

Efficient and Robust Three-Phase Split Computations

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The combination of successive substitution and the Newton method provides a robust and efficient algorithm to solve the nonlinear isofugacity and mass balance equations for two-phase split computations. The two-phase Rachford–Rice equation may sometimes introduce complexity, but the Newton and bisection methods provide a robust solution algorithm. For three-phase split calculations, the literature shows that the computed three-phase region is smaller than measured data indicate. We suggest that an improved solution algorithm for the three-phase Rachford–Rice equations can address the problem. Our proposal is to use a two-dimensional bisection method to provide good initial guesses for the Newton algorithm used to solve the three-phase Rachford–Rice equations. In this work, we present examples of various degree of complexity to demonstrate powerful features of the combined bisection–Newton method in three-phase split calculations. To the best of our knowledge, the use of the bisection method in two variables has not been used to solve the three-phase Rachford–Rice equations in the past. © 2010 American Institute of Chemical Engineers AIChE J, 57: 2555–2565, 2011
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Introduction

Three phase-split computations are important in a variety of chemical engineering problems, including reservoir performance and recovery studies. In such studies, phase behavior effects become important in two different ways; the transfer of species between the phases, and the effect of change in phase composition on phase volumes, viscosity, and interfacial tension. While in the past, the focus has been on two-phase compositional simulation, there are important needs for three-phase compositional models for the injection of CO₂, steam, steam-additives, and solvents. Due to the high solubility of CO₂ in both oil and water phases, and the resulting density increase, rigorous three-phase compositional modeling can be crucial to determine the breakthrough of CO₂ and its proper distribution in the reservoir. In some

CO₂-injection applications, a heavy hydrocarbon-rich liquid phase and a light CO₂-rich liquid phase at high temperatures (as high as 260°F) may form. There are cases where the amounts of the two liquid phases and the gas phase are comparable. Three-phase regions may be much broader at higher than at lower temperatures. Another important application of three-phase computations is in asphaltene precipitation.

Phase-split computations and phase stability analysis can take as much as 50% of the total CPU time in two-phase reservoir simulations. In complicated problems, they may be even more expensive. In three-phase compositional modeling, phase behavior computations can be even more time consuming than in two-phase.

There has been much progress in two-phase stability and two-phase split calculations based on equations of state.^{1,2} On the other hand, three-phase split calculations are not yet mature enough for implementation in commercial compositional reservoir simulators, despite a large number of publications on the subject.^{3–6} Michelsen and Møllerup⁷ point out

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that convergence of successive substitutions and its variants may be problematic in multiphase flash computations.

The requirements in compositional simulations are: (1) robustness, and 2 efficiency (i.e., fast computations for billions of phase splits). Robust methods are often based on direct minimization of Gibbs free energy but are too slow for large scale reservoir simulations.^{8,9} More efficient methods are available, but they do not have the required robustness.

There is a wide range of techniques available to solve the algebraic nonlinear equations which define phase stability and phase-split calculations. This article focuses on the latter. For two-phase split calculations, the combination of successive substitution and the Newton method has proved to be both robust and efficient.¹⁰ The Newton method has quadratic convergence rate. If the Jacobian is not too small and the initial guess is good enough, convergence is achieved in a few iterations. Successive substitution has a linear convergence rate and provides a good initial guess for the Newton method if it is not available from the previous time step of the simulation. It has been our experience that in simulations of gas injection processes in complex problems such as fractured reservoirs, there could be significant variations of composition between time steps. Thus, there is a need for careful selection of techniques for stability and phase-split calculations.

A major difficulty in two-phase split computations is the solution of the deceptively simple Rachford–Rice equation¹¹ which is part of the successive substitution. Here, the Newton method is usually used to solve for the phase fraction. The initial guess is an issue. The method can also run into problems when the derivative with respect to phase fraction is close to zero, as is true for the critical region. In such a case, the bisection method provides a simple and robust solution.¹² The bisection method is very inexpensive and is guaranteed to converge fast for the solution to the two-phase Rachford–Rice equation. As a whole, the combination of stability analysis (for both phase stability testing and obtaining an initial estimate of the equilibrium ratios), successive substitution, and the Newton method is both efficient and robust. In recent years, the use of the reduction variables has added further efficiency.^{13,14}

Examination of the literature shows that the computed three-phase envelopes in pressure–composition space are sometimes much smaller than the measured phase envelopes.^{15–17} While one may suspect the deficiency of the cubic equation used in computations, there may be computational problems that lead to the difference between measured data and predictions. Surprisingly, the solution to the three-phase Rachford–Rice equations that comprise part of the successive substitution is believed to be the problem. The Newton method requires good initial guesses for the phase fractions and if they are not provided, the three-phase region will not be computed properly.

The major goal of this work is to develop an efficient and robust algorithm for three-phase split calculations. Although our interests include both CO₂–crude systems and water–crude systems, the examples presented here are limited to the former. For water–crude systems, simple cubic equations of state such as the Peng–Robinson may not be adequate due to high water polarity and resulting association. Recently, the cubic plus association approach has been shown to adequately describe the phase behavior of water-containing

reservoir fluids with and without CO₂ when cross association is taken into account.¹⁸

Despite the fact that some authors^{19,20} who have specifically dealt with three-phase split computations do not report a problem, solving the three-phase Rachford–Rice expressions is not trivial. Even for the two-phase Rachford–Rice expression, Leibovici and Neoschil⁶ suggest the need for the bisection method and a revised formulation of the two-phase Rachford–Rice equation. These authors remark that the revised formulation cannot be applied in the three-phase and higher phase split calculations. Instead, they propose a modified Newton method. Michelsen⁵ suggested to formulate the multiphase Rachford–Rice problem as a minimization problem of a convex function where the gradient vector consists of the Rachford–Rice expressions. The approach has recently been adopted by Leibovici and Nichita²¹ and Okuno et al.²² These authors use a Newton’s method with a line search technique. However, there is no attempt to predict entire phase envelopes (e.g., in pressure–composition space) that will provide a true test of the algorithms.

This article is structured along the following. We first present the problem formulation. Next, we briefly discuss the solution procedure. A two-dimensional bisection algorithm used to obtain an initial guess for the solution to the three-phase Rachford–Rice expressions is then discussed in detail. The two-dimensional bisection technique is only used to generate an initial guess for the first iteration of a successive substitution loop. Finally, we present complete phase diagrams in pressure–composition space for different petroleum fluids before concluding the article with a few remarks.

