General Strategy for Stability Testing and Phase-Split Calculation in Two and Three Phases

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Summary

Efficient and robust phase equilibrium computation has become a prerequisite for successful large-scale compositional reservoir simulation. When knowledge of the number of phases is not available, the ideal strategy for phase-split calculation is the use of stability testing. Stability testing not only establishes whether a given state is stable, but also provides good initial guess for phase-split calculation. In this research, we present a general strategy for two- and three-phase split calculations based on reliable stability testing. Our strategy includes the introduction of systematic initialization of stability testing particularly for liquid/liquid and vapor/liquid/liquid equilibria. Powerful features of the strategy are extensively tested by examples including calculation of complicated phase envelopes of hydrocarbon fluids mixed with CO_2 in single-, two-, and three-phase regions.

Introduction

Robust and efficient multiphase equilibrium computation of multicomponent fluids is important in large-scale compositional reservoir simulation. It may be performed billions of times and may cost significant CPU time in complex simulation runs. In the past, the focus has been on two-phase compositional simulation. Currently, there is an increasing need to perform three-phase compositional modeling for CO_2- and steam-related enhanced oil recovery (EOR) processes and for asphaltene precipitation problems.

The challenging issue is that the number of phases at equilibrium cannot be determined *a priori*. Two approaches have been adopted to attack the problem. In one approach, phase-split calculation is performed on the basis of a pre-assigned number of phases. If an unphysical solution is obtained [i.e., one or more phases have a negative amount (the so-called "negative flash")], phase-split calculation is repeated based on a consecutively decreasing number of phases until the physical solution is found (Neoschil and Chambrette 1978; Whitson and Michelsen 1989; Leibovici and Neoschil 1995). This approach may be computationally expensive. It may also suffer from the absence of a good initial guess. In another approach, stability testing is used prior to phase-split calculation to determine whether it is necessary to increase the number of phases (Baker et al. 1982; Michelsen 1982a, b). This approach is widely used in compositional reservoir simulation because stability testing has fewer variables and thus is mathematically simpler than direct phase-split calculation. Moreover, stability testing can provide good initial estimate for phase-split calculation when it is not available from the previous timestep. This is particularly important for fractured reservoirs, where composition may change significantly between two consecutive timesteps (Hoteit amnd Firoozabadi 2009). Both stability testing and phase-split calculation can be formulated as either global minimization, or local minimization, or direct solution of nonlinear algebraic equations.

Diverse global minimization techniques have been developed to seek the local minima and global minimum of Gibbs tangent plane distance (TPD) function in stability testing, and the global minimum of Gibbs free energy in phase-split calculation. The homotopy continuation approach was used by Sun and Seider for both stability testing and phase-split calculation (1995). The integral area method by Eubank, Elhassan, Barrufet and Whiting was used to solve the multiphase equilibrium of binary and ternary fluids (Eubank et al. 1992; Elhassan et al. 1996; Hodges et al. 1997). The interval Newton/generalized bisection method was used by Hua et al. for stability testing (Hua et al. 1996, 1998a, b). The generic optimization was used by McKinnon and Mongeau for the chemical and phase equilibrium problems (1998). The simulated annealing was used by Pan and Firoozabadi for various types of phase equilibrium (1998); by Nichita et al. for wax precipitation from hydrocarbon mixtures (2001); and by Zhu for stability testing (2000). The so-called DIviding RECTangles (DIRECT) method was applied to stability analysis by Saber and Shaw (2008). McDonald and Floudas studied the phase- and chemical-equilibrium problem and stability problem by using the deterministic branch and bound algorithm (1995a, b, c, 1996). Nichita et al. proposed a hybrid approach on the basis of the tunneling technique for the multiphase equilibrium calculations (2002a, b). The adoption of these expensive techniques can significantly increase the success to find the global minimum of Gibbs TPD function and Gibbs free energy. These techniques may be still sensitive to the initialization and are generally very slow. They may not be a good fit for compositional reservoir simulation in large scale.

Local minimization of Gibbs TPD function and Gibbs free energy has been used in compositional reservoir simulations. In this method, the zero-gradient condition is adopted, which leads to a set of nonlinear algebraic equations. Numerous techniques are used to solve these equations robustly and efficiently. In stability testing, one example is Michelsen's unconstrained local minimization implemented by the Broyden-Fletcher-Godfarb-Shanno (BFGS) quasi-Newton method (Michelsen 10982a). It has proved to be robust and efficient in our examination. However, stability testing based on local minimization requires multiple initial estimates to avoid missing the instability. In phase-split calculation, the popular methods include the successive substitution iteration (SSI), quasi-Newton, Newton, steepest-descent, and their various modifications and combinations (Michelsen 1982b, 1993; Trangenstein 1987; Lucia et al. 1985; Ammar and Renon 1987). Among them, the SSI combined with Newton method is probably the best option. Good initialization may increase the probability of finding the global minimum of Gibbs free energy in phase-split calculation based on local minimization. Initial guesses from stability testing and from the previous simulation timestep may do the job. For both stability testing and phase-split calculation, the efficiency can be improved if the equations are solved in the reduced space (Firoozabadi and Pan 2000; Pan and Firoozabaadi 2003). It is difficult to distinguish between local minimization and equation-solving methods, but they may not be exactly identical. The working equations and variables in local minimization may not be the same as those in an equation-solving method in a different formulation (Pan and Firoozabadi 2003; Firoozabadi 1999). In addition, while factoring a symmetric and positive Hessian

matrix, local minimization method monitors the numerical iteration to proceed in the direction of lower Gibbs TPD function or Gibbs free energy. There is no such requirement in the equation-solving method and the solution may be only a stationary point.

Direct solution to a set of nonlinear algebraic equations describing both stability testing and phase-split calculation also prevails in compositional reservoir simulation. In stability testing, finding a stationary point with negative TPD value assures the instability of a mixture. However, to provide a good initial guess for phase-split calculation, more than one stationary point may be needed. There are various numerical algorithms used to determine the stationary points of Gibbs TPD function by using multiple initial estimates (Firoozabadi 1999). The conventional technique is using the SSI followed by the Newton method (Hoteit and Firoozabadi 2006). The equation-solving method of stability testing also strongly depends on the initialization, and only one or two initial estimates may not detect the instability. In phase-split calculation, the nonlinear algebraic equations arise from the equal chemical potentials combined with the mass conservation. With good-enough initial estimate either from reliable stability testing or from the previous simulation timestep, the equation-solving method of phase-split calculation normally can converge to the global minimum of Gibbs free energy. For two-phase split calculation, there has been much progress in developing the numerical algorithms. For three-phase split calculation, the combination of SSI and Newton methods has proved to be both robust and efficient (Firoozabadi 1999; Haugen et al. 2011). The SSI provides good initial estimate for the Newton method. The Newton method generally converges within a few iterations if the initial guess is good enough and the Jacobian marix is not nearly singular. Within each SSI step, the nonlinear Rachford-Rice (RR) equation (1952) is solved independently through either bisection or Newton method (Haugen et al. 2011; Michelsen and Mollerup 2004) or minimization of a convex function (Michelsen 1994; Okuno et al. 2010a, b; Leibovici and Nichita 2008). Recently the reduction method has received considerable attention for both stability testing and phase-split calculation because the computational efficiency may be further improved (pan and Firoozabadi 2003; Michelsen 1986; Hendriks 1988; Hendriks and Vanbergen 1992; Nichita and Minescu 2004; Nichita 2006; Nichita et al. 2006, 2007; Okuno et al. 2010b, c).

Early in this project, we found that standard stability testing based on local minimization and equation-solving methods was not always reliable because the initial guesses (Wilson correlation) did not guarantee the detection of instability, especially for liquid/liquid and vapor/liquid/liquid equilibria. In this research, we propose a general strategy for two- and three-phase split calculations based on reliable stability testing. In stability testing, we use the Wilson correlation (1968) and a new expression to provide the initial guesses. We implement stability testing by applying the BFGS-quasi-Newton method based on Michelsen's unconstrained local minimization (1982a). Phase-split calculation uses the initial guesses from stability testing for equilibrium ratios and from the bisection method for phase fractions. The combination of the SSI and Newton methods is adopted in the numerical implementation based on equation-solving method. Both stability testing and phase-split calculation are performed in conventional space. The strategy proposed in this research has been tested extensively by a large number of examples of different degrees of complexity, and it is both robust and efficient. In the future we may examine the methods in reduced space.

