Development of An Augmented Free-Water Three-Phase Rachford-Rice Algorithm for CO_2/Hydrocarbons/Water Mixtures

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ABSTRACT

In this work, we develop a robust and efficient algorithm to perform three-phase flash calculations for CO_2/water/hydrocarbons mixtures on the basis of the assumption that only CO_2 and water are considered in the aqueous phase. We name this new algorithm as the so-called augmented free-water flash, considering that it is a modified version of the conventional free-water flash which assumes the presence of pure water in the aqueous phase. The new algorithm is comprised of two loops: in the outer loop, we first develop a pragmatic method for initializing the equilibrium ratios of CO_2 and water in the aqueous phase with respect to the reference phase (i.e., the hydrocarbon-rich liquid phase); in the inner loop, we solve the Rachford-Rice (RR) equation that has been simplified based on the augmented free-water assumption.

Moreover, this new augmented free-water three-phase flash algorithm is incorporated into a flash package which can handle single-phase, two-phase, and three-phase equilibria calculations. The flash package first tests the stability of the feed. If the feed is found to be stable, a single-phase equilibrium can be concluded. Otherwise, the augmented free-water three-phase flash algorithm is initiated. If the phase fractions obtained from this augmented free-water three-phase algorithm do not belong to [0, 1] or if an open feasible region occurs during the iterations, two-phase flash will be conducted. The flash package that couples the augmented free-water flash requires less computational time and a fewer number of iterations than the conventional full three-phase flash package.

Furthermore, the augmented free-water flash method has been extended to the methane-containing hydrocarbons/water mixtures where the solubility of methane in the aqueous phase might not be negligible under certain conditions. Similarly, in the new algorithm, we only consider the presence of water and methane in the aqueous phase. The general framework of the flash algorithm is the same as the one that is previously developed for the CO_2/hydrocarbons/water mixtures. But, we use the Wilson equation to initialize the *K*-values for the non-water components, but use the equation suggested by Lapene *et al.* (2010) to initialize the *K*-values for water. Two case studies have been used to test the performance of the new algorithm. The testing results show that the amount of methane dissolved in water is less than that of CO_2 under the same conditions. But the solubility of methane in the aqueous phase can be also quite high at high-pressure/high-temperature conditions, justifying the use of our augmented algorithm (instead of the free-water algorithm) to perform flash computations for the methane-containing hydrocarbons/water mixtures.

The example calculations for water/hydrocarbon mixtures using the augmented free-water algorithm prove its robustness and effectiveness over a wide range of pressure and temperature. The results obtained by the augmented free-water method are more accurate than the traditional free-water method since the solubility of methane is considered in the augmented one. The computational time and number of iterations are significantly decreased with the use of the new flash package featuring the augmented algorithm. This is because of the following reasons: 1) A fewer number of parameters are involved in the calculations due to the use of the augmented free-water concept; 2) the number of iterations are reduced due to a more accurate initialization of equilibrium ratios compared with the conventional method; and 3) A fewer number of stability tests are required in the new flash package compared with the conventional method.

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DEDICATION

This dissertation is dedicated to my dearest parents, Mrs. Fengyu Gao and Mr. Xiangyang Pang, and to my everlasting friend, Chocho.

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CHAPTER 1 INTRODUCTION

1.1 Research Background

As a technique widely utilized for enhanced oil recovery (EOR), CO_2 injection has been regarded as one of the most promising and effective tertiary recovery approaches in decades [1]. The factors contributing to incremental oil recovery during miscible and immiscible CO_2 displacement process mainly include: reduced interfacial tension (IFT), lowered crude oil viscosity, higher relative permeability to oil due to oil swelling and solution gas drive [2-11]. Moreover, carbon capture and sequestration (CSS) is considered to be a feasible approach to combating the increasing greenhouse gas emissions. The report delivered by Alberta Economic Development Authority (AEDA) stated that the Government of Alberta invested a 2$ billion CCS Fund to promote the development of CCS technologies within the province [12]. The amount of CO_2 reserved in the formation will reach up to 60% when at CO_2 breakthrough, indicating a great potential of combining CO_2 sequestration with the enhancing oil recovery (EOR) process [13].

Compositional simulations are normally applied to predict the multiphase flow of CO_2/water/hydrocarbons mixtures in the porous media throughout the CO_2 injection projects. Multiphase equilibria computations play an important role in ensuring the reliability and accuracy of compositional-simulation results [14]. During CO_2 injection, the continuous contact of CO_2, water and hydrocarbon can lead to the occurrence of multiphase equilibria of CO_2/hydrocarbons/water under reservoir conditions, such as two-phase and three phase equilibria; under certain circumstances, a vapor-liquid-liquid-aqueous (VLLA) equilibrium can appear in the reservoir [15]. Multiphase flash calculations for water-containing systems remain to be challenging and convergence issues may appear in the stability tests and flash calculations. A robust and efficient algorithm for performing multiphase flash calculations for CO_2/hydrocarbons/water mixtures is required to perform reliable compositional simulations on CO_2 injection projects.

Inspired by the works by Tang and Saha [16] and Iranshahr *et al.* [17], Lapene *et al.* [18] proposed a free-water flash algorithm based on the assumption that the aqueous phase consists of pure water. However, in the case of CO_2/hydrocarbons/water mixtures, such free-water assumption neglects the solubility of CO_2 in the aqueous phase, which can result in significant errors in the flash results. Therefore, the main objective of this work is to develop an improved version of the free-water flash algorithm (i.e., the so-called augmented free-water flash) which can take into account the presence of CO_2 in the aqueous phase.