Problem Formulation

In a three-phase split calculation, we seek three different phases in thermodynamic equilibrium, i.e., the fugacity of each component is the same in all three phases,

$$f_{xi} = f_{yi} = f_{zi}, \quad i = 1 \cdots N. \quad (1)$$

Here, f_{xi} , f_{yi} , and f_{zi} are the fugacities of component i in phases x , y , and z , respectively. N is the total number of components. Choosing phase x to be the reference phase, we can express equilibrium ratios $K_{yi} = y_i/x_i$ and $K_{zi} = z_i/x_i$ as

$$\begin{aligned} \ln K_{yi} &= \ln \phi_{xi} - \ln \phi_{yi}, & i = 1 \cdots N, \\ \ln K_{zi} &= \ln \phi_{xi} - \ln \phi_{zi}, & i = 1 \cdots N, \end{aligned} \quad (2)$$

where ϕ_{xi} , ϕ_{yi} , and ϕ_{zi} are the fugacity coefficients of component i in phases x , y , and z , respectively. In this work, the fugacity coefficients were calculated from the Peng–Robinson equation of state and the van der Waal’s mixing rules.

The system of non-linear equations in Eq. 2 is solved subject to mole fraction constraints which is readily expressed by the three-phase Rachford–Rice equations

$$\begin{aligned} \text{RR}_y &= \sum_{i=1}^N \frac{n_i(K_{yi}-1)}{1+\beta_y(K_{yi}-1)+\beta_z(K_{zi}-1)} = 0, \\ \text{RR}_z &= \sum_{i=1}^N \frac{n_i(K_{zi}-1)}{1+\beta_y(K_{yi}-1)+\beta_z(K_{zi}-1)} = 0. \end{aligned} \quad (3)$$

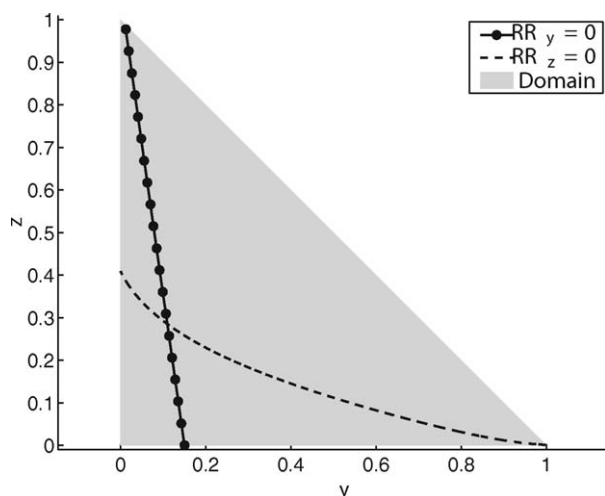


Figure 1. A plot of the search domain and the solutions to the three-phase Rachford-Rice equation.

The equations are simultaneously satisfied at the intersection between the two lines.

In the above expressions, n_i is the feed mole fraction of component i , while β_y and β_z are the mole fractions of phases y and z , respectively. Note that a physical solution requires both phase fractions and their sum to be between zero and unity. Based on mass balance, the mole fractions x_i of the reference phase relate to the equilibrium ratios and phase fractions by

$$x_i = \frac{n_i}{1 + \beta_y(K_{yi} - 1) + \beta_z(K_{zi} - 1)}. \quad (4)$$

The mole fractions in phases y and z can subsequently be found by $y_i = K_{yi}x_i$ and $z_i = K_{zi}x_i$.

Solution Procedure

Our three-phase split algorithm is divided into the following steps:

1. Initial estimate of the equilibrium ratios: The initial estimate can be obtained from correlations, stability analysis or previous time steps.

2. Two-dimensional bisection: The algorithm is used to obtain an initial guess for the phase fractions from the equilibrium ratios.

3. Successive substitution: The method updates the phase fractions and equilibrium ratios iteratively. Note that within each successive substitution the Rachford-Rice equations are solved by the Newton method. In other words, the two-dimensional bisection algorithm is only applied once, i.e., before the first successive substitution.

4. Newton method: Once the switching criterion is met, the successive substitution algorithm is abandoned and the Newton method is used on the system of equations formed by the iso-fugacity and Rachford-Rice equations. The method is used until the convergence criterion is met.

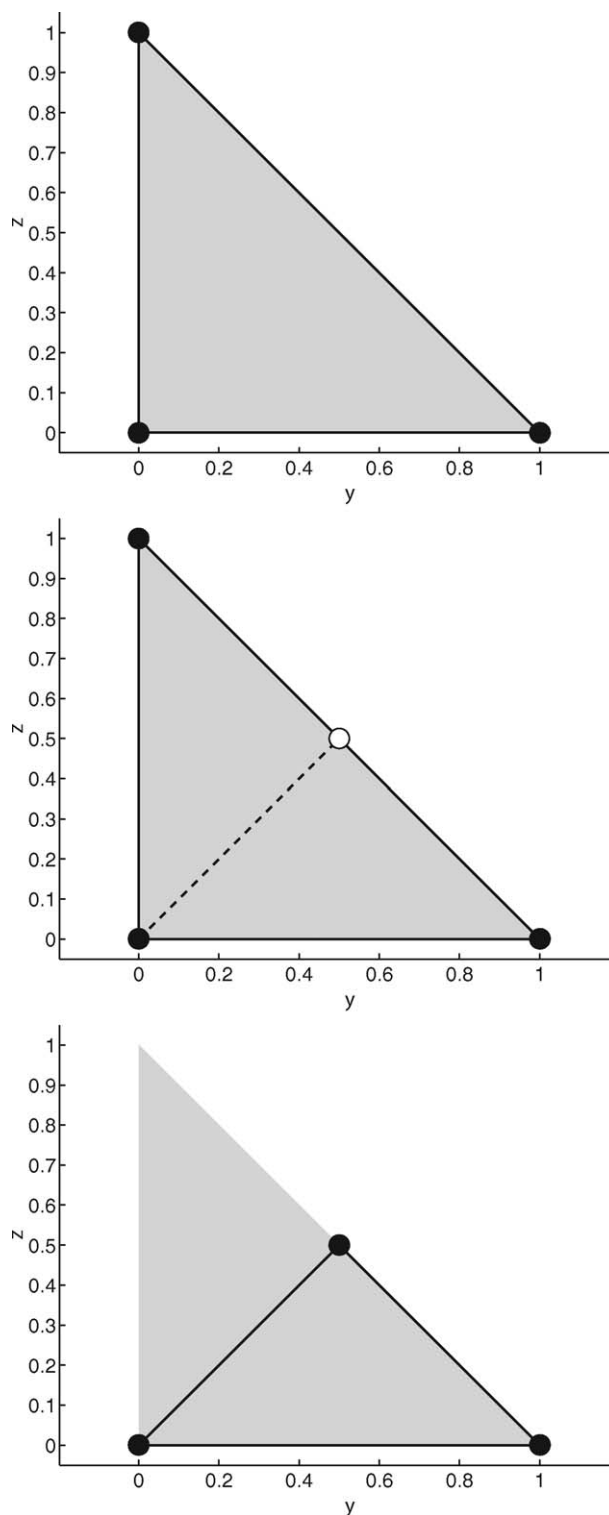


Figure 2. A cartoon showing how a triangle (top) is divided in two by connecting the midpoint of the hypotenuse and the opposite corner (middle).

A subtriangle is discarded (bottom) if either three-phase Rachford-Rice equation does not change sign on its three corners.

