Emirates Journal for Engineering Research, 13 (3), 81-91 (2008)

(Regular Paper)

CONVENTIONAL AND RAPID FLASH CALCULATIONS FOR THE SOAVE-REDLICH-KWONG AND PENG-ROBINSON EQUATIONS OF STATE

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(Received November 2007 and accepted July 2008)

إن عملية حسابات الفصل الطوري الثنائي (Two-phase flash calculations) لموائع البترول تمثل أحد أهم العمليات في النمذجة التركيبية لمكامن البترول. فهي مطلوبة عند حساب ضغط المكمن لكل مرحلة، وقد تمت العديد من الأبحاث لزيادة سرعة هذه الحسابات لاسيما أنها تمثل جزءاً بسيطاً من عملية النمذجة ككل. المعروف أن هناك طريقتين لصياغة معادلات الفصل الطوري الثنائي وهي الطريقة الاعتيادية (Conventional) والطريقة المسرَعة (Rapid). تم في هذا البحث دراسة كلا الطريقتين بتطبيق معادلات الطور لكل من سواف وريدليك ووانج (Soave-Redlich-Kwong) وبنج وروبنسون (Peng-Robinson) وبالتالي برمجتها بطريقة كينونية (Object Oriented). وقد تم حل معادلات الطريقة الاعتيادية بالطريقة التدرجية(Sequential Substitution Iteration SSI) والطريقة المباشرة (Direct Method). وحيث أن الطريقة التدرجية تعتمد على معادلة راشفورد ورايس الغير خطية، فقد استخدمت العديد من الحلول الغير خطية، وبالمثل استخدمت العديد من الحلول للطريقة المباشرة. تم في هذا البحث دراسة الكثير من الأمثلة منها عينة زيت تتكون من خمس مركبات والتي اقترحها مهرا وآخرون في عام 1982م وعينة زيت تتكون من عشرة مركبات والتي اقترحها ناهايم وآخرون في عام 1983م وعينة زيت تتكون من خمسة عشر مركباً والمقترحة من قبل فاسل وآخرون في عام 1978م.بالإضافة إلى عدد مائة وإحدى وثلاثون عينة زيت تمثل تشكيله كبيرة من التراكيب الكيميائية والتي تم حساب الفصل الطوري لـها عند ضغوط تتراوح من مائة إلى عشرة آلاف وحدة ضغط بزيادة خمسة وحدات لكل مرحلة. وقد قورنت النتائج مع النتائج المنشورة وهذا سوف يساعد على إلقاء المزيد من الضوء على هذه العملية المهمة في النمذجة التركيبية لمكامن البترول.

The two-phase flash calculation process represents the bottleneck of compositional reservoir modeling. It is required at each pressure step. There have been many researches to increase the speed of these calculations since they only represent a fraction of the whole compositional modeling. The most common formulations of the flash calculations, however, are the conventional and rapid formulations. In this paper, the conventional and rapid flash calculations for the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS) were extensively studied and programmed in an object-oriented fashion. The conventional flash equations were solved using the sequential substitution iteration (SSI) and the direct methods. The Rachford-Rice equation of the SSI method was solved using many root-finding solvers. Similarly, different nonlinear solvers were used to solve the set of nonlinear equation of the direct and rapid flash equations. The five-component hydrocarbon, reported by Mehra et al[1], the ten-component volatile oil, reported by Nghiem et al[2] and the fifteen-component reservoir oil system, reported by Fussell and Yanosik[3] was used. In addition, a total of 131 crude oil samples representing a wide variety of compositions were flashed at pressures in the range of 100-10000 psia at an increment of 5 psia. Results were compared with reported values and results of comparison should help clarify some problems with vapor/liquid flash calculations.

Keywords: phase behavior; equations of state; flash calculations

1. INTRODUCTION

The flash calculations process is essential to compositional modeling. There have been many solution techniques proposed mainly to speed up this process and to increase its capability to converge near the critical regions. The SSI solution method is common; however, it demonstrates poor convergence near the critical point. To overcome this convergence problem, Fussell and Yanosik[3] have proposed the Minimum Variable Newton-Raphson (MVNR) method. The method minimizes the number of variables for which simultaneous iteration is required. Then it uses the Newton-Raphson method for the correction step. The drawback of the Newton's method, however, is the computation of the Jacobian Matrix and its inverse every iteration. In addition, a good initial guess is required for the solution to proceed.

Nghiem et al[2] have presented an algorithm for flash calculations that uses an equation of state. It first uses a special version of the SSI method and then switches to Powell's method if the SSI method has

shown poor convergence near the critical point. They also presented efficient criteria for switching from one method to another. The Jacobian matrix required by Powell's method was calculated numerically. They stated that their method converges near the critical point and also detects the single-phase region without computing the saturation pressure. Risnes and Dalen[4] described a refined SS method for calculating multiphase flash equilibrium. In this case, the phase behavior procedure proceeds in a stepwise manner and additional phases are introduced. This has been done to avoid trivial solutions and to ensure continuity across phase boundaries. Abhvani and Beaumont[5] have reported results of comparison testing of some of the proposed numerical solution methods. Their comparison criteria were robustness and speed. Robustness refers to the capability of the method to find a solution in difficult regions such as the retrograde condensation and near-critical regions. Speed refers to capability of the method to converge faster. As a result of their study, they proposed a combined SSI/MVNR algorithm.

Nghiem and Li[6] in an attempt to speed up the flash calculations required by compositional simulations, have presented a method for approximating flash calculations with an equation of state. The method consists of solving a system of equations that are simpler than the original flash equations. These equations are obtained by linearizing fugacity equations at an equilibrium condition called the reference condition. Stenby and Wang[7] have developed a non-iterative flash calculation algorithm that requires the solution of two sets of linear equations without solving the Rachford-Rice equation. Wang and Barker[8] have compared several flash algorithms in the context of compositional reservoir simulation. They concluded that the non-iterative flash[7] and the method of Young[9] work well for reservoir simulation. They also pointed out that the flashes which are based on reduced parameters (rapid flashes) offer no significant improvement over conventional flashes.

Michelsen[10] has presented a flash procedure via the use of three reduced parameters. This reduces the flash calculations to the solution of three nonlinear equations regardless of the number of components in the hydrocarbon mixture. The limit of this procedure, however, is that all BIPs are taken to be zero. When there exists BIPs between a single component and the other components, however, Jensen and Fredenslund[11] have proposed the use of five reduced parameters. More recently, Li and Johns[12] have proposed the split of the BIPs into two parameters using a simple quadratic expression. The method is applied for non-zero BIPs. When all BIPs are zero, however, the method reduces to the same three reduced parameters as proposed by Michelsen[10]. When there exists BIPs between a single component and the other components, the method reduces to the same five reduced parameters as proposed by Jensen and Fredenslund[11].