The remainder of this article is organized as follows. The next two sections describe the theoretical background and numerical implementation of stability testing and phase-split calculation. The fourth section illustrates several examples including the computation of complicated phase envelopes in single-, two-, and three-phase regions. Finally, the main results and conclusions are summarized. Appendix A provides the expressions to calculate total compressibility and total partial molar volumes in single-, two-, and three-phase states. These are required in formulation of pressure equation for some compositional models (Moortgat and Firoozabadi 2010; Moortgat et al. 2011a, b).

Theoretical Background

Single-Phase Stability Testing. For a mixture containing C components with overall mole fractions $\{n_i\}$ at given temperature T and pressure p, single-phase stability testing may be needed to examine whether the mixture is stable in a single-phase state. In stability testing, the reduced molar Gibbs TPD function is expressed by (Michelsen 1982a; Firoozabadi 1999)

$$\text{TPD}(\{y_i^{\text{trial}}\})$$
$$= \sum_{i=1}^{C} y_i^{\text{trial}}[\ln\phi_i(\{y_i^{\text{trial}}\}) + \ln y_i^{\text{trial}} - \ln\phi_i(\{z_i^{\text{test}}\}) - \ln z_i^{\text{test}}]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where $\{y_i^{\text{trial}}\}$ and $\{z_i^{\text{test}}\}$ are the compositions of the trial and test phases, respectively; and $\phi_i(\{y_i^{\text{trial}}\})$ and $\phi_i(\{z_i^{\text{test}}\})$ are the fugacity coefficients of component i in the trial and test phases, respectively. For single-phase stability testing, $\{z_i^{\text{test}} = n_i\}$. The stationary points of TPD function satisfy the condition (Firoozabadi 1999)

$$\ln\phi_i(\{Y_i\}) + \ln Y_i - \ln\phi_i(\{z_i^{\text{test}}\}) - \ln z_i^{\text{test}} = 0 \ (i = 1 \text{ to } C),$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where the variable $\{Y_i = y_i^{\text{trial}}e^{-W}\}$, with W being the TPD value at one of the stationary points. The trial phase compositions can be determined from $\{y_i^{\text{trial}} = Y_i / \sum_{i=1}^{C} Y_i\}$. Michelsen introduced the formulation in terms of an unconstrained local minimization and used an alternative function TPD* (in terms of $\{Y_i\}$) to replace TPD function (Michelsen 1982a)

$$\text{TPD}^*(\{Y_i\})$$
$$= 1 + \sum_{i=1}^{C} Y_i[\ln\phi_i(\{Y_i\}) + \ln Y_i - \ln\phi_i(\{z_i^{\text{test}}\}) - \ln z_i^{\text{test}} - 1]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

The functions TPD* and TPD have the same stationary points and the same sign at stationary points.

Two-Phase Split Calculation. Two-phase equilibrium satisfies the condition of equal fugacities of each component in both phases, $f_{xi} = f_{yi}$ ($i=1$ to C), where f_{xi} and f_{yi} are the fugacities of component i in phases x and y, respectively. The equality of fugacities can be further transformed using the natural logarithm of the equilibrium ratios as the primary variables (phase x is chosen as the reference) (Haugen et al. 2011),

$$\ln K_{yi} = \ln\phi_{xi} - \ln\phi_{yi} \ (i = 1 \text{ to } C), \ \cdots\cdots\cdots\cdots (4)$$

where $K_{yi} = y_i/x_i$ is the equilibrium ratio of component i with x_i and y_i being the mole fractions of component i in phases x and y, respectively. ϕ_{xi} and ϕ_{yi} are the corresponding fugacity coefficients. x_i and y_i are restricted by the RR equation (Rachford and Rice 1952)

$$RR_y = \sum_{i=1}^{C}(y_i - x_i) = \sum_{i=1}^{C} \frac{n_i(K_{yi} - 1)}{1 + \beta_y(K_{yi} - 1)} = 0, \ \cdots\cdots (5)$$

where β_y is the mole fraction of phase y. The combination of Eqs. 4 and 5 with $C + 1$ variables, $\{K_{yi}\}$ and β_y, is used to solve two-phase equilibrium. The phase compositions are determined from

$$x_i = \frac{n_i}{1 + \beta_y(K_{yi} - 1)}, y_i = K_{yi}x_i \ (i = 1 \text{ to } C). \ \cdots\cdots (6)$$

Two-Phase Stability Testing. Two-phase stability testing may be needed to examine whether the mixture is stable in a given two-phase state. It is thermodynamically equivalent to testing the stability of one of the two equilibrium phases (Baker et al. 1982). The TPD and TPD* functions are not affected by the selection of

the test phase because the term $\ln\phi_i(\{z_i^{\text{test}}\}) + \ln z_i^{\text{test}}$ in Eqs. 1 and 3 remains the same. In this research, we use the phase with higher molar weight to perform two-phase stability testing; the reason will be provided in the Results and Discussion section.

Three-Phase Split Calculation. Three-phase equilibrium satisfies the condition $f_{xi} = f_{yi} = f_{zi}$ (i=1 to C), where f_{xi}, f_{yi}, and f_{zi} are the fugacities of component i in phases x, y, and z, respectively. Similarly, the equilibrium condition also can be expressed in terms of the natural logarithm of the equilibrium ratios (phase x is chosen as the reference) (Haugen et al. 2011)

$$\begin{cases} \ln K_{yi} = \ln\phi_{xi} - \ln\phi_{yi} \\ \ln K_{zi} = \ln\phi_{xi} - \ln\phi_{zi} \end{cases} (i = 1 \text{ to } C), \quad \dots\dots\dots (7)$$

where $K_{yi} = y_i/x_i$ and $K_{zi} = z_i/x_i$ are equilibrium ratios of component i with x_i, y_i, and z_i being the mole fractions of component i in phases x, y, and z, respectively. ϕ_{xi}, ϕ_{yi}, and ϕ_{zi} are the corresponding fugacity coefficients. The RR equation is given by (Rachford and Rice 1952)

$$\begin{cases} RR_y = \sum_{i=1}^{C}(y_i - x_i) = \sum_{i=1}^{C} \dfrac{n_i(K_{yi} - 1)}{1 + \beta_y(K_{yi} - 1) + \beta_z(K_{zi} - 1)} = 0 \\ RR_z = \sum_{i=1}^{C}(z_i - x_i) = \sum_{i=1}^{C} \dfrac{n_i(K_{zi} - 1)}{1 + \beta_y(K_{yi} - 1) + \beta_z(K_{zi} - 1)} = 0 \end{cases}$$
$$\dots\dots\dots\dots\dots\dots\dots (8)$$

where β_y and β_z are the mole fractions of phases y and z, respectively. Three-phase equilibrium is solved by combining Eqs. 7 and 8. There are $2C + 2$ variables, $\{K_{yi}\}$, $\{K_{zi}\}$, β_y, and β_z. The phase compositions are determined from

$$x_i = \frac{n_i}{1 + \beta_y(K_{yi} - 1) + \beta_z(K_{zi} - 1)},$$
$$y_i = K_{yi}x_i, z_i = K_{zi}x_i \ (i = 1 \text{ to } C). \quad \dots\dots\dots (9)$$

Numerical Implementation

Stability Testing. Local minimization and equation-solving methods of stability testing cannot guarantee the detection of instability. There is a strong dependency on the initial guess of the trial phase compositions $\{y_i^{\text{trial}}\}$ or more practically the equilibrium ratios $\{K_i^{\text{stab}} = y_i^{\text{trial}}/z_i^{\text{test}}\}$. Improper initialization may miss all the stationary points with negative TPD values and fail to detect the instability. The only way to overcome this intrinsic shortcoming is using multiple initial estimates. In standard stability testing, Wilson correlation and its reciprocal are used to provide the initial guesses of $\{K_i^{\text{stab}}\}$. The Wilson correlation is given by (Wilson 1968)

$$K_i^{\text{Wilson}} = \frac{p_{ci}}{p}\exp\left[5.37(1 + \omega_i)\left(1 - \frac{T_{ci}}{T}\right)\right], \quad \dots\dots (10)$$

where T_{ci}, p_{ci}, and ω_i are the critical temperature, critical pressure, and acentric factor of component i, respectively. Canas-Marin et al. (2007) linearly combine $\{K_i^{\text{Wilson}}\}$ and $\{1/K_i^{\text{Wilson}}\}$ to construct a set of initial guesses of $\{K_i^{\text{stab}}\}$ for single-phase stability testing. If instability is not detected, this empirical method will continue refining the linear combination and construct more initial guesses. If instability still cannot be found, the stationary point with the least positive TPD value is used as the initial guess to perform two-phase split calculation. In this suggestion, stability testing may not be in line with phase-split calculation.

