An Improved Algorithm for the Three-Fluid-Phase VLLE Flash Calculation

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The VLLE flash is important in water and hydrocarbons mixtures, hydrocarbon and CO₂ rich mixtures, and hydrocarbon methane rich mixtures that are encountered in reservoir performance and recovery studies. A robust VLLE flash algorithm is proposed. The equilibrium and mass balance equations are solved as a constrained minimization problem. An inverse barrier function is used to handle the inequality constraints to solve for the phase fractions. It warrants always arriving to the solution. The challenging cases analyzed showed that the initialization procedure proposed, together with successive substitution iteration in the outer loop, is a good method for a stable VLLE flash algorithm, even near critical points. Whenever the result is in the region outside the three-phase physical domain, the solution suggests that the system has fewer phases. In one of the cases analyzed, a region with three liquid phases was encountered and the algorithm found two different solutions with positive phase fractions.

Keywords: computational chemistry (kinetics/thermo), phase diagrams, phase equilibrium, vapor-liquid-liquid equilibrium

Introduction

The three-fluid-phase Vapor-Liquid-Liquid Equilibrium (VLLE) flash calculation is important in a variety of problems relevant in chemical engineering. In many processes, three fluid phases may be present when the liquid phase splits into two liquids, consequently, the phase equilibrium calculation has to recognize the regions where one (V or L), two (VL or LL), or three fluid phases (VLL) are present. Such is the case in water and hydrocarbons mixtures, hydrocarbon and CO₂ rich mixtures and hydrocarbon CH₄ rich mixtures found in reservoir performance and recovery studies.

The fluid phase equilibrium problem is formulated as follows: given a mixture whose global composition is known, the compositions and amounts of fluid phases present in equilibrium at a given temperature and pressure, must be determined. The phase with the lowest density is labeled as vapor, the remaining ones as liquids. Thermodynamic models that represent the properties of the fluid phases present in equilibrium at a given temperature and pressure, must be determined.

Over the past three decades, many multiphase algorithms have been proposed to solve the highly nonlinear equilibrium problem. The problem has been formulated in two broad categories: (1) equi-fugacity methods (EFM), and 2) Gibbs free energy minimization methods (GMM). In the EFM method, the formulation pursues the equality of fugacity and the mass balance equations. The EFM method solves for the phase fractions in an inner loop and the phase compositions are updated in the outer loop. The inner loop can be formulated as a minimization problem or as an equation-solving problem. For the two approaches, there are several algorithms recently developed that provide solutions to difficult equilibrium problems. Apparently, both approaches are capable to find the solution even with difficult problems, and the selection of a specific approach is a matter of preferences.

Recent works on the EFM have placed special attention to the solution of the Rachford–Rice (RR) equations to guaranty robustness and stability of the solution. Implementing the negative flash strategy is necessary for a robust algorithm (Whitson and Michelsen). In this approach, a major problem found is that classical Newton’s method fails to converge in difficult regions like near critical points and phase boundaries. Proposals to overcome this deficiency are the formulation of Iranshahr et al. and Leibovici and Neoschil that uses the Newton’s method with a relaxation parameter, of Haugen et al. using the two-dimensional bisection method to obtain initial guesses of phase fractions and then solving the RR equations by Newton’s Method, of Okuno et al. that uses a line search along the Newton’s...
direction and the formulation of Yan and Stenby that analyzes the use of higher order methods. To solve the RR equations, Michelsen proposed the minimization of a function whose derivatives are the RR equations and Leibovici and Nichita added the negative flash concept to Michelsen’s formulation with good results.

Conversely, works on the GMM approach are the formulation of Lucia et al. that uses the full space SQP algorithm, of Bausa and Marquardt that employs homotopy continuation, of Saber and Shaw that uses the so-called DIRECT method, and of Jalali et al. that applies homotopy continuation in the complex domain, of Nichita and Gomez that uses tunneling global optimization and of Petitfrere and Nichita on the trust region method.

To find the correct number of phases present for a given problem, the strategies proposed have been along the following lines: (1) start with a stability analysis to see if the mixture splits in two phases, then solve the two phase flash, follow with a stability analysis to see if the system splits in three phases, and finally, solve the VLLE flash; (2) start with the three-phase VLLE flash, if the solution is in the VLLE region, accept the solution, otherwise, perform the corresponding two phase flash (VL or LL).

As a starting point for any VLLE flash algorithm is the initialization procedure. First, there is the need to provide initial estimates of compositions and fractions of the phases present. Poor estimates can lead to not finding the correct solution or not finding a solution at all. Several algorithms perform first, as pointed out previously, a one-phase stability analysis to provide initial estimates for the two-phase flash problem, then use the results from two-phase split calculation and, if an instability is found with a two-phase stability analysis, a three-phase flash is solved. Another option is to start directly with estimates from ideal Wilson K’s for vapor and one liquid phase and the second liquid phase with the key component as pointed out previously, a one-phase stability analysis to provide initial estimates for the two-phase flash, then use the results from two-phase split calculation and, if an instability is found with a two-phase stability analysis, a three-phase flash is solved. Another option is to start directly with estimates from ideal Wilson K’s for vapor and one liquid phase and the second liquid phase with the key component and, if an instability is found with a two-phase stability analysis, a three-phase flash is solved.

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Problem Formulation

The VLLE flash is formulated as: given a mixture of known global composition, the amounts and compositions of the vapor and two liquid phases present in equilibrium at a given temperature and pressure, must be determined. In the EFM approach, the system of equations that must be solved are the usual equilibrium and material balance relations for each component in the mixture.

