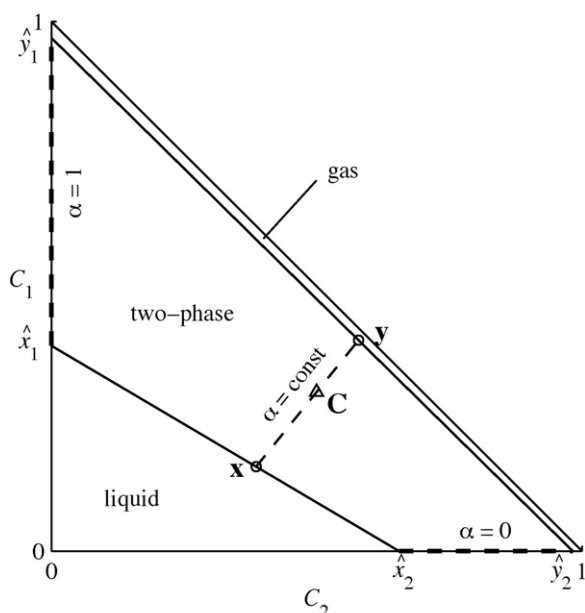


Fig. 6. Ternary diagram for $K_2 > 1$. For positive overall concentrations, the parameter α that uniquely defines the tie-line field may take values in the range $[0, 1]$.

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 Fig. 10, 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 Fig. 9). 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.

3. 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:

$$K_1 > K_2 > K_3 > K_4, \quad K_1 > 1, \quad K_4 < 1. \quad (21)$$

In Fig. 11 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 two-phase regions, are planes. The intersection of the liquid and vapor planes with the C_1 -axis, \hat{x}_1 and \hat{y}_1 , respectively, are:

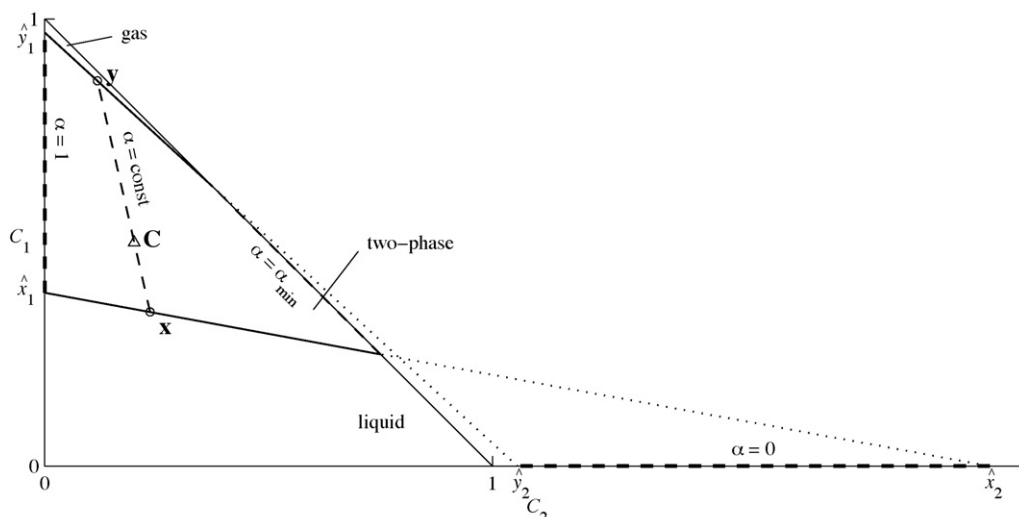


Fig. 7. Ternary diagram for $K_2 < 1$. For positive overall concentrations, the parameter α that uniquely defines the tie-line field may take values in the range $[\alpha_{\min}, 1]$.