2. EQUATIONS OF STATE (EOS)

When the composition of a hydrocarbon mixture is known, an *equation of state* is used to evaluate its compressibility factor, component fugacities, and fugacity coefficients for the vapor and liquid phases at the prevailing pressure and temperature. The most popular equations of state are the Soave-Redlich-Kwong (SRK) and the Peng Robinson (PR). These equations are expressed in terms of the compressibility factor as follows:

$$Z^3 + a_2 Z^2 + a_1 Z + a_0 = 0 \tag{1}$$

When Eq. 1 is solved for Z, it yields three real roots in the two-phase region. The largest root corresponds to the compressibility of the vapor phase, Z^V, while the smallest positive root is the compressibility of the liquid phase, Z^L. Physical properties of the mixture components along with the system pressure and temperature are used to evaluate the equation parameters as follows:

$$\begin{aligned} a_2 &= (u_1 + u_2 - 1)B - 1 \\ a_1 &= A - (u_1 + u_2)B - (u_1 + u_2 - u_1 u_2)B^2 \\ a_0 &= -AB - u_1 u_2 (1 + B)B^2 \end{aligned} \tag{2}$$

The parameters u_1 and u_2 are switching parameters; i.e. for the SRK EOS, $u_1=0$ and $u_2=1$ and for the PR EOS, $u_1=1+\sqrt{2}$ and $u_2=1-\sqrt{2}$. A and B are, respectively, the attraction and repulsion dimensionless parameters, which are given by:

$$A = \frac{P}{(RT)^2} a_m \tag{3}$$

$$B = \frac{P}{RT} b_m$$

where:

$$\begin{aligned} a_m &= \sum_{i=1}^{N} x_i \Psi_i \\ b_m &= \sum_{i=1}^{N} x_i b_i \end{aligned} \tag{4}$$

$$\Psi_i = \sum_{j=1}^{N} x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j \alpha_i \alpha_j}\,(1 - k_{ij}) \tag{5}$$

$$a_i = \Omega_a R^2 \frac{T_{ci}^2}{P_{ci}} \tag{6}$$

$$b_i = \Omega_b R \frac{T_{ci}}{P_{ci}}$$

The constants Ω_a and Ω_b, are best determined through regression in such a way that the EOS is forced to predict the phase behavior of the hydrocarbon mixture. For the SRK EOS, $\Omega_a=0.427480$ and $\Omega_b=0.086640$. For the PR EOS, $\Omega_a=0.457235$ and $\Omega_b=0.077796$. Other parameters are given by:

$$\alpha_i = \left[1 + m_i\left(1 - \sqrt{T_r}\right)\right]^2$$
$$m_i = \begin{cases} 0.480 + 1.574\omega_i - 0.176\omega_i^2 & SRK\ EOS \\ m_0 + m_1\left(1 + \sqrt{T_r}\right)(0.7 - T_r) & PR\ EOS \end{cases} \quad (7)$$

$$m_0 = \begin{cases} 0.378893 + 1.4897153\omega_i & \\ -0.17131848\omega_i^2 + 0.0196554\omega_i^3 & \omega \geq 0.49 \\ 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 & \omega < 0.49 \end{cases}$$
$$m_1 = \begin{cases} 0 & T_r \geq 0.7 \\ Table\,1 & T_r < 0.7 \end{cases} \quad (8)$$
$$T_r = T \diagup T_{ci}$$

k_{ij} is the binary interaction parameter (BIP) between components *i* and *j* that is tuned to match PVT data. The fugacity and fugacity coefficient of component *i* in the liquid phase given by:

$$\ln\Phi_i^L = \frac{B_i}{B}(Z^L - 1) - \ln(Z^L - B) - \left(\frac{A}{(u_1 - u_2)B}\right)\left[2\frac{A_{ij}^L}{A} - \frac{B_i}{B}\right]\ln\left(\frac{Z^L + u_1 B}{Z^L + u_2 B}\right) f_i^L = x_i p \Phi_i^L \quad (9)$$

where:

$$B_i = \frac{P}{RT} b_i \quad (10)$$
$$A_{ij}^L = \frac{P}{(RT)^2}\Psi_i^L = \frac{P}{(RT)^2}\sum_{j=1}^{N} x_j a_{ij}$$

Similar expressions are written for the fugacity and fugacity coefficient of component *i* in the vapor phase.

Table 1. Stryjek and Vera[15]. m_1 parameter for pure components

Compound	m_1	Compound	m_1
N_2	0.01996	C_7	0.04648
O_2	0.01512	C_8	0.04464
CO_2	0.04285	C_9	0.04104
NH_3	0.00100	C_{10}	0.04510
H_2O	-0.06635	C_{11}	0.02919
Hcl	0.01989	C_{12}	0.05426
C_1	-0.00159	C_{13}	0.04157
C_2	0.02669	C_{14}	0.02686
C_3	0.03136	C_{15}	0.01892
n-C_4	0.03443	C_{16}	0.02665
n-C_5	0.03946	C_{17}	0.04048
C_6	0.05104	C_{18}	0.08291

3. CONVENTIONAL FLASH CALCULATIONS

Flash calculations refer to the process of calculating the liquid and vapor mole fractions, x_i and y_i, at the prevailing pressure and temperature when given the overall composition of the hydrocarbon mixture, z_i. The liquid and vapor mole fractions are constrained by the following equation:

$$\sum_{i=1}^{N} y_i = \sum_{i=1}^{N} x_i = 1 \quad (11)$$

The equilibrium ratio or the K-value of component *i* given by:

$$K_i = \frac{y_i}{x_i} \qquad \Rightarrow \qquad y_i = x_i K_i \quad (12)$$

On the basis of one mole; the sum of the liquid and vapor mole fractions is 1; i.e. L+V=1. A material balance on the i^{th} component results in:

$$z_i = V y_i + L x_i$$
$$z_i = V y_i + (1 - V) x_i \quad (13)$$

Substitution of y_i from Eq. 12 into Eq. 13 yields:

$$z_i = V x_i K_i + (1 - V) x_i \quad (14)$$

Solving for x_i yields:

$$x_i = \frac{z_i}{1 + V(K_i - 1)} \quad (15)$$

Solving for y_i yields:

$$y_i = x_i K_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (16)$$

Substitution of Eq. 15 and 16 into Eq. 11 yields:

$$\sum_{i=1}^{N} y_i - \sum_{i=1}^{N} x_i = \sum_{i=1}^{N}(y_i - x_i) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \quad (17)$$

Writing Eq. 17 in a function form gives the *Rachford-Rice* equation:

$$g(V) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \quad (18)$$

This equation represents a single nonlinear equation in V. Abhvani and Beaumont[5] have investigated various algorithms for the solution of this equation. Amongst of which are second-order, third-order, and third-order with approximations Newton methods. They found that the second order Newton is the most efficient method.

In this study, however, many root-finding solvers were used to solve the Rachford-Rice equation. Amongst of which are: the False-Position, Bisection, Newton-Raphson, Newton-Raphson Bisection, Ridder, Secant, and Brent's method, Press et al[13]. They were extensively used to solve the equation resulting from the solution of flash calculations of 134 oil samples at different pressures in the range 100-10000 psia at an increment of 5 psia. The only method that gave physically-acceptable roots of V for all cases and compared well with reported values is Brent's method.

