DEVELOPMENT OF A VAPOR-LIQUID-EQUILIBRIUM MODULE FOR RESERVOIR SIMULATION

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Abstract. *This work presents the study and implementation of a vapor-liquid-equilibrium (VLE) module that to be used in reservoir simulation models. The formulation assumes an arbitrary number of components distributed in the oil and gas phases, with the chemical equilibrium being solved only in oil and gas phases. In the model, flash calculations and the stability test based on the minimization of Gibbs free energy are solved using a more advanced and robust procedure, combining the Newton method with a successive substitution procedure. To validate the model, comparisons are made with the results obtained with a commercial PVT simulator and the results showed good agreement. The model implementation and all the numerical modules used in this work were done with advanced programming techniques in C++, allowing code reuse for solving multicomponent thermodynamic problems, which require the use of a cubic equation of state. Moreover, is it presented a procedure for calculating black oil model properties based on a compositional analysis which can be useful in order to generate input fluid data for black-oil reservoir simulators.*

Keywords: *vapor-liquid equilibrium, compositional model, reservoir simulation, black-oil*

1 INTRODUCTION

Flash calculations, which consist of a type of phase equilibria solution are the workhorse of any compositional reservoir simulation (Whitson & Brulé, 2000). Determining the local vapor and liquid conditions inside the reservoir for a given pressure and temperature is extremely important so that phase properties are correctly calculated and the fluxes from the conservation equations are precisely computed. A compositional reservoir simulation consists of the solution of a set of differential conservation equations by an appropriate discretization procedure, e.g., Finite Differences, Finite Elements or Finite Volume method (Maliska, 2004). In a porous media, it is usually reasonable to assumed that local thermodynamic equilibrium is a reasonable hypothesis, so that, at each solution timestep one can perform flash calculations in order to determined the mixture conditions at a given reservoir point.

The development of a vapor-liquid equilibrium module is not only important for reservoir simulation, but also for flow assurance problems (Bendiksen et al., 1991), where production operation may be affected by very complex phenomena such as hydrate formation (Ali, 2014; Ballard & Jr, 2004; Segtovich, 2014). In the following sections, it will be presented a hybrid numerical procedure to solve vapor-liquid equilibrium problems, which consists of combining two numerical techniques: successive substitutions and the Newton method.

2 MODEL FORMULATION

This work will use the *Peng-Robsinson* equation of state, which is given by

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)}, \tag{1}$$

where v is the molar volume and the parameters a and b are given as functions of the critical temperature and pressure of the component,

$$a = \frac{\Omega_a \left(RT_c\right)^2}{P_c}\alpha, \tag{2}$$

where $\Omega_a = 0,45724$ and,

$$b = \frac{\Omega_b RT_c}{P_c}, \tag{3}$$

with $\Omega_b = 0,07780$. The coefficient α is a function of the temperature,

$$\alpha = \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right], \tag{4}$$

and

$$m = 0,37464 + 1,54226\omega - 0,26992\omega^2, \tag{5}$$

when $\omega < 0,49$ and, for heavier ($\omega > 0,49$), m is given by

$$m = 0,3796 + 1,485\omega - 0,1644\omega^2 - 0,01667\omega^3. \tag{6}$$

The critical properties used in the previous definitions are: critical pressure (P_c), critical temperature (T_c) and acentric factor (ω). In case of a phase with various components, a quadratic mixture rule is used for a and a linear one for b as follow,

$$a = a_{\text{mix}} = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij}, \tag{7}$$

$$b = b_{\text{mix}} = \sum_{i=1}^{N_c} x_i b_i = 1, \tag{8}$$

$$a_{ij} = a_{ji} = \sqrt{a_i a_j}\,(1 - \kappa_{ij})\,, \tag{9}$$

where a_i and b_i are parameters for the pure component and κ_{ij} is the *binary interaction coefficient*, that composes the *binary interaction matrix*. This matrix is symmetric with $\kappa_{ii} = 0$. The parameters Ω_a and Ω_b from Eqs. (2) and (3) have the already mentioned default values, but they might be modified for each component in cases where the Equation of State (EoS) parameters are adjusted to experimental data. This procedure is usually done when grouping a large number of components are grouped into pseudo-components in order to reduce the number of unknowns of the problem.

If,

$$A = \frac{aP}{(RT)^2},\ B = \frac{bP}{RT},\ Z = \frac{Pv}{RT}, \tag{10}$$

then Eq. (1) gives the following cubic equation

$$Z^3 - (1 - B)\,Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0, \tag{11}$$

where the roots can be easily obtained by an analytical formula (Soprano, 2013).