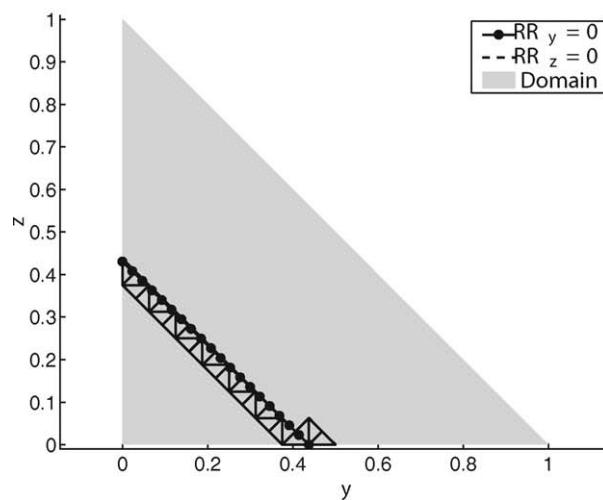
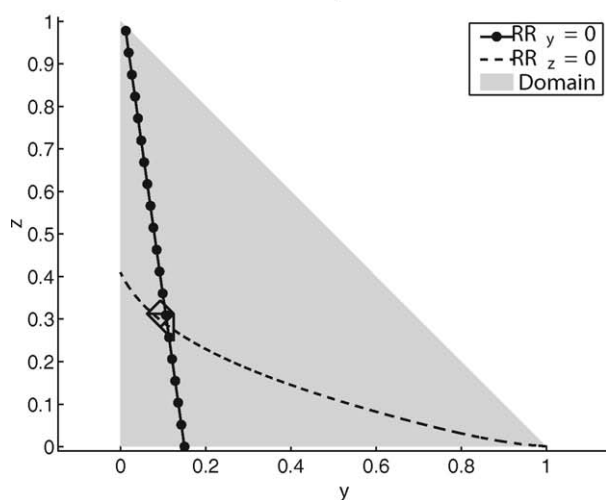
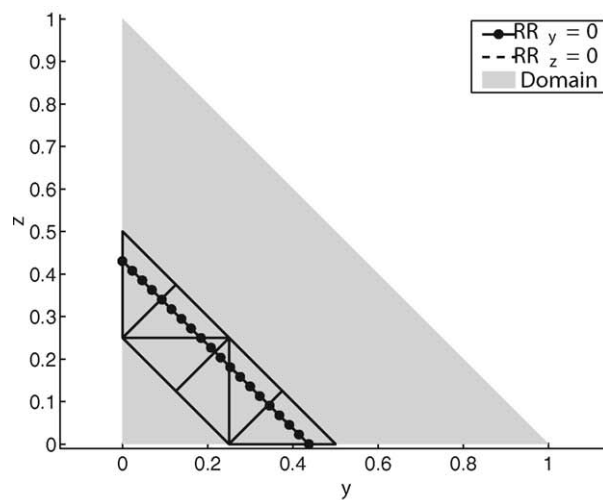
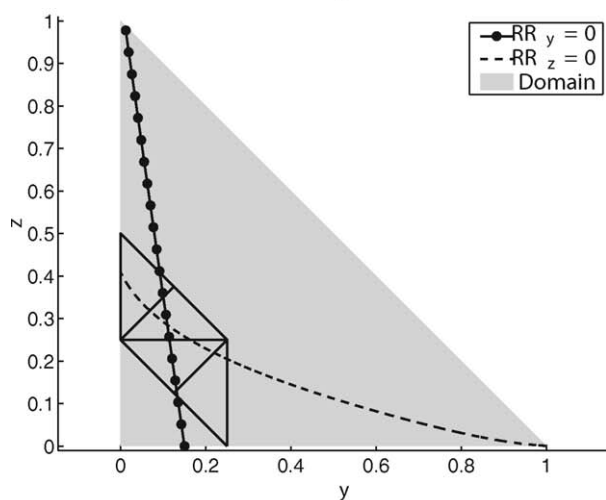
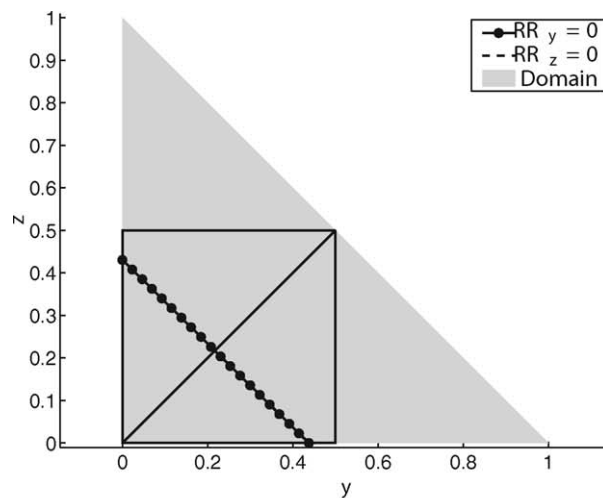
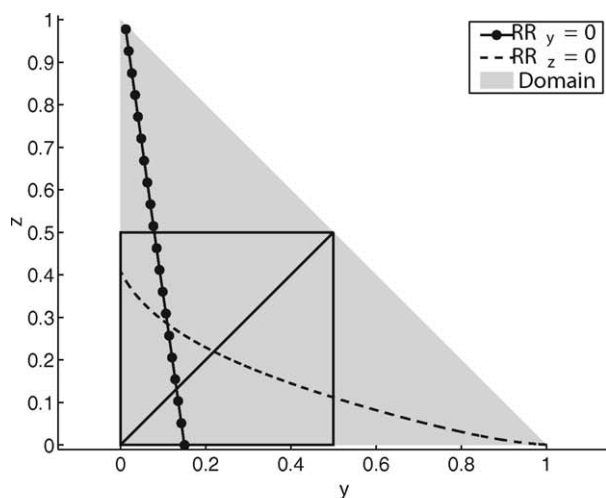


Figure 3. A cartoon showing how the bisection algorithm quickly locates the solution when the lines defined by $RR_y = 0$ and $RR_z = 0$ intersect at a sufficiently large angle.

The snapshots are taken after 2, 5, and 9 iterations.

Figure 4. A cartoon showing how the bisection algorithm fails to find the solution when the lines defined by $RR_y = 0$ and $RR_z = 0$ are essentially parallel.

The snapshots are taken after 2, 5, and 9 iterations.