1.2. Problem Statement

The phase behavior of water-containing mixtures is complex, resulting in difficulties with regards to how to ensure the convergence of the multiphase flash algorithms for these mixtures. Free-water flash method assumes the aqueous phase is pure water based on the fact that the solubility of most hydrocarbons in the aqueous phase is small; it provides an effective alternative algorithm for performing multiphase flash calculations for the water/hydrocarbons mixtures. However, in the case of CO_2/water/hydrocarbons mixtures, the solubility of CO_2 in the aqueous phase can be quite large, rendering the free-water flash method inaccurate in describing the phase behavior of CO_2/water/hydrocarbons mixtures. A modified version of the free-water flash method needs to be developed to improve the accuracy of the multiphase flash calculations for the CO_2/water/hydrocarbons mixtures.

1.3. Research Objectives

The objectives of this research include the following:

- To derive a new objective function for solving Rachford-Rice (RR) equations based on the augmented free-water flash assumption for CO_2/hydrocarbons/water mixtures.
- To develop a robust and efficient new algorithm for carrying out so-called augmented free-water flash calculations.
- To develop a full three-phase flash package that incorporates this new algorithm and can handle single-phase, two-phase and three-phase flash calculations.
- To apply augmented free-water flash algorithm to model the phase behaviour of water/hydrocarbons mixtures by considering the dissolution of only methane in the aqueous phase.
- To examine the effect of water presence on the phase behaviour of CO_2/hydrocarbons/water mixtures.

1.4. Thesis Structure

This thesis is a paper-based thesis, organized as follows:

In Chapter 2, an augmented free-water flash method is presented for CO_2/hydrocarbons/water mixtures. The new objective function is derived based on the assumption that only CO_2 and water are considered in the aqueous phase. Empirical correlations are proposed to initialize the equilibrium ratios. Moreover, a new flash package incorporating the augmented free-water algorithm is developed to handle single-phase, two-phase and three-phase equilibrium calculations. The flash results given by the augmented free-water flash algorithm are compared to those by the conventional full three-phase flash algorithms as well as those by the free-water flash algorithms. The computation efficiency of the proposed algorithm is also assessed.

In Chapter 3, the augmented free-water method has been extended to the water/hydrocarbons mixtures on the basis of the assumption that only methane and water are considered in the aqueous phase. Again, the flash results given by the augmented algorithm are compared to those by the conventional full three-phase flash algorithms as well as those by the free-water flash algorithms. The computation efficiency of the proposed algorithm is also assessed.

Chapter 4 gives the conclusions achieved in the thesis research, together with recommendations for future works.

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CHAPTER 2 AN AUGMENTED FREE-WATER THREE-PHASE RACHFORD-RICE ALGORITHM FOR CO_2/HYDROCARBONS/WATER MIXTURES

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Abstract

Multiphase equilibria for CO_2/water/hydrocarbons mixtures are frequently encountered in using CO_2 for flooding or storing CO_2 in depleted reservoirs. The presence of an aqueous phase in multiphase equilibrium poses difficulties associated with how to ensure the convergence of stability test. The free-water assumption, where the aqueous phase is considered as pure water, provides a better solution to this problem compared with the conventional full three-phase flash method. As for CO_2/hydrocarbons/water mixtures, the free-water assumption might not be valid since the solubility of CO_2 in the aqueous phase may not be negligible. This research presents a robust and efficient algorithm to perform three-phase flash calculation for CO_2/hydrocarbons/water mixtures based on the assumption that only the presence of CO_2 and water is considered in the aqueous phase, i.e., the so-called augmented free-water concept. The new algorithm is comprised of two loops. In the outer loop, we first develop a pragmatic method for initializing the equilibrium ratios of CO_2 and water in the aqueous phase with respect to the reference phase (i.e., the hydrocarbon-rich liquid phase). In the inner loop, we solve the Rachford-Rice (RR) equation that has been simplified based on the augmented free-water assumption. In addition, we incorporate this new augmented free-water three-phase flash algorithm to a flash package which can deal with the single-phase, two-phase, and three-phase equilibria. Both positive and negative flashes have been applied in the flash package. Also, a new criterion is developed to properly switch between two-phase flash and three-phase flash; such criterion has been used as the supplementary judgment for the negative flash, which is proven to be reliable and efficient after extensive testing. The example calculations using the new algorithm show that the augmented free-water method is more accurate than the traditional free-water method since the solubility of CO_2 is considered in the augmented one. The flash package that couples the augmented free-water flash requires less computational time and a fewer number of iterations than the conventional full three-phase flash package.

Keywords: Augmented free-water method, Three-phase equilibrium, Negative flash, CO_2 flooding, CO_2 storage

2.1. Introduction

CO_2 flooding has been proven to be an efficient approach for enhancing oil recovery. CO_2 storage in depleted oil reservoirs is also an important strategy for reducing the presence of greenhouse gas in the air [1]. During CO_2 flooding and CO_2 storage in an oil reservoir, the interaction of CO_2 and hydrocarbons can lead to the occurrence of multiphase equilibria, up to vapor-liquid-liquid three-phase equilibrium. It is worthwhile mentioning that the presence of water, either as an injected fluid or in the form of an aquifer, is inevitable in petroleum reservoirs, resulting in the continuous contact of the aqueous phase with hydrocarbon phases [2]. As such, a multi-phase equilibrium, up to vapor-liquid-liquid-aqueous four-phase equilibrium may ensue under reservoir conditions.

Phase equilibrium calculations for CO_2/hydrocarbons/water mixtures are very important for performing accurate and reliable compositional reservoir simulations. Currently, there is an increasing demand in developing a robust and efficient algorithm for modeling the complex phase behavior of mixtures in compositional simulations (e.g., CO_2/hydrocarbons/water mixtures). For example, in CO_2 sequestration, an accurate phase-equilibrium calculation is the basis for predicting the amount of CO_2 dissolved in the reservoir under *in-situ* conditions. The multiphase equilibrium calculation of water-containing systems remains a challenge due to the initialization and convergence problem of the stability test and flash calculations [3]. The most common way to bypass these issues is to neglect the influence of the aqueous phase and consider only two phases instead of a real three-phase equilibrium [4]. However, several researchers mentioned that in compositional simulations, the use of two-phase equilibrium calculation only is significantly different from that being applied to a three-phase flash calculation, resulting in a non-convergence of the simulation because of the inconsistent change of the physical properties [5-8].