The component fugacity, f_i, can be calculated by

$$\ln\left(\frac{f_i}{x_i P}\right) = \frac{1}{RT} \int_{V\to\infty}^{V=ZnRT/P} \left(\frac{RT}{V} - \left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}}\right) dV - \ln Z, \tag{12}$$

which for the *Peng-Robinson* EoS results into the following expression

$$\begin{aligned}\ln\phi_i = \ln\left(\frac{f_i}{x_i P}\right) &= \frac{B_i}{B}\,(Z-1) - \ln\,(Z-B) \\ &+ \frac{A}{2\sqrt{2}B}\left(\frac{B_i}{B} - \frac{2}{A}\sum_j A_{ij}x_j\right)\ln\left(\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right).\end{aligned} \tag{13}$$

For the equation above, ϕ_i is known as the *fugacity coefficient* (Sandler, 2006). Note that Eq. (13) depends on the correct choice of the compressibility factor Z, that is the root of Eq. (11). Since it is a cubic equation, it can have at most three roots, but the correct solution is the one where the free Gibbs energy is at the minimum value. In order to accomplish that, it is possible to use the normalized Gibbs energy which is defined as (Johns, 2004)

$$g^* = \sum_{i=1}^{n_c} x_i \ln f_i. \tag{14}$$

In the case where Eq. (11) has three real roots, the middle one is discarded and f_i is calculated with the remaining roots. The root that results in the minimum value for g^*, given by Eq. (14), is the correct one to be chosen. In many cases, when the phase is liquid, $Z = Z_{\text{min}}$ and when the phase is in the vapor state, $Z = Z_{\text{max}}$, however the correct choice can only be ensured when the Gibbs energy is calculated. In the present work, the compressibility factor is always chosen to be the one that results in the minimum value for the normalized Gibbs energy g^*.

2.1 Phase equilibria and the flash routine

In order to establish the phase equilibria one must determine the state of a system for the given conditions of pressure, temperature and composition. One of the fundamental conditions for phase equilibria is that the fugacity of each component in a given phase is equal to the fugacity in the other phase,

$$f_{iL} = f_{iV}. \tag{15}$$

The demonstration of this condition can be found in Sandler (2006) and Gomes (1990). It must be noted that the expression above is a necessary condition of the system to be in equilibrium, however it is not a sufficient one, since the Gibbs free energy must also be at its minimum, which implies in testing if the condition is stable and the correct choice of the compressibility factors for each phase, Z_L and Z_V.

The flash routine is the main procedure used to solve phase equilibrium problems involving equations of state. The P-T flash problem is stated as: *for given values for pressure, temperature and global mole fractions for each component, find the component mole fraction in each phase (x_{ip}), as well as molar phase fraction (F_p), i.e., the amount occupied by each phase in the system*. In order to put the previous statement into a mathematical model, some properties must be defined. The molar balance of a two-phase system may be written as,

$$n = n_V + n_L, \tag{16}$$

since $x_{iP} = \frac{n_{iP}}{n_P}$ for a given phase P, then

$$nz_i = n_V x_{iV} + n_L x_{iL}. \tag{17}$$

If the vapor mole fraction is $F_V = \frac{n_V}{n}$, we get

$$z_i = F_V x_{iV} + (1 - F_V) x_{iL}. \tag{18}$$

The sum of the global mole fractions and component phase mole fraction must sum to unity, therefore

$$\sum_{i=1}^{N_c} x_{iV} = \sum_{i=1}^{N_c} x_{iL} = \sum_{i=1}^{N_c} z_i = 1. \tag{19}$$

Then,

$$\sum_{i=1}^{N_c} (x_{iV} - x_{iL}) = 0. \tag{20}$$

The equilibrium coefficient, also known as K-values (Smith et al., 1996), K_i, is defined by

$$K_i = \frac{x_{iV}}{x_{iL}}. \tag{21}$$

It is possible to use the definition above to obtain an equation that depend solely on F_V and K_i, based on Eqs. (18) and (20). If K_i is known, it is possible to define a function $h = h(F_V)$ such that

$$h(F_V) = \sum_{i=1}^{N_c}(x_{iV} - x_{iL}) = \sum_{i=1}^{N_c} \frac{z_i(K_i - 1)}{1 + F_V(K_i - 1)} = 0. \tag{22}$$

With F_V and K_i (note that z_i are input values) determined, the phase compositions can then be calculated by

$$x_{iL} = \frac{z_i}{F_V(K_i - 1) + 1} \text{ and } x_{iV} = \frac{z_i K_i}{F_V(K_i - 1) + 1} = K_i x_{iL}. \tag{23}$$

The solution procedure of Eq. (22) and Eq. (23) is know as *Rachford-Rice* method (Rachford & Rice, 1952).

The solution procedure for the flash routine may be based on any non-linear solution method, e.g., successive substitutions or a Newton-like method. It is assumed that there is a solution for this problem, where it can be a solution that represents the phase compositions at equilibrium or the trivial solution (when $K_i = 1$ and $x_{iL} = x_{iV} = z_i$). A common initial estimate for the K-values is obtained by Wilson (1969),

$$K_i = \frac{P_{ci}}{P} \exp\left[5,37\left(1 + \omega_i\left(1 - \frac{T_{ci}}{T}\right)\right)\right]. \tag{24}$$

Note that the K-values estimates obtained from Eq. (24) are not effective for high-pressure situations and the flash routine may not converge. The most suitable approach is to determine K_i from a stability analysis before initializing the flash routine.

2.2 Stability analysis

Even if the result obtained from the flash routine seems physically consistent, one must perform a thorough verification of the solution by a stability analysis test. Moreover, it is possible perform a stability analysis before initiating the flash routine. This procedure does require more calculations, but the results obtained from the stability test may provide good estimates for the K-values in the flash routine.

The stability test consists in determine whether a single-phase system will split in two (or more) phases. This is a very challenging task and even more complex than the solution of the flash routine. Michelsen (1982) and Baker et al. (1982) present an algorithm for determine the thermodynamic stability by a Gibbs energy tangent plane criteria. The goal is to determine if a mixture has the minimum Gibbs energy at the single-phase state or the Gibbs energy is smaller if this mixture splits into two or more phases (Johns, 2004).