It is well recognized that when the equilibrium is between vapor and liquid, $\{K_i^{\text{Wilson}}\}$ and $\{1/K_i^{\text{Wilson}}\}$ often provide good initial guesses of $\{K_i^{\text{stab}}\}$ for stability testing. It is the standard approach in virtually all of the commercial simulation softwares. However, when there is more than one liquid phase (e.g., liquid/liquid and vapor/liquid/liquid equilibria), stability testing becomes

unreliable if only $\{K_i^{\text{Wilson}}\}$ and $\{1/K_i^{\text{Wilson}}\}$ are adopted for the initialization. There is no universally accepted practice to guarantee the detection of instability. Michelsen suggested that the trial phase can be initially assumed to be a pure substance (Michelsen 1982a). This suggestion is significant but further improvement is needed because the trial phase may be very different from pure substance. On the basis of Michelsen's suggestion, we propose that the initial composition of one of the components is 90 mol% and the others equally share 10 mol% in the trial phase, and suggest the following expression:

$$\begin{cases} K_i^{\text{new}} = 0.9/z_i^{\text{test}} \\ K_j^{\text{new}} = [0.1/(C-1)]/z_j^{\text{test}} \quad (j \neq i). \end{cases} \quad \dots\dots\dots (11)$$

Any component can be assumed to have the initial mole fraction of 90% in the trial phase. For our general purpose, all of the components are tried. In our research, we combine Eqs. 10 and 11 to provide the initial guesses of $\{K_i^{\text{stab}}\}$ for stability testing:

$$\{K_i^{\text{stab}}\}(\text{init})$$
$$= [\{K_i^{\text{Wilson}}\}, \{1/K_i^{\text{Wilson}}\}, \{\sqrt[3]{K_i^{\text{Wilson}}}\}, \{1/\sqrt[3]{K_i^{\text{Wilson}}}\}, \{K_i^{\text{new}}\}].$$
$$\dots\dots\dots\dots\dots\dots (12)$$

The first four terms are identical to Haugen's four-sided initialization for stability testing (private communication). There are C initial guesses in the last term. We use all the $C + 4$ initial estimates in Eq. 12 to perform both single- and two-phase stability testings. Eq. 12 has been extensively tested in this research, in our compositional simulation (Moortgat et al. 2011), and in the challenging phase-behavior computations of asphaltene precipitation (Li and Firoozabadi 2010a, b). If we know in advance that only vapor and liquid phases may exist, it is often safe to use the first two terms in Eq. 12.

We adopt the BFGS-quasi-Newton method to implement stability testing within the framework of Michelsen's unconstrained local minimization of TPD* function (i.e., Eq. 3). The details can be found in Michelsen (1982a) and Hoteit and Firoozabadi (2006). After extensive examination, we find this approach works both robustly and efficiently. Despite the multiple initial guesses, at most three non-trivial solutions are found. For single-phase stability testing, the trivial solution is $\{K_i^{\text{1P-stab}} = 1\}$. For two-phase stability testing, the trivial solutions are $\{K_i^{\text{2P-stab}} = 1\}$ and $\{K_i^{\text{2P-stab}} = K_i^{\text{2P-split}}\}$ (or $\{K_i^{\text{2P-stab}} = 1/K_i^{\text{2P-split}}\}$, depending on the reference phase). Trivial solutions are also the local minima of TPD* hypersurface. The state is practically considered stable if all the non-trivial solutions have the TPD* value higher than -10^{-10}. On the basis of our tests, the number of iterations generally does not exceed 100 for the tolerance of 10^{-10} (Hoteit and Firoozabadi 2006).

The BFGS-quasi-Newton method based on unconstrained local minimization is like other algorithms and may also meet convergence difficulty in both single- and two-phase stability testings. That is probably because sometimes the TPD* hypersurface only contains the saddle points and trivial solutions, and the iteration process encounters one saddle point. Passing through the saddle point to reach the trivial solution needs a large number of iterations. This convergence issue has been systematically studied in Nichita et al. (2007). In that case, the solution is safely considered trivial when the number of iterations is higher than 1,000. We set the default number of iterations at 1,000 for a successful outcome.

Phase-Split Calculation. In reservoir simulation, if the previous timestep cannot provide good initial guesses of equilibrium ratios and phase fractions, we must provide them to implement phase-split calculation. In two-phase split calculation, generally the initial guess of $\{K_{yi}\}$ is $\{K_i^{\text{1P-stab}}\}$ with the lowest TPD* value in single-phase stability testing. In three-phase split calculation, the initial guesses of $\{K_{yi}\}$ and $\{K_{zi}\}$ are $\{K_i^{\text{2P-stab}}\}$ with the lowest

TABLE 1—COMPONENT DATA FOR N_2/C_2, N_2/C_1/C_2, C_1/CO_2, C_1/CO_2/H_2S, AND C_1/CO_2/H_2S/H_2O MIXTURES								
Component	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,C1}$	$k_{i,N2}$	$k_{i,CO2}$	$k_{i,H2S}$
C_1	190.6	46.0	0.008	16		0.038		
C_2	305.4	48.8	0.098	30	0.021	0.08		
N_2	126.2	33.9	0.04	28				
CO_2	304.2	73.8	0.225	44	0.095[a],0.1005[b],0.13[c]			
H_2S	373.2	89.4	0.1	34	0.0755[b],0.095[c]		0.0999[b],0.097[c]	
H_2O	647.3	220.5	0.344	18	0.4928			0.04

[a] C_1/CO_2 mixture
[b] C_1/CO_2/H_2S mixture at first four conditions and C_1/CO_2/H_2S/H_2O mixture
[c] C_1/CO_2/H_2S mixture at last two conditions

TPD* value in two-phase stability testing and $\{K_i^{\text{2P-split}}\}$ (or $\{1/K_i^{\text{2P-split}}\}$, depending on the reference phase) in previous two-phase split calculation, respectively. The initial guess of β_y in two-phase split calculation is obtained by 1D bisection method to solve Eq. 5 in the range [0, 1] (Michelsen and Mollerup 2004). Similarly, solving Eq. 8 by 2D bisection method can generate the initial guesses of β_y and β_z within [0, 1] in three-phase split calculation (Haugen et al. 2011). Compared with alternatives, 2D bisection method does not require the starting guess and should always work. We significantly improve both efficiency and robustness of 2D bisection method even near phase boundaries and bicritical points. These features have been demonstrated in Li and Firoozabadi (2012). Note that the bisection method is adopted only for the initialization of phase fractions.

