Calculation of convergence pressure/temperature and stability test limit loci of mixtures with cubic equations of state

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Abstract

The convergence locus (CL) and stability test limit locus (STLL) are important underlying properties of multicomponent system phase diagrams. In the pressure–temperature plane, the CL separates the region where the negative flash has non-trivial solutions. The mathematical domain of flash calculations is significantly wider than the physical domain; if a negative flash is performed, the equilibrium constants are continuously derivable when a phase boundary is crossed. Criticality criteria are met for the phase compositions resulting from the negative flash and the minimum eigenvalue of a quadratic form evaluated with these compositions (which are intrinsically stable) is used to locate the CL. An efficient negative flash procedure is also proposed. The STLL is important because in its vicinity the number of iterations for phase stability testing increases dramatically and divergence may occur. Outside the STLL the tangent plane distance function has only a trivial solution; between STLL and the phase boundary, there is a non-trivial positive solution. The spinodal criterion is met at the STLL for trial phase compositions. The CL and STLL are located at given pressure or temperature based on rigorous thermodynamic criteria in only few Newton iterations. The proposed method avoids repeated expensive negative flash calculations in the vicinity of the CL and phase stability calculations in the vicinity of the STLL. Results are presented for representative hydrocarbon mixtures with different amounts of classical contaminants and different shapes of phase envelopes.
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1. Introduction

The convergence locus (CL) and stability test limit locus (STLL) are remarkable phase properties of multicomponent mixtures, yet their calculation is extremely difficult and time consuming. Efficient calculation algorithms for these properties are needed to facilitate and extend their use.

In the temperature–pressure plane, the CL of a given multicomponent mixture delineates the region where "negative flash" (Whitson and Michelsen [1]) calculations give two distinct solutions for the compositions (x_i for the liquid phase and y_i for the vapor phase), i.e. the solution is non-trivial. Solutions of "negative flash" are obtained by allowing phase mole fractions V and L of the vapor and liquid phases to lie outside the physical domain [0,1]. The CL is indeed much larger than the phase envelope, and both loci join at the mixture critical point. The CL is in fact a line of critical points (see next section), which explains the computational difficulty to find this boundary from an equation of state.

There are many applications of negative flash and convergence pressure concepts. Historically, before the spectacular development of cubic EoS in the 1970s, compositional simulators have used for a long time interpolation in K-value charts based on convergence pressures [2]. Equilibrium constants K_i are continuously derivable when a phase boundary is crossed, and some modern reservoir compositional simulators [3] and process simulators [4] take advantage of this property for phase stability testing and phase identification. Some empirical relations for generating K-values are using the convergence pressure [5]. The negative flash is also important for flash calculations at different specifications (other than pressure and temperature, see Michelsen [6,7]), and for pseudo-component delumping [8–10]. The negative flash was extended to multiphase equilibrium calculations by Leibovici and Neoschil [11]. One of the most important negative flash applications and maybe the most important application of the convergence pressure concept is the

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calculation of the minimum miscibility pressure (MMP) in multicomponent hydrocarbon/injected gas systems [12,13] in the case of a pure condensing or vaporizing drive.

Phase stability analysis is an important problem in phase equilibrium calculations. The phase stability problem is posed in terms of Gibbs tangent plane distance (TPD) criterion. Stability of a phase requires that all stationary points of the TPD function are positive, i.e. the global minimum of the TPD function is zero. It is known that in the single-phase region, the TPD function may have non-trivial positive stationary points. The STLL encloses the domain in the temperature–pressure plane where stability testing has non-trivial solutions. Outside this envelope (located between phase boundaries and the CL), the only stationary point of the TPD function is trivial. The vicinity of the STLL is an extremely difficult region for any stability testing algorithm.

In this work, we devise and test computational algorithms for calculating the CL and STLL of multicomponent mixtures from cubic equations of state. All codes are based on reduction methods and are written for a general form of two-parameter cubic EoS (including the SRK EoS, Soave [14], and the PR EoS, Peng and Robinson [15]). The outline is as follows. In the next two sections we present the proposed criteria and algorithms for CL and STLL, then several applications for some representative hydrocarbon mixtures; a brief discussion precedes the conclusions of this paper.

2. Convergence locus

The Rachford–Rice (RR) equation:

$$F(V) = \sum_{i=1}^{nc} \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \tag{1}$$

is usually solved for physical values of vapor mole fraction, $V \in [0,1]$. If V is allowed to go out of its physical bounds, a "negative flash" is performed. The function $F(V)$ has nc (number of components) asymptotes at $V = 1/(1 - K_i)$; the two asymptotes that bound the mathematical domain are $V_L = 1/(1 - K_{max})$ and $V_H = 1/(1 - K_{min}) > 1$.

The negative flash concept was presented and discussed in detail by Whitson and Michelsen [1]. For flash calculations, the mathematical domain is wider than the physical domain. The convergence locus bounds the mathematical domain; at conditions outside the convergence locus, a negative flash has only trivial solutions. By extending flash calculations outside the physical domain, continuous derivability is ensured when phase boundaries are crossed; this property is very useful for various practical applications. The solution of the negative flash is a saddle point of the Gibbs free energy. Negative flash calculations in the vicinity of the CL are even more difficult than flash calculations at near-critical conditions. More careful initialization is required for negative flashes [1].