The method combines root bracketing, bisection, and inverse quadratic interpolation to converge to a root. It combines the sureness of bisection with the speed of a higher-order method *when appropriate*. The method is guaranteed to converge, so long as the function can be evaluated within the initial interval known to contain a root. It is highly recommended for the solution of the Rachford-Rice equation over the Newton-Raphson method; which rushes to a solution only when the function behaves smoothly. It can, however, dash rapidly to infinity without warning if measures are not taken to avoid such behavior, Press et a[13].

4. SSI SOLUTION OF THE CONVENTIONAL FLASH

This method represents the traditional way of solving the conventional flash equations. When given the overall composition of a hydrocarbon mixture, z_i, the system pressure P, and the system temperature T, the parameters V, L, y_i, x_i, and K_i can be calculated via SSI flash calculation process as follows (A flow chart of the SSI flash process is shown in Figure 1):

1. Assume component equilibrium ratios from Wilson's correlation as:

$$K_i = \frac{P_{ci}}{P}\exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{19}$$

2. Solve the Rachford-Rice equation, Eq. 18, for V. Brent's method of solution is used.
3. Calculate component liquid and vapor mole fractions using Eq. 15 and 16 respectively.
4. Solve Eq. 1 for the compressibility of the liquid and vapor phases, Z^L and Z^V.
5. Calculate fugacities and fugacity coefficients of all components for both liquid and vapor phases using Eq. 9.
6. Calculate new sets of equilibrium ratios as:

$$K_i = \frac{\Phi_i^L}{\Phi_i^V} \tag{20}$$

7. Steps 2-6 are repeated until the following criteria are satisfied:

$$\varepsilon_f = \sum_{i=1}^{N}\left[\frac{f_i^L}{f_i^V}-1\right]^2 < 10^{-15} \tag{21}$$
$$\varepsilon_V = \left[V - V^0\right]^2 < 10^{-15}$$

5. DIRECT SOLUTION OF THE CONVENTIONAL FLASH

In the direct solution of the conventional flash, we solve for the following set of equations:

$$\frac{f_i^V}{f_i^L}-1=0 \qquad i=1,...,N$$
$$g(V)=\sum_{i=1}^{N}\frac{z_i(K_i-1)}{1+V(K_i-1)}=0 \tag{22}$$

Eq. 22 represents a set of (N+1) nonlinear equations. These equations may be solved for the following sets of variables: VY iteration, LX iteration, and VK iteration. According to Abhvani and Beaumont[5] the VK iteration scheme requires less iteration and takes less overall CPU time. In this study, we implemented the VK iteration. Many nonlinear solvers were used to solve this set of equations. Amongst of which are: the Newton-Raphson, Globally-Convergent Newton, and Broyden's method, Press et al[13]. The Globally-Convergent Newton along with Broyden methods gave physically-acceptable roots for all cases. Broyden's method, however, failed to converge for 5 cases out of the 134 samples, while the Globally-Convergent Newton converged for all cases. This method has given identical results to those obtained with the rapid flash as will be seen next. The method is used for estimating variables with a tolerance in fugacity of 10^{-15}. The direct method of solution is summarized as follows (A flow chart of the direct flash is shown in Figure 2). Assume component equilibrium ratios from Wilson's correlation as:

$$K_i = \frac{P_{ci}}{P}\exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{23}$$

Assume an initial guess of V from the Rachford-Rice equation, Eq. 18. Calculate fugacities and fugacity coefficients of all components for both liquid and vapor phases using Eq. 9. Update component equilibrium ratios K_i and V, using the Globally-Convergent Newton. Steps 3-4 are repeated until the following criteria are satisfied:

$$\varepsilon_f = \sum_{i=1}^{N}\left[\frac{f_i^L}{f_i^V}-1\right]^2 < 10^{-15} \tag{24}$$
$$\varepsilon_V = \left[V - V^0\right]^2 < 10^{-15}$$

6. RAPID FLASH CALCULATIONS

The rapid flash as proposed by Li and Johns[12] is implemented. The authors formulated the rapid flash equations for the PR EOS and used Newton's method of solution with analytic Jacobian. The rapid flash is fruitful for hydrocarbon mixture with extended analysis. However, for lumped mixtures, it offers no significant improvement over conventional flashes. In this study, however, the rapid flash equations were formulated for both the SRK and the PR EOS.

Following the convention used by Li and Johns, Eq. 4 is written in terms of the liquid phase reduced parameters as follows (See Appendix A for detailed derivation of reduced parameters):

$$\begin{aligned} a_m^L &= \left(\Theta_1^L\right)^2 + 2\left(\Theta_2^L\right)^2 - 2\Theta_3^L\Theta_4^L \\ b_m^L &= \Theta_5^L \\ \Psi_i^L &= \sqrt{a_i\alpha_i}\,\Theta_1^L + 2\sqrt{a_i\alpha_i}\,h_i g_i\Theta_2^L \\ &\quad -\sqrt{a_i\alpha_i}\,g_i\Theta_3^L - \sqrt{a_i\alpha_i}\,h_i^2 g_i\Theta_4^L \end{aligned} \tag{25}$$

where, for the liquid phase, there are six independent reduced parameters given by:

$$\begin{aligned} \Theta_1^L &= \sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i} \\ \Theta_2^L &= \sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i g_i \\ \Theta_3^L &= \sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i^2 g_i \\ \Theta_4^L &= \sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,g_i \\ \Theta_5^L &= \sum_{i=1}^{N} x_i b_i \\ \Theta_6^L &= L \end{aligned} \tag{26}$$

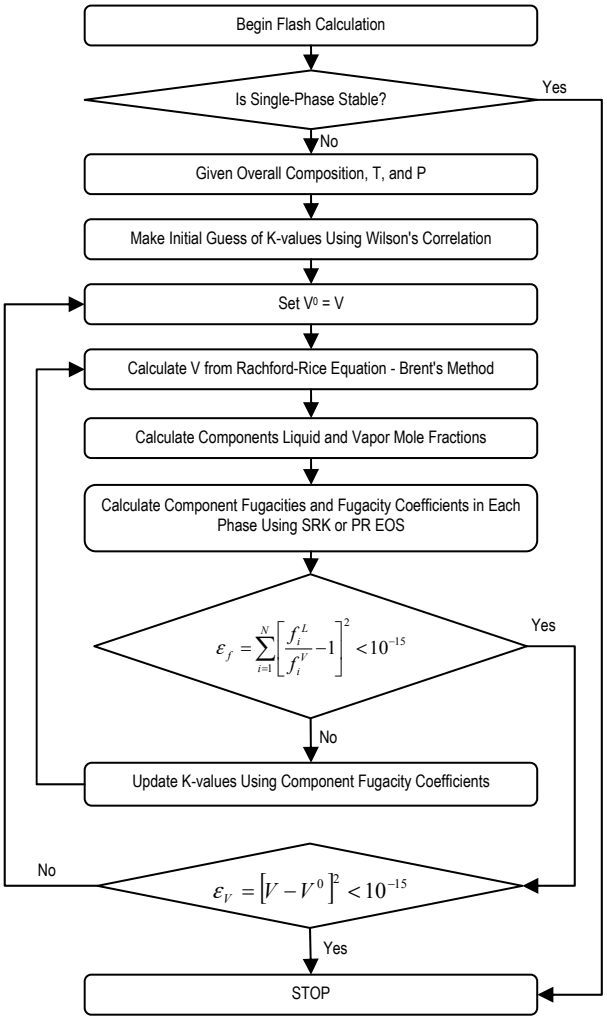

Figure 1. Flow chart of the SSI solution method.