Table 1. Mole Fractions (x_i , y_i , and z_i) and Phase Fractions (β_j) for a Liquid–Gas–Water Example

	n_i	x_i	y_i	z_i	K_{iy}	K_{iz}
C ₂	0.20	$6.7344 \cdot 10^{-2}$	$2.9260 \cdot 10^{-1}$	–	4.3449	–
C ₃	0.50	$5.0745 \cdot 10^{-1}$	$5.7674 \cdot 10^{-1}$	–	1.1366	–
C ₄	0.20	$4.2509 \cdot 10^{-1}$	$1.2932 \cdot 10^{-1}$	–	0.3042	–
H ₂ O	0.10	$1.1495 \cdot 10^{-4}$	$1.3308 \cdot 10^{-3}$	1	11.577	8699.3
β_j		0.2823	0.6185	0.0991		

The labels x , y , and z refer to first liquid, gas, and water phases, respectively. Feed mole fractions (n_i) and equilibrium ratios (K_{iy} and K_{iz}) are from Michelsen.⁵

In the following, we discuss the successive substitution and Newton algorithms in some detail. An elaborate discussion of the two-dimensional bisection technique is deferred to the next section.

In a Newton iteration, the equilibrium conditions in Eq. 2 and the Rachford–Rice expressions in Eq. 3 are solved simultaneously. For an N -component mixture, Eqs. 2 and 3 form a set of $2N + 2$ equations in $2N + 2$ unknowns. We choose our primary unknowns to be the phase fractions β_y , and β_z , and the natural logarithm of the equilibrium ratios K_{yi} , and K_{zi} . Equilibrium ratios are preferred over mole fractions because the latter choice leads to an ill-defined Jacobian close to the phase boundaries, and using the natural logarithm stabilizes the Newton method when the equilibrium ratios span several orders of magnitude. In the Newton algorithm, we define the residual vector \vec{e} as

$$\vec{e} = \begin{bmatrix} [e_{yi}] \\ [\text{RR}_y] \\ [e_{zi}] \\ [\text{RR}_z] \end{bmatrix}, \quad (5)$$

where

$$e_{yi} = \ln K_{yi} - \ln \phi_{xi} + \ln \phi_{yi}, \quad (6a)$$

$$e_{zi} = \ln K_{zi} - \ln \phi_{xi} + \ln \phi_{zi}. \quad (6b)$$

In each iteration, equilibrium ratios and phase fractions are updated by solving for $\vec{\Delta}$ in the following matrix equation,

$$\mathbf{J} \cdot \vec{\Delta} = -\vec{e}. \quad (7)$$

Here $\vec{\Delta}$ contains the increments of our primary variables, i.e.,

$$\vec{\Delta} = \begin{bmatrix} [\Delta \ln K_{yi}] \\ [\Delta \beta_y] \\ [\Delta \ln K_{zi}] \\ [\Delta \beta_z] \end{bmatrix}, \quad (8)$$

and \mathbf{J} is the Jacobian defined by

$$\mathbf{J} = \begin{bmatrix} \left[\frac{\partial e_{yi}}{\partial \ln K_{yj}} \right] & \left[\frac{\partial e_{yi}}{\partial \beta_y} \right] & \left[\frac{\partial e_{yi}}{\partial \ln K_{zj}} \right] & \left[\frac{\partial e_{yi}}{\partial \beta_z} \right] \\ \left[\frac{\partial \text{RR}_y}{\partial \ln K_{yj}} \right] & \left[\frac{\partial \text{RR}_y}{\partial \beta_y} \right] & \left[\frac{\partial \text{RR}_y}{\partial \ln K_{zj}} \right] & \left[\frac{\partial \text{RR}_y}{\partial \beta_z} \right] \\ \left[\frac{\partial e_{zi}}{\partial \ln K_{yj}} \right] & \left[\frac{\partial e_{zi}}{\partial \beta_y} \right] & \left[\frac{\partial e_{zi}}{\partial \ln K_{zj}} \right] & \left[\frac{\partial e_{zi}}{\partial \beta_z} \right] \\ \left[\frac{\partial \text{RR}_z}{\partial \ln K_{yj}} \right] & \left[\frac{\partial \text{RR}_z}{\partial \beta_y} \right] & \left[\frac{\partial \text{RR}_z}{\partial \ln K_{zj}} \right] & \left[\frac{\partial \text{RR}_z}{\partial \beta_z} \right] \end{bmatrix}. \quad (9)$$

The Newton method has a quadratic convergence rate and, in our work, it generally converges in 2–3 iterations. However, the convergence radius is small and the Newton method is only applied after a sufficiently good initial estimate has been obtained by successive substitutions.

In a successive substitution, the equilibrium ratios are first assumed constants and the three-phase Rachford–Rice equations are solved for the phase fractions β_y and β_z . The updated phase fractions allow us to update the mole fractions and hence the fugacity coefficients of each component in the three phases. The equilibrium ratios are then updated by the use of Eq. 2. Successive substitutions have a linear convergence rate and the change in phase fractions between iterations is often small. In our experience, the phase fractions from one iteration is a good enough initial estimate for the phase fractions at the next iteration to allow for the use of the Newton method to solve the Rachford–Rice equations. The method generally converges in 2–5 iterations. The problem is that when the initial estimate of the equilibrium ratios comes from a correlation or from stability analysis, we do not have an initial estimate for the phase fractions for the first iteration of the successive substitution. Our solution to the problem is the introduction of a two-dimensional bisection technique.

Two-Dimensional Bisection

When the equilibrium ratios are kept constant, each three-phase Rachford–Rice equation is a function of two independent variables, i.e., β_y and β_z . The solution to these equations will therefore form a line in the β_y – β_z -plane (see Figure 1).

Table 2. Mole Fractions (x_i , y_i , and z_i) and Phase Fractions (β_j) for a Liquid–Liquid–Gas Example

	n_i	x_i	y_i	z_i	K_{iy}	K_{iz}
C ₁	0.66	$1.0014 \cdot 10^{-1}$	$9.7613 \cdot 10^{-1}$	$6.9548 \cdot 10^{-1}$	9.7474	6.9448
C ₂	0.03	$1.5340 \cdot 10^{-2}$	$4.3470 \cdot 10^{-3}$	$6.6386 \cdot 10^{-2}$	0.2834	4.3275
C ₃	0.01	$4.1399 \cdot 10^{-3}$	$1.6052 \cdot 10^{-4}$	$2.4111 \cdot 10^{-2}$	0.0388	5.8241
CO ₂	0.05	$7.3085 \cdot 10^{-2}$	$1.2983 \cdot 10^{-2}$	$7.3598 \cdot 10^{-2}$	0.1776	1.0070
H ₂ S	0.25	$8.0729 \cdot 10^{-1}$	$6.3769 \cdot 10^{-3}$	$1.4043 \cdot 10^{-1}$	0.0079	0.1740
β_j		0.2422	0.3873	0.3706		

The labels x , y , and z refer to first liquid, gas, and second liquid phases, respectively. Feed mole fractions (n_i) and equilibrium ratios (K_{iy} and K_{iz}) are from Michelsen.⁵