We should note that on the convergence locus, even though all K-values are equal to unity (and $V = +\infty$ or $V = -\infty$), component mole fractions are different from feed composition z (i.e. non-trivial). For a given convergence point (say at T, p_{conv}), the mole fractions from the negative flash are identical to the composition of a mixture at its critical point at these conditions, hereafter referred to as critical composition (for which $V = L = 0.5$). Moreover, the results of an isothermal flash for any pressure below the convergence pressure are identical for the feed composition and for the critical composition. This interesting property is the basis of the corresponding states approach (see for instance Rowe [16], and Kaliappan and Rowe [17]) used in the early work on compositional simulation [2].

For locating the convergence pressure on an isotherm, using bisection or some similar method is very costly; besides, it can be misleading because at the upper limit of the interval the solution is always trivial.

The idea behind the proposed method is to approach the solution by keeping all iterates in the negative flash region ($p < p_{conv}$), and by performing a reduced number of (negative) flash calculations. A criterion for the convergence locus is needed.

As the convergence pressure is approached, mole fractions of both "equilibrium" phases tend to the critical composition. For this composition the criticality conditions must be fulfilled. Let us note that "equilibrium" phases from negative flash are at their saturation points (liquid at its bubblepoint and vapor at its dewpoint) at flash pressure and temperature, thus they are both intrinsically stable (outside the spinodal). Therefore $\lambda_{min}(p, x(p)) \geq 0$ (λ_{min} is the minimum eigenvalue of the matrix **Q** containing second order partial derivatives of Helmholtz free energy with respect to mole numbers [18]), for any pressure between the saturation pressure and the convergence pressure at a given temperature (equality holds only on the convergence locus). Furthermore, continuity of phase mole fractions ensures the continuity of positive λ_{min} as CL is approached. The above considerations suggest that even though we search for a critical point, we can safely retain only one criticality condition (i.e. the spinodal equation [18]), thus the convergence locus criterion is:

$$\lambda_{min}(p, x(p)) = 0 \tag{2}$$

where x contains mole fractions of any of the two "equilibrium" phases obtained from negative flash.

We need only λ_{min} and the corresponding eigenvector; inverse iteration (Peters and Wilkinson [19]) is used to calculate the eigenvalue–eigenvector pair. Matrix **Q** is scaled as suggested by Michelsen [20] to **B** with elements:

$$B_{ij} = \delta_{ij} + (x_i x_j)^{1/2} \frac{\partial \ln \varphi_i}{\partial n_j} \tag{3}$$

Eq. (2) is solved for pressure using the Newton–Raphson (NR) method with numerical derivatives. If the function is convex, the use of backward finite differences for approximating the derivative ensure that $p^{(\nu)} < p_{conv}$ at any iteration level ν. The function $\lambda_{min}(p)$ may not be convex and needs to be scaled; it is crucial to have a convex function for keeping all iterates at $p^{(\nu)} < p_{conv}$. We use $\lambda^* = [\lambda/\lambda^{(0)}]^{\alpha}$; $\alpha > 1$. A value of $\alpha < 4$ was found suitable in all test problems; as a safety feature, if at the first iteration the negative flash returns the trivial solution then α is increased.

Summarizing, the proposed algorithm consists in:

(1) Start at saturation pressure.
(2) At subsequent iterations perform a negative flash; the results at $p^{(v)}$ are used as initial guesses for negative flash calculations at $p^{(v+1)}$.
(3) Calculate the minimum eigenvalue λ_{min} of matrix **B**.
(4) Calculate by numerical derivation $\partial\lambda_{min}/\partial p$.
(5) Update pressure by the NR method.
(6) If convergence criteria are not met go to step (2).

The algorithm converges usually in just a few NR iterations. For calculating the convergence temperature at a given pressure the algorithm is quite similar.

We need a powerful algorithm for negative flash calculations, since at least at last iteration levels calculations are performed at near-singular conditions. We found appropriate the use of the reduction method for flash calculations, which seems to be more robust than conventional flash (note, however, that the method could work also by using conventional variables). The M reduction parameters are defined as [21]:

$$Q_\alpha = \sum_{i=1}^{nc} q_{\alpha i} x_i; \quad \alpha = 1, m; \quad Q_M = B \qquad (4)$$

where m is the number of non-zero eigenvalues β_α of the matrix **C** with elements $(1 - k_{ij})$, $M = m + 1$ and $q_{\alpha i}$ are elements of the eigenvectors corresponding to β_α [22].

The $M + 1$ error equations for flash calculations are:

$$e_\alpha \equiv \sum_{i=1}^{nc} q_{\alpha i} x_i - Q_\alpha = 0; \quad \alpha = 1, M \qquad \text{and}$$

$$e_{M+1} \equiv \sum_{i=1}^{nc} (y_i - x_i) = 0 \qquad (5)$$

Iteration variables are selected depending on whether the mixture is predominantly in liquid or vapor state: QBL iterations with $\mathbf{Q} = (Q_{L1}, \ldots, Q_{LM}, L)^T$ for $V < L$ and QBV iterations with $\mathbf{Q} = (Q_{V1}, \ldots, Q_{VM}, V)^T$ otherwise. The algorithm is presented in detail elsewhere [23,24]. It combines successive substitution iterations (SSI) and Newton–Raphson iterations. The switching (from SSI to NR) criteria from Ref. [25] are used; in the case of a too early switch the code reverts to SSI. For SSI, RR equation is solved using the method of Leibovici and Neoschil [11]; for NR iterations, V is an independent variable and the RR equation is not directly solved (it is one of the error equations). No attempts were made to use convergence acceleration procedures such as dominant eigenvalue method, because they are risky for negative flashes, mainly near the CL [1].