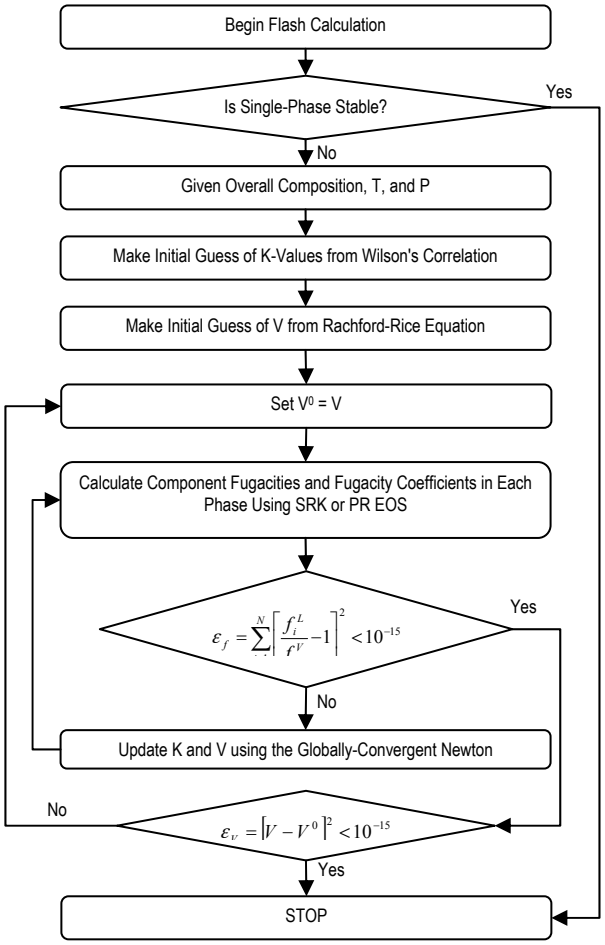

Figure 2. Flow chart of the direct solution method.

It is obvious now that all parameters in the flash calculation, including component fugacities and fugacity coefficients for each phase are only functions of these six reduced parameters. Thus, regardless of the number of components in the hydrocarbon mixture, the flash calculation is reduced to finding only these six reduced parameters with the following objective functions:

$$
\begin{aligned}
R_1 &= \Theta_1^L - \sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i} = 0 \\
R_2 &= \Theta_2^L - \sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, h_i g_i = 0 \\
R_3 &= \Theta_3^L - \sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, h_i^2 g_i = 0 \\
R_4 &= \Theta_4^L - \sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, g_i = 0 \\
R_5 &= \Theta_5^L - \sum_{i=1}^{N} x_i b_i = 0 \\
R_6 &= \sum_{i=1}^{N} \frac{z_i (1 - K_i)}{K_i + \Theta_6^L (1 - K_i)} = 0
\end{aligned}
\qquad (27)
$$

Many nonlinear solvers were used to solve the set of equations for the reduced parameters. Amongst of which are: the Newton-Raphson, Globally-Convergent Newton-Raphson, and Broyden's method. The quasi-Newton methods provide cheap approximations to the Jacobian. These methods are often called secant methods. The best of these is Broyden's Method. This method converges superlinearly once we get close enough to a root. It is almost as robust as Newton's method, and often needs far fewer functions evaluations to determine a zero, Press et al[13]. They were extensively used for the solution of flash equations of 134 oil samples at different pressures in the range 100-10000 psia at an increment of 5 psia. The only method that gave physically-acceptable roots for all cases and compared well with reported values is Broyden's method. For completeness, the Jacobian matrix for the SRK and PR equations of state is given in Appendix B.

Broyden's method is used for estimating these parameters with a tolerance in fugacity of 10^{-15}. Once reduced parameters for the liquid phase are determined, reduced parameters for the vapor phase are found by a simple material balance as follows:

$$\Theta_k^F = L\Theta_k^L + (1-L)\Theta_k^V \qquad k = 1,.....,5 \tag{28}$$

Solving for the vapor phase reduced parameters yields:

$$\Theta_k^V = \frac{\Theta_k^F - L\Theta_k^L}{(1-L)} \qquad k = 1,.....,5 \tag{29}$$

where feed reduced parameters are written in terms of the overall mole fractions, z_i, and $\Theta_6^F = 1$.

7. THE RAPID FLASH SOLUTION PROCEDURE

The steps for solving the rapid flash are presented here. When given the overall composition of a hydrocarbon mixture, z_i, the system pressure, P, and the system temperature T, the rapid flash is performed as follows (A flow chart of this flash process is shown in Figure 3):

1. Assume component equilibrium ratios from Wilson's correlation as:

$$K_i = \frac{P_{ci}}{P}\exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{30}$$

2. Solve for component mole fractions in the liquid phase, x_i, from Eq. 15, with V=1.
3. Assume reduced parameters of the liquid phase from Eq. 26, with L=0.
4. Calculate the fugacity coefficients of all components for both liquid and vapor phases using Eq. 9
5. Update reduced parameters using Eq. 27-29 (Broyden's method is used).
6. Steps 4-5 are repeated until the following criteria are satisfied:

$$\varepsilon_f = \sum_{i=1}^{N}\left[\frac{f_i^L}{f_i^V} - 1\right]^2 < 10^{-15} \tag{31}$$
$$\varepsilon_V = \left[V - V^0\right]^2 < 10^{-15}$$

8. RESULTS

The conventional and rapid flash calculations formulated in this study were extensively used to flash a total of 134 crude oil samples at different pressures from 100 to 10000 psia at an increment of 5 psia. The oil samples include: the five-component hydrocarbon reported by Mehra et al[1], the ten-component volatile oil reported by Nghiem et al[2] and the fifteen-component reservoir oil system reported by Fussell and Yanosik[3]. In addition, 131 crude oil samples, compiles by Elsharkawy[14], were used. Saturation pressures of all oil samples were calculated via flash calculations and compared with reported values.

The initial guesses for both flash methods were obtained by conventional flash until component fugacities converged to within a relative error of 10^{-4}.