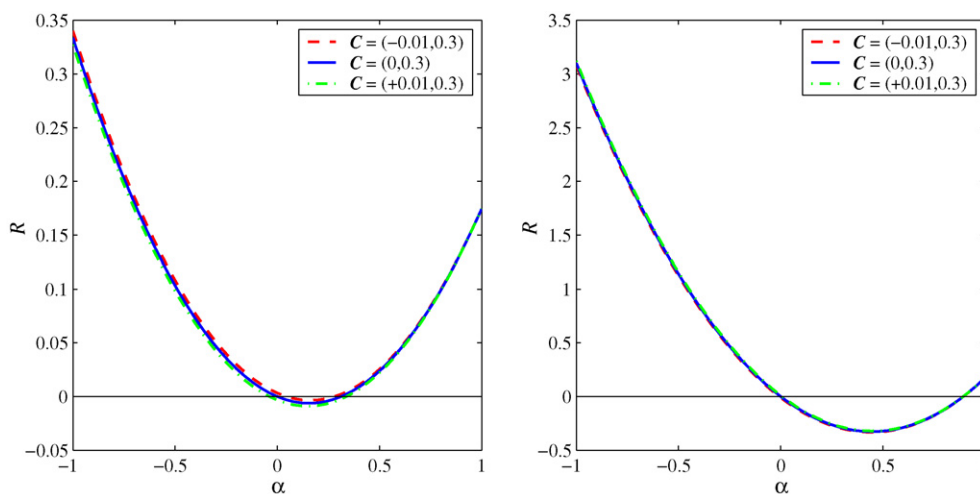


Fig. 8. Plot of the residual, $R(\alpha)$, for $K_2 > 1$ (left) and $K_2 < 1$ (right), for three different overall compositions. Note the continuous dependence of the residual on the overall composition, and the smooth behavior at the root.

$$\hat{\mathbf{x}}_1 = \begin{bmatrix} \hat{x}_1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{x}_1 = \frac{1 - K_4}{K_1 - K_4}, \quad \hat{\mathbf{y}}_1 = \begin{bmatrix} \hat{y}_1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{y}_1 = K_1 \frac{1 - K_4}{K_1 - K_4}, \quad (22)$$

$$\hat{\mathbf{x}}_2 = \begin{bmatrix} 0 \\ \hat{x}_2 \\ 0 \end{bmatrix}, \quad \hat{x}_2 = \frac{1 - K_4}{K_2 - K_4}, \quad \hat{\mathbf{y}}_2 = \begin{bmatrix} 0 \\ \hat{y}_2 \\ 0 \end{bmatrix}, \quad \hat{y}_2 = K_2 \frac{1 - K_4}{K_2 - K_4}, \quad (23)$$

$$\hat{\mathbf{x}}_3 = \begin{bmatrix} 0 \\ 0 \\ \hat{x}_3 \end{bmatrix}, \quad \hat{x}_3 = \frac{1 - K_4}{K_3 - K_4}, \quad \hat{\mathbf{y}}_3 = \begin{bmatrix} 0 \\ 0 \\ \hat{y}_3 \end{bmatrix}, \quad \hat{y}_3 = K_3 \frac{1 - K_4}{K_3 - K_4}. \quad (24)$$

In Fig. 11 we also show the tie line passing through an overall composition state \mathbf{C} , defined by the equilibrium liquid and gas compositions, \mathbf{x} and \mathbf{y} , respectively.

3.1. 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:

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

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

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

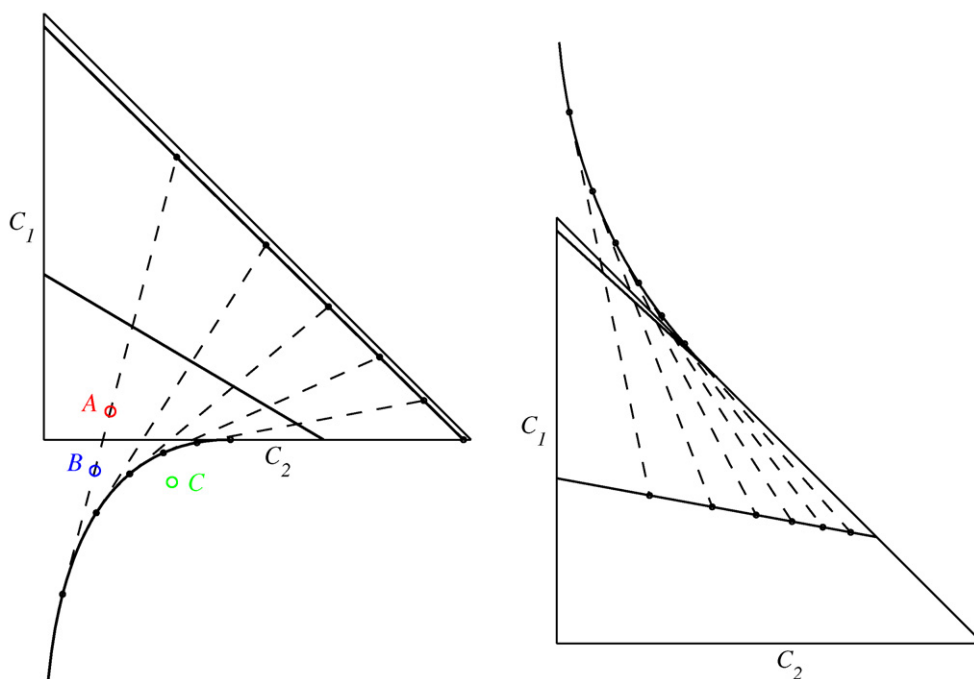


Fig. 9. Tie-line envelope curves for $K_2 > 1$ (left) and $K_2 < 1$ (right). Three overall concentration states are indicated for the case of a high-volatility intermediate component. State A is inside the unit triangle, and all the components have positive concentrations. State B is outside the unit 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.

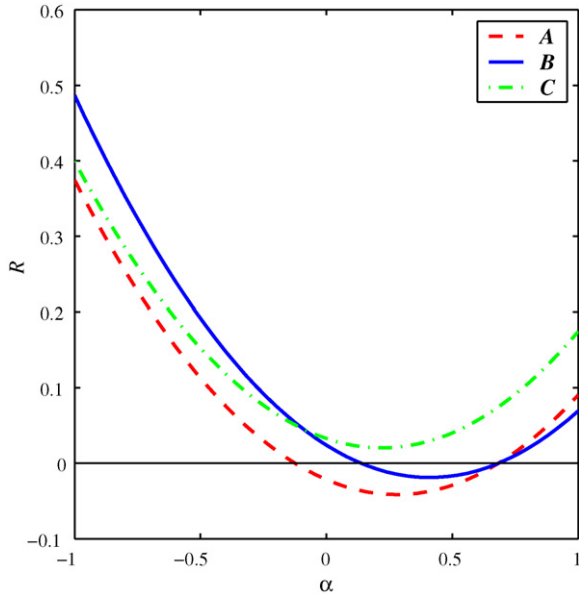


Fig. 10. Residual $R(\alpha)$ for all three composition states, A–C, depicted in Fig. 9(left). (A) Two solutions exist: one positive and one negative. The negative root corresponds to a tie-line extension outside the unit triangle and is therefore unphysical. (B) Two solutions exist, both of them positive. The root closest to α_1 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.

and gas compositions:

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

Solving for S in the last equation,

$$S = \frac{C_3 - x_3}{y_3 - x_3}, \quad (28)$$

and substituting into the first two equations:

$$(C_1 - x_1)(y_3 - x_3) = (C_3 - x_3)(y_1 - x_1), \quad (29)$$

$$(C_2 - x_2)(y_3 - x_3) = (C_3 - x_3)(y_2 - x_2). \quad (30)$$

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

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

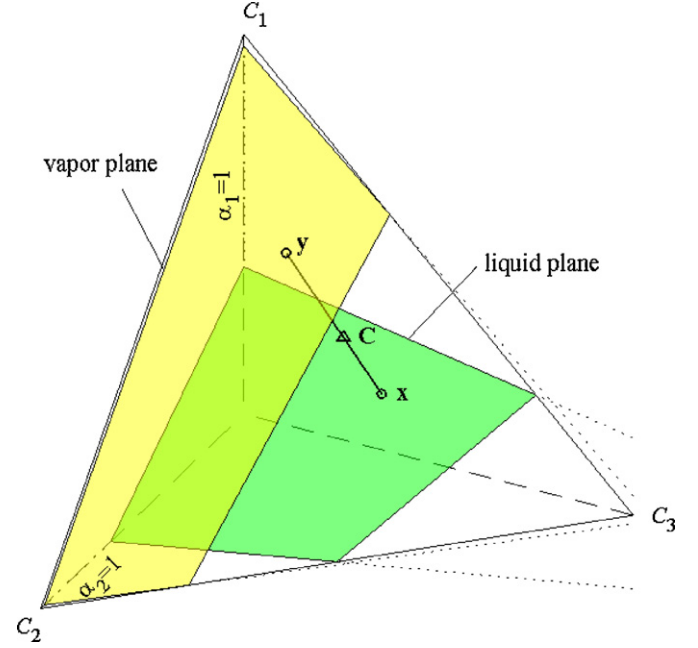


Fig. 11. Quaternary diagram for $K_2 > 1 > K_3$.