Since for negative flash $x_i, y_i \in (0,1)$, the reduced variables $Q_\alpha \in (Q_{\alpha min}, Q_{\alpha max})$ for any $V \in (-\infty, +\infty)$, where the bounds of reduced variables are $Q_{\alpha min} = \min_{i=1,nc}(q_{\alpha i})$ and $Q_{\alpha max} = \max_{i=1,nc}(q_{\alpha i})$.

A procedure similar to that proposed by Cismondi and Michelsen [26] for calculating critical loci of binary mixtures can be used to obtain initial estimates. Supposing the critical composition is already calculated, it can be updated using the equation:

$$n_i = z_i + s\sqrt{z_i} u_i; \quad i = 1, nc \qquad (6)$$

where s is a parameter (distance from a critical point), $z_i = n_i / \sum n_i$ and u_i are the elements of the eigenvector **u**. Then critical point is calculated (using a reduction method [27,28]) for z_i and critical pressure is a very good approximation of convergence pressure at $T = T_c$, provided s is reasonably small. From our experience, use of Eq. (6) gives always (T, p) values inside the convergence envelope.

Exact calculation of CL is rather difficult because it involves the unknown composition on the CL. It requires the resolution of Eq. (6) together with the criticality conditions for z, p or T, and s.

3. Stability test limit

Phase stability testing is based on Michelsen's tangent plane distance function [20]. The TPD function is given by the difference between the Gibbs free energy surface in **x** (composition of a trial phase), and the tangent plane to this surface in **z** (composition of the phase whose stability is asserted). A mixture is stable if and only if the TPD function is non-negative at *all* stationary points [20,29], i.e. $D(\mathbf{x}) \geq 0(\forall)\mathbf{x}$.

The dimensionless TPD function is:

$$D(\mathbf{x}) = \sum_{i=1}^{nc} x_i(\ln f_i(\mathbf{x}) - \ln f_i(\mathbf{z})) \qquad (7)$$

The phase stability problem is solved either by direct minimization of D or by the resolution of a non-linear system corresponding to stationarity conditions. Initial guesses for Michelsen's two-sided initialization [20] of phase stability testing are obtained from Wilson's equation [30] ($Y_i^{(0)} = z_i/K_i$ and $Y_i^{(0)} = z_i K_i$).

The STLL bounds the region where non-trivial positive solutions exist for phase stability testing in the single-phase region. At temperature and pressure conditions outside the STLL, only the trivial solution exists. STLL was also called "limit of parallel tangent plane" [1].

For stability testing of two-phase systems, we can distinguish the following cases in the T–p plane:

(i) Inside the limit of intrinsic stability (spinodal), there are two negative minima of TPD function;
(ii) between spinodal and phase boundary, a minimum is negative and the other one corresponds to the trivial solution $\mathbf{x} = \mathbf{z}$;
(iii) on the phase boundary, the two minima (one non-trivial and one trivial) correspond to $D = 0$;
(iv) between phase boundary and STLL, one minimum is trivial and the other one is positive; the non-trivial solution corresponds to the "shadow phase" [31];
(v) at the STLL, the non-trivial stationary point becomes a saddle point;
(vi) outside the STLL, the only solution is a trivial minimum.

To illustrate the behavior of the TPD function in the single-phase region, TPD is plot in Fig. 1a–e for a binary mixture C_1-nC_{10} (80% mole methane) at different pressures above bubblepoint and $T = 350$ K (PR EoS, $k_{12} = 0.035$). The bubblepoint pressure is 341.7 bar, and STLL pressure is 352.8 bar. Fig. 1a–c