The tangent plane criteria can be illustrated by a case presented in Baker et al. (1982), where it is calculated the mixture Gibbs energy of CO_2 and toluene at $38,1\ ^\circ\mathrm{C}$ and $1379\ \mathrm{kPa}$.

Figure 1 shows the mixture Gibbs energy as a function of the CO_2 mole fraction. This curve is calculated by assuming that the mixture is always in the single-phase state, even if this is not the real state of the mixture. Note that in the range between x_V and x_L, the solid line is not the equilibrium Gibbs energy, but the dashed one is and the mixture is slit into two phases. If the global CO_2 composition is z, then the equilibrium Gibbs energy will be g_{mix} and the vapor mole fraction of the new system is given by

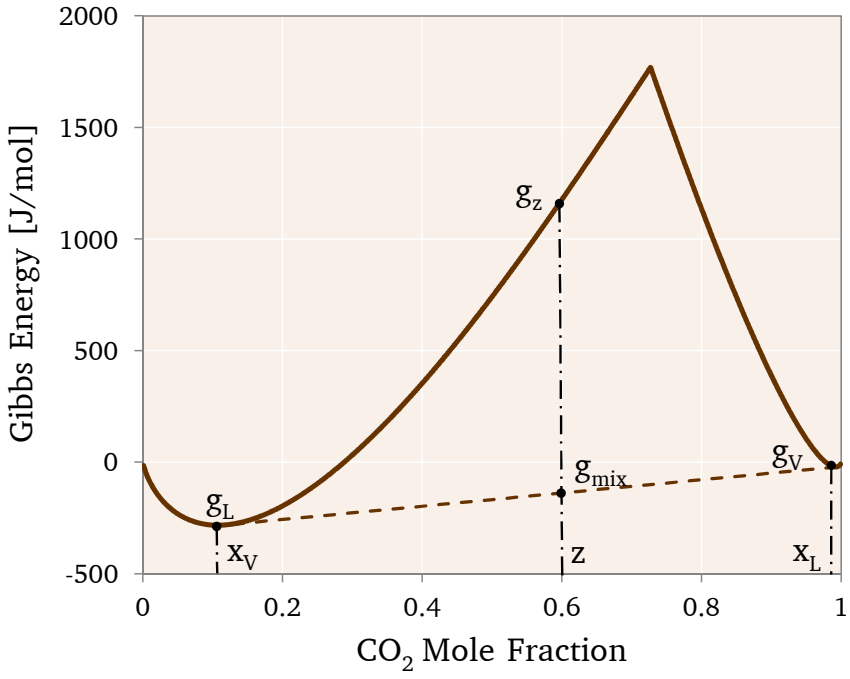


Figure 1: Mixture Gibbs energy for CO_2/toluene at $38,1\ ^{\circ}\text{C}$ and $1379\ \text{kPa}$.

$$F_V = \frac{z - x_V}{x_L - x_V}, \tag{25}$$

with a CO_2 composition equals to x_V in the vapor phase and x_L in the liquid phase. In practice, an algorithm for this method is hard to implement.

3 NUMERICAL PROCEDURE

The numerical methods used in the following sections consist of combining successive substitutions and a Newton-like method. Note that there are various techniques for approximate the Jacobian matrix needed for the Newton method solution. Hence, the approximation in the present work was made by finite differences (Balay et al., 2008) with matrix coloring (Gebremedhin et al., 2005). The linear systems that need to be solved at each Newton iteration are solved using the GMRES method (Saad, 2000; Lucianetti, 2000).

As it has been mentioned, the flash routine consist in the solution of a set of non-linear equations, Eq. (15) for $i = 1, \ldots, N_c$ and Eq. (22). Two common approaches are available: the *successive substitutions* approach and by solving a coupled system of equations using the Newton method.

3.1 Flash routine

Successive substitutions. The procedure for using *successive substitutions* is based in the fugacity coefficient relations $\phi_{iL} = \frac{f_{iL}}{x_{iL}P}$ and $\phi_{iV} = \frac{f_{iV}}{x_{iV}P}$. The ratio between them is given by

$$\frac{\phi_{iL}}{\phi_{iV}} = \frac{f_{iL}}{f_{iV}} \frac{x_{iV}}{x_{iL}}. \tag{26}$$

As $K_i = \frac{x_{iV}}{x_{iL}}$ and at equilibrium we have $f_{iL} = f_{iV}$, then

$$\frac{\phi_{iL}}{\phi_{iV}} = \frac{x_{iV}}{x_{iL}} = K_i,$$

therefore Eq. (26) defines the following iterative relation

$$K_i^{n+1} = K_i^n \frac{f_{iL}^n}{f_{iV}^n}. \tag{27}$$

The algorithm steps can be summarized as follows

1. Estimate values for K_i, by using Eq. (24) or the estimate obtained from the stability analysis;
2. Solve Eq. (22), through an one-dimensional Newton method, using F_V as the unknown;
3. Calculate x_{iL} and x_{iV} through Eq. (23);
4. Calculate the component fugacity for each phase, f_{iL} and f_{iV}, Eq. (13);
5. Check convergence, i.e., $|f_{iL} - f_{iV}| < \epsilon$. If true, finish the procedure;
6. Update the values for K_i by using Eq. (27);
7. Go to step 2, until convergence is achieved.