1. Equilibrium equations

\[ f_i^V = f_i^L = f_i^{b} \]  \hspace{1cm} i = 1, \ldots, n  \hspace{1cm} (1)

In terms of equilibrium constants, they are expressed as

\[ K_{ii} = \frac{y_i}{x_i} = \frac{\theta_{ii}^{V}}{\theta_{ii}^{L}} \quad K_{ij} = \frac{w_i}{x_i} = \frac{\theta_{ij}^{V}}{\theta_{ij}^{L}} \quad i = 1, \ldots, n \hspace{1cm} (2) \]

The fugacity coefficients for the three fluid phases are calculated with the PR EOS and are functions of temperature, pressure, and phase composition.

2. Material balance equations

\[ z_i = \beta_1 y_i + \beta_2 w_i + (1 - \beta_1 - \beta_2) x_i \quad i = 1, \ldots, n \hspace{1cm} (3) \]

The phase fractions are

\[ \frac{V}{P} = \beta_1 \quad \frac{L_2}{P} = \beta_2 \quad \frac{L_1}{P} = (1 - \beta_1 - \beta_2) \hspace{1cm} (4) \]

Equations 2 and 3 are combined in the usual manner to give the equations for the phase compositions in terms of phase fractions and equilibrium constants

\[ x_i = \frac{z_i}{1 + \beta_1 (K_{ii} - 1) + \beta_2 (K_{ji} - 1)} \quad i = 1, \ldots, n \hspace{1cm} (5) \]

\[ y_i = \frac{z_i K_{ji}}{1 + \beta_1 (K_{ii} - 1) + \beta_2 (K_{ji} - 1)} \quad i = 1, \ldots, n \hspace{1cm} (6) \]

\[ w_i = \frac{z_i K_{ij}}{1 + \beta_1 (K_{ij} - 1) + \beta_2 (K_{jj} - 1)} \quad i = 1, \ldots, n \hspace{1cm} (7) \]

The system formed by Eqs. 2 and 5–7, together with the restriction that the phase mole fractions have to add to unity should be recursively solved. The unknowns are the phase fractions \( \beta_1, \beta_2 \), and the phase component mole fractions \( x_i, y_i, w_i \), \( i = 1, \ldots, n \). The number of unknowns is: 2 phase fractions (the third one adds to unity) and 3(n–1) phase component mole fractions (the remaining one adds to unity for each phase.)

In the EFM approach, it is usual to combine Eqs. 5–7 to give the RR equations

\[ \text{RR}_{xy} = \sum_{i=1}^{n} \frac{z_i (K_{ii} - 1)}{1 + \beta_1 (K_{ii} - 1) + \beta_2 (K_{ji} - 1)} = 0 \hspace{1cm} (8) \]

\[ \text{RR}_{yx} = \sum_{i=1}^{n} \frac{z_i (K_{ji} - 1)}{1 + \beta_1 (K_{ii} - 1) + \beta_2 (K_{ji} - 1)} = 0 \hspace{1cm} (9) \]

The general EFM strategy is to solve Eqs. 8 and 9 for \( \beta_1 \) and \( \beta_2 \) for a given set of equilibrium constants \( K_{ii} \) and \( K_{jj} \) for...
As it can be seen in the previous work mentioned above, many strategies have been proposed to solve the RR equations in the inner loop. In the present work, we adopted the modification of Leibovici and Nichita to Michelsen’s formulation as a constrained minimization problem. We introduced an inverse barrier function to construct a composite function that combines the objective function and the inequality constrained functions in such a way as to introduce a barrier along the constrained boundary.

The formulation is as follows.

Following Leibovici and Nichita, given a set of equilibrium constants $K_i$, and $K_m$, for $i = 1, \ldots, n$, find the phase fractions $\theta = (\beta_1, \beta_2)$ that minimizes the objective function

$$Q(\theta) = 1 - \frac{1}{2} \sum_{i=1}^{n} z_i \ln [1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)]^2$$

Subject to the inequality constraints

$$E_i = 1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1) > 0 \quad i = 1, \ldots, n$$

The inequality constraints warrant that the component mole fractions in all phases are positive. Equation 11 defines the feasible region. The phase fractions are allowed to take values in the feasible region even if a negative value for some phase fraction is found. A solution is sought in all the domain of the feasible region.

The inequality constraints are combined with the objective function through the inverse barrier function

$$B(\theta, r) = Q(\theta) + r \sum_{i=1}^{n} \frac{1}{\beta_i^2}$$

The problem is now to solve for the phase fractions $\beta_1, \beta_2$ that minimize the augmented function $B(\theta, r)$. The barrier parameter has to be chosen so that the trial values of the phase fractions remain in the feasible region. It must adopt a non-negative value. In subsequent iterations it has to diminish and become zero as the solution is approached. If the barrier parameter is properly chosen, an unconstrained search technique can be implemented.

The minimum of the augmented function is found if the derivatives of the augmented function are equal to zero

$$B_{\theta_1} = \frac{\partial B}{\partial \beta_1} = -\sum_{i=1}^{n} \frac{z_i (K_i - 1)}{1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)}$$

$$B_{\theta_2} = \frac{\partial B}{\partial \beta_2} = -\sum_{i=1}^{n} \frac{z_i (K_m - 1)}{1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)}$$