corresponds to pressures between bubblepoint and the STLL. On the STLL (Fig. 1d) a saddle point can be seen. For pressures above the STLL the only stationary point is the trivial solution. However, two different cases can be distinguished: at pressures just above the STLL, the TPD function has an inflex-
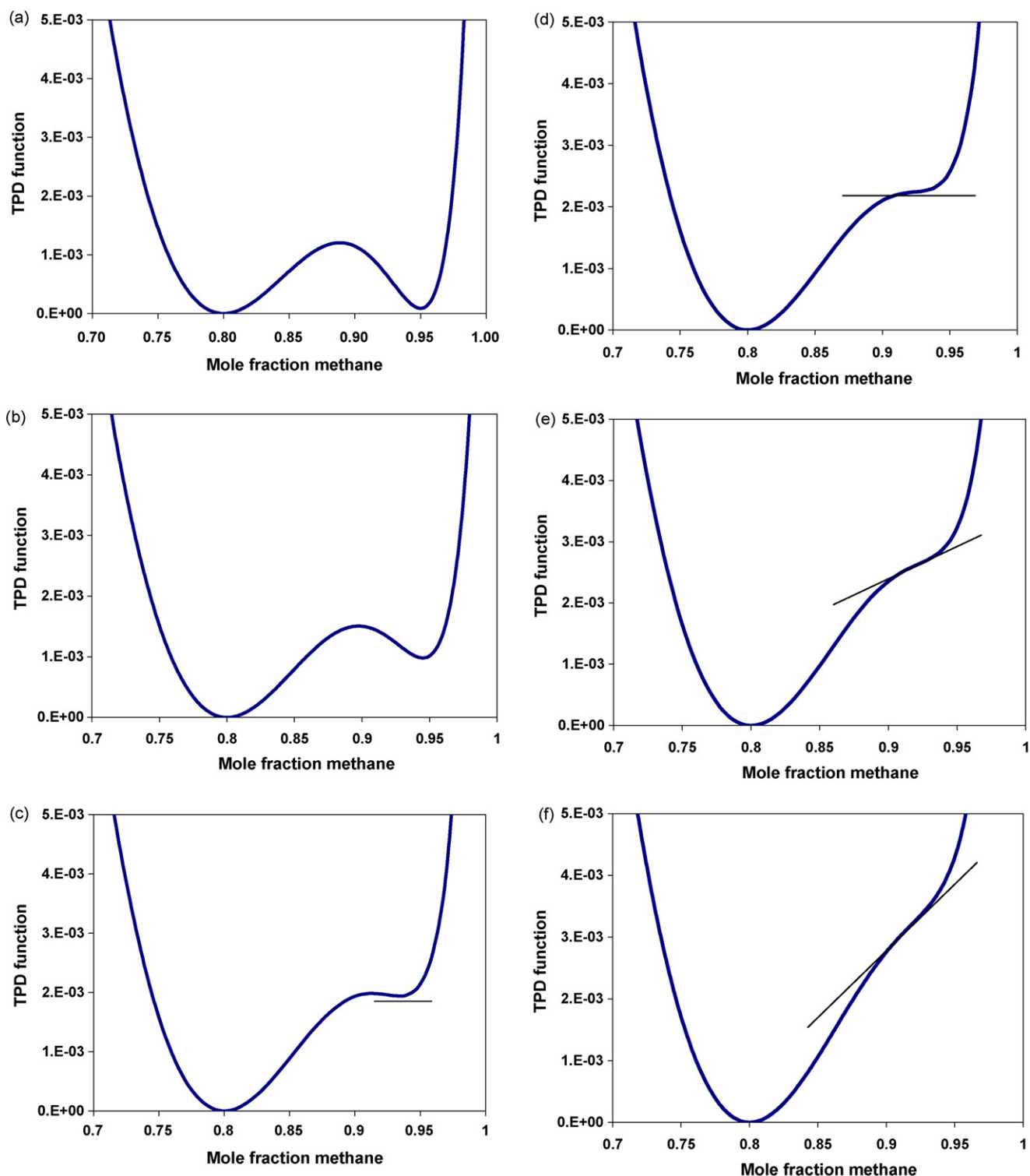

Fig. 1. TPD function at different pressures in the single-phase region for a C_1/nC_{10} binary mixture at $T = 350$ K: (a) 341.7 bar, (b) 345 bar, (c) 350 bar, (d) 352.8 bar, (e) 355 bar and (f) 360 bar.

ion point (see Fig. 1e and f), while at a higher pressure this point disappears.

Fig. 1a–e reveals why by starting from one of the two initial points [20], the phase stability problem is so difficult for second order methods and many fixed-point methods in the vicinity of the STLL. They have to be able to "cross" the vicinity of a saddle point to reach the global minimum valley. The picture is far more complicated for multicomponent systems, for which the convergence path of iterative methods depends on the topology of TPD hypersurface in an nc-dimensional space.

As the STLL is approached, the number of iterations increases dramatically for any method of phase stability testing, and divergence occurs in the immediate vicinity of STLL, which is the most difficult region for phase stability calculations.

The proposed algorithm for STLL pressure calculation at given temperature (or STLL temperature at given pressure) is similar with that described for CL calculation. The criterion to be met at the STLL is:

$$\lambda_{min}(p, \mathbf{x}) = 0 \tag{8}$$

that is, the spinodal condition, where $\mathbf{x}$ is here the trial phase composition vector.

The eigenvalue λ_{min} is always positive between saturation points and STLL. Eq. (8) is solved for pressure using NR iterations by starting from the saturation pressure. As stated earlier, proper scaling is required for $\lambda_{min}(p)$ since it may not be convex.

A reduction method for phase stability testing (Nichita et al. [25]) is used in this work. A non-linear system of only $M = m + 1$ equations (stationary point conditions expressed in terms of reduced variables) is solved by a globally convergent NR method. The M unknowns are the reduced variables corresponding to the trial phase composition. In addition to its reduced dimensionality, it is advantageous to use the reduction method because the TPD surface is smoother in the reduced variable space than in the compositional space [32,33].

The STLL is located between (and closer to) the phase boundary and the CL. In the critical region, both curves are very close to the phase boundary; the distance from the phase boundary to the convergence locus is at least four times larger than the distance to the STLL [1]. The critical point is common for the three curves.

4. Results

The proposed method is tested for a model gas–condensate system (Y8) and for mixtures Y8/N$_2$. Then, a reservoir fluid (composition and component properties provided by Total) and its mixtures with different amounts of carbon dioxide are studied.