The SSI method is carried out first with the initial guesses of equilibrium ratios and phase fractions. Within each SSI step, the equilibrium ratios are updated iteratively through Eq. 4 or 7 in the outer loop. The phase fractions are solved for independently through Eq. 5 or 8 by the Newton method in the inner loop using updated equilibrium ratios. The phase compositions are updated through Eq. 6 or 9. We define the maximal absolute increment between two successive iteration steps to describe the convergence as $\Delta = \max(\{|\Delta \ln K_{yi}|\}, |\Delta \beta_y|)$ and $\Delta = \max(\{|\Delta \ln K_{yi}|\}, \{|\Delta \ln K_{zi}|\}, |\Delta \beta_y|, |\Delta \beta_z|)$ for two- and three-phase split calculations, respectively. Once Δ is smaller than a predefined switching criterion 10^{-5}, we turn to the Newton method to solve for both the natural logarithm of equilibrium ratios and phase fractions simultaneously until Δ is smaller than a predefined tolerance 10^{-10}. The Newton method has a quadratic convergence rate and can locate the solution within a few iteration steps if its initial guess is close enough to the solution. According to our tests, the number of iterations is usually not higher than 100 for the SSI and not higher than 3 for the Newton method. Two-phase split calculation generally needs far fewer SSI steps than three-phase split calculation. The Newton method also can be formulated by solving for the natural logarithm of equilibrium ratios and phase fractions separately. It reduces the dimension of Jacobian matrix but needs more iteration steps.

Phase-split calculation in the critical region is very challenging. In the critical region, the TPD* value for nontrivial solutions of stability testing could be very close to zero. Our initial guess of equilibrium ratios is very close to the final solution, but the initial guess of phase fractions from bisection method could be far from the final solution. The Newton method may fail when the Jacobian matrix is nearly singular or Δ keeps fluctuating or even diverges in phase-split calculation. In that case, the SSI is switched back until the tolerance is satisfied. Although the SSI would eventually converge after enough iteration steps (Michelsen and Mollerup 2004), at the beginning Δ may not have a decreasing trend for a very large number of steps and even at later stage Δ also converges very slowly (Gibbs free energy always decreases as the SSI proeeds). We do not accelerate the SSI by using methods such as the General Dominant Eigenvalue method (Crowe and Nishio 1975) suggested by Michelsen (1982b) because that may lead to the divergence of Δ and the phase-split calculation may

fail especially close to the critical point. Phase fractions may converge to the tolerance much slower than the natural logarithm of equilibrium ratios in critical region. Because our simulation requires total compressibility to update the pressure field, control over the accuracy of phase fractions is particularly important in the critical region because inaccurate phase fractions may result in a negative total compressibility and cause the fluctuation of the pressure field. However, if total compressibility is not required, one may consider using the initial guesses of equilibrium ratios and phase fractions directly as phase-split result because the two critical phases are nearly indistinguishable.

Results and Discussion

Our strategy has been successfully implemented in our two- and three-phase compositional simulations (Moortgat et al. 2011a) with outstanding efficiency and robustness. We discuss various examples to illustrate the powerful features of our algorithm. We follow the stand-alone calculation to test these examples, from single-phase stability testing to two-phase split calculation (if the single-phase state is unstable) to two-phase stability testing to three-phase split calculation (if the two-phase state is unstable). In reservoir simulation, because the previous timestep is frequently used to provide initial guesses for phase-split calculation, the procedure can be significantly expedited by avoiding some modules (e.g., stability testing, bisection method, and the SSI in phase-split calculation). We use the Peng-Robinson equation of state (PR-EOS) to implement both stability testing and phase-split calculation (Peng and Robinson 1976; Robinson et al. 1985). All the runs are executed on a Dell Inspiron E1505 laptop with Intel® Core™ Duo Processor T2300 (1.66GHz) and 1GB RAM, a 6-year-old machine.

We start with some well-defined fluids including N_2/C_2, N_2/C_1/C_2, C_1/CO_2, C_1/CO_2/H_2S, and C_1/CO_2/H_2S/H_2O. Their phase behavior computations at certain conditions have been described as "challenging" (Sofyan et al. 2003). **Table 1** lists the critical temperature T_C, critical pressure p_C, acentric factor ω, molecular weight M_W, and the nonzero binary interaction coefficients k_{ij}. M_W is used to estimate the mass density. **Table 2** shows the CPU time for both stability testing and phase-split calculation at various (T, p, $\{n_i\}$) conditions by using our strategy. Note that each CPU time is only for the particular computation stated in the table. For instance, the CPU time for three-phase split calculation does not include those for single-phase stability testing, two-phase split calculation, and two-phase stability testing. For C_1/CO_2/H_2S/H_2O mixture, Sofyan et al. (2003) may have typographical errors in TPD values of single-phase stability testing for the first and third conditions. The mixture is in three-phase state at the last condition but Sofyan et al. (2003) do not show that. For all the conditions, our strategy can always locate the global minimum of TPD function in single-phase stability testing and find the correct results of phase-split calculation. Although multiple initial estimates in Eq. 12 are used, stability testing does not significantly increase the computational cost and has similar CPU time as two-phase split calculation. But three-phase split calculation is much slower.

The other examples include the calculation of complicated phase envelopes for CO_2 mixing with six hydrocarbon fluids.

TABLE 2—CPU TIME OF STABILITY TESTING AND PHASE-SPLIT CALCULATION FOR N_2/C_2, $N_2/C_1/C_2$, C_1/CO_2, $C_1/CO_2/H_2S$, AND $C_1/CO_2/H_2S/H_2O$ MIXTURES AT INDIVIDUAL CONDITIONS

Mixture	T (K)	P (bar)	n	CPU Time (Sec)			
				1P-Stab	2P-Split	2P-Stab	3P-Split
N_2/C_2	270	76	(0.1,0.9)	8.91e–5			
	270	76	(0.18,0.82)	1.03e–4	9.53e–5	1.13e–4	
	270	76	(0.3,0.7)	1.06e–4	1.03e–4	1.14e–4	
	270	76	(0.44,0.56)	1.00e–4	1.05e–4	1.09e–4	
	270	76	(0.6,0.4)	1.44e–4			
$N_2/C_1/C_2$	270	76	(0.3,0.1,0.6)	1.83e–4	1.64e–4	1.59e–4	
	270	76	(0.15,0.3,0.55)	2.00e–4	2.78e–4	1.73e–4	
	270	76	(0.08,0.38,0.54)	2.13e–4			
	270	76	(0.05,0.05,0.9)	1.22e–4			
C_1/CO_2	220	60.8	(0.9,0.1)	9.06e–5			
	220	60.8	(0.8,0.2)	1.19e–4	2.42e–4	1.23e–4	
	220	60.8	(0.7,0.3)	1.11e–4	2.77e–4	1.25e–4	
	220	60.8	(0.57,0.43)	1.19e–4	2.22e–4	1.25e–4	
	220	60.8	(0.4,0.6)	2.58e–4			
$C_1/CO_2/H_2S$	208.5	55.1	(0.4989,0.0988,0.4023)	2.52e–4	4.34e–4	2.44e–4	
	210.5	57.5	(0.4989,0.0988,0.4023)	2.80e–4	5.47e–4	2.42e–4	
	210.5	57.5	(0.48,0.12,0.4)	2.67e–4	5.63e–4	2.61e–4	
	227.55	48.6	(0.4989,0.0988,0.4023)	2.02e–4	1.39e–4	1.86e–4	
	190.16	36.82	(0.4989,0.0988,0.4023)	2.13e–4	1.78e–4	2.75e–4	2.23e–3
	202.65	50.33	(0.4989,0.0988,0.4023)	5.64e–4	2.30e–4	3.06e–4	2.27e–3
$C_1/CO_2/H_2S/H_2O$	310.95	76	(0.1488,0.2991,0.0494,0.5027)	2.11e–4	1.17e–4	2.23e–4	
	380.35	129.3	(0.1496,0.3009,0.0498,0.4997)	2.13e–4	1.23e–4	1.97e–4	
	449.85	181.7	(0.0496,0.0494,0.4,0.5)	2.28e–4	1.92e–4	2.30e–4	
	310.95	62.6	(0.0504,0.0503,0.3986,0.5008)	2.72e–4	1.39e–4	2.34e–4	1.98e–3

They are the acid gas from Pan and Firoozabadi (1998; Haugen et al. 2011), Oil B from Shelton and Yarbourough (Haugen et al. 2011; Nichita et al. 2006; Shelton and Yarborough 1977), Maljamar reservoir oil from Orr et al. (Haugen et al. 2011; Orr et al. 1981), Maljamar separator oil also from Orr et al. (Haugen et al. 2011; Orr et al. 1981), Bob Slaughter Block oil from Khan et al. (1992; Okuno et al. 2010d) and North Ward Estes oil from Khan et al. (1992; Okuno 2010b For the last two oils, the mixing gas contains 95 mol% CO_2 and 5 mol% C_1. **Tables 3 through 8** list the component data of the six fluids. The calculated phase envelopes for CO_2 mixing with these six hydrocarbon mixtures are displayed in **Figs. 1 through 6.** We approximately locate the bicritical points based on four criteria. First, TPD* ≈ 0 (approximately -10^{-10}) in two-phase stability testing. Second, $\{K_{yi} \approx K_{zi}\}$ or $\{K_{yi} \approx 1\}$ or $\{K_{zi} \approx 1\}$. Third, the two physically similar phases have nonnegligible amounts; Finally, the mixture enters the two-phase region when the pressure is slightly increased (0.001 bar). The phase boundaries are captured with the accuracy of 0.001 bar.