In 2010, Lapene *et al.* [4] developed a new three-phase free-water method with a modified Rachford-Rice equation [9], which was applied in the simulation of some thermal recovery processes. The approach is based on the assumption that only water is considered in the aqueous phase because of the ultra-small solubility of hydrocarbons (typically in the order of 10^{-4}) in the aqueous phase. Hence, the inner loop of the flash calculation can be simply regarded as a pseudo-two-phase problem. Their newly modified RR function guarantees the convergence of the inner loop as it is decreasing monotonically between two adjacent asymptotes, while the previous formulation of RR function is not monotonic and can lead to some convergence problems in some specific cases [4, 10]. However, this new algorithm cannot be applicable for the CO_2/hydrocarbons/water mixtures because the dissolution of CO_2 in the aqueous phase can be significant under reservoir conditions; as a result, the pure-water assumption results in an inaccurate solution of the phase equilibrium calculations.

To simulate the phase behavior of the CO_2/hydrocarbons/water mixtures, we propose an augmented free-water method to take the solubility of CO_2 in the aqueous phase into account. The major novelty in our algorithm is that the CO_2 dissolution can be effectively approximated with our algorithm, while the conventional free-water approach neglects CO_2 solubility in the aqueous phase. Additionally, the augmented three-phase free-water algorithm has been coupled into a flash package that can handle single-phase, two-phase and three-phase equilibria. This proposed flash package combines the classical stability test and negative flash together so that the overall computational cost is decreased without compromising its robustness and accuracy. Compared with the free-water three-phase flash method, the augmented free-water flash algorithm provides more accurate representation of the true multiphase equilibrium than the original free-water approach.

2.2. Mathematical Formulations for Multiphase Split Calculations

In multiphase equilibrium, the following equations must be satisfied for the purpose of minimizing the Gibbs free energy of the mixtures to obtain the phase equilibrium [11]:

$$f_{ix} = f_{iy} = f_{iw},\ i = 1,\ldots,N_c \tag{1}$$

where f_{ix} is the fugacity of component *i* in phase *x*, f_{iy} is the fugacity of component *i* in phase *y*, f_{iw} is the fugacity of component *i* in phase *w*, N_c is the number of components, *x*, *y*, and *w* represent the oleic phase, vapor phase and aqueous phase, respectively. The fugacity-equality equations in terms of fugacity coefficient are shown as follows:

$$\ln\left(x_i\varphi_{ix}\right) - \ln\left(y_i\varphi_{iy}\right) = \ln\left(x_i\varphi_{ix}\right) - \ln\left(w_i\varphi_{iw}\right) = 0,\ i = 1,\ldots,N_c \tag{2}$$

where x_i, y_i and w_i are molar compositions of component *i* in the oleic phase, vapor phase and aqueous phase, respectively, φ_{ix}, φ_{iy} and φ_{iw} are the fugacity coefficients of the i^{th} component in the oleic phase, vapor phase and aqueous phase, respectively. Here we choose the hydrocarbon-rich phase as the reference phase, the equilibrium ratios can be defined as:

$$\begin{cases} K_{iy} = \dfrac{y_i}{x_i} = \dfrac{\varphi_{ix}}{\varphi_{iy}} \\ K_{iw} = \dfrac{w_i}{x_i} = \dfrac{\varphi_{ix}}{\varphi_{iw}} \end{cases} \tag{3}$$

where K_{iy} is the equilibrium ratio of the i^{th} component in the vapor phase with respect to the oleic phase, and K_{iw} is the equilibrium ratio of the i^{th} component in the aqueous phase with respect to the oleic phase.

In the augmented free-water assumption, the aqueous phase consists of water and CO_2 only. Namely, the w_i for the other components are 0. In this case, the set of equilibrium ratios in the aqueous phase with respect to the oleic phase contain only two K values, i.e., K_{ww} and $K_{CO_2 w}$ for water and CO_2, respectively. The material balance equations can be obtained for the mixtures,

$$\begin{cases} z_i = \beta_x x_i + \beta_y y_i + \beta_w w_i,\ i = \text{water, CO}_2 \\ z_i = \beta_x x_i + \beta_y y_i,\ i \neq \text{water, CO}_2 \end{cases} \tag{4}$$

$$\beta_x + \beta_y + \beta_w = 1 \tag{5}$$

where z_i is the fraction of i^{th} component in the feed, β_x, β_y and β_w are the fractions of the hydrocarbon-rich liquid phase, the vapor phase and the aqueous phase, respectively.