4.1. Synthetic hydrocarbon mixture

Test calculation has been performed on a synthetic mixture of six normal-alkanes (feed mole fractions: $0.8097C_1$, $0.0566C_2$, $0.0306C_3$, $0.0457nC_5$, $0.033nC_7$, $0.0244nC_{10}$), known in the literature as the Y8 mixture (Yarborough [34]). The
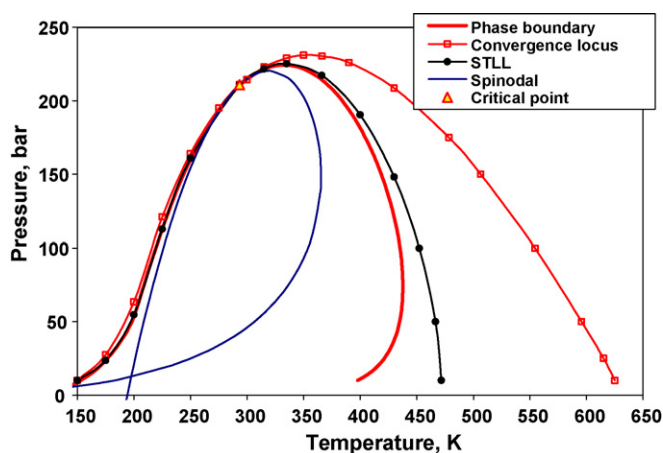

Fig. 2. Phase envelope, CL, STLL and spinodal for Y8 mixture.

Peng–Robinson EoS is used, with all BIPs zero. There is only one non-zero eigenvalue of $\mathbf{C}$ ($m = 1$, $\beta_1 = 6$); the non-linear systems have only three equations for flash calculations [35] and two equations for phase stability.

The phase envelope of Y8 mixture is given in Fig. 2. The critical point is at $T = 293.78$ K and $p = 210.67$ bar. The spinodal curve, the convergence locus and STLL are also drawn. Note that phase envelopes (saturation points) and spinodal curves are also constructed using a reduction method.

At $T = 335$ K (dewpoint at $p = 224.39$ bar, CL at $p = 229.06$ bar, and STLL at $p = 225.26$ bar), Fig. 3 depicts minimum eigenvalues of $\mathbf{B}$ evaluated for both vapor and liquid phase compositions at pressures between the dewpoint and the CL. For stability calculations, the dimensionless TPD function and λ_{min} are drawn versus pressure in Fig. 4.

Different amounts of nitrogen are combined with the Y8 mixture. The BIPs between N$_2$ and hydrocarbon components are taken equal to 0.1 (giving $m = 2$, $\beta_1 = 6.8332$, $\beta_2 = 0.1668$). The non-linear systems have four equations for flash and three equations for stability. Phase envelopes are drawn in Fig. 5 (for 25% N$_2$, critical point at $T = 232.89$ K and $p = 313.18$ bar.) and Fig. 6 (for 50% N$_2$, no critical point), together with spinodal curves, CL and STLL. Note the different shapes of characteristic loci.
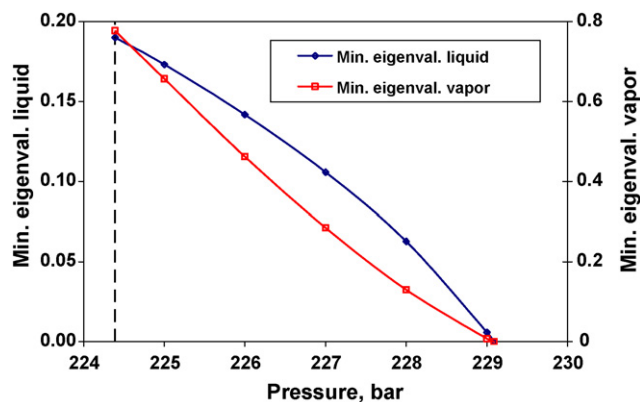

Fig. 3. Minimum eigenvalues (phase compositions from negative flash) vs. pressure for Y8 mixture at $T = 335$ K.
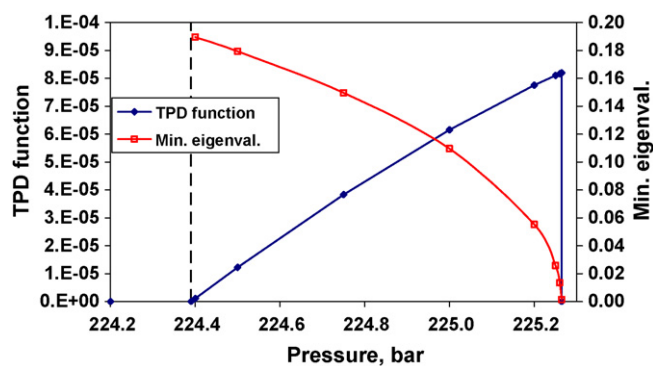
Fig. 4. Minimum eigenvalues (trial phase composition from phase stability testing) vs. pressure and TPD function for Y8 mixture at $T = 335$ K.