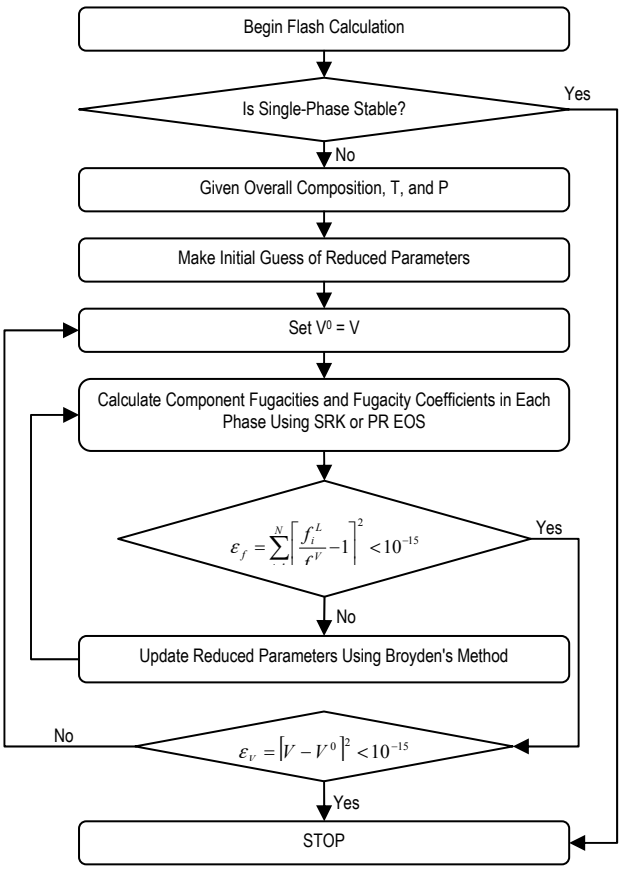

Figure 3. Flow chart of the rapid flash solution method.

Then the rapid flash continues in the same manner as presented by Li and Johns[12]. Both SSI and direct methods for the solution of the conventional flash converged to a solution for all tested examples at all pressure ranges. The rapid method converged to a trivial solution (the overall compositions) only for five cases. On the other hand, Li and Johns[12] reported that their rapid and SSI flash calculations were performed for 52 random overall compositions, temperatures and pressures. Of those eight rapid flash calculations and sixteen SSI flash calculations failed to converge or converged to a trivial solution. While this is not an absolute test, it, however, indicates that the solvers proposed in this study are more robust than the Newton's method of solution.

8.1 Five Component System

Mehra et al[1] presented a five-component hydrocarbon system, the composition of which is shown in Table 2. The mixture was flashed at a temperature of 240.4 EF and different pressures. Mehra et al. reported a mixture's critical point close to 805 psia and at a temperature slightly below 240.4EF. In this study, the calculated critical points of the mixture, using the different methods, are shown in Table 3. Figure 4 shows the vapor mole fraction plotted versus pressure for pressures from 600 to 850.

Table 2. Mehra et al. five component system

#	Component	Overall mole fraction
1	C_2	0.39842
2	C_3	0.29313
3	n-C_4	0.20006
4	n-C_5	0.07143
5	n-C_6	0.03696

Table 3. Saturation pressures

#	Method	Critical Pressure, psia
1	SSI - SRK	804.87
2	SSI - PR	NA
3	Rapid - SRK	857.75
4	Rapid - PR	900.18

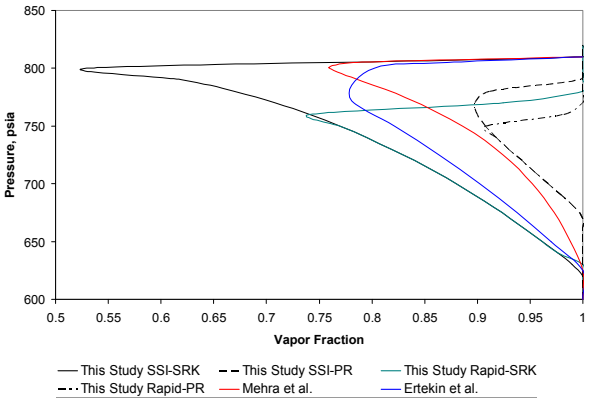

Figure 4. Plot of vapor mole fraction versus pressure for the five component system of Mehra et al.

8.2 Ten Component System

Nghiem et al[2] presented a ten-component volatile oil, the composition of which is shown in Table 4. The mixture was flashed at a temperature of 324 °F and different pressures from 2700 to 2810 psia. Nghiem et al. reported a mixture's critical point pressure of 2813 psia at 324 °F. The calculated critical point pressure in case of SRK is 3029 psia and 2891 psia in case of PR. Figure 5 shows the vapor mole fraction plotted versus pressure. As stated by Nghiem et al., method 2 (NL or NV iteration) appears to be slightly better than the other two methods. In this study, however, both methods SSI and rapid gave identical trends. The trends follow the same trend of V values as reported by Nghiem et al. The difference in results may be due to differences in BIPs used in this study.

Table 4. Nghiem et al. ten component system

#	Component	Overall mole fraction
1	C_1	0.6436
2	C_2	0.0752
3	C_3	0.0474
4	nC_4	0.0412
5	nC_5	0.0297
6	nC_6	0.0138
7	nC_7	0.0303
8	nC_8	0.0371
9	nC_9	0.0415
10	nC_{10}	0.0402

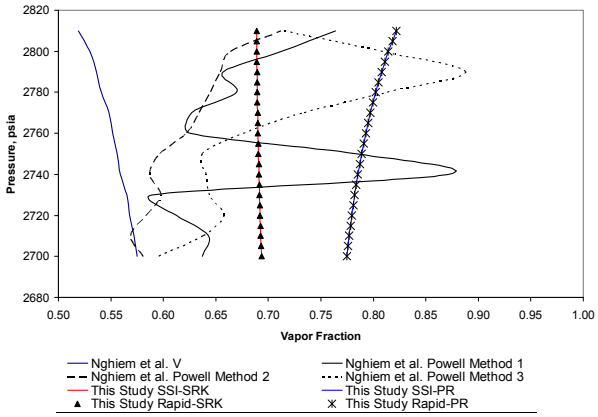

Figure 5. Plot of vapor mole fraction versus pressure for the ten component system of Nghiem et al.

8.3 Fifteen-Component Oil System

Fussell and Yanosik[3] presented a fifteen-component reservoir oil system, the composition of which is shown in Table 5. The mixture was flashed at a temperature of 235 °F and different pressures. The authors have used physical properties of the C_{7+} fraction pseudocomponents as shown in Table 5. In this study, however, properties of the lumped C_{7+} fraction were used as shown in Table 6 to match the mixture's bubble-point pressure of 4952 psia. Properties of the C7+ fraction were estimated using Riazi and Daubert method[16]. The calculated bubble-point pressure in case of SRK is 4952 psia and 4959 psia in case of PR. Figure 6 shows the vapor mole fraction plotted versus pressure for all methods.

Table 5. Fussell and Yanosik reservoir oil composition

#	Component	Overall mole fraction
1	N_2	0.00808
2	CO_2	0.01501
3	C_1	0.56990
4	C_2	0.12714
5	C_3	0.07596
6	i-C_4	0.01075
7	n-C_4	0.03055
8	i-C_5	0.00849
9	n-C_5	0.01074
10	C_6	0.01272
11	180 BP*	0.01716
12	230 BP	0.01764
13	280 BP	0.01416
14	330 BP	0.01115
15	380 BP	0.07055

**BP represents boiling point fractions of the C_{7+}, °F*

Table 6. Properties of the C7+ fraction of Fussell and Yanosik reservoir oil

Property	Value
z	0.13066
SG	0.9668
MW	145.944 lb/mole
Tb	431.0 °F

8.4 Data Sets Compiled by Elsharkawy

Elsharkawy[14] has compiled data sets of a total of 131 crude oil samples from the Middle East and other parts of the world (see Appendix C for a full list of all data). Data included experimentally-measured compositions and saturation pressures along with the SRK and PR-predicted saturation pressures. In addition, data of the C_{7+} fraction, such as specific gravity and molecular weight were also included. In this study, saturation pressures of all samples were generated using the SSI and rapid methods. They were then compared with Elsharkawy data. Plots of saturation pressures versus sample numbers are shown in Figures 7-11.