Table 3. Mole Fractions (x_i , y_i , and z_i) and Phase Fractions (β_j) for a Liquid–Liquid–Solid Example

	n_i	x_i	y_i	z_i	K_{iy}	K_{iz}
C ₁	0.66	$9.7801 \cdot 10^{-2}$	$7.9150 \cdot 10^{-1}$	–	8.0930	–
C ₂	0.03	$7.7979 \cdot 10^{-3}$	$3.5193 \cdot 10^{-2}$	–	4.5132	–
C ₃	0.01	$1.9961 \cdot 10^{-3}$	$1.1872 \cdot 10^{-2}$	–	5.9477	–
CO ₂	0.05	$5.1475 \cdot 10^{-2}$	$4.9655 \cdot 10^{-2}$	–	0.9646	15.318
H ₂ S	0.25	$8.4093 \cdot 10^{-1}$	$1.1178 \cdot 10^{-1}$	–	0.1329	1.1972
β_j		0.1896	0.8104	0		

The labels x , y , and z refer to first liquid, second liquid, and solid phases, respectively. Feed mole fractions (n_i) and equilibrium ratios (K_{iy} and K_{iz}) are from Michelsen.⁵

The three-phase Rachford–Rice equations are simultaneously satisfied where the two lines intersect. Three-phase solutions must lie inside an equilateral triangle defined by the β_y – β_z -coordinates (0,1), (0,0), and (1,0). In our implementation of the two-dimensional bisection technique, the search domain is limited to this triangle.

In the first step of the bisection algorithm, we propose to divide the initial domain into two subdomains. This is done by connecting the midpoint of the hypotenuse and the opposite corner (see Figure 2). The approach divides the parent triangle into subtriangles of identical shapes. Thus, the refined mesh exhibits no directional bias. Next, the three-phase Rachford–Rice expressions are evaluated on the corners of each subtriangle. If either one of them has the same sign on all three corners, we assume it does not equal zero anywhere inside that subtriangle and the subtriangle is discarded. In subsequent iterations, the above procedure is repeated for each accepted subtriangle. Note that dividing a triangle in two only requires calculating the coordinates of one additional point. The other coordinates are available from the parent triangle. The same is true for the values of the three-phase Rachford–Rice expressions. Thus, each iteration is very inexpensive. Due to the additional dimension, two-dimensional bisection refines the domain by a factor of $\sqrt{2}$ per iteration while its one-dimensional counterpart refines the domain by a factor of 2. In our three-phase split algorithm, we use 20 bisection iterations. At that point, the average value of the coordinates of the remaining triangles are used as an initial guess for the Newton method. Provided the mixture is not too close to a bicritical point where two of the phases have almost identical compositions, the combination of two-dimensional bisection and the Newton method proves to be a robust and efficient way of solving the three-phase Rachford–Rice equations. Figure 3 shows snapshots of our proposed bisection technique for a noncritical mixture. Using 20 bisection iterations is a very conservative choice. In most cases, 5–10 iterations is more than sufficient. Thus, implementing a switching criterion to dynamically determine the number of bisection iterations is an alternative.

Close to a bicritical point, two of the phases have very similar compositions. If one of these phases is the reference phase x , one set of equilibrium ratios K_{yi} or K_{zi} will be close to unity. If not, the two sets of equilibrium ratios are close to one another. In a bicritical case, the two lines defined by the three-phase Rachford–Rice expressions will be close to parallel. As a result, finding the solution requires a very high resolution perpendicular to the lines. The two-dimensional bisection method does not have a directional bias. Consequently, there will be a large number of triangles clustering along the lines (see Figure 4). This will eventually make each bisection iteration unacceptably expensive, both in terms of memory usage and CPU time. One solution to the problem is to introduce a directional bias by using triangles with a very small aspect ratio, i.e., with a much smaller dimension perpendicular to the lines than parallel to them. We choose an alternative approach. If at any iteration the number of accepted triangles in the two-dimensional bisection algorithm exceeds 50, we assume the mixture is close to a bicritical point and exit the loop. Then, we perform a one-dimensional bisection along a straight line lying very close to the near-parallel solutions $RR_y = 0$ and $RR_z = 0$. When $K_{yi} \simeq 1$ (or $K_{zi} \simeq 1$) an inspection of Eq. 3 reveals that the solution must lie very close to the line $\beta_z = \beta$ (or $\beta_y = \beta$) where β is the solution to the two-phase Rachford–Rice equation. When $K_{yi} \simeq K_{zi}$, it is helpful to rewrite Eq. 3 in the following way:

$$\begin{aligned} RR_y &= \sum_{i=1}^N \frac{n_i(K_{yi}-1)}{1+(\beta_y+\beta_z)(K_{yi}-1)+\beta_z(K_{zi}-K_{yi})} = 0, \\ RR_z &= \sum_{i=1}^N \frac{n_i(K_{zi}-1)}{1+(\beta_y+\beta_z)(K_{zi}-1)-\beta_y(K_{zi}-K_{yi})} = 0. \end{aligned} \quad (10)$$

Note that the rightmost term in both denominators are negligible when $K_{yi} \simeq K_{zi}$. Thus, both three-phase Rachford–Rice expressions are essentially equal to their two-phase counterpart. Conclusively, the solution must lie very close to the line $\beta_y + \beta_z = \beta$. Performing a one-dimensional

Table 4. Feed Mole Fractions (n), Critical Temperatures T_C , Critical Pressures P_C , Acentric Factors ω and Nonzero Binary Interaction Coefficients k_{ij} for Sour Gas

Component	n	T_C (K)	P_C (bar)	ω	k_{i,CO_2}	k_{i,N_2}	$k_{i,\text{H}_2\text{S}}$
CO ₂	0.7059	304.2	73.9	0.225	–	–	–
N ₂	0.0703	126.2	33.5	0.040	–0.020	–	–
H ₂ S	0.0197	373.2	89.4	0.081	0.120	0.200	–
C ₁	0.0686	190.6	45.4	0.008	0.125	0.031	0.100
C ₂	0.1056	305.4	48.2	0.098	0.135	0.042	0.080
C ₃	0.0297	369.8	41.9	0.152	0.150	0.091	0.080

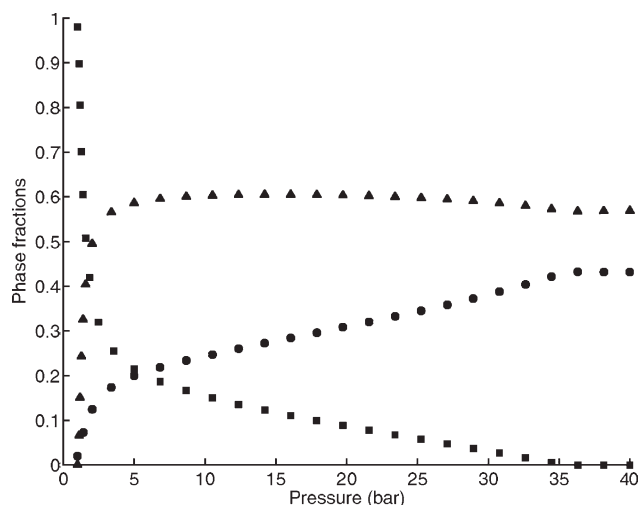


Figure 5. A plot showing how the phase amounts of liquid 1 (disks), liquid 2 (triangles), and vapor (squares) change across the three phase envelope for the sour gas at $T = 178.8$ K.