Newton method. The solution of the flash routine by Newton's method consists in simultaneously solving Eqs. (15) and (22), which in residual form are given by

$$R_{f_i} = f_{iL} - f_{iV}, \text{ for } i = 1 \dots N_c, \tag{28}$$

$$R_m = \sum_{i=1}^{N_c} \frac{z_i(K_i - 1)}{1 + F_V(K_i - 1)}. \tag{29}$$

The problem unknowns are the equilibrium coefficients K_i and the vapor molar fraction F_V and therefore the goal is to find the solution of $\vec{R} = [R_{f_i} \;\; R_m]^T$ for $\vec{x} = [K_i \;\; F_V]^T$. This problem has $N_c + 1$ unknowns and can be solved by using an approximated Jacobian matrix using finite differences approximations and matrix coloring as it is shown in Soprano (2013).

According to Chen et al. (2006a), the successive substitution method is easier to implement, and more reliable, even near critical points. However, it has a slower convergence for a desired precision. The Newton method requires less iterations, but needs a good initial guess in order to converge properly and it still can diverge near critical points.

In the present work, the flash routine is solved by a hybrid approach between successive substitutions and the Newton method. First, the successive substitution method is used, performing only a few iterations. The goal is to obtain a better approximation of the initial guess for Newton method. This procedure provides a better robustness to Newton method. Moreover, in case that the Newton method still can't converge, the problem is restarted and solved by successive substitutions.

3.2 Stability test

The previously presented graphical procedure by finding the tangent plane over the Gibbs energy function (Fig. 1) is not most suitable approach for performing the stability test. Michelsen (1982) presents a practical criteria that determines whether the mixture will remain single-phase or split in more than one phase. The resulting algorithm is similar to the flash routine, but faster and more robust (Johns, 2004), because good estimates for K_i are not necessary. For instance, Eq. (24), is sufficient enough for calculating the initial values of K_i. The criteria is based in Michelsen (1982) and consists in evaluate the values of the function defined by

$$F(x_1, \ldots, x_{N_c}) = \sum_{i=1}^{N_c} x_i \left[\mu_i(x_1, \ldots, x_{N_c}) - \mu_i(z_1, \ldots, z_{N_c})\right], \tag{30}$$

which measures the difference between the tangent plane and the Gibbs energy for an original composition z_i and a new composition x_i. The goal is to determine whether the mixture with composition z_i is stable or not. The system will be stable if $F(x_1, \ldots, x_{N_c}) \geq 0$ for all x_i. The problem can also be written using fugacities (Whitson & Brulé, 2000). In this case, the algorithm consists in finding the composition of a secondary phase with fugacity equals to the mixture fugacity $f_{i,z}$ times a constant. This procedure is done in two steps: first assuming a vapor-like phase and second assuming a liquid-like phase. After performing both procedures, the results are evaluated in order to determine whether the system is stable or not. The goal is to solve

$$f_{i,z} - f_{i,x_P} S_P = 0, \tag{31}$$

with $f_{i,z} = f_i(P, z_1, z_2, \ldots, z_{N_c})$ and $f_{i,x_P} = f_i(P, x_{1P}, x_{2P}, \ldots, x_{N_cP})$ evaluated by Eq. (13) and $P = L, V$. In case of a vapor-like phase V, x_{iV} is given by

$$x_{iV} = \frac{1}{S_V} \left(K_{iV} z_i\right), \tag{32}$$

where,

$$S_V = \sum_{i}^{N_c} K_{iV} z_i, \tag{33}$$

and for the liquid-like phase ($P = L$),

$$x_{iL} = \frac{1}{S_L} \left(\frac{z_i}{K_{iL}}\right), \tag{34}$$

with,

$$S_L = \sum_i^{N_c} \frac{z_i}{K_{iL}}. \tag{35}$$

The problem unknowns are K_{iV} and K_{iL} for the vapor and liquid, respectively. The initial estimates are calculated from Eq. (24). The system will be unstable if $S_V > 1$ or $S_L > 1$. For an unstable system the K_i estimates are calculated by

$$K_i = K_{iV} K_{iL}, \tag{36}$$

Successive substitutions. The stability test is performed in two steps for $P = V$ and $P = L$:

1. Calculate the fugacity f_{z_i}, Eq. (13);
2. Calculate the initial estimates for K_{iV} or K_{iL}, using Eq. (24);
3. Calculate S_V through Eq. (33) or S_L through Eq. (35);
4. Calculate x_{iV} through Eq. (32) or x_{iL} through Eq. (34);
5. Calculate the fugacity f_{i,x_P}, Eq. (13);
6. Check for convergence, i.e., $|f_{i,z} - f_{i,x_P} S_P| < \epsilon$, for $P = V$ or $P = L$. If true, finalize the procedure.
7. Update K_i by

$$K_{iV}^{n+1} = K_{iV}^{n} \left(\frac{f_{i,z}}{f_{i,x_V} S_V} \right), \tag{37}$$

   for vapor-like case and,

$$K_{iL}^{n+1} = K_{iL}^{n} \left(\frac{f_{i,x_L} S_L}{f_{i,z}} \right), \tag{38}$$

   for the liquid-like case;
8. Return to step 3, until reaching convergence;
9. After finalizing the tests for the vapor-like and the liquid-like cases, check if the system is unstable, i.e., $S_V > 1$ or $S_L > 1$.