4.2. Reservoir fluid

The reservoir fluid (gas–condensate) composition is described by 29 components (mixture composition, component properties and non-zero BIPs are given in Table 1). The PR EoS is used. BIPs were adjusted to match available experimental data at reservoir temperature. Seven components have non-zero BIPs with the remaining ones, giving 15 non-zero eigenvalues of the matrix **C** ($m = 15$). Non-linear systems have 17 and 16 equations for flash and stability, respectively. The critical point is at $T = 412.89$ K and $p = 338.81$ bar. The phase envelope, the spinodal, the convergence locus and STLL of the reservoir
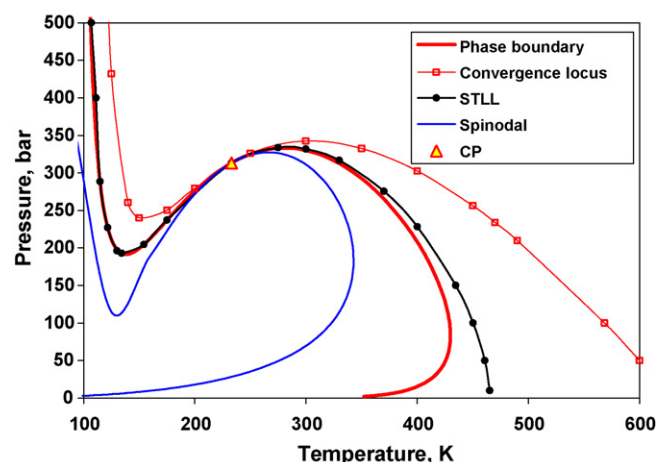

Fig. 5. Phase envelope, CL, STLL and spinodal for Y8/25% N_2 mixture.

fluid are plotted in Fig. 7. Carbon dioxide was added in various amounts; here we present in Fig. 8 the phase, convergence and stability envelopes for a 50% CO_2 mixture. This mixture has a high-pressure (671.66 bar) critical point at a low temperature (232.43 K). For very large amounts of CO_2, the mixtures have no critical points; envelopes are qualitatively similar to those drawn in Fig. 6.

For the gas–condensates studied here the negative flash region is very tiny on the bubblepoint side of the phase envelope, and

Table 1
Reservoir fluid composition and component properties

| Composition	Mole number	M_i	T_{ci} (K)	p_{ci} (bar)	ω_i	$k_{N_2 j}$	$k_{CO_2 j}$	$k_{H_2S j}$	$k_{COS j}$	$k_{C_1 j}$	$k_{C_2 j}$	$k_{C_3 j}$
N_2	1.150	28.01	126.20	33.90	0.0400	0.00	−0.02	0.180	0.00	0.04	0.05	0.08
CO_2	4.120	44.01	304.20	73.80	0.2250	−0.02	0.00	0.100	0.00	0.10	0.13	0.13
H_2S	14.690	34.08	373.20	89.37	0.1000	0.18	0.10	0.000	0.00	0.00	0.15	0.09
CH_3S	0.012	48.11	469.95	72.30	0.1530	0.00	0.00	0.000	0.00	0.15	0.00	0.00
C_2H_6S	0.016	62.13	499.00	54.90	0.1910	0.00	0.00	0.000	0.00	0.15	0.00	0.00
COS	0.002	60.07	378.80	63.50	0.1050	0.00	0.00	0.000	0.00	0.00	0.00	0.00
C_1	48.210	16.04	190.60	46.00	0.0115	0.04	0.10	0.000	0.00	0.00	0.00	0.00
C_2	7.320	30.07	305.40	48.80	0.0908	0.05	0.13	0.150	0.00	0.00	0.00	0.00
C_3	4.430	44.10	369.80	42.50	0.1454	0.08	0.13	0.090	0.00	0.00	0.00	0.00
iC_4	0.860	58.12	408.10	36.50	0.1760	0.10	0.13	0.075	0.00	0.00	0.00	0.00
nC_4	1.930	58.12	425.20	38.00	0.1928	0.09	0.13	0.050	0.00	0.00	0.00	0.00
iC_5	0.890	71.76	468.77	35.58	0.2202	0.10	0.12	0.060	0.00	0.00	0.00	0.00
nC_5	0.880	72.15	469.6	33.70	0.2273	0.10	0.12	0.060	0.00	0.00	0.00	0.00
C_6	1.270	85.36	511.98	33.19	0.2606	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_6H_6	0.049	78.11	562.20	48.90	0.2120	0.10	0.10	0.060	0.10	0.07	0.03	0.00
C_7	1.591	99.08	549.75	30.63	0.2807	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_7H_8	0.178	92.14	591.8	41.00	0.2630	0.10	0.10	0.060	0.10	0.07	0.03	0.00
C_8	1.702	113.24	574.715	28.30	0.3270	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_8H_{10}(XYL)	0.343	106.16	621.13	36.00	0.3230	0.10	0.10	0.060	0.10	0.07	0.03	0.00
C_8H_{10}(EB)	0.057	106.16	617.10	36.10	0.3011	0.10	0.10	0.060	0.10	0.07	0.03	0.00
C_9	1.250	125.19	618.15	27.58	0.3440	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_{10}	1.330	137.83	638.15	25.85	0.3780	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_{11}	1.050	149.00	658.15	24.57	0.3960	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_{12}	0.840	163.00	676.15	23.20	0.4140	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_{13}	0.780	176.00	690.15	21.96	0.4320	0.10	0.10	0.060	0.10	0.00	0.00	0.00
C_{14}	0.620	191.00	708.15	20.78	0.4590	0.10	0.10	0.060	0.10	0.00	0.00	0.00
PC1[a]	2.388	230.85	741.78	18.19	0.5129	0.10	0.10	0.060	0.10	0.02	0.00	0.00
PC2[a]	1.762	325.39	906.15	16.80	0.6950	0.10	0.10	0.060	0.15	0.08	0.04	0.03
PC3[a]	0.310	500.00	1113.15	14.35	0.8300	0.10	0.10	0.060	0.15	0.08	0.04	0.03