The CO_2 mole fraction is fixed at 0.60.

bisection on the three-phase Rachford–Rice expressions along the appropriate line, provides the initial guess for the Newton method. In our experience, the approach always puts the initial guess inside the convergence radius of the Newton method. This simple procedure makes our proposed method very robust, even in the bicritical region.

Note that the three different kinds of bicritical regions, $K_{yi} \simeq 1$, $K_{zi} \simeq 1$, and $K_{yi} \simeq K_{zi}$, are a result of phase labeling. In our implementation, we only treat the case when $K_{yi} \simeq K_{zi}$. If the cases $K_{yi} \simeq 1$ or $K_{zi} \simeq 1$ are encountered, we simply switch the reference phase.

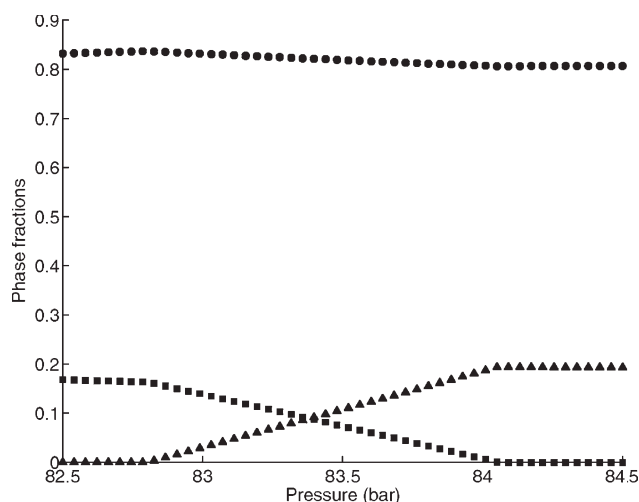


Figure 6. A plot showing how the phase amounts of liquid 1 (disks), liquid 2 (triangles), and vapor (squares) change across the three phase envelope for Oil B at $T = 307.6$ K.

The CO_2 mole fraction is fixed at 0.75.

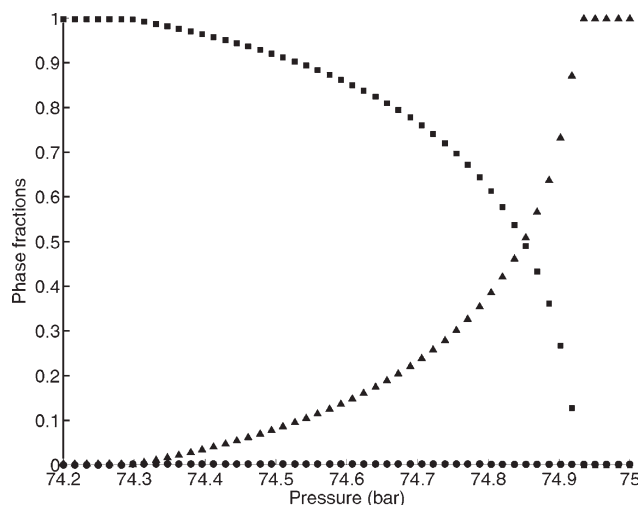


Figure 7. A plot showing how the phase amounts of liquid 1 (disks), liquid 2 (triangles), and vapor (squares) change across the three phase envelope for the Maljamar separator oil at $T = 305.4$ K.

The CO_2 mole fraction is fixed at 0.977.

Results

The challenge of finding a good initial guess for the three-phase Rachford–Rice equation is nearly ignored in the literature. One notable exception is Michelsen⁵ who obtains phase fractions from the minimization of an alternative objective function. The approach is valid for any number of phases. Moreover, as the objective function is convex, a unique solution is guaranteed to exist. Michelsen argues that the main complexity of calculating the phase distribution in multi-phase problems is that phases may appear or disappear

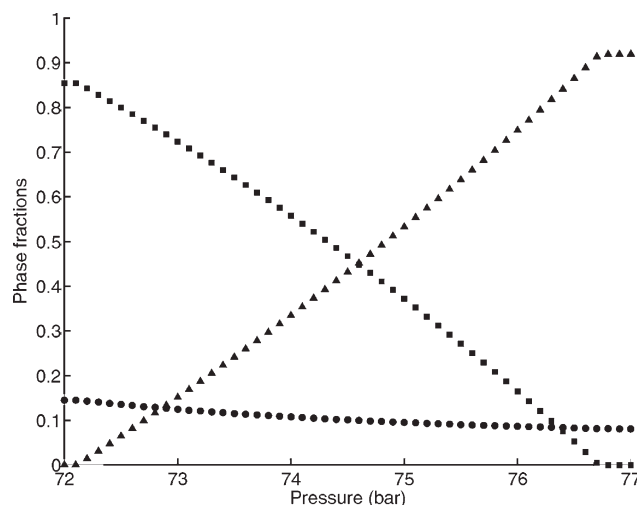


Figure 8. A plot showing how the phase amounts of liquid 1 (disks), liquid 2 (triangles), and vapor (squares) change across the three phase envelope for the Maljamar reservoir oil at $T = 305.4$ K.

The CO_2 mole fraction is fixed at 0.90.

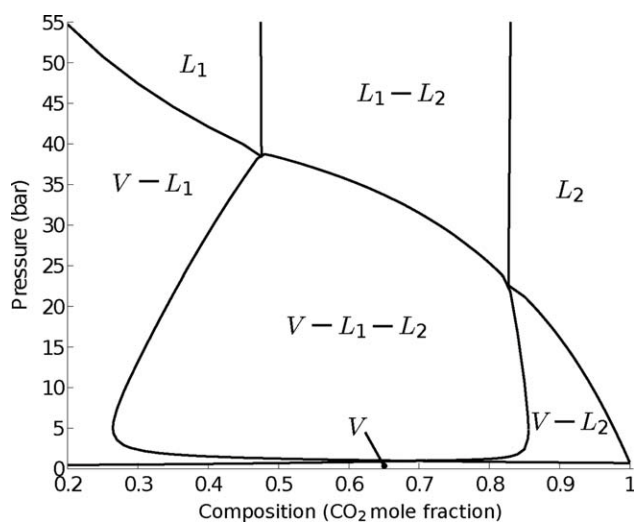


Figure 9. A phase diagram for the sour gas at $T = 178.8$ K showing the single-phase, two-phase, and three-phase regions. V denotes vapor and L_1 and L_2 denote the two liquid phases.