Then we can obtain the following RR equations:

$$\begin{cases} \sum_{i=1}^{N_c} \left(x_i - y_i \right) = 0 \\ \sum_{i=1}^{N_c} \left(x_i \right) - w_w - w_{CO_2} = 0 \end{cases} \tag{6}$$

The molar compositions in the oleic phase can be obtained by combining Eqs. 3, 4, and 5:

$$\begin{cases} x_i = \dfrac{z_i}{1+\beta_y\left(K_{iy}-1\right)-\beta_w}, \ i \neq \text{water, CO}_2 \\ x_i = \dfrac{z_i}{1+\beta_y\left(K_{iy}-1\right)+\beta_w\left(K_{iw}-1\right)}, \ i = \text{water, CO}_2 \end{cases} \tag{7}$$

By substituting Eq. 7 to Eq. 6, the newly modified RR equations are given as,

$$\begin{cases} RR_y : \dfrac{z_w\left(1-K_{wy}\right)}{1+\beta_y\left(K_{wy}-1\right)+\beta_w\left(K_{ww}-1\right)} + \dfrac{z_{\text{CO}_2}\left(1-K_{\text{CO}_2 y}\right)}{1+\beta_y\left(K_{\text{CO}_2 y}-1\right)+\beta_w\left(K_{\text{CO}_2 w}-1\right)} \\ + \sum\limits_{\substack{i\neq\text{water} \\ i\neq\text{CO}_2}}^{N_c} \dfrac{z_i\left(1-K_{iy}\right)}{1+\beta_y\left(K_{iy}-1\right)-\beta_w} = 0 \\ RR_w : \dfrac{z_w\left(1-K_{ww}\right)}{1+\beta_y\left(K_{wy}-1\right)+\beta_w\left(K_{ww}-1\right)} + \dfrac{z_{CO_2}\left(1-K_{\text{CO}_2 w}\right)}{1+\beta_y\left(K_{\text{CO}_2 y}-1\right)+\beta_w\left(K_{\text{CO}_2 w}-1\right)} \\ + \sum\limits_{\substack{i\neq\text{water} \\ i\neq\text{CO}_2}}^{N_c} \dfrac{z_i}{1+\beta_y\left(K_{iy}-1\right)-\beta_w} = 0 \end{cases} \tag{8}$$

The two RR equations given in formula 8 are solved in the inner loop of the three-phase split algorithm. In this work, we solve the two RR equations based on a minimization method which originated from the works by Michelsen [12] and Okuno *et al.* [13]. Leibovici and Nichita [14] firstly presented an approach to solving the phase fractions by minimizing the objective function subjected to the feasible region proposed by Leibovici and Neoschil [15]. In order to improve the robustness of the RR algorithm, Okuno *et al.* [13] developed a new set of constraints that result in a smaller feasible region. These new constraints are derived based on the fact that all of the phase-component mole fractions are within the range of [0, 1]. They applied both positive and negative flashes in their algorithm. According to Okuno *et al.* [13], the mathematical formulation of the objective function and constraints for a three-phase equilibrium calculation are given as below,

$$\begin{cases} \text{minimize}: \; F\left(\beta\right) = \sum_{i=1}^{N_c} \text{-} z_i \ln\left[1 \text{-} \beta_y\left(1 \text{-} K_{iy}\right) \text{-} \beta_w\left(1 \text{-} K_{iw}\right)\right] \\ \text{subject to}: \; \beta_y\left(1 \text{-} K_{iy}\right) + \beta_w\left(1 \text{-} K_{iw}\right) \leq \min\left\{1 \text{-} z_i, 1 \text{-} K_{iy} z_i, 1 \text{-} K_{iw} z_i\right\}, \; i = 1, \ldots, N_c \end{cases} \tag{9}$$

The above objective function contains $2N_c+2$ variables. Considering the augmented free-water concept where only CO_2 and water are present in the aqueous phase, the objective function and constraints given by formula 9 can be simplified as:

$$\begin{cases} \text{minimize}: \; F\left(\beta\right) = \sum_{\substack{i \neq water \\ i \neq CO_2}}^{N_c} -z_i \ln\left[1 - \beta_y\left(1 - K_{iy}\right) - \beta_w\right] \\ +\left(-z_w\right)\ln\left|1 - \beta_y\left(1 - K_{wy}\right) - \beta_w\left(1 - K_{ww}\right)\right| + \left(-z_{CO_2}\right)\ln\left|1 - \beta_y\left(1 - K_{CO_2 y}\right) - \beta_w\left(1 - K_{CO_2 w}\right)\right| \\ \text{subject to}: \; \begin{cases} \beta_y\left(1 - K_{iy}\right) + \beta_w \leq \min\left\{1 - z_i, 1 - K_{iy} z_i\right\}, \; i \neq water, \; CO_2 \\ \beta_y\left(1 - K_{wy}\right) + \beta_w\left(1 - K_{ww}\right) \leq \min\left\{1 - z_w, 1 - K_{wy} z_w, 1 - K_{ww} z_w\right\} \\ \beta_y\left(1 - K_{CO_2 y}\right) + \beta_w\left(1 - K_{CO_2 w}\right) \leq \min\left\{1 - z_{CO_2}, 1 - K_{CO_2 y} z_{CO_2}, 1 - K_{CO_2 w} z_{CO_2}\right\} \end{cases} \end{cases} \tag{10}$$

The above formula can be also obtained by integrating the modified RR equation (i.e., Eq. 8). As such, the objective function contains N_c+4 variables including $\{K_{iy}\}$, K_{ww}, $K_{\mathrm{CO_2}w}$, β_y and β_w, among which the first N_c+2 variables are fed from the outer loop of the flash algorithm. The modified objective function is also convex, whose proof is similar to the one given by Michelsen [12].

2.3. Algorithm for the Augmented Free-Water Three-Phase Flash

2.3.1. Initialization of Equilibrium Ratios

For augmented free-water three-phase split calculations, the constant-*K* flash [13] is used. This three-phase split calculation consists of two iteration loops: an outer iteration loop for updating equilibrium ratios based on fugacity coefficients and an inner iteration loop for solving both phase fractions and phase compositions. Both positive flash and negative flash are adopted in this work. The Peng-Robinson equation of state (PR-EOS) is selected to perform the calculations of thermodynamic properties for the phase-split calculation [16].