$$R_2(\alpha_1, \alpha_2) \equiv a_2(\alpha_1\alpha_2 + \alpha_2^2) + c_2\alpha_1 + (b_2 + c_2)\alpha_2 - c_2 = 0. \quad (32)$$

where the coefficients are:

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

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

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

This is a system of *quadratic* equations in $[\alpha_1, \alpha_2]$. In Fig. 12 we plot the residual surfaces, R_1 and R_2 , for a particular choice of K -values and overall composition.

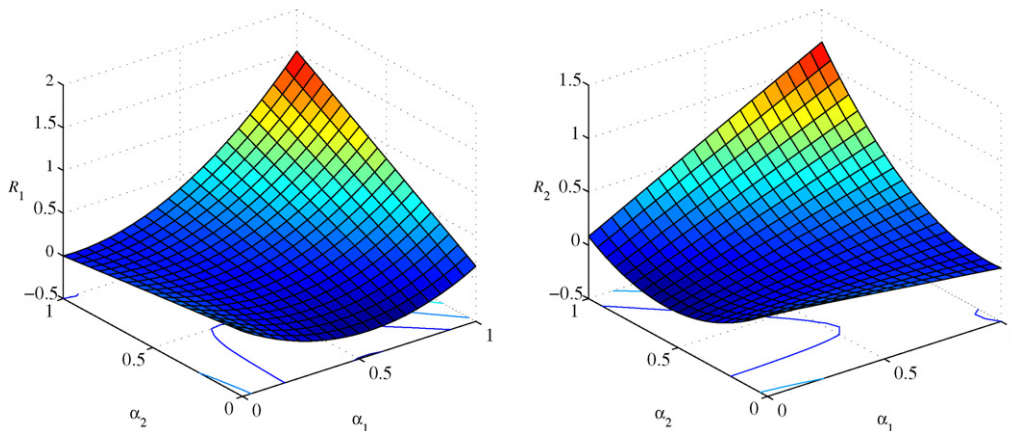


Fig. 12. Surface plot of the residuals R_1 and R_2 as functions of the tie-line parameters α_1 and α_2 . The case shown corresponds to the K -values $(K_1, K_2, K_3, K_4) = (2.5, 1.5, 0.5, 0.05)$ and the overall composition $(C_1, C_2, C_3, C_4) = (0.25, 0.25, 0.25, 0.25)$.