It should be noted that the usual RR equations are fulfilled if the barrier parameter is equal to zero. The problem is transformed to find a solution of Eqs. 13 and 14 for the phase fractions $\beta_1, \beta_2$. To do so, we have selected a Newton’s search method. The necessary derivatives for the gradient are

$$\frac{\partial B_{\theta_1}}{\partial \beta_1} = \sum_{i=1}^{n} \frac{z_i (K_i - 1)}{[1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)]^2}$$

$$\frac{\partial B_{\theta_2}}{\partial \beta_2} = \sum_{i=1}^{n} \frac{z_i (K_m - 1)}{[1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)]^2}$$

$$\frac{\partial B_{\theta_1}}{\partial \beta_1} = \sum_{i=1}^{n} \frac{z_i (K_m - 1)}{[1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)]^2}$$

$$\frac{\partial B_{\theta_2}}{\partial \beta_2} = \sum_{i=1}^{n} \frac{z_i (K_i - 1)}{[1 + \beta_1 (K_i - 1) + \beta_2 (K_m - 1)]^2}$$
11, are always meet. Substituting Eqs. 15 and 16 into Eq. 11, the following expression is obtained

\[ E_i = (E_i)_0 + \frac{a_i + b_i r + c_i r^2}{A + B r + C r^2} \quad i = 1, \ldots, n \quad (17) \]

Where

\[ (E_i)_0 = 1 + (\beta_1)_0 (K_{i1} - 1) + (\beta_2)_0 (K_{i1} - 1) \]
\[ a_i = (-S_1 S_4 + S_2 S_3) (K_{i1} - 1) + (-S_2 S_3 + S_1 S_4) (K_{i2} - 1) \]
\[ b_i = (-2 S_1 S_4 + 2 S_2 S_3) (K_{i1} - 1) + (-2 S_2 S_4 + 2 S_1 S_3) (K_{i2} - 1) \]
\[ c_i = (-2 S_1 S_4 + 2 S_2 S_3) (K_{i2} - 1) + (-2 S_1 S_4 + 2 S_2 S_3) (K_{i1} - 1) \]
\[ A = S_2 S_3 - S_4 \]
\[ B = 4 S_4 S_{10} - 2 S_4 S_5 - 2 S_3 S_9 \]
\[ C = 4 (S_{10} - S_3 S_9) \]

The equations \( E_i = 0 \) are quadratic with respect to the barrier parameter \( r \) and are solved for \( r \) in each component in the mixture. The barrier parameter \( r \), substituted in Eqs. 15 and 16 to update the phase fractions is chosen as 1.5 times the maximum real root encountered in solving Eq. 17 equated to zero for all components. If a negative value is found, then \( r \) is set equal to zero. In this case, the algorithm is equivalent to a Newton’s second-order convergence because imposing a barrier was not necessary to ensure the convergence. The barrier parameter has to be zero when the convergence is reached.

The previous formulation warrants finding a solution whenever a solution exists. If, for the given set of equilibrium constants a solution does not exist, the iterations proceed to negative values of increasing magnitude for one of the phases.

Solution Procedure

The algorithm proposed in this work for the VLLE flash problem is as follows:

1. Initial estimates of the phase fractions are set to \( \beta_1 = 0.3 \) and \( \beta_2 = 0.3 \).
2. Initial estimates of the phase compositions are given by

   For the vapor phase \( y_i = z_i K_i^W \quad i = 1, \ldots, n \)

   For the first liquid phase \( x_i = z_i / K_i^W \quad i = 1, \ldots, n \)

Where the \( K_i^W \) is the usual Wilson’s VL equilibrium constant

\[ K_i^W = \frac{P_{ci}}{P} \exp \left( 5.373 (1 + \omega_i) \left( 1 - \frac{T_{ci}}{T} \right) \right) \quad i = 1, \ldots, n \]

For the second liquid phase, we choose it to be almost a pure component.\(^\text{19,20}\) The proposed mole fraction value for the key component of Li and Firoozabadi\(^\text{5}\) is 0.90. However, we tested several values (0.9, 0.95, and 0.98) and adopted a mole fraction equal to 0.98 for the key component as it gave the most consistent results for the systems studied in this work. The remaining 0.02 is evenly distributed among the rest of the components. In principle, all components are chosen to be key components.

3. Calculate the fugacity coefficients for each component in every phase using the EOS. For the first iterations, the algorithm of Mathias et al.\(^\text{23}\) is implemented to avoid trivial solutions. Then, the equilibrium constants are calculated with Eq. 2.

4. Solve the inner loop to find the phase fractions \( \theta = (\beta_1, \beta_2) \) for the equilibrium constants calculated in Step 3 with the augmented barrier function formulation presented in this work, as explained earlier. The phase fractions are allowed to take values in the feasible region even if a negative phase is encountered. Continue the iterations until the residual of the barrier function Eqs. 13 and 14 are lower than a specified tolerance. If the iterations proceed to negative values of increasing magnitude for one of the phases the iteration is stopped and a warning is issued stating that for the conditions given either (a) there is not a solution of the RR equations for the given set of equilibrium constants, (b) the solution is very close to the limit of the feasible region, or (c) the problem is very close to a critical point.

5. Update the phase component mole fraction with Eqs. 5–7. Normalize so that they add to unity.

6. Check for convergence and go back to Step 3 for the next iteration if needed. This is the SSI in the outer loop.

Results

Haugen et al.\(^\text{4}\) stress the importance of finding the solution in the inner loop where a solution of the three-phase flash is sought for a given set of equilibrium constants. This is a necessary requisite for a stable VLLE flash algorithm. To illustrate the convergence properties of the algorithm proposed in this work for the inner loop, in Figures 1 and 2 we present results of Examples 3 and 4 given by Okuno et al.\(^\text{7}\) in their Table 2. The feasible zone is located in the usual manner delimited by the lines drawn where the inequality constraints given by Eq. 11 are set equal to zero. The feasible zone is divided into two sectors depending on the convergence properties of a Newton’s algorithm. If the initial estimates of the phase fractions fall in Sector B, the Newton’s algorithm will converge, but if it fall in Sector A the Newton algorithm will not converge because in one of the iterations the phase fractions will adopt values outside the feasible zone. The solution to the flash problem always lies in the Newton’s convergence sector. For these examples, the Newton’s convergence Sector B is very narrow and therefore can be used to prove the convergence characteristics of the inner loop algorithms. As it is shown in Figure 1, the barrier method proposed in this work is capable during all iterations to maintain the successive values of phase fractions.
in the feasible zone. This is done by using a positive value of the barrier parameter. In this particular example, a positive value of the barrier parameter was needed in the second iteration. As shown in Figure 2 for Example 3, the proposed algorithm can find a solution starting with different initial estimates. It takes a few iterations to drive the solution to the Newton’s sector where convergence is located.