Proper estimates of equilibrium ratios are prerequisite for building a robust and efficient algorithm. If the previous time-step in numerical simulations cannot provide a good initial guess, the Wilson correlation can be used to set the initial equilibrium ratios [17]:

$$K_{iy} = \frac{p_{ci}}{p} \exp\left[5.37\left(1+\omega_i\right)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{11}$$

where p_{ci}, ω_i and T_{ci} represent the critical pressure, acentric factor and critical temperature of the i^{th} component, respectively, T and P represent the system's temperature and pressure, respectively. We use the correlation proposed by Lapene *et al.* to estimate the equilibrium ratio for the water component in the gas phase with respect to the aqueous phase [4]:

$$K_{wy} = \frac{p}{p_{cw}} \frac{T_{cw}}{T} \tag{12}$$

We also find that Eq. 12 performs better for the flash calculations for CO_2/hydrocarbons/water mixtures than the one originally proposed by Peng and Robinson [3]. The initial guess of water fraction in the vapor phase is based on the correlation proposed by Lapene *et al.* [4],

$$y_w = \frac{p_{sat}^{w}}{p} \tag{13}$$

where p_{sat}^{w} is the saturation pressure of pure water that can be calculated by an empirical correlation given by Bridgeman and Aldrich [18]. Based on the definition of the equilibrium ratios, we can obtain:

$$x_w = \frac{w_w}{K_{ww}} \tag{14}$$

$$K_{wy} = \frac{y_w}{x_w} \tag{15}$$

The equilibrium ratio of water in the aqueous phase with respect to the oleic phase is,

$$K_{ww} = \frac{K_{wy}}{y_w} w_w \tag{16}$$

Here, the initial value of w_w can be set to 1 when the pressure of interest is relatively low. However, a lower value of K_{ww} can be expected at higher pressures where CO_2 dissolution becomes significant, leading to convergence issues of the algorithm. Based on the solutions provided by the conventional full three-phase flash calculations, we propose an empirical approach as follows: if the K_{ww} calculated from Eq. 16 is smaller than 3.2, then the new K_{ww} value will be replaced by,

$$K_{ww}^{'} = -0.1K_{ww}^{2} + 1.9K_{ww} \tag{17}$$

where K_{ww} is evaluated based on Eq. 16. As for the equilibrium ratio of CO_2 in the aqueous phase with respect to the oleic phase, we propose another empirical correlation that shows a superior performance in guaranteeing convergence:

$$K_{\mathrm{CO_2}w} = \frac{0.5}{K_{ww}} \tag{18}$$

2.3.2. Flash Package Incorporating the Augmented Free-Water Three-Phase Flash Algorithm

This new augmented free-water three-phase flash algorithm is incorporated into a flash package where single-phase, two-phase, and three-phase equilibria can be all considered. In the conventional approach, a stability test is always performed prior to the split calculation because the possibility to perform a further flash calculation depends on the value of tangent plane distance (*TPD*). The solution of the *TPD* function can also provide an initial estimation for the split calculation. It is suggested to use the (N_c+4) sets of initial estimates [19] in the stability analysis to increase the possibility of locating the global minimum in the Gibbs free energy. However, the use of such exhaustive approach leads to an undesirable computational cost for multiphase equilibrium calculations (e.g., a three-phase equilibrium calculation), which prevents its wide use in commercial compositional simulators.

For the purpose of improving the computational efficiency, we propose an approach to reducing the number of stability tests without losing robustness and efficiency based on the negative flash method. Negative flash was firstly proposed by Whitson and Michelsen [20]. In order to cover the negative flash region, Leibovici and Nichita [14] extended Michelsen's multiphase flash method [13] by replacing the bound-constrained minimization of Michelsen's convex function with a linearly-constrained unbounded minimization of the same function. Iranshahr *et al.* [21] developed a multi-stage negative-flash procedure to identify the state of a mixture for which the maximum number of phases is arbitrary. Yan and Stenby [22] solved the multiphase negative flash for ideal solutions by an unconstrained minimization method. Recently, Hinojosa-Gomez *et al.* [23] proposed a robust and stable improved algorithm for vapor-liquid-liquid flash calculations based on the combined use of the inverse barrier function method and negative flash; their solution is able to suggest that the system has fewer phases if the calculated phase fractions stay outside the three-phase physical domain. To sum up, one distinct advantage of negative flash lies in that, unlike the conventional flash, it can be conducted without the phases being deleted or added [22].

Given that: 1) the number of variables are reduced by the augmented three-phase free-water flash calculation from $2N_c$+2 to N_c+4, and 2) all the initial estimates of equilibrium ratios we need to perform a three-phase flash calculation are determined by empirical formulas, the three-phase flash calculation can be directly initiated without necessarily conducting the two-phase spilt calculation if the feed is proven to be unstable. The flow chart of this algorithm is shown in **Figure 2.1** and the procedure of the algorithm is briefly explained as follows:

Perform the stability test for the feed compositions with N_c+4 initial guesses of equilibrium ratios. The expression of *TPD* function was proposed by Michelsen [24]:

$$TPD = 1 + \sum_{i=1}^{C} Y_i \left[\ln\phi_i\left(\vec{Y}\right) + \ln Y_i - \ln\phi_i\left(\vec{z}\right) - \ln z_i - 1 \right] \tag{19}$$

$$y_i = \frac{Y_i}{\sum_{i=1}^{C} Y_i} \tag{20}$$

where y_i is the mole fraction of the i^{th} component in the trial phase, and Y_i is formally the mole number of the i^{th} component. We use the equilibrium ratios to properly initialize the trial phase compositions,

$$Y_i = K_i^{\text{stab}} z_i \tag{21}$$

Inspired by the works by Michelsen [24] and Cañas-Marín *et al.* [25], Li and Firoozabadi [19] proposed the use of N_c+4 sets of initial guesses of K_i^{stab} for stability testing:

$$\left\{K_i^{\text{stab}}\right\} = \left[\left\{K_i^{\text{Wilson}}\right\}, \left\{\frac{1}{K_i^{\text{Wilson}}}\right\}, \left\{\sqrt[3]{K_i^{\text{Wilson}}}\right\}, \left\{\frac{1}{\sqrt[3]{K_i^{\text{Wilson}}}}\right\}, \left\{K_i^{\text{new}}\right\}\right] \tag{22}$$

where

$$\begin{cases} K_i^{\text{new}} = \dfrac{0.9}{z_i} \\ K_j^{\text{new}} = \dfrac{\frac{0.1}{N_c - 1}}{z_j} \quad \left(j \neq i\right) \end{cases} \tag{23}$$

where K_i^{Wilson} refer to the equilibrium ratios given by the Wilson correlation.