Newton method. The stability test using Newton method considers $\vec{R} = [R_{f_i P}]$ with $R_{f_i P} = f_{i,z} - f_{i,x_P} S_P$, for $i = 1, \ldots, N_c$ and $\vec{x} = [K_{iP}]$. The present work also uses a hybrid approach for the stability analysis, with an analogous procedure used for the flash routine.

4 RESULTS

In the following subsections it will be presented the validation of the flash routine solution strategy adopted in the present work and also the methodology and validation for black-oil properties calculation.

4.1 Flash routine validation

The model validation was performed by comparing with the commercial PVT package WINPROP (CMG, 2011). The original mixture consists of 22 components, with properties detailed in Kenyon & Behie (1987). However, this 22 components were reduced to a smaller set of pseudo-components. The full characterization is presented in Chen et al. (2006a). The properties of each pseudo-component are shown is Table 1 and the binary interaction parameters (κ_{ij}) used in Eq. (9) are shown in Table 2. The mixture composition is presented in Table 3. The components were grouped in pseudo-components (Chen et al., 2006b) as follows: (CH_4,N_2),(C_2H_6,CO_2), (C_3H_8,C_4H_{10}), (C_5H_{12},C_6H_{14}), (C_{7+}^1), (C_{7+}^2), (C_{7+}^3), where the last three correspond to a heavier hydrocarbon distribution with more than 7 carbon molecules.

Table 1: Pseudo-component properties.

Component	P_c (atm)	T_c (K)	ω	M_i	Ω_a	Ω_b
P_1	45.45	189.2	0.00891	16.38	0.344772	0.063282
P_2	51.29	305.4	0.11352	31.77	0.521974	0.099825
P_3	39.89	395.8	0.17113	50.64	0.514972	0.107479
P_4	31.95	485.1	0.26910	77.78	0.419169	0.093455
P_5	27.91	592.0	0.34196	118.44	0.485943	0.074860
P_6	17.71	697.1	0.51730	193.95	0.570583	0.101206
P_7	12.52	804.4	0.72755	295.30	0.457236	0.077796

Table 2: Binary Interaction Matrix.

Component	P_1	P_2	P_3	P_4	P_5	P_6	P_7
P_1	0						
P_2	0.000622	0					
P_3	-0.002471	$-0,001540$	0				
P_4	0.011418	0.010046	0.002246	0			
P_5	-0.028367	0.010046	0.002246	0	0		
P_6	-0.1	0.010046	0.002246	0	0	0	
P_7	0.206868	0.010046	0.002246	0	0	0	0

Initially the component phase molar fractions and the equilibrium coefficients are compared for a given point at the P-T diagram. The chosen point is $T = 366.5\,\mathrm{K}$ e $P = 15000\,\mathrm{kPa}$ (point A, as indicated in Fig. 2).

Table 3: Molar mixture composition.

Pseudo-component	Components	z_i
P_1	CH_4,N_2	0.6793
P_2	C_2H_6,CO_2	0.099
P_3	C_3H_8,C_4H_{10}	0.1108
P_4	C_5H_{12},C_6H_{14}	0.045
P_5	C_{7+}^1	0.05011
P_6	C_{7+}^2	0.0134
P_7	C_{7+}^3	0.00239