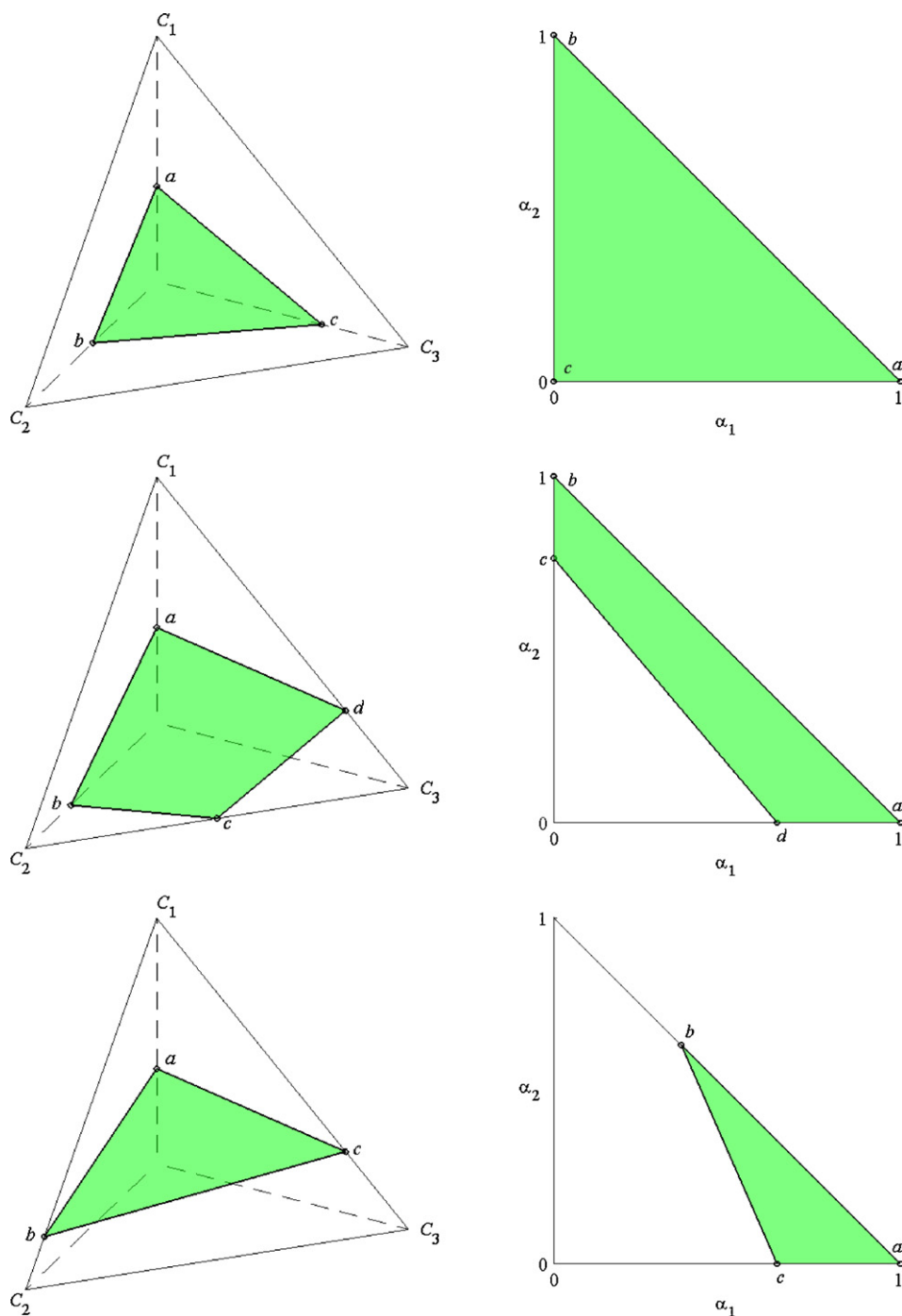


Fig. 13. Plots of the liquid locus on the ternary diagram (left column) and the corresponding region of admissible solutions to the negative flash problem on the (α_1, α_2) space (right column). From top to bottom: (a) $K_2 > K_3 > 1$, (b) $K_2 > 1 > K_3$, and (c) $1 > K_2 > K_3$.

3.2. Existence of solutions

The solution to the flash problem consists in finding the intersection of the two quadratic curves (conic sections) (31) and (32). The range of admissible values of the solution (α_1, α_2) depends on the K -values. In Fig. 13 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 Fig. 14). The surface that bounds this region is called envelope surface [13].

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 Fig. 14 are three overall composition states: a state inside the unit tetrahedron (A), a state outside the unit tetra-