For a multicomponent system of given global composition at a specified temperature and pressure, the solution of the three-phase flash VLLE problem can fall into one of the following situations: (a) convergence to the physical feasible solution for which all phase fractions are positive, (b) convergence in the negative flash region where one of the phase fractions is negative, or (c) there is not solution to the VLLE problem. The last situation arises when the stated conditions for the VLLE flash problem are beyond the asymptotes, as discussed by Leibovici and Nichita.

To test the proposed algorithm in this work, we systematically analyzed five challenging problems addressed by Haugen et al. and Li and Firoozabadi (CO₂ injection for Oil B, Malhamar Reservoir Oil, Malhamar Separator Oil, Bob Slaughter Block Oil, and North Ward Estes Oil). For the Bob Slaughter Block Oil and North Ward Estes Oil, we injected pure CO₂, as it is done with the other three systems. Haugen et al. and Li and Firoozabadi injected impure CO₂ (95% CO₂ + 5% CH₄) for these systems, so our results are not quite comparable with Haugen et al. and Li and Firoozabadi results for these two systems. We used the PR EOS for the fugacity coefficients calculations in all phases. The compositions, critical properties, acentric factors, and nonzero binary interaction coefficients were taken from the Tables 4–8 in Li and Firoozabadi.

In Figures 3–7, we present the phase diagrams for the systems studied. All the phase diagrams were constructed with the VLLE algorithm proposed in this work. The results we obtained compare well with the results of Haugen et al. and Li and Firoozabadi. Note that for the North Ward Estes Oil system there is not a CO₂-rich bicritical point in our calculations as compared with Haugen et al. results due to the difference in composition of the CO₂ injected.

At a specified pressure and CO₂ mole fraction, the VLLE flash was solved with the algorithm outlined in Solution Procedure Section, always starting from the stand-alone initial estimate. The negative-flash algorithm always converged to a solution if the specified conditions fall inside the VLLE flash convergence limits. Whenever a phase boundary line is crossed, a new phase appears or disappears depending on the direction that the line is crossed. Then, along the phase boundary line, the phase fraction of one of the phases in equilibrium is equal to zero. To locate the points in the phase diagrams presented in this work, an interpolation of the VLLE negative-flash solutions was performed. The enlargements around the bicritical points show a retrograde behavior not reported by

**Figure 2. Iteration path for Example 3 from Okuno et al.**

Newton’s iterations (dot) and proposed method (triangles). Feasible zone above solid line and below dashed lines. The gross solid line divides the Sector B (Newton’s method converges) and Sector A (Newton’s method fails).

**Figure 3. The phase diagram for CO₂ mixing with Oil B at 307.6 K showing the phase regions.**

V, L₁, L₂ are the vapor, CO₂-lean, and CO₂-rich liquid phases. The solid lines are the phase boundaries and the dashed lines are the VLLE flash convergence limit. The solid circle represents the bicritical point. (a) Complete phase diagram and (b) enlargement around the CO₂-rich bicritical point.
previous works on the same systems. The convergence limits lines drawn on the phase diagrams correspond to solutions of the VLLE negative-flash for which a phase fraction for one of the phases is equal to +\frac{1}{5} or −\frac{2}{5}. With these limits, we make sure to be close to the asymptotes. The VLLE region enclosed by the convergence limits cover a much wider area than the physically feasible three phase VLLE region enclosed by the phase boundaries. As the convergence limit is approached, the difference in composition of two of the phases becomes very small. The two phases with this behavior are the ones with the phase fraction large in magnitude, one positive and the other one negative. Therefore, close to the convergence limit a VLLE algorithm is prompt to fail due to convergence to a trivial solution. This region constitutes a good area to test the robustness of a VLLE algorithm. The algorithm proposed in this work handled this region quite well. A closer look at the enlargements around the bicritical points shows that the convergence limit for the feasible region is very close to the three-phase boundary in the neighborhood of a few thousands in the mole fraction of CO₂.

In Figures 8–11, the phase behavior along pressure trajectories across the three phase envelop for constant CO₂ global mole fraction are presented. We have selected two CO₂ compositions for the Oil B system close to the bicritical point, one to the left at 99% mol. (see Figures 8 and 9) and one to the right at 99.45% mol. in the retrograde zone (see Figures 10 and 11). The smooth change shown in Figures 8 and 9, even when the system crosses the phase boundaries is the typical behavior encountered in VLLE. In Figure 9 is appreciated how the vapor V and the CO₂-rich liquid L₂ approach each other in composition as the convergence limit is reached.