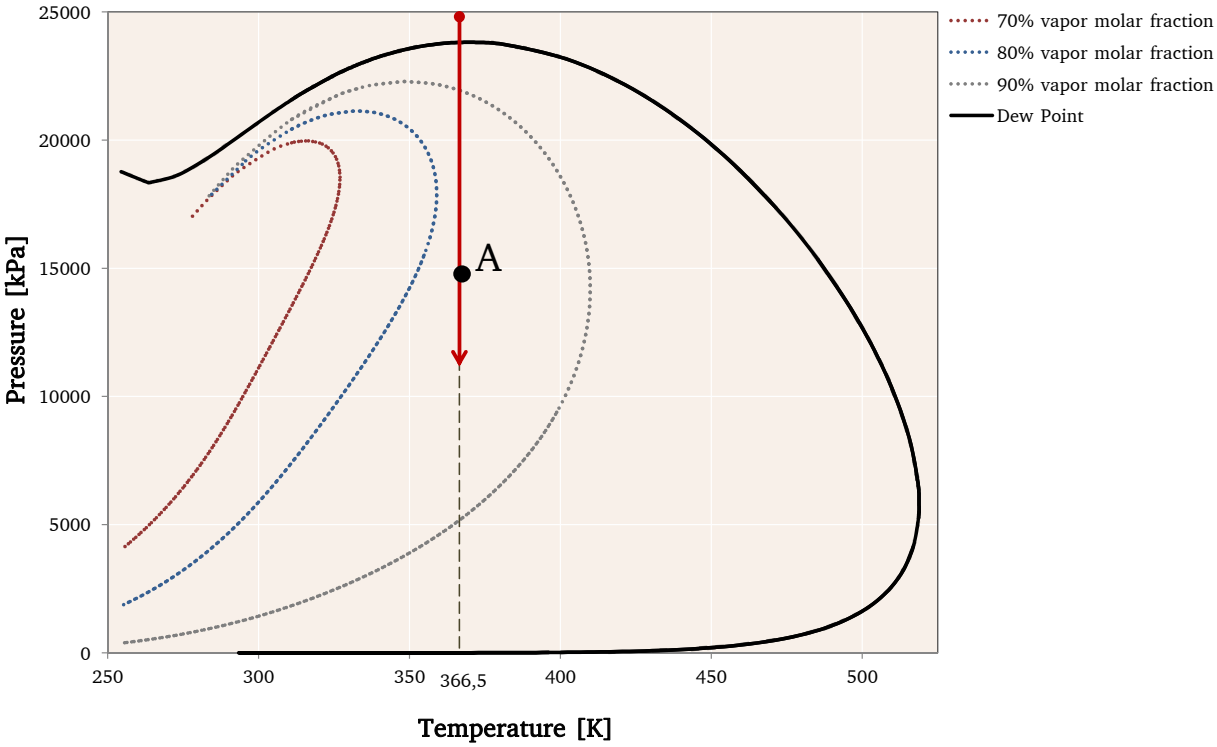


Figure 2: P-T diagram for the mixture composition given by Table 3.

Table 4 shows the values for the liquid molar fractions obtained by the flash routine developed in this work versus the values obtained from WINPROP. In Table 5 it is shown the comparisons for the vapor molar fractions. Finally, Table 6 shows the comparisons between equilibrium coefficients (K_i). Note that the differences are considerably small.

Table 4: Comparisons between the liquid component molar fractions (x_{iL}) for $T = 366.5$ K and $P = 15000$ kPa.

Property	WINPROP	Present work	Difference
x_{P_1L}	0.41237	0.41272	3.4×10^{-4}
x_{P_2L}	0.08802	0.08804	2.0×10^{-5}
x_{P_3L}	0.13263	0.13226	3.7×10^{-4}
x_{P_4L}	0.07581	0.07578	3.2×10^{-5}
x_{P_5L}	0.21340	0.21342	1.6×10^{-5}
x_{P_6L}	0.06412	0.06413	7.2×10^{-6}
x_{P_7L}	0.01364	0.01366	1.3×10^{-5}

Table 5: Comparisons between the vapor component molar fractions (x_{iV}) for $T = 366.5$ K and $P = 15000$ kPa.

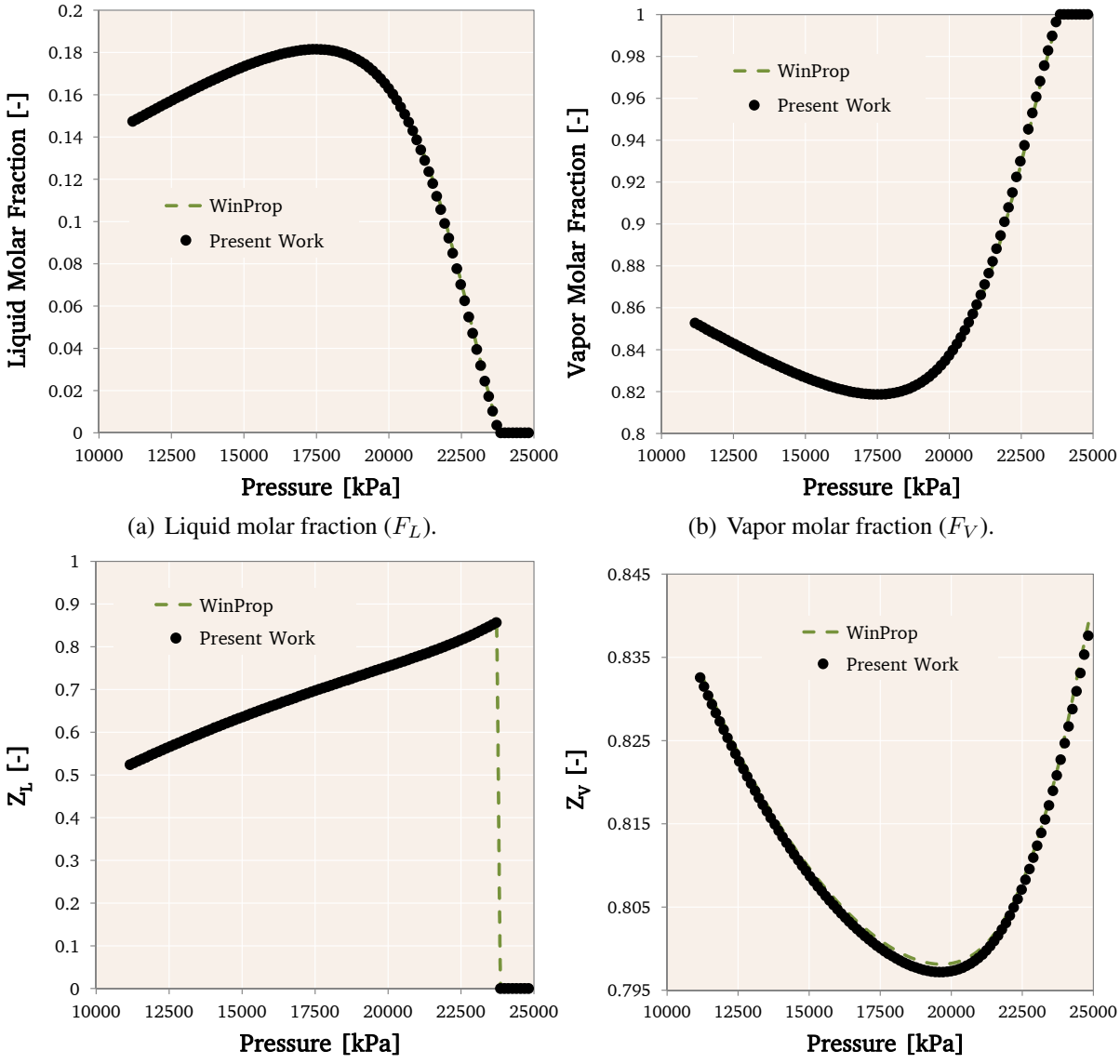
Property	WINPROP	Present work	Difference
x_{P_1V}	0.73532	0.73518	1.4×10^{-4}
x_{P_2V}	0.10131	0.10130	7.0×10^{-6}
x_{P_3V}	0.10622	0.10630	8.3×10^{-5}
x_{P_4V}	0.03853	0.03855	1.5×10^{-5}
x_{P_5V}	0.01584	0.01588	3.9×10^{-5}
x_{P_6V}	0.00275	0.00277	1.2×10^{-5}
x_{P_7V}	0.00003	0.00003	2.1×10^{-7}