The CO_2 mixing with acid gas (Fig. 1) has the most complex phase envelope with three single-phase, three two-phase, and one three-phase regions. The single vapor phase only appears when the pressure is lower than 1 bar. The phase envelope has the largest three-phase region. It terminates at three points and each point also connects to two two-phase and one single-phase regions. When CO_2 overall mole fraction is less than 0.469 and higher than 0.832, the three-phase region has a "retrograde" behavior. The amount of one liquid phase (L_2 on the left side and L_1 on the right side) first increases and then decreases as the pressure increases. Fig 2 presents the computed phase envelope for CO_2 mixing with Oil B. It shows a very narrow three-phase region. On the left side, the three-phase region is terminated by a point analogous to those three points in Fig. 1. On the right side, the three-phase region ends at a bicritical point at which the vapor and L_2 phase become indistinguishable. The three-phase region of CO_2 mixing with Maljamar reservoir oil is completely immersed in the two-phase region and ends at two bicritical points (Fig. 3). The CO_2 mixing with Maljamar separator oil has the phase envelope similar to that for Oil B (Fig. 4). Bob Slaughter Block oil mixed with impure CO_2 has nearly similar phase envelope as Oil B and Maljamar separator oil except for an obvious single L_2 phase region when the mixture is almost the pure mixing gas (Fig. 5). A "retrograde" behavior is observed when CO_2 overall mole fraction is higher than that of the bicritical point. Fig. 6 shows the phase

TABLE 3—COMPONENT DATA OF ACID GAS

Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$	$k_{i,N2}$	$k_{i,H2S}$
CO_2	0.70592	304.211	73.819	0.225	44			
N_2	0.07026	126.2	33.9	0.039	28	–0.02		
H_2S	0.01966	373.2	89.4	0.081	34.1	0.12	0.2	
C_1	0.06860	190.564	45.992	0.01141	16	0.125	0.031	0.1
C_2	0.10559	305.322	48.718	0.10574	30.1	0.135	0.042	0.08
C_3	0.02967	369.825	42.462	0.15813	44.1	0.150	0.091	0.08

TABLE 4—COMPONENT DATA OF OIL B							
Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$	$k_{i,N2}$	$k_{i,C1}$
CO_2	0.0011	304.211	73.819	0.225	44.01			
N_2	0.0048	126.2	33.5	0.04	28.01	−0.02		
C_1	0.1630	190.6	45.4	0.008	16.04	0.075	0.08	
C_2	0.0403	305.4	48.2	0.098	30.07	0.08	0.07	0.003
C_3	0.0297	369.8	41.9	0.152	44.1	0.08	0.07	0.01
iC_4	0.0036	408.1	36	0.176	58.12	0.085	0.06	0.018
nC_4	0.0329	425.2	37.5	0.193	58.12	0.085	0.06	0.018
iC_5	0.0158	460.4	33.4	0.227	72.15	0.085	0.06	0.025
nC_5	0.0215	469.6	33.3	0.251	72.15	0.085	0.06	0.026
C_6	0.0332	506.35	33.9	0.299	84	0.095	0.05	0.036
PC_1	0.181326	566.55	25.3	0.3884	112.8	0.095	0.1	0.049
PC_2	0.161389	647.06	19.1	0.5289	161.2	0.095	0.12	0.073
PC_3	0.125314	719.44	14.2	0.6911	223.2	0.095	0.12	0.098
PC_4	0.095409	784.93	10.5	0.8782	304.4	0.095	0.12	0.124
PC_5	0.057910	846.33	7.5	1.1009	417.5	0.095	0.12	0.149
PC_6	0.022752	919.39	4.76	1.4478	636.8	0.095	0.12	0.181

TABLE 5—COMPONENT DATA OF MALJAMAR RESERVOIR OIL							
Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$	$k_{i,C1}$
CO_2		304.211	73.819	0.225	44		
C_1	0.2939	190.6	45.4	0.008	16	0.115	
C_2	0.1019	305.4	48.2	0.098	30.1	0.115	
C_3	0.0835	369.8	41.9	0.152	44.1	0.115	
nC_4	0.0331	425.2	37.5	0.193	58.1	0.115	
C_{5-7}	0.1204	516.667	28.82	0.2651	89.9	0.115	0.045
C_{8-10}	0.1581	590	23.743	0.3644	125.7	0.115	0.055
C_{11-14}	0.0823	668.611	18.589	0.4987	174.4	0.115	0.055
C_{15-20}	0.0528	745.778	14.8	0.6606	240.3	0.115	0.06
C_{21-28}	0.0276	812.667	11.954	0.8771	336.1	0.115	0.08
C_{29+}	0.0464	914.889	8.523	1.2789	536.7	0.115	0.28

envelope for North Ward Estes oil mixed with impure CO_2. The three-phase region is not connected to the single L_1 phase region. It ends at two bicritical points, similar to that for Maljamar reservoir oil.

All the terms, particularly the last one in Eq. 12, facilitate to detect the instability in both single- and two-phase stability testings. We have examined totally 2394 conditions in Figs. 1 through 6. For single-phase stability testing, 613 conditions (true

TABLE 6—COMPONENT DATA OF MALJAMAR SEPARATOR OIL						
Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$
CO_2		304.211	73.819	0.225	44	
C_{5-7}	0.2354	516.667	28.82	0.2651	89.9	0.115
C_{8-10}	0.3295	590	23.743	0.3644	125.7	0.115
C_{11-14}	0.1713	668.611	18.589	0.4987	174.4	0.115
C_{15-20}	0.1099	745.778	14.8	0.6606	240.3	0.115
C_{21-28}	0.0574	812.667	11.954	0.8771	336.1	0.115
C_{29+}	0.0965	914.889	8.523	1.2789	536.7	0.115

TABLE 7—COMPONENT DATA OF BOB SLAUGHTER BLOCK OIL						
Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$
CO_2	0.0337	304.2	73.77	0.225	44.01	
C_1	0.0861	160	46	0.008	16.04	0.055
PC_1	0.6478	529.03	27.32	0.481	98.45	0.081
PC_2	0.2324	795.33	17.31	1.042	354.2	0.105