We use these N_c+4 sets of initial guesses for performing stability test on the feed. If the value of *TPD* is non-negative, the feed is stable; otherwise, it is unstable.

If the instability of the feed is detected (i.e., *TPD*<0), the augmented free-water three-phase flash calculation is executed.

If the final results of phase fractions calculated by the augmented free-water three-phase algorithm are shown to be unphysical (e.g. beyond the range of [0, 1]) or an open feasible region is discovered during the successive substitution iteration, a two-phase split calculation is required.

Given the feed composition, the CO_2/hydrocarbons/water mixtures can be single-phase, two-phase or three-phase. In order to guarantee the correctness and robustness of the results obtained by the augmented three-phase flash, a reasonable switching criterion is developed to judge whether the phase is stable and how to distinguish between the different circumstances. In the augmented free-water method, the maximum phase number is set to be three, which becomes one of the preconditions to conduct three-phase algorithm directly. By combining the conventional stability analysis and the negative flash, we firstly check the stability of the feed, and perform the augmented three-phase free-water flash algorithm if the instability is indicated. Newton with line search method is used to minimize the objective function.

Appendix A shows the flow chart of the augmented free-water three-phase algorithm. This newly proposed algorithm with Newton's iterations and successive substitution iterations consists of two iteration loops: the inner iteration loop and the outer iteration loop. *K*-values are updated in the outer loop, while the phase fractions and phase compositions are solved in the inner loop to satisfy the RR equations. Furthermore, three different cases can be encountered when we are running the augmented free-water three-phase algorithm.

The first case is that all of the phase mole fractions and phase compositions lie in [0, 1], which indicates that a three-phase equilibrium exists. The second case is that the phase mole fractions are beyond [0, 1], while the phase compositions fall within [0, 1]. Although the phase fractions are unphysical, the algorithm still yields nonnegative compositions, with material balance and fugacity equations being satisfied. Under this circumstance, we proceed with a lower level of phase split calculation, i.e., a two-phase split. The third case corresponds to an open feasible region of phase fractions that might occur in the inner iteration loop using the Newton and line search method. In the RR equations, the trivial solution will appear if either $\{K_{iy}\}=\{1\}$ or $\{K_{iw}\}=\{1\}$. Moreover, if one set of the K value becomes 1, the constraints of its related phase fractions will no longer exist, resulting in an open feasible region. Therefore, if an open feasible region occurs in any of the inner iteration loop, the solution of the minimization is considered as having a trivial solution only. Under this circumstance, we switch to a two-phase split.

Convergence issues may also occur in three-phase split calculations due to the existence of saddle points. A similar issue is mentioned by other researchers in *TPD* analysis [19, 26] and is possibly because the *TPD* surface only contains saddle points and trivial solutions, and a considerable number of iterations are needed to escape the saddle points. In this work, we set the maximum number of iterations to 1000, and the solution is regarded as trivial if the number of iterations is higher than 1000.

2.4. Results and Discussion

Three representative mixtures, containing one water/CO_2/C_1/n-C_{16} mixture and two reservoir fluid/water/CO_2 mixtures, are used as examples to validate the robustness, accuracy, and efficiency of the newly developed augmented free-water flash algorithm for CO_2/hydrocarbons/water mixtures. We compare the performance of the new algorithm against both the free-water three-phase flash algorithm and the conventional three-phase flash algorithm.

Herein, the so-called conventional three-phase flash algorithm relies on the use of stability test and considers the presence of all the components in the aqueous phase. The effect of introducing water on the phase behavior of CO_2/hydrocarbons/water mixtures is also discussed.

2.4.1. Comparison of Robustness and Accuracy of Augmented Free-water Three-Phase Flash Algorithm, Free-water Three-phase Flash Algorithm and Conventional Three-phase Flash Algorithm

2.4.1.1. Water/CO_2/C_1/n-C_{16} Mixture

This synthetic mixture consists of pure water, CO_2, CH_4, and n-C_{16}. The properties of the pure components and the binary interaction parameters (BIPs) are detailed in **Table 2.1**. This case was also used by Mohebbinia *et al*. [2] to investigate the four-phase region when water is introduced into the mixtures at low temperatures. Here we choose the feeds that avoid the presence of four-phase region. **Figure 2.2 (a)** compares the mole fractions of individual components as calculated by the augmented free-water method and those calculated by the conventional full three-phase flash method at P=100 bar and different temperatures. **Figure 2.2 (b)** shows the same comparison for the oleic phase. The absolute deviations of the mole fractions between those two methods are presented in **Figure 2.3 (a)** for the gas phase and **Figure 2.3 (b)** for the oleic phase, respectively. The largest absolute deviations are found to be 9.9×10^{-5} in the gas phase and 3.7×10^{-5} in the oleic phase, respectively, showcasing an accurate prediction of the phase compositions as given by the augmented free-water three-phase flash method. **Figure 2.4** compares the phase fractions of each phase calculated by the augmented free-water method and the conventional three-phase flash method at P=100 bar and different temperatures, while **Figure 2.5** shows the absolute deviations of phase fractions between these two methods. A good agreement of phase fractions calculated by these two methods can be clearly observed in **Figure 2.5**.