The three-phase region terminates at the points where the three single-phase regions touch the three-phase boundary.

between iterations. Thus, he finds it convenient to treat all phase fractions as independent unknowns. Conclusively, for a given number of phases, Michelsen's approach involves one more unknown than the corresponding Rachford-Rice equation where the fact that the sum of all phase fractions equals unity is used to eliminate one of them. Our solution procedure does not have issues with the number of phases changing between iterations. The two-dimensional bisection algorithm is only used to provide initial guesses for the

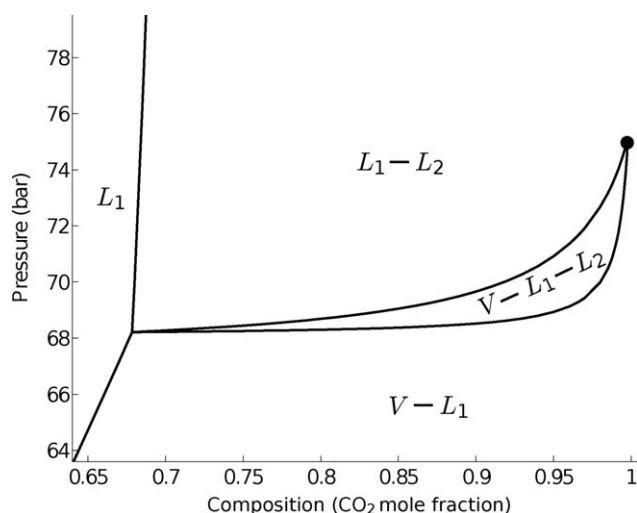


Figure 11. A phase diagram for the Maljamar separator oil at $T = 305.4$ K showing the single-phase, two-phase and three-phase regions.

V denotes vapor and L_1 and L_2 denote the two liquid phases. The three-phase region terminates at a bicritical point (●) and at the point where the single liquid-phase region touches the three-phase boundary.

phase fractions for the first successive substitution. Subsequent iterations use phase fractions from the previous iteration as initial guesses.

Michelsen⁵ provides the results of four example calculations. In addition to feed compositions and phase fractions, he also reports the fugacity coefficients of each component in all phases for each mixture. After choosing a reference phase, the information can be used to calculate equilibrium ratios. We can then compare Michelsen's results to those

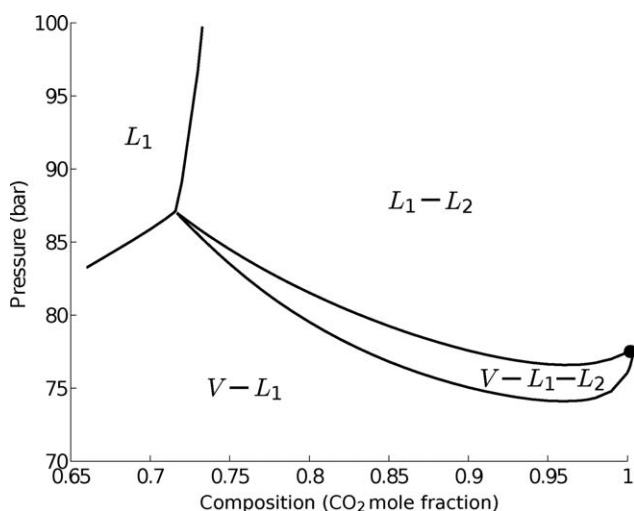


Figure 10. A phase diagram for Oil B at $T = 307.6$ K showing the single-phase, two-phase and three-phase regions.

V denotes vapor and L_1 and L_2 denote the two liquid phases. The three-phase region terminates at a bicritical point (●) and at the point where the single liquid-phase region touches the three-phase boundary.

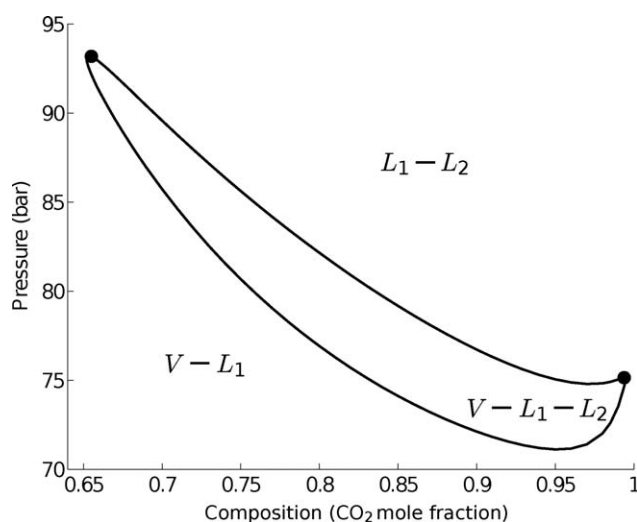


Figure 12. A phase diagram for the Maljamar reservoir oil at $T = 305.4$ K showing the two-phase and three-phase regions.

V denotes vapor and L_1 and L_2 denote the two liquid phases. The three-phase region terminates at two bicritical points (●).

Table 5. Feed Mole Fractions (n), Critical Temperatures T_C , Critical Pressures P_C , Acentric Factors ω and Nonzero Binary Interaction Coefficients k_{ij} for Oil B

Component	n	T_C (K)	P_C (bar)	ω	k_{i,CO_2}	k_{i,N_2}	k_{i,C_1}
CO ₂	0.0011	304.2	73.9	0.225	—	—	—
N ₂	0.0048	126.2	33.5	0.040	−0.020	—	—
C ₁	0.1630	190.6	45.4	0.008	0.075	0.080	—
C ₂	0.0403	305.4	48.2	0.098	0.080	0.070	0.003
C ₃	0.0297	369.8	41.9	0.152	0.080	0.070	0.010
iC ₄	0.0036	408.1	36.0	0.176	0.085	0.060	0.018
nC ₄	0.0329	425.2	37.5	0.193	0.085	0.060	0.018
iC ₅	0.0158	460.4	33.4	0.227	0.085	0.060	0.025
nC ₅	0.0215	469.6	33.3	0.251	0.085	0.060	0.026
C ₆	0.0332	506.4	33.9	0.299	0.095	0.050	0.036
PC1	0.1813	566.6	25.3	0.389	0.095	0.100	0.049
PC2	0.1614	647.1	19.1	0.529	0.095	0.120	0.073
PC3	0.1253	719.4	14.2	0.691	0.095	0.120	0.098
PC4	0.0954	784.9	10.5	0.878	0.095	0.120	0.124
PC5	0.0579	846.3	7.5	1.101	0.095	0.120	0.149
PC6	0.0228	919.4	4.8	1.448	0.095	0.120	0.181

obtained from our own three-phase split calculations. Michelsen's first example is a three-phase four-component mixture (see Table 1). One of the phases is pure water. The calculated phase fractions are in perfect agreement with those reported by Michelsen. Example 2a is a four-phase mixture in five components (see Table 2). The solid phase is only present in a tiny amount and, as our algorithm is only applicable to three-phase mixtures, we simply ignored it. The calculated phase fractions show excellent agreement with Michelsen's results. Example 2b is the only case where our results do not agree with those reported from Michelsen. He finds a three-phase mixture with two liquid and one solid phases, while in our case, there is no solid present (see Table 3). Taking a closer look at Michelsen's results reveals that the sum of mole fractions in the solid phase does not equal unity, implying that the solution is not valid. This may be due to an error in the reported fugacity coefficients. All example calculations were initialized with five bisection iterations. The subsequent algorithm for the solution of the three-phase Rachford–Rice equations requires five newton iterations.