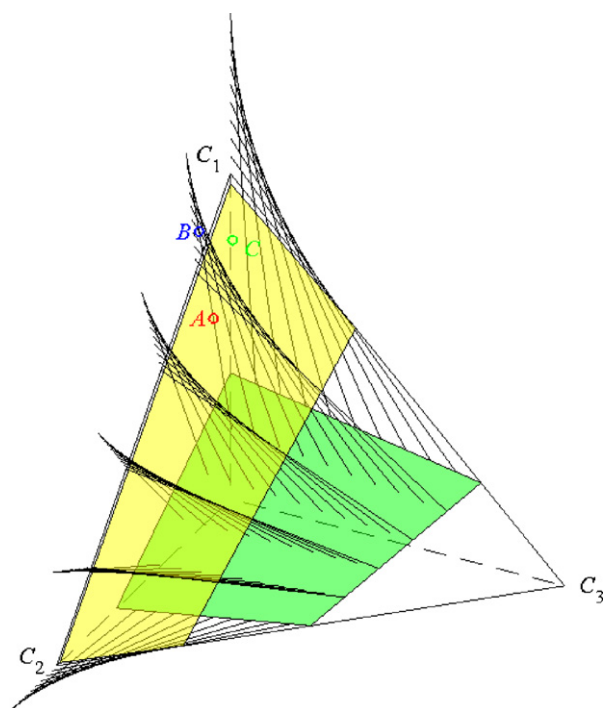


Fig. 14. Plots of the tie-line field for the case $K_2 > 1 > K_3$, and its associated envelope surface. Also shown are three composition states. A, a state inside the unit tetrahedron; B, a state outside the unit tetrahedron, but inside the envelope surface; and C, a state outside the envelope surface.

hedron but inside the envelope surface (B), and a state outside the envelope surface (C). In Fig. 15 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 [5]: 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

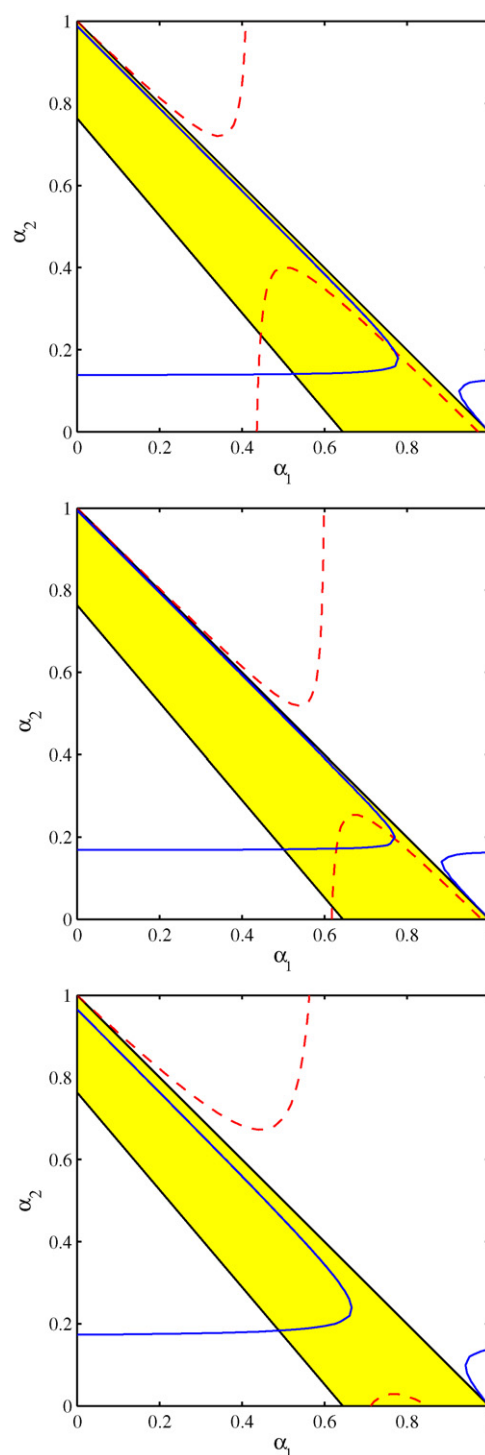


Fig. 15. Plots of the curves $R_1(\alpha_1, \alpha_2) = 0$ and $R_2(\alpha_1, \alpha_2) = 0$ on the (α_1, α_2) -plane, corresponding the K -values and composition states depicted in Fig. 14. From top to bottom: A–C.

a single quadratic equation. Similarly, the extremum of each hyperbola (the point at which $\partial R_i / \partial \alpha_i = 0$) may also be found analytically. This information allows one to approximate (circumscribe) each hyperbola by linear segments, as shown in Fig. 16. 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.