2.4.1.2. Water/CO$_2$/North Ward Estes (NWE) Oil Mixture

The augmented free-water flash calculation is applied to assess the phase behavior of water/CO$_2$/NEW-oil/ mixtures; the properties of the reservoir fluids are calculated by the fluid characterization method presented by Khan *et al.* [5]. **Table 2.2** lists the component properties, while **Table 2.3** lists the BIPs used in the PR EOS model. In this case, the feed is comprised of water, CO$_2$ and NWE-oil with the molar ratios of water:CO$_2$:NWE oil being equal to 2:1:1. The BIPs for the non-aqueous phase are based on Khan *et al.* [5], while the BIPs for the aqueous phase are from Mohebbinia *et al.* [2].

Figure 2.6 shows the three-phase envelopes for the water/CO$_2$/NWE-oil mixture as calculated by the conventional three-phase flash method, free-water method and augmented free-water method, respectively. **Figure 2.6** also shows the two-phase envelope calculated for the CO$_2$/NWE oil mixture; the large difference between the two-phase envelope and the three-phase envelope indicates that the presence of water has a large impact on the phase behavior of the CO$_2$/NWE oil mixture. It can be seen from **Figure 2.6** that our augmented free-water method gives a three-phase envelope that matches well with that calculated by the conventional three-phase flash method, while the free-water method provides a phase envelope that is deviating from the one calculated by the conventional flash.

Figure 2.7 plots the phase fractions calculated by the above three different methods at P=400 bar. Again, the augmented free-water method provides phase-fraction predictions that are close to those by the three-phase flash method, while the free-water method provides good predictions of the phase fraction of the oleic phase, but gives less accurate predictions for the vapor phase and aqueous phase. **Figure 2.8** compares the absolute deviations of phase fractions between the augmented free-water method and free-water method in the three-phase zone at *P*=400 bar. The absolute error is calculated by subtracting the phase fraction obtained by either one of these two methods and the phase fraction obtained by the conventional three-phase flash. Note that the maximum absolute error of augmented free-water method is found to be 8.7×10^{-4}, which indicates a more accurate prediction compared to the free-water method (its maximum absolute error: 2.4×10^{-2}). **Table 2.4** shows the comparison of the phase compositions obtained by applying the augmented free-water three-phase flash method, and those by the full three-phase flash method and free-water flash method for water/CO_2/NWE oil mixture at 400 bar and 600 K. It can be observed that the compositions of the components in the aqueous phase, calculated by the conventional three-phase flash, are nearly zero except for water and CO_2. This is a further validation of the underlying assumption adopted in the new algorithm that only the presence of water and CO_2 is considered in the aqueous phase. Moreover, the gas-phase compositions calculated by the augmented free-water three-phase method are much closer to those obtained by conventional method compared to the free-water three-phase flash method; similar conclusion can be also made for the oleic phase.

Figure 2.9 compares the phase fractions calculated by performing the standalone augmented algorithm that is not coupled into the flash package and those calculated by performing the conventional three-phase flash at *T*=480 K. Note that the phase fractions obtained by the augmented free-water three-phase flash agree well with the results obtained by conventional full three-phase flash when the system is at a three-phase equilibrium. As shown by the calculation results, a two-phase equilibrium occurs when pressure is higher than 330 bar. In the two-phase zone, we can encounter two scenarios as aforementioned in Section 3.2. The first scenario refers to that the unphysical phase fractions are beyond the range of [0, 1], but still can be calculated; this corresponds to the second case as mentioned in Section 3.2. The second scenario, which is depicted in **Figure 2.9**, shows that if the pressure is close to 360 bar, the phase fractions of the gas and oleic phase tend to be infinite, resulting in an open feasible region during successive substitution iterations; this corresponds to the third case as mentioned in Section 3.2. The switching criteria introduced in Section 3.2 are deployed to deal with these two scenarios and have been used in our augmented free-water flash package. Results show that the phase boundaries calculated by our flash package with such methodology are consistent with the results obtained by the full three-phase flash method.

2.4.1.3. Water/CO_2/Bob Slaughter Block (BSB) Oil Mixture

Three-phase equilibrium calculations are conducted for a water/CO_2/BSB oil mixture. This case study uses a feed where the molar ratios of water:CO_2:BSB oil is 15:2:3. The characterization of BSB oil was given by Khan *et al.* [5]. The feed composition, the component properties and BIPs are listed in **Table 2.5** and **2.6**. The resulting phase envelopes for the water/CO_2/BSB oil mixture by the augmented free-water method, the free-water method and the conventional three-phase flash method are shown in **Figure 2.10**. It clearly shows that there is a small discrepancy between phase boundary obtained by the augmented free-water three-phase method and that by the conventional flash method at conditions of 590-620 K and 360-470 bar. This is caused by an increased solubility of other components in the aqueous phase under these conditions, while the assumption of our augmented free-water method is that only water and CO_2 exist in the aqueous phase. Nonetheless, in comparison to the free-water method, our augmented free-water method is able to compute a three-phase envelope that is more consistent with the one given by the conventional full three-phase flash method.

Table 2.7 lists the comparison between phase compositions for the water/CO2/BSB oil mixture obtained by the three methods at 220 bar and 500 K. It is obvious that the augmented free-water method yields a more accurate prediction of compositions for the oleic and gas phases compared with the free-water method.