Figures 10 and 11 show the behavior in the retrograde region right to the bicritical point. In the increasing pressure trajectory, as one crosses the VLL-three-phase boundary, the
CO₂-rich liquid $L_2$ appears as is the case left to the bicritical point trajectory (see Figure 8). As pressure is increased, the $L_2$ phase fraction increases as for a normal case, but it reaches a maximum and then falls down. As pressure is further increased, the $L_2$ phase disappears as the phase boundary is crossed at a higher pressure, contrary to the normal behavior. The CO₂ mole fractions of the three phases are reported in Figure 11. It is worth to mention that the difference in CO₂ mole fraction between the vapor $V$ and CO₂-rich liquid $L_2$ is just a few thousandths, consequently, the properties of the two phases $V$ and $L_2$ are very close to each other in the vicinity of the bicritical point. Left of the bicritical point in CO₂ composition, the system leaves the three-phase region and enters the two-phase region at the upper pressure phase boundary as CO₂-lean liquid $L_1$ and CO₂-rich liquid $L_2$. Right to the bicritical point in CO₂ composition, the system leaves the three-phase region and enters the two-phase region at the upper pressure phase boundary as CO₂-lean liquid $L_1$ and vapor $V$. The label $V$ or $L_2$, for phases at pressures above the phase boundaries, is just a matter of convenience therefore, continuity is preserved. As a final remark for these systems, we analyzed the SSI convergence for the outer loop. In Figure 12, we present the convergence evolution for phase fractions and in Figure 13 for phase CO₂ mole fractions, for CO₂ mixing with Oil B to give 75% mol. of CO₂ at 307.6 K and 83.5 bar. This point calculation is typical of systems away from critical points. The
convergence is stable and comes close to the solution after a few iterations.

In Figure 14, we present the convergence evolution for phase fractions and in Figure 15 for phase CO$_2$ mole fractions, for CO$_2$ mixing with Oil B to give 99.3% mol. of CO$_2$ at 307.6 K and 72 bar. This point calculation is typical of systems that are close to critical points. The convergence becomes more erratic and it takes longer to arrive close to the solution.

The initial estimates in Step 2 of Solution Procedure Section requires the election of a component as an almost pure component for the second liquid phase composition estimate. For the cases studied in this work, the CO$_2$ was chosen as the almost pure component. At selected points, all other components were tested. The result was that the algorithm never converged when other component besides CO$_2$ was chosen. In almost all the tests, the initial equilibrium constants did not yield a solution for the inner loop.

A further test of the algorithm proposed was performed using the PEMEX Gas Condensate A fluid enriched with CO$_2$. The original fluid composition before the addition of CO$_2$ is presented in Table 1, along with the critical properties and nonzero temperature dependent binary interaction parameters. At a given temperature, the binary interaction parameters are calculated with the following expression

$$k_{ij} = k^0_{ij} + \left( \frac{T}{1000} \right) k^1_{ij}$$  \hspace{1cm} (18)

In Figure 16, we present the phase diagram of the original fluid with the experimental data that was used to obtain the nonzero binary interaction parameters. It shows a narrow VLLE region at low temperatures and pressures. The original fluid was mixed with CO$_2$ to give a 16% mol. of CO$_2$. This system was analyzed and the resulting phase diagram is shown in Figure 17. This system shows regions of two and three liquid phases in equilibrium. That is, besides the one- and two-phase regions, it has regions of three phases: VLL and LLL, and a four phase region: VLLL. A thorough search covering the whole P-T plane was conducted to test the performance of the VLLE flash algorithm. The results of the VLLE algorithm proposed in this article also served to construct the phase diagram. The procedure for the test was the following:

1. Perform calculations for the VLLE flash for a pressure vector at a given temperature. Select all the components as key components. If more than one solution is found, keep the ones that are different.
2. Locate the VLL phase boundaries whenever a phase fraction is equal to zero. Interpolation between solutions may be necessary.

3. Repeat the two previous steps for a temperature vector at a given pressure.

The general results of the test are: (a) solutions were found only when CO₂, CH₄, or N₂ were selected as key components.
In cases when a solution is found with \( \text{N}_2 \) as the key component, it was identical to the solutions found with \( \text{CO}_2 \) or \( \text{CH}_4 \). (b) In the VLL three-phase regions, the solutions were physically feasible with positive phase fractions. As the four-phase VLLL region was approached, the VLLE algorithm found two physically feasible solutions, one with \( \text{CO}_2 \) and the other with \( \text{CH}_4 \) as the key component. We retained the solution based on the minimum Gibbs energy criteria. (c) The liquid phases found in the physically feasible solutions were labeled as follows: \( L_1 \) as the heavy hydrocarbon components (PC1 through PC5) rich liquid phase; \( L_2 \) as the \( \text{CO}_2 \)-rich liquid phase; and \( L_3 \) as the \( \text{CH}_4 \)-rich liquid phase. (d) In the \( V-L_1-L_2 \) region, the solution was always the one found with \( \text{CO}_2 \) as the key component. (e) In the \( V-L_1-L_3 \) region, the solution was always the

**Figure 16.** The phase diagram for PEMEX Gas Condensate A showing the phase regions.

\( V, L_1, L_2 \) are the vapor, heavy hydrocarbons-rich, and \( \text{CO}_2 \)-rich liquid phases. The solid lines are the phase boundaries and the open squares are experimental data. (a) Complete phase diagram. The solid circle represents the VL critical point. (b) Enlargement around the VLL phase region. The solid circle represents the bicritical point.

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**Table 1.** Composition, Critical Properties, and Binary Interaction Coefficients for the PEMEX Gas Condensate A