TABLE 8—COMPONENT DATA OF NORTH WARD ESTES OIL						
Component	n (initial)	T_C (K)	P_C (bar)	ω	Mw (g/mol)	$k_{i,CO2}$
CO_2	0.0077	304.2	73.77	0.225	44.01	
C_1	0.2025	190.6	46	0.008	16.04	0.12
PC_1	0.118	343.64	45.05	0.13	38.4	0.12
PC_2	0.1484	466.41	33.51	0.244	72.82	0.12
PC_3	0.2863	603.07	24.24	0.6	135.82	0.09
PC_4	0.149	733.79	18.03	0.903	257.75	0.09
PC_5	0.0881	923.2	17.26	1.229	479.95	0.09
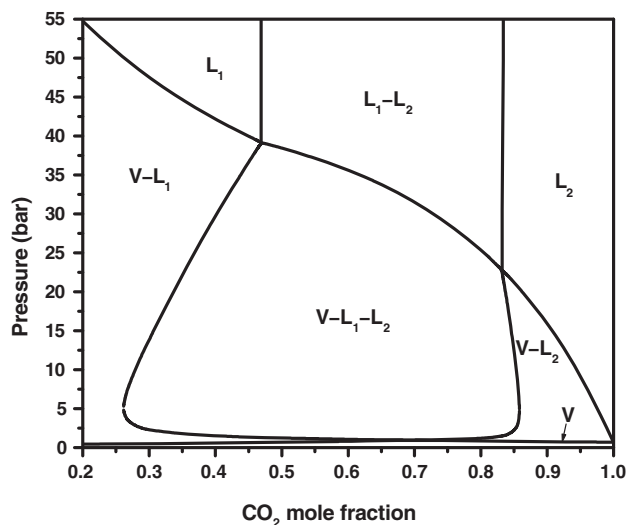
Fig. 1—The phase envelope for CO_2 mixing with acid gas at 178.8 K showing the single-, two-, and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. Note the single-phase V appears when the pressure is lower than 1 bar.
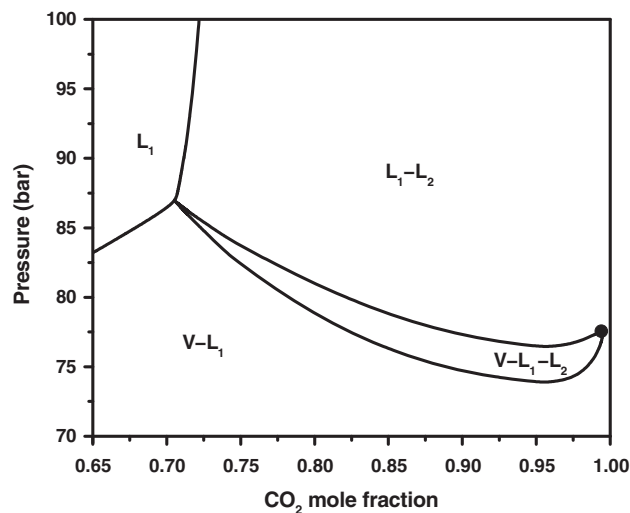

Fig. 2—The phase envelope for CO_2 mixing with Oil B at 307.6 K showing the single-, two-, and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. The solid circle represents the bicritical point.

solution) are stable in single-phase state when all the terms are used. It becomes 671 without the first and second terms, 617 without the third and fourth terms, and 670 without the last term. For two-phase stability testing, 1,340 conditions (true solution) are stable in two-phase state when all the terms are used. It becomes

1,366 without the first and second terms, 1,364 without the third and fourth terms, and 1,508 without the last term. If we replace the values 0.9 and 0.1 in Eq. 11 by 0.99 and 0.01 or by 0.8 and 0.2, Eq. 12 may fail to detect the instability. Although the TPD and TPD* functions remain the same for different test phases in two-phase stability testing, choosing the phase with lower molar weight as the test phase produces six failures among a total of
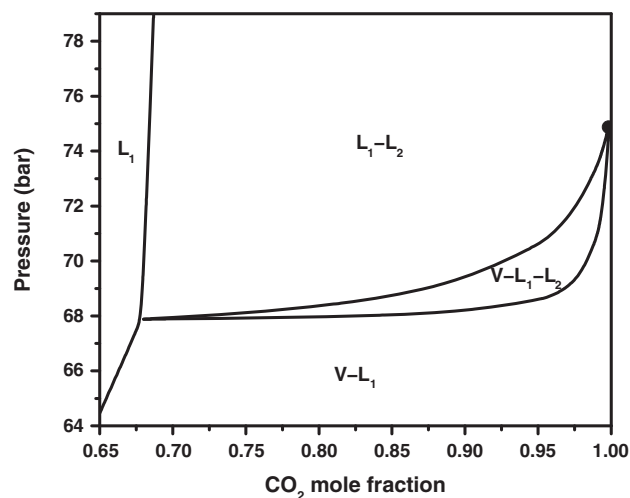

Fig. 3—The phase envelope for CO_2 mixing with Maljamar reservoir oil at 305.35 K showing the two- and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. The solid circles represent the bicritical points.

Fig. 4—The phase envelope for CO_2 mixing with Maljamar separator oil at 305.35 K showing the single-, two-, and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. The solid circle represents the bicritical point.
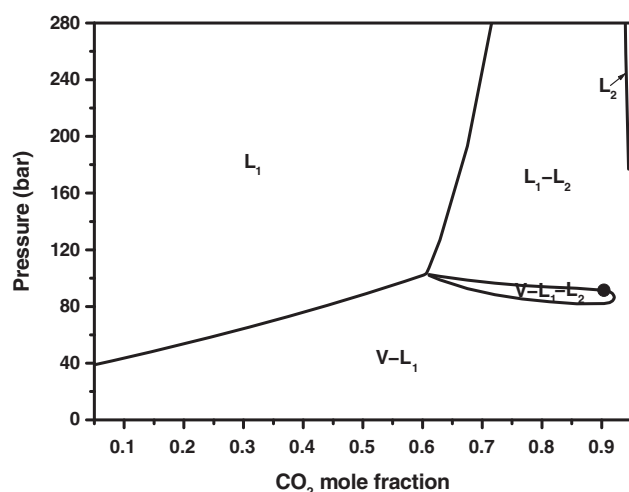
Fig. 5—The phase envelope for impure CO_2 (95 mol% CO_2 + 5 mol% C_1) mixing with Bob Slaughter Block oil at 313.71 K showing the single-, two-, and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. The solid circle represents the bicritical point. Note the single-phase L_2 appears when the mixture is almost the pure mixing gas.
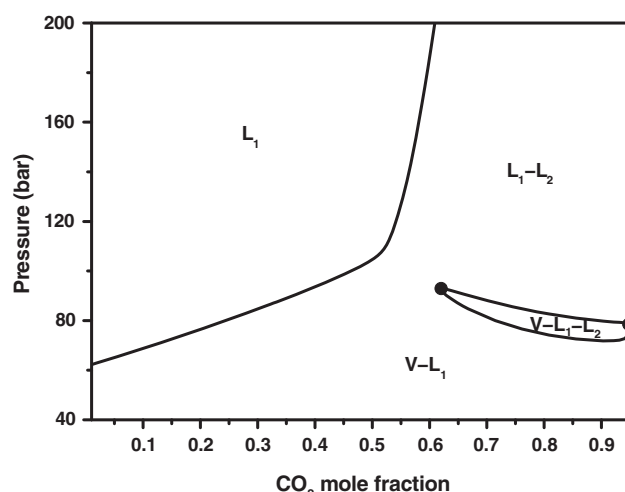

Fig. 6—The phase envelope for impure CO_2 (95 mol% CO_2 + 5 mol% C_1) mixing with North Ward Estes oil at 301.48 K showing the single-, two-, and three-phase regions. V, L_1, and L_2 denote the vapor, CO_2-lean, and CO_2-rich liquid phases. The solid circles represent the bicritical points.

1,781 conditions where two-phase stability testing is required. That is because the initial guess of $\{y_i^{trial}\}$ depends on the test phase despite the fact that the same initial guess of $\{K_i^{stab}\}$ is used; the iteration may take the wrong path when the phase with lower molar weight is the test phase.

In **Table 9,** we randomly choose one condition for CO_2 mixing with each hydrocarbon fluid and estimate the CPU time for both stability testing and phase-split calculation by using our strategy. As before, both single- and two-phase stability testings have simi-

lar CPU time as two-phase split calculation, but three-phase split calculation is much more expensive. The computational cost increases with the number of components. In **Table 10,** we estimate the total CPU time used to calculate each phase envelope, including bicritical points. Each phase envelope only needs a few seconds, although there are many single-, two-, and three-phase states. Because we require very high accuracy for both equilibrium ratios and phase fractions, in our strategy the CPU time increases close to the critical point.