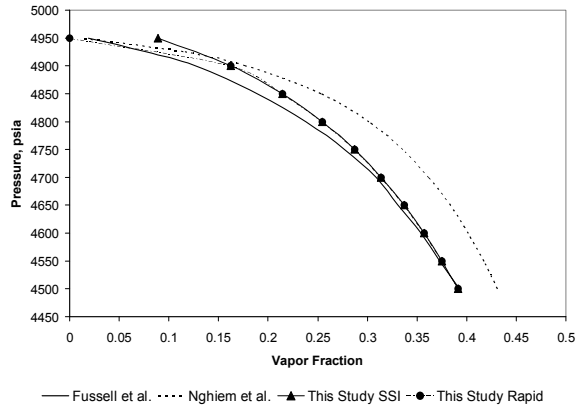

Figure 6. Plot of vapor mole fraction versus pressure for the fifteen-component system

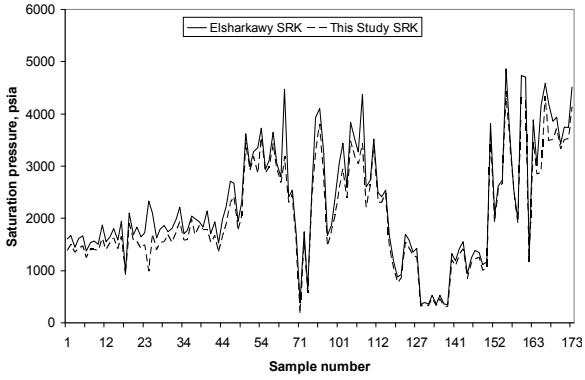

Figure 7. Plot of SRK-predicted saturation pressures versus sample numbers for Elsharkawy and this study

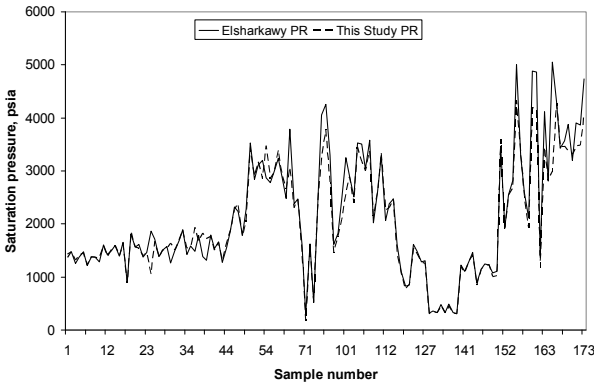

Figure 8. Plot of PR-predicted saturation pressures versus sample numbers for Elsharkawy and this study

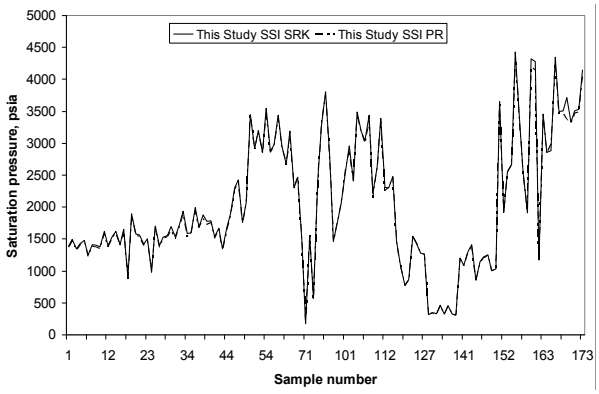

Figure 9. Plot of SRK- and PR-predicted saturation pressures versus sample numbers for this study

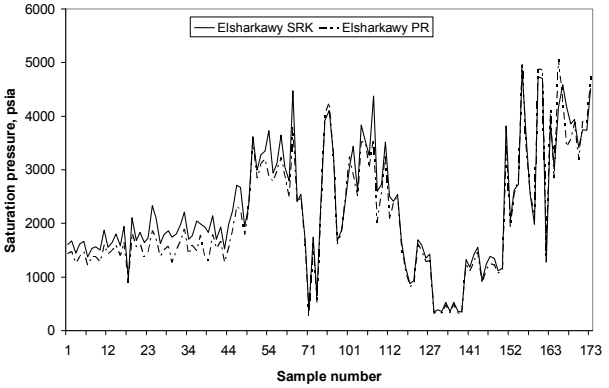

Figure 10. Plot of SRK- and PR-predicted saturation pressures versus sample numbers for Elsharkawy

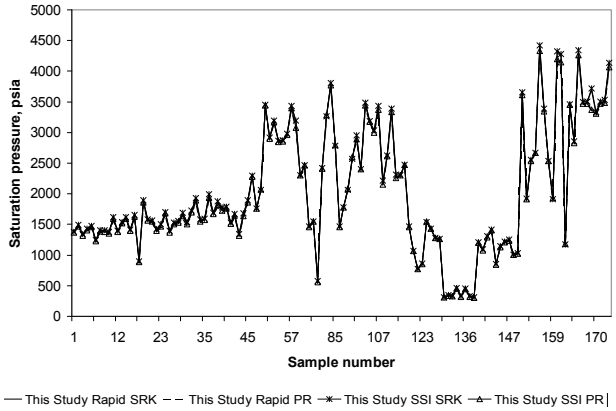

Figure 11. Plot of Rapid and SSI flash calculations for both SRK and PR equations of state

9. CONCLUSIONS

In this paper, conventional and rapid flashes with both SRK and PR EOS were studied and programmed in an object-oriented fashion. We managed to reproduce all saturation pressures for a total of 134 oil samples that cover a wide range of compositions. All oil samples were flashed at pressures in the range of 100-10000 psia at an increment of 5 psia. We have investigated different solvers for the conventional and rapid solution methods. Results of this study should help clarify some problems with flash calculations. The

following conclusions were drawn based on these results:

1. Brent's method is highly recommended for the solution of the Rachford-Rice equation over the Newton-Raphson method. It combines the sureness of bisection with the speed of a higher-order method when appropriate. The method is guaranteed to converge, so long as the function can be evaluated within the initial interval known to contain a root. On the other hand, Newton-Raphson method rushes to a solution only when the function behaves smoothly. It can, however, dash rapidly to infinity without warning if measures are not taken to avoid such behavior.
2. The SSI solution, when combined with Brent's method, is robust, fast, and converges to a physically-acceptable solution in almost all cases.
3. Quasi-Newton methods provide cheap approximations to the Jacobian. These methods are often called *secant methods*. The best of these is *Broyden's Method*. This method converges superlinearly once we get close enough to a root. It is almost as robust as Newton's method, and often needs far fewer functions evaluations to determine a zero.
4. For both conventional and rapid solution methods, a new round of calculations is necessary to make sure that there is no significant change in the calculated values of V. This condition is satisfied via the second criterion of Eq. 21 or 31.
5. Both conventional and rapid flashes slow down close to the critical point. This in turn renders the rapid flash obsolete when no extended analysis is used.
6. The selection of the nonlinear solver may have a critical impact on the convergence of the method to a solution. The Globally-Convergent Newton did work well with the direct conventional, whereas Broyden's method worked better for the rapid flash. Both methods gave identical results for all cases studied.