<table>
<thead>
<tr>
<th>Component</th>
<th>( n ) (initial)</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (bar)</th>
<th>( \omega )</th>
<th>( k_{i,j}^{\text{C1}} )</th>
<th>( k_{i,j}^{\text{C1}} )</th>
<th>( k_{i,\text{CO}_2} )</th>
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<td>( \text{N}_2 )</td>
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<td>126.20</td>
<td>34.00</td>
<td>0.0373</td>
<td>0.36513</td>
<td>-0.36513</td>
<td>-0.017</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>0.009530</td>
<td>304.21</td>
<td>73.83</td>
<td>0.2236</td>
<td>0.14205</td>
<td>-0.1200</td>
<td>0.0974</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>0.001380</td>
<td>373.53</td>
<td>89.63</td>
<td>0.0942</td>
<td>0.1322</td>
<td>0.1200</td>
<td>0.0919</td>
</tr>
<tr>
<td>( \text{C}_1 )</td>
<td>0.615960</td>
<td>190.56</td>
<td>45.99</td>
<td>0.0115</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0974</td>
</tr>
<tr>
<td>( \text{C}_2 )</td>
<td>0.056020</td>
<td>305.32</td>
<td>48.72</td>
<td>0.0995</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0919</td>
</tr>
<tr>
<td>( \text{C}_3 )</td>
<td>0.026280</td>
<td>369.83</td>
<td>42.48</td>
<td>0.1523</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0974</td>
</tr>
<tr>
<td>( \text{iC}_4 )</td>
<td>0.003890</td>
<td>407.80</td>
<td>36.40</td>
<td>0.1835</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0919</td>
</tr>
<tr>
<td>( \text{nC}_4 )</td>
<td>0.014010</td>
<td>425.12</td>
<td>37.96</td>
<td>0.2002</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0974</td>
</tr>
<tr>
<td>( \text{iC}_5 )</td>
<td>0.005400</td>
<td>460.40</td>
<td>33.80</td>
<td>0.2279</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0919</td>
</tr>
<tr>
<td>( \text{nC}_5 )</td>
<td>0.007400</td>
<td>469.70</td>
<td>33.70</td>
<td>0.2515</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0974</td>
</tr>
<tr>
<td>( \text{C}_6 )</td>
<td>0.027930</td>
<td>519.73</td>
<td>30.50</td>
<td>0.2987</td>
<td>0.1222</td>
<td>0.1200</td>
<td>0.0919</td>
</tr>
<tr>
<td>( \text{PC}_1 )</td>
<td>0.041020</td>
<td>563.595</td>
<td>30.527</td>
<td>0.3396</td>
<td>0.14205</td>
<td>-0.36513</td>
<td>0.1200</td>
</tr>
<tr>
<td>( \text{PC}_2 )</td>
<td>0.069706</td>
<td>632.811</td>
<td>24.921</td>
<td>0.4540</td>
<td>0.14205</td>
<td>-0.36513</td>
<td>0.1200</td>
</tr>
<tr>
<td>( \text{PC}_3 )</td>
<td>0.060786</td>
<td>724.857</td>
<td>17.962</td>
<td>0.6635</td>
<td>0.14205</td>
<td>-0.36513</td>
<td>0.1200</td>
</tr>
<tr>
<td>( \text{PC}_4 )</td>
<td>0.032821</td>
<td>820.911</td>
<td>12.419</td>
<td>0.9533</td>
<td>0.14205</td>
<td>-0.36513</td>
<td>0.1200</td>
</tr>
<tr>
<td>( \text{PC}_5 )</td>
<td>0.010158</td>
<td>916.547</td>
<td>8.592</td>
<td>1.3164</td>
<td>0.14205</td>
<td>-0.36513</td>
<td>0.1200</td>
</tr>
</tbody>
</table>
The global CO2 composition is held constant at 16% mol. Vapor one encountered with CH4 as the key component. (f) At high pressures and low temperatures, three phases were found with positive phase fractions. The vapor phase has a liquid like density, therefore, the solution can be labeled as a LLL.

As examples of the phase behavior encountered, two trajectories were analyzed, one at 155 K and other at 30 bar. In Figure 18, phase fractions at 155 K are depicted as function of pressure for the solutions with CO2 or CH4 as the key components. At pressures below 9.5 bar and above 12.04 bar, the two solutions are identical. Between 9.5 and 12.04 bar, two different solutions were found. In the interval from 9.5 to 10.07 bar, the solution found with CO2 as the key component has a lower Gibbs energy. In the interval from 10.07 to 12.04 bar, the solution found with CH4 as the key component has a lower Gibbs energy. The solution with the greater Gibbs energy is shown with dotted lines. The phase boundary V-L1-L2 to L1-L3 is found when V = 0 at 11.67 bar when the CH4 is the key component. The four-phase VLLL boundary is found with an incipient phase search that does not alter the VLLE algorithm. We introduce a fourth phase with zero phase fraction so that the VLLE equations are not modified. The initial estimate for the composition is based again on the key component concept. As initialization procedure for the fourth phase, a second key component is proposed, different from the one used in the VLLE calculation. For the Gas and Condensate A studied, the second key component was CH4 or CO2 depending on which component was selected in the VLLE calculation. Then, calculate fugacity coefficients and equilibrium constants as

\[
K_{new}^{i} = \frac{q_{i}^{V}}{q_{i}^{new}} \quad i = 1, \ldots, n
\]  

Table 2. Component Phase Mole Fractions for the Phase Boundaries in the Pressure Trajectory at 155 K for the CO2 Mixing with PEMEX Gas Condensate A