Because the equal fugacity condition is necessary but not sufficient for phase equilibrium, an improper initial guess may

TABLE 9—CPU TIME OF STABILITY TESTING AND PHASE-SPLIT CALCULATION FOR CO_2 MIXING WITH ACID GAS, OIL B, MALJAMAR RESERVOIR OIL, MALJAMAR SEPARATOR OIL, BOB SLAUGHTER BLOCK OIL, AND NORTH WARD ESTES OIL AT INDIVIDUAL CONDITIONS

				CPU Time (sec)			
Mixture	T (K)	P (bar)	n (CO_2)	1P-Stab	2P-Split	2P-Stab	3P-Split
Acid gas	178.8	20	0.5	8.89e–4	2.13e–4	1.08e–3	3.50e–3
Oil B	307.6	76	0.9	4.14e–3	3.97e–3	6.43e–3	2.02e–2
Maljamar reservoir oil	305.35	79	0.8	1.80e–3	2.58e–3	2.08e–3	8.36e–3
Maljamar separator oil	305.35	71	0.98	4.44e–4	4.84e–4	6.69e–4	4.06e–3
Bob Slaughter Block oil	313.71	91	0.85837	2.70e–4	3.06e–4	3.14e–4	3.03e–3
North Ward Estes oil	301.48	79	0.80866	6.73e–4	1.18e–3	1.03e3	4.56e–3

TABLE 10—CPU TIME TO CALCULATE PHASE ENVELOPES AND BICRITICAL POINTS FOR CO_2 MIXING WITH ACID GAS, OIL B, MALJAMAR RESERVOIR OIL, MALJAMAR SEPARATOR OIL, BOB SLAUGHTER BLOCK OIL, AND NORTH WARD ESTES OIL

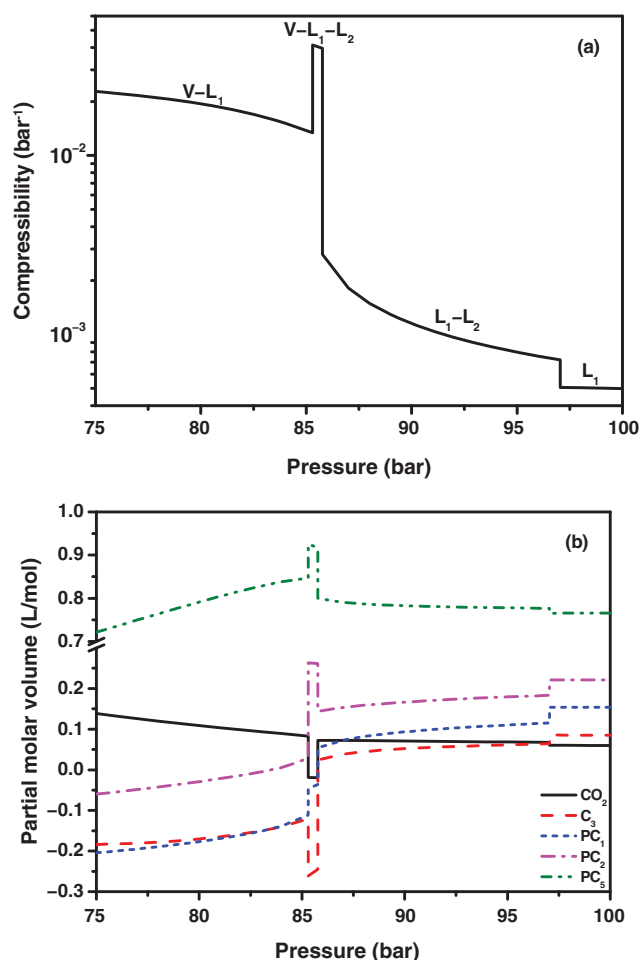|	Number of States			CPU time (sec)	
Mixture	1P	2P	3P	Phase Envelope	Bicritical Point
Acid gas	166	249	221	1.68	
Oil B	39	133	54	5.02	0.42
Maljamar reservoir oil	0	133	52	6.81	5.01
Maljamar separator oil	65	173	46	0.81	0.09
Bob Slaughter Block oil	224	320	30	0.51	0.08
North Ward Estes oil	119	332	38	1.81	0.61

Fig. 7—(a) Total compressibility and (b) total partial molar volumes of CO_2, C_3, PC_1, PC_2, and PC_5 as function of pressure for CO_2 mixing with Oil B at 307.6 K and CO_2 mole fraction 0.72.

produce an incorrect phase-split solution with a local minimum of Gibbs free energy. Reliable stability testing can effectively avoid the blind selection of the initial guess for phase-split calculation. Very often, $\{K_i^{1P\text{-stab}}\}$ with the lowest TPD* value is the best initial guess for two-phase split calculation. However, in a few cases, that may lead to an incorrect two-phase solution. The incorrect solution could be either VL or LL type. It is "unstable," but three-phase solution does not exist. The correct two-phase solution can be obtained by trying another initial guess [e.g., $\{K_i^{2P\text{-stab}}\}$ with the lowest TPD* value in two-phase stability testing after the incorrect two-phase split calculation]. The correct solution is stable, and three-phase split calculation is not required. The correct solution has a Gibbs free energy only slightly lower than the incorrect one. The same observation has been made in Ref.[20]

In **Fig. 7,** we use Oil B mixed with CO_2 ($n_{CO_2} = 0.72$) as an example to show the single-, two-, and three-phase total compressibility and total partial molar volumes. As the pressure increases, the state changes from VL_1 to VL_1L_2 to L_1L_2 to L_1, accompanied by several discontinuities in both total compressibility and total partial molar volumes.[31,34] Fig. 7a shows that the total compressibility spans two orders of magnitude. The VL_1L_2 state is the most compressible, followed by the VL_1 state and then the L_1L_2 state. The L_1 state is the least compressible. The total partial molar volumes of different components reveal complicated behavior changing from one state to another state. Fig. 7b shows the selected results having different trends. To the best of our knowledge, the three-phase total compressibility and total partial molar volumes have not been discussed in literature except in our recent research for three-phase systems containing an aqueous phase (Moortgat et al. 2011a).

Conclusions

We present a general strategy for two- and three-phase split calculations based on reliable stability testing. By using the Wilson correlation and a new expression to provide the initial estimates, we adopt the BFGS-quasi-Newton method within unconstrained local minimization to implement stability testing. For all the tests examined in this research, in our compositional simulation, and in the challenging phase-behavior computations of asphaltene precipitation, our algorithm can always correctly predict the instability. Phase-split calculation uses stability testing and the bisection method to provide initial guesses, and is implemented by combining the SSI and Newton methods based on equation-solving approach. A number of examples are used to demonstrate the powerful aspects of the proposed strategy.

Nomenclature

f = fugaciy of a component
K = equilibrium ratio of a component
n, x, y, z = mole fraction of a component
β = mole fraction of a phase
ϕ = fugacity coefficient of a component

Acknowledgments

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Appendix A—Total Compressibility and Total Partial Molar Volumes in Single-, Two-, and Three-Phase States

For an individual phase α, $\{n_{\alpha,k}\}$ is the number of moles for components, $N_\alpha = \sum_k n_{\alpha,k}$ is the total number of moles, $v_\alpha^{EOS} = Z_\alpha RT/p$ is the molar volume without volume shift, Z_α is the compressibility factor, and $\{f_{\alpha,k}\}$ is the fugacity for components. For the whole system, $\{n_k = \sum_\alpha n_{\alpha,k}\}$ is the number of moles for components, $N = \sum_k n_k = \sum_{\alpha,k} n_{\alpha,k}$ is the total number of moles, $V^{EOS} = \sum_\alpha V_\alpha^{EOS} = \sum_\alpha Z_\alpha N_\alpha RT/p$ is the total volume without volume shift, and $V = \sum_\alpha V_\alpha = \sum_\alpha (Z_\alpha N_\alpha RT/p + \sum_k n_{\alpha,k}c_k)$ is

the total volume with volume shift $\{c_k\}$. In the following expressions, the subscripts $\mathbf{n} = \{n_k\}$, $\mathbf{n}_{\neq k} = \{n_1, ..., n_{k-1}, n_{k+1}, ..., n_C\}$, $\mathbf{n}_\alpha = \{n_{\alpha,k}\}$, and $\mathbf{n}_{\alpha,\neq k} = \{n_{\alpha,1}, ..., n_{\alpha,k-1}, n_{\alpha,k+1}, ..., n_{\alpha,C}\}$.