Table 6: Comparisons between the equilibrium coefficients (K_i) for $T = 366.5$ K and $P = 15000$ kPa.

Coefficient	WINPROP	Present work	Difference
K_{P_1}	1.78315	1.78132	1.8×10^{-3}
K_{P_2}	1.15096	1.15061	3.5×10^{-4}
K_{P_3}	0.80089	0.80374	2.9×10^{-3}
K_{P_4}	0.50827	0.50869	4.1×10^{-4}
K_{P_5}	0.07421	0.07438	1.8×10^{-4}
K_{P_6}	0.04295	0.04313	1.8×10^{-4}
K_{P_7}	0.00207	0.00209	1.3×10^{-5}

Another validation of the flash routine was performed by reducing the pressure of a system at constant pressure. The procedure is indicated in the P-T diagram shown in Fig. 2 for the 7 pseudo-components. The fixed temperature is 366.5 K with an initial pressure of 25 MPa decreasing until 11 MPa. As it can be noted in Fig. 2, this is a typical case of retrogade condensate reservoir. Initially, there exists only gas and with the reductions of pressure, the liquid phase starts to appear. However, further reductions in pressure results in a reduction of the liquid phase (there is a maximum value of liquid molar fraction that can exist in the system).

The results for this case are shown in Fig. 3. The good agreement of the results suggests that the proposed methodology is suitable for solving vapor-liquid equilibrium problems. It is important to note that for a compositional reservoir simulation, the flash routine is only an internal module, so it is important that it is solved correctly. The conservation equations should not be affected by possible errors due to incorrect flash calculations.



(a) Liquid molar fraction (F_L).

(b) Vapor molar fraction (F_V).

(c) Liquid compressibility factor (Z_L).

(d) Vapor compressibility factor (Z_V).

Figure 3: Comparisons between results of the molar fraction for each phase.

4.2 Black-oil properties calculation

Black-oil properties are the solubility ratio (R_s), the oil formation volume fraction (B_o) and the gas formation volume fraction (B_g). These variables are function of pressure, temperature and global composition. The black-oil model assumes that composition remains constant (Dake, 1978) throughout the entire process. The following expression can be used for calculating the

solubility ratio

$$R_s(P,T) = \frac{V_{g,\text{SC}}}{V_{o,\text{SC}}}. \tag{39}$$

where the SC subscript stands for surface conditions. The formation volume fraction is defined as

$$B_o(P,T) = \frac{V_o(P,T)}{V_{o,\text{SC}}}. \tag{40}$$

where V_o is the oil volume at formation conditions and $V_{o,\text{SC}}$ is the oil volume at surface conditions. The gas formation volume factor may be calculated with reasonable accuracy (Ahmed, 2006) by calculation the ratio of the gas volume at reservoir conditions and the volume at surface conditions as it behaves like an ideal gas, in which the expression $Pv = RT$ is valid. Hence,

$$B_g(P,T) = \frac{V_g(P,T)}{V^{\text{IG}}_{g,\text{SC}}}. \tag{41}$$

The superscript IG stands for ideal gas, i.e., volume is computed as the gas behaves like an ideal gas at surface conditions. Black-oil properties can be obtained by the use of correlations (Ahmed, 2006; Johns, 2004) or by experimental tests. Another approach is to calculate them numerically based in Eqs. (39)-(41). Details of the numerical experiment can be found in Soprano (2013). The numerical process considers the following equation

$$Pv = ZRT, \tag{42}$$

from which one can obtain the following relations

$$B_g(P,T) = \frac{Z_g T}{P}\left(\frac{P}{T}\right)_{\text{SC}}, \tag{43}$$

$$B_o(P,T) = \frac{Z_o T}{P}\left(\frac{P}{F_o Z_o T}\right)_{\text{SC}}, \tag{44}$$

$$R_s(P,T) = \left(\frac{F_g Z_g}{F_o Z_o}\right)_{\text{SC}}, \tag{45}$$

where F_o and F_g are the molar fractions of the gas and oil phases resulting from the flash calculation. It is important to note that, for the calculation of R_s and B_o, the phase equilibrium calculations is performed by considering as the global composition of the system, the oil composition at reservoir conditions. It can be different from the global composition of the mixture in the reservoir if there exists free gas at reservoir conditions.