NOMENCLATURE

a = attraction parameter for an EOS, psia-ft3/lbm-mol
A = attraction parameter for an EOS, dimensionless
b = repulsion parameter for an EOS, ft3/lbm-mol
B = repulsion parameter for an EOS, dimensionless
F = number of moles of the hydrocarbon mixture
f_i^V = fugacity of component *i* in the vapor phase.
f_i^L = fugacity of component *i* in the liquid phase.
g = BIP Parameter for the rapid flash, dimensionless.
h = BIP Parameter for the rapid flash, dimensionless.
K_i = equilibrium ratio of component i at p and T.
L = number of moles of the hydrocarbon mixture in the liquid phase.
N = number of components in the hydrocarbon mixture.
P = system pressure, psia.
T = system temperature, °F.
V = number of moles of the hydrocarbon mixture in the vapor phase.
x_i = mole fraction of component i in the liquid phase.
y_i = mole fraction of component i in the vapor phase.
z_i = overall mole fraction of component i in the entire hydrocarbon mixture.
Z^V = compressibility factor of the vapor phase as calculated by the EOS.
Z^L = compressibility factor of the liquid phase as calculated by the EOS.
Φ_i^V = fugacity coefficient of component *i* in the vapor phase.
Φ_i^L = fugacity coefficient of component *i* in the liquid phase.

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Appendix A:
Rapid Flash Reduced Parameters

The key point to the rapid flash, as proposed by Li and Johns[12] is to decompose the BIPs into two parts using the following expression:

$$k_{ij} = \left(h_i - h_j\right)^2 g_i g_j \tag{32}$$

where h_i and g_i are parameters for component i that are tuned to match PVT data. Substitution of Eq. 32 into Eq. 5 yields:

$$a_{ij} = \left(1 - \left(h_i - h_j\right)^2 g_i g_j\right)\sqrt{a_i a_j \alpha_i \alpha_j} \tag{33}$$

As stated by Li and Johns[12] the use of Eq. 33 guarantees that the BIP matrix remains symmetric and that the diagonal elements of the BIP matrix are zero. Expanding Eq. 33 and rearranging yields:

$$\begin{aligned} a_{ij} &= \sqrt{a_i a_j \alpha_i \alpha_j} + 2\sqrt{a_i a_j \alpha_i \alpha_j}\, h_i h_j g_i g_j \\ &\quad - \sqrt{a_i a_j \alpha_i \alpha_j}\, h_i^2 g_i g_j - \sqrt{a_i a_j \alpha_i \alpha_j}\, h_j^2 g_i g_j \end{aligned} \tag{34}$$

Substitution of Eq. 34 into Eq. 4 yields:

$$\begin{aligned} \Psi_i &= \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j} + 2\sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_i h_j g_i g_j \\ &\quad - \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_i^2 g_i g_j - \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_j^2 g_i g_j \\ a_m &= \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j} + 2\sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_i h_j g_i g_j \\ &\quad - \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_i^2 g_i g_j - \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j \sqrt{a_i a_j \alpha_i \alpha_j}\, h_j^2 g_i g_j \\ b_m &= \sum_{i=1}^{N} x_i b_i \end{aligned} \tag{35}$$

Rearranging Eq. 35 yields:

$$\begin{aligned} \Psi_i &= \sqrt{a_i \alpha_i}\left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\right) + 2\sqrt{a_i \alpha_i}\, h_i g_i \left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, h_j g_j\right) \\ &\quad - \sqrt{a_i \alpha_i}\, h_i^2 g_i \left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, g_j\right) - \sqrt{a_i \alpha_i}\, g_i \left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, h_j^2 g_j\right) \\ a_m &= \left(\sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\right)\left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\right) + 2\left(\sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, h_i g_i\right)\left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, h_j g_j\right) \\ &\quad - \left(\sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, h_i^2 g_i\right)\left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, g_j\right) - \left(\sum_{i=1}^{N} x_i \sqrt{a_i \alpha_i}\, g_i\right)\left(\sum_{j=1}^{N} x_j \sqrt{a_j \alpha_j}\, h_j^2 g_j\right) \\ b_m &= \sum_{i=1}^{N} x_i b_i \end{aligned} \tag{36}$$

Realizing that i and j are interchangeable yields:

$$\Psi_i = \sqrt{a_i\alpha_i}\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\right) + 2\sqrt{a_i\alpha_i}\,h_i g_i\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i g_i\right) - \sqrt{a_i\alpha_i}\,g_i\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i^2 g_i\right) - \sqrt{a_i\alpha_i}\,h_i^2 g_i\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,g_i\right) \quad (37)$$

$$a_m = \left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\right)^2 + 2\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i g_i\right)^2 - 2\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,h_i^2 g_i\right)\left(\sum_{i=1}^{N} x_i\sqrt{a_i\alpha_i}\,g_i\right)$$

$$b_m = \sum_{i=1}^{N} x_i b_i$$

Following the convention used by Li and Johns[12] Eq. 37 is written in terms of the reduced parameters as follows:

$$\Psi_i = \sqrt{a_i\alpha_i}\,\Theta_1^L + 2\sqrt{a_i\alpha_i}\,h_i g_i \Theta_2^L - \sqrt{a_i\alpha_i}\,g_i\Theta_3^L - \sqrt{a_i\alpha_i}\,h_i^2 g_i \Theta_4^L$$
$$a_m = \left(\Theta_1^L\right)^2 + 2\left(\Theta_2^L\right)^2 - 2\Theta_3^L\Theta_4^L$$
$$b_m = \Theta_5^L \quad (38)$$

Appendix B: Jacobian Matrix for SRK/PR

The entries of the Jacobian matrix are given here for both equations of state, the SRK and the PR. The rows of the Jacobian matrix in a dimensionless form are given by:

$$\frac{\partial R_{D1}}{\partial \Theta_{Dk}^L} = \delta_{1k} - \sum_{i=1}^{N}\sqrt{A_i}\frac{\partial x_i}{\partial \Theta_{Dk}^L}$$
$$\frac{\partial R_{D2}}{\partial \Theta_{Dk}^L} = \delta_{2k} - \sum_{i=1}^{N}\sqrt{A_i}\,h_i g_i\frac{\partial x_i}{\partial \Theta_{Dk}^L}$$
$$\frac{\partial R_{D3}}{\partial \Theta_{Dk}^L} = \delta_{3k} - \sum_{i=1}^{N}\sqrt{A_i}\,h_i^2 g_i\frac{\partial x_i}{\partial \Theta_{Dk}^L}$$
$$\frac{\partial R_{D4}}{\partial \Theta_{Dk}^L} = \delta_{4k} - \sum_{i=1}^{N}\sqrt{A_i}\,g_i\frac{\partial x_i}{\partial \Theta_{Dk}^L}$$
$$\frac{\partial R_{D5}}{\partial \Theta_{Dk}^L} = \delta_{5k} - \sum_{i=1}^{N}B_i\frac{\partial x_i}{\partial \Theta_{Dk}^L}$$
$$\frac{\partial R_{D6}}{\partial \Theta_{Dk}^L} = \sum_{i=1}^{N}\left(\frac{\partial x_i}{\partial \Theta_{Dk}^L} - \frac{\partial y_i}{\partial \Theta_{Dk}^L}\right) \quad (39)$$

where δ_{ik} is the Kronecker delta function; which equals 1 when i = k and 0 otherwise.