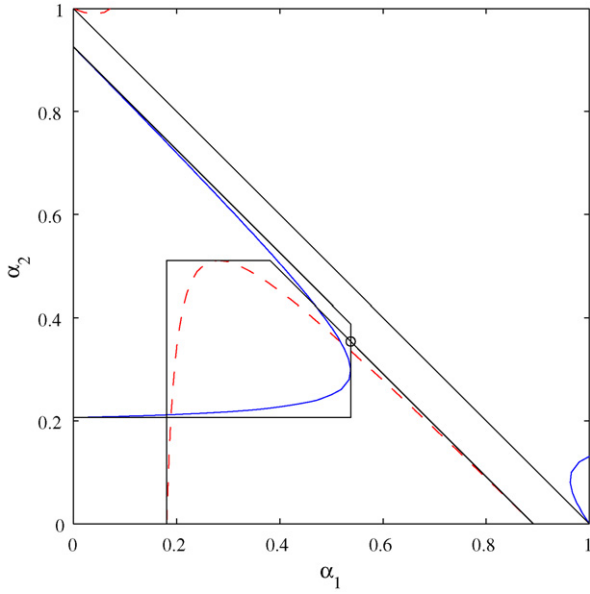


Fig. 16. Intersection of the conics $R_1 = 0$ and $R_2 = 0$ defining the solution in (α_1, α_2) -space. The initial guess for Newton iteration (marked with a circle) is obtained as the intersection of a piecewise linear approximation that circumscribes the conic sections.

4. 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: $K_1 > K_2 > \dots > K_{N-1} > K_N$, with $K_1 > 1$ and $1 > K_N > 0$. Let the overall composition $\mathbf{C} = [C_1, \dots, C_{N-1}]^T$ 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, $\hat{\mathbf{x}}_i$ and $\hat{\mathbf{y}}_i$, respectively, are:

$$\hat{\mathbf{x}}_i = \begin{bmatrix} 0 \\ \vdots \\ \hat{x}_i \\ \vdots \\ 0 \end{bmatrix}, \quad \hat{x}_i = \frac{1 - K_N}{K_i - K_N}, \quad \hat{\mathbf{y}}_i = \begin{bmatrix} 0 \\ \vdots \\ \hat{y}_i \\ \vdots \\ 0 \end{bmatrix},$$

$$\hat{y}_i = K_i \hat{x}_i, \quad i = 1, \dots, N-1. \quad (36)$$

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

$$\mathbf{x} = \sum_{j=1}^{N-2} \alpha_j \hat{\mathbf{x}}_j + \left(1 - \sum_{j=1}^{N-2} \alpha_j\right) \hat{\mathbf{x}}_{N-1}, \quad (37)$$

$$\mathbf{y} = \sum_{j=1}^{N-2} \alpha_j \hat{\mathbf{y}}_j + \left(1 - \sum_{j=1}^{N-2} \alpha_j\right) \hat{\mathbf{y}}_{N-1}. \quad (38)$$

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

$$C_i = x_i + S(y_i - x_i), \quad i = 1, \dots, N-1. \quad (39)$$

Solving for S in the last equation,

$$S = \frac{C_{N-1} - x_{N-1}}{y_{N-1} - x_{N-1}}, \quad (40)$$

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

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

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

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

where the coefficients are:

$$a_i = \hat{x}_{N-1}(\hat{y}_i - \hat{x}_i) - \hat{x}_i(\hat{y}_{N-1} - \hat{x}_{N-1}), \quad (43)$$

$$b_i = (C_{N-1} - \hat{x}_{N-1})\hat{y}_i - (C_{N-1} - \hat{y}_{N-1})\hat{x}_i, \quad (44)$$

$$c_i = C_i(\hat{y}_{N-1} - \hat{x}_{N-1}). \quad (45)$$

The flash problem reduces to finding the vector $\boldsymbol{\alpha} = [\alpha_1, \dots, \alpha_{N-2}]$, solution to the $N-2$ quadratic equation (42). Once this is known, the liquid and gas compositions are immediately obtained from Eqs. (37) and (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. [11]). 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 [5], 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.

5. 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 [14,20,21], in which the iteration may converge to a spurious root, either due to convergence difficulties or because the non-linear 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 [13]. 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 [12,13,20,21]. We are currently working on a direct extension of the method—based on a parameterization of the tie-line field—for non-constant K -values.

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