<table>
<thead>
<tr>
<th>Component</th>
<th>V</th>
<th>9.72 bar</th>
<th>10.73 bar</th>
<th>11.67 bar</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>0.03917</td>
<td>0.00281</td>
<td>0.00108</td>
<td>0.00412</td>
<td>0.08479</td>
<td>0.00661</td>
<td>0.00263</td>
</tr>
<tr>
<td>CO2</td>
<td>0.01365</td>
<td>0.13940</td>
<td>0.86402</td>
<td>0.22133</td>
<td>0.01272</td>
<td>0.13641</td>
<td>0.85662</td>
</tr>
<tr>
<td>H2S</td>
<td>0.00001</td>
<td>0.01919</td>
<td>0.00787</td>
<td>0.0121</td>
<td>0.00001</td>
<td>0.0159</td>
<td>0.00666</td>
</tr>
<tr>
<td>C1</td>
<td>0.94534</td>
<td>0.33386</td>
<td>0.12570</td>
<td>0.63660</td>
<td>0.90119</td>
<td>0.33166</td>
<td>0.13343</td>
</tr>
<tr>
<td>C2</td>
<td>0.00178</td>
<td>0.08065</td>
<td>0.00614</td>
<td>0.06008</td>
<td>0.00126</td>
<td>0.05984</td>
<td>0.00473</td>
</tr>
<tr>
<td>C3</td>
<td>0.00004</td>
<td>0.03851</td>
<td>0.00154</td>
<td>0.02525</td>
<td>0.00003</td>
<td>0.02974</td>
<td>0.00125</td>
</tr>
<tr>
<td>C4</td>
<td>0.00000</td>
<td>0.00572</td>
<td>0.00009</td>
<td>0.00355</td>
<td>0.00000</td>
<td>0.00450</td>
<td>0.00007</td>
</tr>
<tr>
<td>C5</td>
<td>0.00000</td>
<td>0.02061</td>
<td>0.00355</td>
<td>0.01163</td>
<td>0.00000</td>
<td>0.01678</td>
<td>0.0031</td>
</tr>
<tr>
<td>C6</td>
<td>0.00000</td>
<td>0.00796</td>
<td>0.00005</td>
<td>0.00420</td>
<td>0.00000</td>
<td>0.00661</td>
<td>0.0005</td>
</tr>
<tr>
<td>C7</td>
<td>0.00000</td>
<td>0.00896</td>
<td>0.00004</td>
<td>0.00002</td>
<td>0.00000</td>
<td>0.00594</td>
<td>0.0000</td>
</tr>
<tr>
<td>C8</td>
<td>0.00000</td>
<td>0.001498</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.001732</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

The global CO2 composition is held constant at 16% mol. Vapor V, heavy hydrocarbons-rich liquid L1, CO2-rich liquid L2, CH4-rich liquid L3.
The global CO$_2$ composition is held constant at 16% mol. Vapor $V$, heavy hydrocarbons-rich liquid $L_1$ (triangles), CO$_2$-rich liquid $L_2$ (asterisks), CH$_4$-rich liquid $L_3$ (squares) for temperature trajectory across the phase diagram for CO$_2$ mixing with PEMEX Gas Condensate A at 30 bar K.

The global CO$_2$ composition is held constant at 16% mol. Hollow symbols are for solutions with CO$_2$ key component and full symbols are for either CO$_2$ or CH$_4$ key component. The continuation dotted lines are for solutions with CH$_4$ key component. The phase boundaries are marked with vertical lines.

In the outer loop of the VLLE algorithm, we generate a new estimate for the composition of the fourth phase

$$u_i = K_{gew} x_i \quad i = 1, \ldots, n \quad (20)$$

Then, calculate the summation of the mole fractions of the fourth phase and normalize the mole fractions with

$$S_u = \sum_{i=1}^{n} u_i \quad (21)$$

Finally, calculate the following error function to verify the equilibrium conditions

$$Error = \sum_{i=1}^{n} [x_i^0 - u_i^0]_2^{f_{new}} \quad (22)$$

As the VLLE flash approaches convergence, the summation $S_u$ and error function Error approach limiting values. The fourth phase will be in equilibrium with the other three phases at a given temperature and pressure when the summation $S_u$ is equal to unity and the error function Error approaches zero within a tolerance.

At 155 K, the transition to the four phase region was found at 9.72 bar when the key component was CO$_2$ in the VLLE flash and CH$_4$ in the fourth phase; and at 10.73 bar, when the key component was CH$_4$ in the VLLE flash and CO$_2$ in the fourth phase. In Table 2, we report the compositions at equilibrium for the pressures of the phase transitions for the trajectory at 155 K. Note the distinct phase component mole fractions for all the phases. The summation $S_u$ had values greater than 1 inside the four phase region and less than 1 outside this region.

In Figure 19, the phase fractions at 30 bar are depicted as function of temperature for the solutions with CO$_2$ or CH$_4$ as the key component. For the CO$_2$ solution, the vapor phase adopted a liquid like density for temperatures lower than 170.5 K, so it was labeled as liquid. At temperatures above 170.5 K, the two solutions are identical. For temperatures below 170.5 K, two different solutions were found. For temperatures below 151 K, the solution with CO$_2$ has positive phase fractions and the solution with CH$_4$ the vapor has a negative phase fraction; therefore, the solution for CO$_2$ is the correct one. The phase boundary $V-L_1-L_3$ to $V-L_1$ is found when $L_3 = 0$ at 188.1 K when either CH$_4$ or CO$_2$ is selected as the key component. The phase boundary $V-L_1-L_3$ to $L_1-L_3$ is found when $V = 0$ at 182.4 K when CH$_4$ or CO$_2$ is the key component. The phase boundary $L_1-L_2-L_3$ to $L_1-L_2$ is found when $L_3 = 0$ at 151.4 K when CO$_2$ is the key component. In Table 3, we report the compositions at equilibrium for the temperatures of the phase transitions for the trajectory at 30 bar. Note the distinct phase component mole fractions for all the phases.