[a] Pseudo-components.
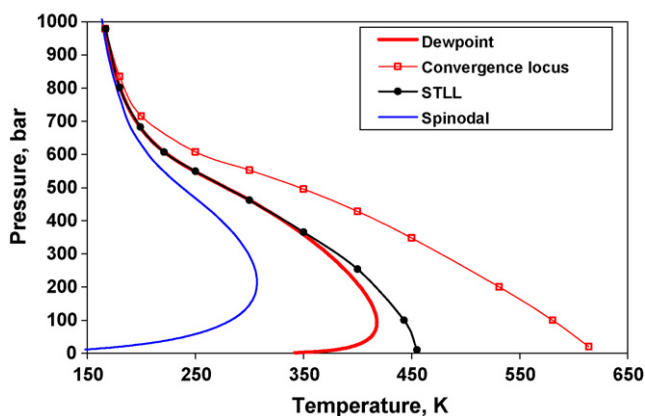
Fig. 6. Phase envelope, CL, STLL and spinodal for Y8/50% N_2 mixture.
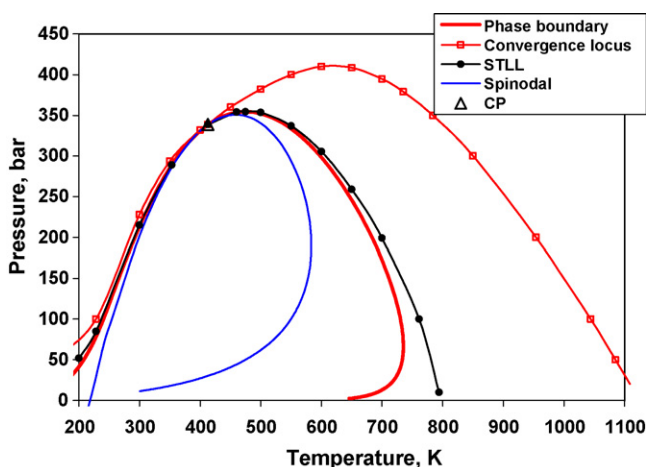
Fig. 7. Phase envelope, CL, STLL and spinodal for reservoir fluid.

larger on the dewpoint side; it becomes wider as we move away from the critical point. Larger negative flash regions on the bubblepoint side are characteristic to mixtures with higher amounts of heavy components such as reservoir oils.
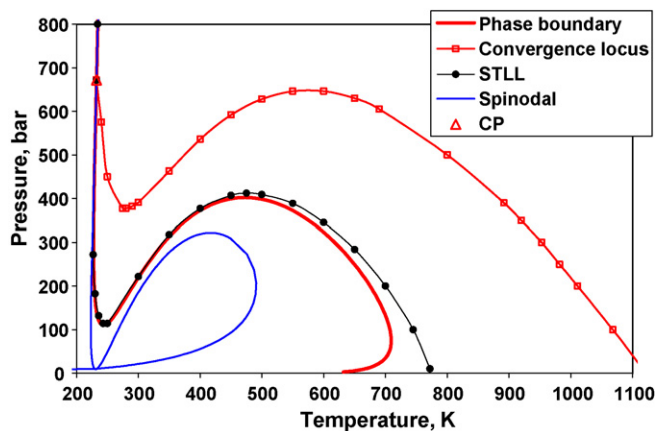
Fig. 8. Phase envelope, CL, STLL and spinodal for reservoir fluid/50% CO_2 mixture.

5. Discussion

Hoteit and Firoozabadi [36] recently state that the cause of this problem is the discontinuity of the TPD function in the single-phase state at the STLL. In fact, this is one of the effects. The cause of convergence problems in phase stability calculations, as well as of the existence of that discontinuity (we would rather say endpoint, because the trivial minimum is continuous starting from the spinodal towards high pressures), is the topology of the TPD surface. At the STLL, the stationary point of the TPD function is a saddle point and for pressures just above the STLL there is an inflexion point (for more than one independent variable, i.e. nc > 2, a non-stationary point where the Hessian matrix is singular) of the TPD surface. For pressures close to the STLL, a region where the Hessian is indefinite belongs to the basin attraction for iterates starting from one of the two Michelsen's initial guesses. This makes stability testing in the vicinity of the STLL really challenging.