$$A_i = \frac{P}{(RT)^2}a_i\alpha_i \quad (40)$$

$$B_i = \frac{P}{RT}b_i$$

$$\frac{\partial x_i}{\partial \Theta_{Dk}^L} = -\frac{z_i\left[(1-K_i)\delta_{6k} + \left(1-\Theta_{D6}^L\right)\frac{\partial K_i}{\partial \Theta_{Dk}^L}\right]}{\left[\Theta_{D6}^L + K_i\left(1-\Theta_{D6}^L\right)\right]^2} \quad (41)$$

$$\frac{\partial y_i}{\partial \Theta_{Dk}^L} = -\frac{z_i\left[K_i(1-K_i)\delta_{6k} + \Theta_{D6}^L\frac{\partial K_i}{\partial \Theta_{Dk}^L}\right]}{\left[\Theta_{D6}^L + K_i\left(1-\Theta_{D6}^L\right)\right]^2}$$

$$\frac{\partial K_i}{\partial \Theta_{Dk}^L} = K_i\left(\sum_{l}^{N}\frac{\partial \ln\Phi_i^V}{\partial \Theta_{Dl}^V}\frac{\partial \Theta_{Dl}^V}{\partial \Theta_{Dk}^L} - \frac{\partial \ln\Phi_i^V}{\partial \Theta_{Dk}^V}\right) \quad (42)$$

with:

$$\frac{\partial \Theta_{Dl}^V}{\partial \Theta_{Dk}^L} = \begin{cases} -\dfrac{1-\Theta_{D6}^L}{\Theta_{D6}^L} & for\ l = k = 1,\ldots,5 \\ \dfrac{\Theta_{Dk}^L - \Theta_{Dk}^V}{\left(1-\Theta_{Dk}^L\right)^2} & for\ l = 6, k = 1,\ldots,5 \\ -1 & for\ l = k = 6 \\ 0 & otherwise \end{cases} \quad (43)$$

Differentiating Eq. 9 and rearranging yields:

$$\frac{\partial \ln\Phi_i}{\partial \Theta_{Dk}} = \frac{B_i}{B}\frac{\partial Z}{\partial \Theta_{Dk}} - \frac{B_i(Z-1)}{B^2}\frac{\partial B}{\partial \Theta_{Dk}} - \frac{1}{(Z-B)}\left(\frac{\partial Z}{\partial \Theta_{Dk}} - \frac{\partial B}{\partial \Theta_{Dk}}\right)$$
$$-\left(\frac{A}{(u_1-u_2)B}\right)\left[2\frac{A_{ij}}{A} - \frac{B_i}{B}\right]\left[\frac{1}{(Z+u_1B)}\left(\frac{\partial Z}{\partial \Theta_{Dk}} + u_1\frac{\partial B}{\partial \Theta_{Dk}}\right)\right.$$
$$\left. - \frac{1}{(Z+u_2B)}\left(\frac{\partial Z}{\partial \Theta_{Dk}} + u_2\frac{\partial B}{\partial \Theta_{Dk}}\right)\right] - \ln\left(\frac{Z+u_1B}{Z+u_2B}\right)$$
$$\left[\frac{2}{(u_1-u_2)B}\frac{\partial A_{ij}}{\partial \Theta_{Dk}} - \frac{2A_{ij}}{(u_1-u_2)AB}\frac{\partial A}{\partial \Theta_{Dk}} + \frac{AB_i}{(u_1-u_2)B^3}\frac{\partial B}{\partial \Theta_{Dk}}\right]$$
$$-\left[2\frac{A_{ij}}{A} - \frac{B_i}{B}\right]\ln\left(\frac{Z+u_1B}{Z+u_2B}\right)\left(\frac{1}{(u_1-u_2)B}\frac{\partial A}{\partial \Theta_{Dk}} - \frac{A}{(u_1-u_2)B^2}\frac{\partial B}{\partial \Theta_{Dk}}\right) \quad (44)$$

Similarly, differentiating Eq. 1 and rearranging yields:

$$\frac{\partial Z}{\partial \Theta_{Dk}} = -\frac{1}{\left(3Z^2 + 2a_2Z + a_1\right)}\left(Z^2\frac{\partial a_2}{\partial \Theta_{Dk}} + Z\frac{\partial a_1}{\partial \Theta_{Dk}} + \frac{\partial a_0}{\partial \Theta_{Dk}}\right)$$
$$\frac{\partial a_2}{\partial \Theta_{Dk}} = (u_1+u_2-1)\frac{\partial B}{\partial \Theta_{Dk}}$$
$$\frac{\partial a_1}{\partial \Theta_{Dk}} = \frac{\partial A}{\partial \Theta_{Dk}} - u_2\frac{\partial B}{\partial \Theta_{Dk}} - 2(u_1+u_2-u_1u_2)B\frac{\partial B}{\partial \Theta_{Dk}}$$
$$\frac{\partial a_0}{\partial \Theta_{Dk}} = -A\frac{\partial B}{\partial \Theta_{Dk}} - B\frac{\partial A}{\partial \Theta_{Dk}} - 2u_1u_2(1+B)B\frac{\partial B}{\partial \Theta_{Dk}} - u_1u_2B^2\frac{\partial B}{\partial \Theta_{Dk}} \quad (45)$$

$$\frac{\partial A}{\partial \Theta_{Dk}} = \begin{bmatrix} 2\Theta_{D1} & 4\Theta_{D2} & -2\Theta_{D4} & -2\Theta_{D3} & 0 & 0 \end{bmatrix}$$
$$\Theta_{Dk} = \begin{bmatrix} \left(\sqrt{P}/RT\right)\Theta_1 & \left(\sqrt{P}/RT\right)\Theta_2 & \left(\sqrt{P}/RT\right)\Theta_3 \\ \left(\sqrt{P}/RT\right)\Theta_4 & (P/RT)\Theta_5 & \Theta_6 \end{bmatrix}$$
$$R_{Dk} = \begin{bmatrix} \left(\sqrt{P}/RT\right)R_1 & \left(\sqrt{P}/RT\right)R_2 & \left(\sqrt{P}/RT\right)R_3 \\ \left(\sqrt{P}/RT\right)R_4 & (P/RT)R_5 & R_6 \end{bmatrix}\frac{\partial B}{\partial \Theta_{Dk}} = \delta_{5k} \quad (46)$$

$$\frac{\partial A_{ij}}{\partial \Theta_{Dk}} = \begin{bmatrix} \sqrt{A_i} & 2\sqrt{A_i}\,h_i g_i & -\sqrt{A_i}\,g_i & -\sqrt{A_i}\,h_i^2 g_i & 0 & 0 \end{bmatrix}$$