The general findings based on the results of the six systems studied in this work, are the following:

Table 3. Component Phase Mole Fractions for the Phase Boundaries in the Temperature Trajectory at 30 bar for the CO$_2$ Mixing with PEMEX Gas Condensate A

<table>
<thead>
<tr>
<th>Component</th>
<th>$V$</th>
<th>$L_1$</th>
<th>$L_2$</th>
<th>$L_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.01143</td>
<td>0.00413</td>
<td>0.01805</td>
<td>0.08533</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.12355</td>
<td>0.86969</td>
<td>0.01933</td>
<td>0.03300</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.00154</td>
<td>0.00061</td>
<td>0.00085</td>
<td>0.00004</td>
</tr>
<tr>
<td>C1</td>
<td>0.32549</td>
<td>0.12036</td>
<td>0.69645</td>
<td>0.87722</td>
</tr>
<tr>
<td>C2</td>
<td>0.05626</td>
<td>0.00365</td>
<td>0.03976</td>
<td>0.00412</td>
</tr>
<tr>
<td>C3</td>
<td>0.02826</td>
<td>0.00092</td>
<td>0.01701</td>
<td>0.00025</td>
</tr>
<tr>
<td>iC4</td>
<td>0.02482</td>
<td>0.00005</td>
<td>0.00012</td>
<td>0.00001</td>
</tr>
<tr>
<td>nC4</td>
<td>0.01614</td>
<td>0.00021</td>
<td>0.00811</td>
<td>0.00002</td>
</tr>
<tr>
<td>iC5</td>
<td>0.00638</td>
<td>0.00003</td>
<td>0.00002</td>
<td>0.00000</td>
</tr>
<tr>
<td>nC5</td>
<td>0.00898</td>
<td>0.00004</td>
<td>0.00008</td>
<td>0.00000</td>
</tr>
<tr>
<td>C6</td>
<td>0.03593</td>
<td>0.00005</td>
<td>0.01286</td>
<td>0.00000</td>
</tr>
<tr>
<td>PC1</td>
<td>0.07072</td>
<td>0.00006</td>
<td>0.03031</td>
<td>0.00000</td>
</tr>
<tr>
<td>PC2</td>
<td>0.12388</td>
<td>0.00001</td>
<td>0.00919</td>
<td>0.00000</td>
</tr>
<tr>
<td>PC3</td>
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<td>0.00000</td>
<td>0.00229</td>
<td>0.00000</td>
</tr>
<tr>
<td>PC4</td>
<td>0.05929</td>
<td>0.00000</td>
<td>0.00001</td>
<td>0.00000</td>
</tr>
<tr>
<td>PC5</td>
<td>0.01835</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Phase Fractions</td>
<td>0.4693</td>
<td>-0.0001</td>
<td>0.5307</td>
<td>-0.0027</td>
</tr>
</tbody>
</table>

The global CO$_2$ composition is held constant at 16% mol. Vapor $V$, heavy hydrocarbons-rich liquid $L_1$, CO$_2$-rich liquid $L_2$, CH$_4$-rich liquid $L_3$.  

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1. If only one solution is found with positive phase fractions, it corresponds to a valid VLLE solution.
2. If more than one solution is found with positive phase fractions, the minimum Gibbs energy criteria is used to select a solution. A fourth phase is proposed and tested using the $S_n$ summation. If $S_n < 1$, the system is in a VLLE region and the solution is valid. If $S_n > 1$, the system is in a VLLLE region and the solution is not valid, consequently a further VLLLE flash must be solved.
3. If a negative VLLLE flash solution is found or no solution is found at all, the system lies in a region with two phases at most. The equilibrium solution must be found by the appropriate two phase flash.

**Concluding Remarks**

The algorithm proposed in this work for the solution of a stand-alone three-phase VLLL equilibrium flash calculation is stable and robust. The inverse barrier function to solve for the phase fractions in the inner loop always warrants arriving to the solution whenever it exists. This methodology is easy to implement in any algorithm that solves the RR equations. The SSI in the outer loop has a slow rate of convergence, nevertheless it is a good method as a starting point for a higher order method, even close to critical points. The challenging cases analyzed showed that the initialization procedure proposed in this work is a good starting point for a stable three-phase VLLLE flash algorithm. The key component concept is robust and allowed to generate the liquid phases present in equilibrium at the different three-phase regions. For the CH$_4$ and CO$_2$ rich mixture of the Gas and Condensate A fluid, the Gibbs energy criteria helped to determine the valid solution when two physically feasible solutions were found. A simple extension was presented to calculate the VLL phase boundary when a third liquid phase was present.

The results found for the negative flash in the region outside the three-phase physical domain are continuous; therefore, it allowed us to calculate the VLL phase boundaries.

**Acknowledgment**

The authors acknowledge the invitation to contribute to this homage to Prof. John M. Prausnitz, an outstanding professor for many of us that learned to love thermodynamics with him.

**Notation**

- $B = \text{augmented inverse barrier function}$
- $B_{\text{inv}}, B_{\text{res}} = \text{augmented inverse barrier function residuals}$
- $E = \text{inequality material balance equation}$
- $\text{Error} = \text{Error function for the fourth phase}$
- $f = \text{fugacity}$
- $K_1 = \text{vapor to first liquid equilibrium constant}$
- $K_2 = \text{second liquid to first liquid equilibrium constant}$
- $K_{\text{new}} = \text{fourth phase to first liquid equilibrium constant}$
- $n = \text{number of components}$
- $Q = \text{objective function for minimization}$
- $r = \text{radius parameter}$
- $\text{RR}_{\text{inv}}, \text{RR}_{\text{res}} = \text{Rachford–Rice residuals}$
- $u = \text{fourth-phase mole fraction}$
- $v = \text{second liquid mole fraction}$
- $x = \text{first liquid mole fraction}$
- $y = \text{vapor mole fraction}$
- $z = \text{global mole fraction}$
- $\beta_1, \beta_2 = \text{vapor and second liquid phase fractions}$
- $\phi = \text{fugacity coefficient}$
- $\theta = \text{phase fractions vector}$

**Subscripts**

- $i = \text{component}$
- $w_1 = \text{second minus first liquid}$
- $x = \text{vapor minus first liquid}$

**Superscripts**

- $V = \text{vapor phase label}$
- $L_1 = \text{first liquid phase label}$
- $L_2 = \text{second liquid phase label}$
- $L_3 = \text{third liquid phase label}$

**Literature Cited**


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