A new convergence locus related to stability calculations in the single-phase region can be defined in a somewhat similar manner than the CL for negative flashes. Let us introduce it by a numerical example. For Y8 mixture at $T = 366.5$ K, dewpoint pressure is at $p = 214.078$ bar and STLL at $p = 217.502$ bar. "Equilibrium" constants calculated in the single-phase vapor region ($y_i \equiv z_i$) using the trial phase ("shadow phase") composition, $K_i = z_i/x_i$, (at the dewpoint, K_i are identical with the K_i's resulting from saturation pressure or negative flash calculations) are plotted in Fig. 9. Extrapolation of these K-values at pressures above the STLL indicates the existence of a convergence point. For conditions above bubblepoint ($x_i \equiv z_i$) the "stability"
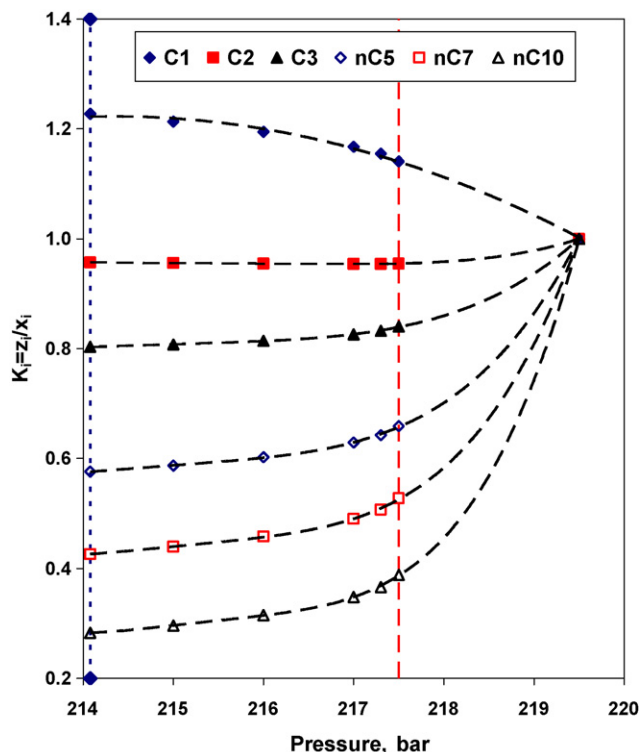
Fig. 9. K-Values ($K_i = z_i/x_i$) above DP for Y8 mixture at $T = 366.5$ K.

K-values are defined similarly as $K_i = y_i/z_i$. The pressures for which all K_i converge to unity define a locus that could be called as "stability convergence locus" (SCL), located between the STLL and the CL, where "shadow phase" composition becomes equal to feed composition. It seems that this interesting property has not been yet reported in the literature.

Compositions corresponding to K-values between STLL and SCL can be calculated. They correspond to a stationary point of the modified objective function for phase stability as defined by Stateva and Tsvetkov [37]; for details on finding these stationary points by global optimization see Nichita and Gomez [38]. Locating the SCL is more difficult and is not the subject of the present paper.

Jensen and Michelsen [12] proposed the calculation of convergence pressures by solving a modified flash with V as a specification (for example, $V = \pm 10$). Their procedure is very well suited for automatic construction of the CL. It is not possible to calculate the "exact" value (for $V = \pm \infty$) of convergence pressures (with an extremely high degree of accuracy, as for example in saturation pressure calculation) using algorithms such those from Ref. [12] or proposed in this work simply because these methods diverge at the "exact" solution.

Negative flashes seem unavoidable for CL calculation, unless some appropriate modification of the procedure described by Cismondi and Michelsen [26] is set up. However, the latter seems extremely difficult. Finding scaling laws and critical exponents in the negative flash region in a similar manner to Dalton [39] or Michelsen [40] could also be useful.

We are currently investigating a CL calculation procedure very simple to implement, that avoids any calculation near singularities, and its application to MMP calculations.

6. Conclusions

The convergence pressure/temperature locus and the stability test limit locus (which can be considered as fingerprints for mixtures phase behavior) have been calculated from rigorous thermodynamic criteria. Loci equations are obtained by equating to zero the minimum eigenvalue of the matrix containing second order partial derivatives of Helmholtz free energy, evaluated for compositions resulting from negative flash (convergence locus) and trial phase compositions from phase stability testing (stability test limit). Powerful numerical algorithms based on the reduction method are used for negative flash calculations and phase stability testing. The proposed calculation methods are successfully tested for representative hydrocarbon systems and their mixtures with injection gases, with different shapes of phase, convergence and stability envelopes.

List of symbols

D	tangent plane distance function
f_i	fugacity of component i in the mixture
k_{ij}	binary interaction parameter between components i and j
K_i	equilibrium constant
L	liquid mole fraction
m	number of non-zero eigenvalues of matrix $\mathbf{C}$

M	number of reduction parameters
n_i	number of moles
nc	number of components
p	pressure
$q_{\alpha i}$	elements of eigenvectors of matrix $\mathbf{C}$
$\mathbf{Q}$	matrix containing second order derivatives of A
$\mathbf{Q}$	vector of reduction parameters
Q_α	reduction parameters
s	distance parameter in Eq. (6)
T	temperature
V	vapor mole fraction
x_i	liquid mole fraction, component i
y_i	vapor mole fraction, component i
z_i	feed mole fraction, component i

Greek letters
β	eigenvalue of the matrix $\mathbf{C}$
λ	eigenvalue of the matrix $\mathbf{B}$
φ_i	fugacity coefficient of component i in a mixture

Subscripts
conv	convergence
i,j	component
L	liquid phase
V	vapor phase
α	reduction parameter

Superscripts
T	transposed
ν	iteration level

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