Single-Phase State. When the mixture is in single-phase state, the compressibility and partial molar volumes are given by

$$\kappa_T = \frac{V^{EOS}}{V}\left[\frac{1}{p} - \frac{1}{Z}\left(\frac{\partial Z}{\partial p}\right)_{T,\mathbf{n}}\right] \quad \dots\dots\dots\dots \text{(A-1)}$$

$$\bar{v}_i = \frac{NRT}{p}\left(\frac{\partial Z}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}} + v^{EOS} + c_i \ (i = 1 \text{ to } C). \quad \dots\dots \text{(A-2)}$$

Two-Phase State. When the mixture is in two-phase state, the total compressibility and total partial molar volumes are given by

$$\kappa_T = \frac{V^{EOS}}{Vp} - \frac{1}{V}\sum_{\alpha=1}^{2}\left\{\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial p}\right)_{T,\mathbf{n}_\alpha}\right.$$
$$\left. + \sum_{k=1}^{C}\left[\begin{array}{c}\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial n_{\alpha,k}}\right)_{T,p,\mathbf{n}_{\alpha,\neq k}}\\ + v_\alpha^{EOS} + c_k\end{array}\right]\left(\frac{\partial n_{\alpha,k}}{\partial p}\right)_{T,\mathbf{n}}\right\} \quad \dots \text{(A-3)}$$

$$\bar{v}_i = \sum_{\alpha=1}^{2}\sum_{k=1}^{C}\left[\begin{array}{c}\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial n_{\alpha,k}}\right)_{T,p,\mathbf{n}_{\alpha,\neq k}}\\ + v_\alpha^{EOS} + c_k\end{array}\right]\left(\frac{\partial n_{\alpha,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}} \ (i = 1 \text{ to } C)$$
$$\dots\dots\dots\dots\dots\dots \text{(A-4)}$$

The unknowns in Eqs. A-3 and A-4 can be solved from

$$\sum_{k=1}^{C}\left[\left(\frac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}} + \left(\frac{\partial f_{2,j}}{\partial n_{2,k}}\right)_{T,p,\mathbf{n}_{2,\neq k}}\right]\left(\frac{\partial n_{2,k}}{\partial p}\right)_{T,\mathbf{n}}$$
$$= \left(\frac{\partial f_{1,j}}{\partial p}\right)_{T,\mathbf{n}_1} - \left(\frac{\partial f_{2,j}}{\partial p}\right)_{T,\mathbf{n}_2} \ (j = 1 \text{ to } C) \quad \dots\dots \text{(A-5)}$$

$$\sum_{k=1}^{C}\left[\left(\frac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}} + \left(\frac{\partial f_{2,j}}{\partial n_{2,k}}\right)_{T,p,\mathbf{n}_{2,\neq k}}\right]\left(\frac{\partial n_{2,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}}$$
$$= \sum_{k=1}^{C}\delta_{ki}\left(\frac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}} \ (j = 1 \text{ to } C) \quad \dots\dots\dots \text{(A-6)}$$

combined with the mass balance $\{n_k = \sum_{\alpha=1}^{2} n_{\alpha,k}\}$. δ_{ki} is the Kronecker delta function. Note $\kappa_T = \infty$ for $C = 1$.

Three-Phase State. When the mixture is in three-phase state, the total compressibility and total partial molar volumes are given by

$$\kappa_T = \frac{V^{EOS}}{Vp} - \frac{1}{V}\sum_{\alpha=1}^{3}\left\{\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial p}\right)_{T,\mathbf{n}_\alpha}\right.$$
$$\left. + \sum_{k=1}^{C}\left[\begin{array}{c}\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial n_{\alpha,k}}\right)_{T,p,\mathbf{n}_{\alpha,\neq k}}\\ + v_\alpha^{EOS} + c_k\end{array}\right]\left(\frac{\partial n_{\alpha,k}}{\partial p}\right)_{T,\mathbf{n}}\right\}$$
$$\dots\dots\dots\dots\dots\dots \text{(A-7)}$$

$$\bar{v}_i = \sum_{\alpha=1}^{3}\sum_{k=1}^{C}\left[\begin{array}{c}\frac{N_\alpha RT}{p}\left(\frac{\partial Z_\alpha}{\partial n_{\alpha,k}}\right)_{T,p,\mathbf{n}_{\alpha,\neq k}}\\ + v_\alpha^{EOS} + c_k\end{array}\right]\left(\frac{\partial n_{\alpha,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}} \ (i = 1 \text{ to } C)$$
$$\dots\dots\dots\dots\dots\dots \text{(A-8)}$$

The unknowns in Eqs. A-7 and A-8 can be solved from

$$
\left\{
\begin{array}{l}
\sum_{k=1}^{C}\left\{
\begin{array}{l}
\left[\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\right]\left(\dfrac{\partial n_{2,k}}{\partial p}\right)_{T,\mathbf{n}}+\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\left(\dfrac{\partial n_{3,k}}{\partial p}\right)_{T,\mathbf{n}}\\[2mm]
+\left(\dfrac{\partial f_{2,j}}{\partial n_{2,k}}\right)_{T,p,\mathbf{n}_{2,\neq k}}\quad=\left(\dfrac{\partial f_{1,j}}{\partial p}\right)_{T,\mathbf{n}_1}-\left(\dfrac{\partial f_{2,j}}{\partial p}\right)_{T,\mathbf{n}_2}
\end{array}
\right\}\\[8mm]
\sum_{k=1}^{C}\left\{
\begin{array}{l}
\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\left(\dfrac{\partial n_{2,k}}{\partial p}\right)_{T,\mathbf{n}}+\left[\begin{array}{c}\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\\[1mm]+\left(\dfrac{\partial f_{3,j}}{\partial n_{3,k}}\right)_{T,p,\mathbf{n}_{3,\neq k}}\end{array}\right]\left(\dfrac{\partial n_{3,k}}{\partial p}\right)_{T,\mathbf{n}}\\[4mm]
\quad=\left(\dfrac{\partial f_{1,j}}{\partial p}\right)_{T,\mathbf{n}_1}-\left(\dfrac{\partial f_{3,j}}{\partial p}\right)_{T,\mathbf{n}_3}
\end{array}
\right\}
\end{array}
\right\}(j=1\text{ to }C)
$$

$$\dotfill (A\text{-}9)$$

$$
\left\{
\begin{array}{l}
\sum_{k=1}^{C}\left\{
\begin{array}{l}
\left[\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\right]\left(\dfrac{\partial n_{2,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}}+\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\left(\dfrac{\partial n_{3,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}}\\[2mm]
+\left(\dfrac{\partial f_{2,j}}{\partial n_{2,k}}\right)_{T,p,\mathbf{n}_{2,\neq k}}\quad=\sum_{k=1}^{C}\delta_{ki}\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}
\end{array}
\right\}\\[8mm]
\sum_{k=1}^{C}\left\{
\begin{array}{l}
\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\left(\dfrac{\partial n_{2,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}}+\left[\begin{array}{c}\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}\\[1mm]+\left(\dfrac{\partial f_{3,j}}{\partial n_{3,k}}\right)_{T,p,\mathbf{n}_{3,\neq k}}\end{array}\right]\left(\dfrac{\partial n_{3,k}}{\partial n_i}\right)_{T,p,\mathbf{n}_{\neq i}}\\[4mm]
\quad=\sum_{k=1}^{C}\delta_{ki}\left(\dfrac{\partial f_{1,j}}{\partial n_{1,k}}\right)_{T,p,\mathbf{n}_{1,\neq k}}
\end{array}
\right\}
\end{array}
\right\}(j=1\text{ to }C)
$$

$$\dotfill (A\text{-}10)$$

combined with the mass balance $\left\{n_k=\sum_{\alpha=1}^{3}n_{\alpha,k}\right\}$. A special case of three-phase total compressibility and total partial molar volumes for the system containing water and two hydrocarbon phases has been recently presented in Ref. 53.

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