The above example calculations are very useful for benchmarking purposes. However, they do not give any indication of the robustness of the method. For instance, all of the mixtures are far away from any bicritical points. A more thorough test is to use the three-phase split algorithm to compute three-phase envelopes. The procedure involves phase split calculations across the three-phase regions. We constructed three-phase envelopes of four CO₂–hydrocarbon mixtures:

(1) Sour gas from Robinson et al.²³ with the modified composition from Pan and Firoozabadi,²⁴ (2) Oil B from Shelton and Yarbrough,²⁵ (3) Maljamar separator oil from Orr et al.,²⁶ and (4) Maljamar reservoir oil also from Orr et al.²⁶ We provide the composition, critical properties, acentric factors, and nonzero binary interaction coefficients for the oils in Tables 4–7.

The sour gas has the largest three-phase region of the four petroleum fluids (see Figure 9). Its three-phase envelope is terminated at three points where the three single-phase regions touch the three-phase boundary. The same three points separate the three two-phase regions. The sour gas phase diagram is the most complex in the sense that it contains all possible equilibrium states. On the other hand, there are no bicritical points. Therefore, the sour gas three-phase envelope is the easiest one to compute. Figure 5 shows variations in phase fractions for a given feed composition.

Oil B has a fairly narrow three-phase region (see Figure 10). Unlike the sour gas, there is a bicritical point on the three-phase boundary. Our three-phase split algorithm is able to get very close to either side of the bicritical point. The three-phase envelope for Oil B is fundamentally different from that of the sour gas. It is terminated at only two points, i.e., the bicritical point where the vapor and one of the liquid phases become indistinguishable and the point where the single liquid phase region touches the three-phase boundary. Figure 6 shows an example of how phase fractions change across the three-phase region.

Table 6. Feed Mole Fractions (n), Critical Temperatures T_C , Critical Pressures P_C , Acentric Factors ω and Nonzero Binary Interaction Coefficients k_{ij} for the Maljamar Separator Oil

Component	n	T_C (K)	P_C (bar)	ω	k_{i,CO_2}
CO ₂	—	304.2	73.9	0.225	—
C _{5–7}	0.2354	516.7	28.8	0.265	0.115
C _{8–10}	0.3295	590.0	23.7	0.364	0.115
C _{11–14}	0.1713	668.6	18.6	0.499	0.115
C _{15–20}	0.1099	745.8	14.8	0.661	0.115
C _{21–28}	0.0574	812.7	12.0	0.877	0.115
C ₂₉₊	0.0965	914.9	8.5	1.279	0.115

Table 7. Feed Mole Fractions (n), Critical Temperatures T_C , Critical Pressures P_C , Acentric Factors ω and Nonzero Binary Interaction Coefficients k_{ij} for the Maljamar Reservoir Oil

Component	n	T_C (K)	P_C (bar)	ω	k_{i,CO_2}	k_{i,C_1}
CO ₂	—	304.2	73.8	0.225	—	—
C ₁	0.2939	190.6	45.4	0.008	0.115	—
C ₂	0.1019	305.4	48.2	0.098	0.115	—
C ₃	0.0835	369.8	41.9	0.152	0.115	—
nC ₄	0.0331	425.2	37.5	0.193	0.115	—
C _{5–7}	0.1204	516.7	28.8	0.265	0.115	0.045
C _{8–10}	0.1581	590.0	23.7	0.364	0.115	0.055
C _{11–14}	0.0823	668.6	18.6	0.499	0.115	0.055
C _{15–20}	0.0528	745.8	14.8	0.661	0.115	0.060
C _{21–28}	0.0276	812.7	12.0	0.877	0.115	0.080
C ₂₉₊	0.0464	914.9	8.5	1.279	0.115	0.280

As for Oil B, the three-phase envelope is terminated at a bicritical point and at the point where a single liquid-phase region touches the three-phase boundary. Therefore, the three-phase envelope for the Maljamar separator oil can be perceived as lying between those of the sour gas and Oil B. As we will discuss shortly, our computed three-phase envelope is wider than those detected by other authors. The reason may be that when the three-phase region becomes very narrow, the phase fractions change rapidly with composition and pressure. Consequently, the phase fractions from one three-phase split calculation is not necessarily a good guess for the next one. In our approach, the problem is alleviated by using two-dimensional bisection to provide the initial guess. Figure 7 shows phase fraction variations near the bicritical point.

The three-phase region associated with the Maljamar reservoir oil is completely immersed in a two-phase region (see Figure 12). This is due to the fact that the three-phase region is terminated by two bicritical points. There is, therefore, a smooth transition between the two two-phase regions at either extreme of the three-phase region. Figure 8 shows variations in phase fractions for a fixed feed composition (Figure 8).

In the past, a number of authors have computed the three-phase region for Oil B.^{15,16,27} Nghiem and Li,¹⁵ and Cultinho et al.¹⁶ compute a narrower region for the three-phase region than we do. Nichita et al.²⁷ do a fine job except toward the bicritical point on the right side of Figure 6 and they fail to detect the single phase liquid at the extreme right in.¹¹ For the Maljamar separator oil, Cultinho et al.¹⁶ show a termination of the three-phase region to the left different from ours. Perschke²⁸ computes a much narrower three-phase region than we do.

Concluding Remarks

There are two ways of solving the three-phase split problem. One approach is based on minimization techniques. Another approach is based on a direct solution of the Rachford–Rice expressions. In this work, we show that a combination of a two-dimensional bisection technique and Newton's method provides a robust and efficient solution algorithm for the second approach. The robustness is demonstrated by consistent phase diagrams, which is perhaps the

best measure of validity. In our algorithm, each iteration of the bisection method is very inexpensive. Moreover, the two-dimensional bisection is only used to provide an initial guess the first time the Rachford–Rice expressions are solved within a successive substitution loop. Subsequently, the initial guess is taken from the previous iteration. Thus, the computational overhead is negligible. Problems in the bicritical region are avoided by putting an upper limit on the number of triangles. If the limit is exceeded, we perform a one-dimensional search along a straight line to which the solution must be close. In our testing, the bisection method never failed. Without the use of the bisection method we would not be able to construct complete three-phase regions.

Acknowledgments

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Notation

\vec{e} = vector of residuals
 f = fugacity
 J = Jacobian
 K = equilibrium ratio
 N = number of components
 n = feed mole fraction
RR = Rachford–Rice residuals
 x = mole fraction (first phase)
 y = mole fraction (second phase)
 z = mole fraction (third phase)
 β = phase fraction
 Δ = vector of updates of the independent variables for the Newton method
 ϕ = fugacity coefficient

Subscripts

i = component label
 x = phase label (first phase)
 y = phase label (second phase)
 z = phase label (third phase)

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