The results are compared with simulations performed in WINPROP (CMG, 2011), which also allows the user to calculate black-oil properties based on a compositional analysis. The mixture used for the numerical experiments consists of 6 components: CH_4, C_3H_8, FC_6, FC_{10}, FC_{15}, FC_{20}, where the last two are pseudo-components obtained from the existing internal component library of WINPROP. The molecular properties of each component are given in Table 7 and the binary interaction matrix is shown in Table 8. The global molar composition

Table 7: Component properties.

Component	P_c (atm)	T_c (K)	ω	M_i	Z_c
CH_4	45.40	190.6	0.008	16.04	0.2876
C_3H_8	41.90	369.8	0.152	44.10	0.2805
FC_6	32.46	507.5	0.27504	86.0	0.2682
FC_{10}	25.01	622.1	0.443774	134.0	0.25527
FC_{15}	18.25	718.6	0.651235	206.0	0.2405
FC_{20}	14.36	782.9	0.816053	275.0	0.2296

Table 8: Binary interaction matrix.

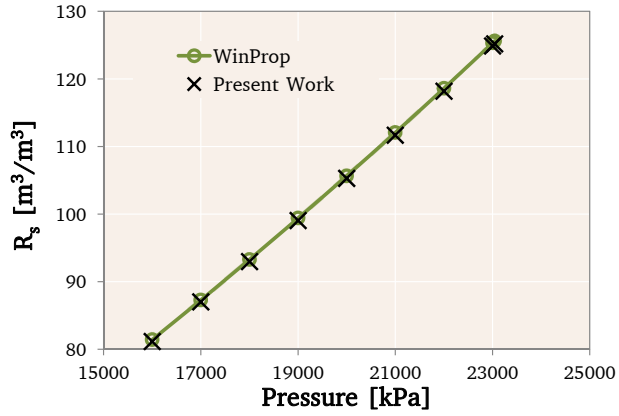
Component	CH_4	C_3H_8	FC_6	FC_{10}	FC_{15}	FC_{20}
CH_4	0					
C_3H_8	0.008537	0				
FC_6	0.025345	0.004620	0			
FC_{10}	0.044372	0.014638	0.002866	0		
FC_{15}	0.067047	0.029340	0.010971	0.002657	0	
FC_{20}	0.085139	0.042358	0.019634	0.007631	0.001296	0

of the mixture is shown in Table 9. This fluid characterization is based in Killough & Kossack (1987), also known as 5th SPE project, a benchmark problem in the reservoir simulation field.

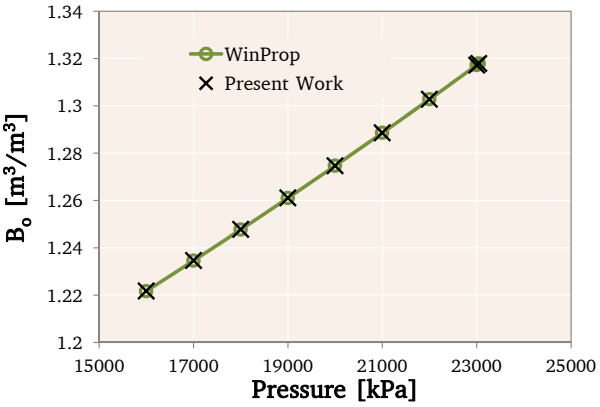
Table 9: Global molar composition.

Component	z_i
CH_4	0.5
C_3H_8	0.03
FC_6	0.07
FC_{10}	0.2
FC_{15}	0.15
FC_{20}	0.05

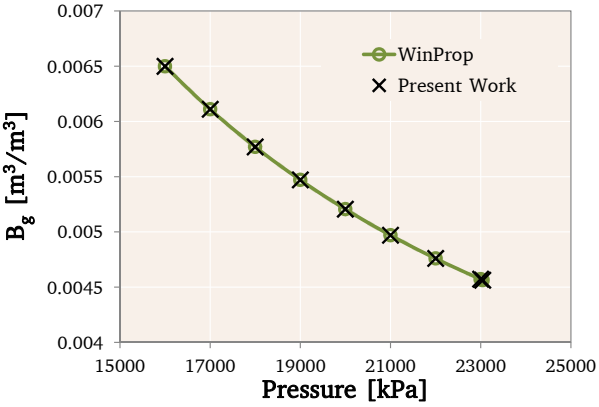
It is considered a reservoir with $70°\mathrm{C}$ and the pressure is reduced from the bubble point ($P_b = 23043,5\,\mathrm{kPa}$) until $P = 16000\,\mathrm{kPa}$. Figure 4 show the results comparisons.



(a) Solution gas ratio (R_s).



(b) Oil formation volume fraction (B_o).



(c) Gas formation volume fraction (B_g).

Figure 4: Black-oil properties curves.

5 CONCLUSIONS

In this work, a hybrid approach for performing flash calculations as well as stability tests was proposed. The combination of successive substitutions and the Newton method showed a reasonable agreement to the reference commercial software. The development of this vapor liquid equilibrium module was employed to a compositional reservoir simulation model (Soprano, 2013) and recently extracted to a separated module so that it can also serve for future developments such as three-phase flash problems, with high CO_2 content or to hydrate formation calculation.

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