A comparison of phase fractions given by the three methods at T=500 K is presented in **Figure 2.11**. The results show that both the augmented free-water method and the free-water method exhibit good agreement with the conventional full three-phase flash method. **Figure 2.12** gives the absolute error of phase fractions in the three-phase zone given by these two methods at T=500 K. Note that the maximum deviation given by the augmented free-water method for the gas phase is 9.19×10^{-4}. In comparison, the maximum deviation given by the free-water method is 1.83×10^{-2}; this deviation is much larger than 9.19×10^{-4}, demonstrating that the augmented free-water method is more accurate than the free-water method.

Figure 2.13 compares the phase fractions calculated by applying the standalone augmented three-phase free-water method against those calculated by applying the conventional full three-phase flash at P=220 bar. Again one can observe from Figure 13 how the switching criteria have been used to assist the determination of phase equilibrium for this mixture.

2.4.2. Comparison of Computational Efficiency between Augmented Free-Water Flash Method and Conventional Full Three-Phase Flash Method

In this section, we compare the number of iterations and computational time consumed by the augmented free-water flash method and the conventional full three-phase flash method to simulate the phase behavior of the two mixtures: the water/CO_2/NWE oil mixture and the water/CO_2/BSB oil mixture. The calculations are performed by successive substitution iterations followed by constant *K*-flash. To make consistent comparisons, we use the Newton and line search in the optimization routine used for solving the phase fractions in the inner loop of both the augmented free-water method and the conventional full three-phase flash method. As such, the differences of these two methods are embodied in the initialization of equilibrium ratios, the negative flash and the number of stability tests required.

Figure 2.14 (a) and **(b)** compare the number of iterations given by the augmented free-water method and the conventional full three-phase flash method for water/CO_2/NWE oil mixture at P=80 bar and P=400 bar, respectively. It is found from Figure 14 that a higher number of iterations will be required at higher temperature/pressure conditions. The comparison of these two methods being implemented at a given pressure shows that: 1) our approach needs a fewer number of iterations compared to the conventional approach; and 2) the reduction of iteration numbers achieved by our approach tends to be more significant at a lower temperature. Similarly, **Figure 2.15 (a)** and **(b)** present the comparison of the number of iterations given by the two methods for the water/CO_2/BSB oil mixture at P=100 bar and T=400 K, respectively. It can be clearly observed that a fewer number of iterations is required in our method to converge, which indicates it is more efficient than the conventional one.

The comparison of computational time between the augmented free-water flash package and the full three-phase flash method for the water/CO_2/NWE-oil mixture at P=250 bar is shown in **Figure 2.16**. Note that the increase in the computational cost can be found for both methods near the phase-boundary temperature. Although they have shared a similar tendency in the computational cost, the augmented one is superior since it requires less computational time.

Figure 2.17 compares the computational cost between these two methods being applied to the water/CO_2/BSB-oil mixture at P=150 bar and different temperatures. As can be seen from Figure 17, similarly, the augmented free-water flash package consumes much less computational time compared with the conventional full three-phase flash method.

2.5. Conclusions

In this work, we propose a robust and efficient algorithm to conduct three-phase flash calculations for CO_2/hydrocarbons/water mixtures based on the assumption that only CO_2 and water are present in the aqueous phase. This new augmented free-water three-phase flash algorithm is incorporated into a flash package where both positive and negative flash are allowed, and single-phase, two-phase, and three-phase equilibria can be handled. The flash package first tests the stability of the feed. If the feed is found to be stable, a single-phase equilibrium can be concluded. Otherwise, the augmented free-water three-phase algorithm is initiated. Switching criteria for the negative flash have been proposed. If the phase fractions obtained from this augmented free-water three-phase algorithm do not belong to [0, 1] or if an open feasible region occurs during the iterations, two-phase flash will be conducted.

We test the robustness and performance of the newly developed augmented algorithm, together with the flash package for several typical CO_2/hydrocarbons/water mixtures. The test results show that the augmented free-water three-phase flash algorithm can provide flash results that agree well with those given by the full three-phase flash algorithm. The augmented free-water three-phase flash algorithm is more accurate than the traditional free-water flash method since the solubility of CO_2 in the aqueous phase has been taken into account. The three-phase envelopes for CO_2/hydrocarbons/water mixtures that are calculated by using the augmented free-water three-phase algorithm is consistent with those obtained by the conventional full three-phase flash. The computational time and number of iterations are significantly decreased with the use of the new flash package featuring the augmented algorithm. This is because of the following reasons: 1) A fewer number of parameters are involved in the calculations due to the use of the augmented free-water concept; 2) the number of iterations are reduced due to a more accurate initialization of equilibrium ratios compared with the conventional method; and 3) A fewer number of stability tests are required in the new flash package compared with the conventional method.

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Nomenclature

err = error

f_{iw} = fugacity of i^{th} component in the aqueous phase

f_{ix} = fugacity of i^{th} component in the gas phase

f_{iy} = fugacity of i^{th} component in the hydrocarbon-rich phase

F = objective function

$iter$ = number of iterations

K_{CO_2w}= equilibrium ratio of CO_2 component in the aqueous phase with respect to the reference phase

K_{CO_2y} = equilibrium ratio of CO_2 component in the gas phase with respect to the reference phase

K_{iw}= equilibrium ratio of the i^{th} component in the aqueous phase with respect to the reference phase

K_{iy} = equilibrium ratio of the i^{th} component in the gas phase with respect to the reference phase

K_{ww}= equilibrium ratio of water component in the aqueous phase with respect to the reference phase

K_{wy} = equilibrium ratio of water component in the gas phase with respect to the reference phase

N_c = number of components

N_p = number of phases

P = pressure, bar

P_c = critical pressure, bar

T = temperature, K

T_c = critical temperature, K

w_i = mole fraction of i^{th} component in the aqueous phase

x_i = mole fraction of i^{th} component in the hydrocarbon-rich phase

y_i = mole fraction of i^{th} component in the gas phase

z_i = mole fraction of i^{th} component in the feed

β_w = phase fraction of the aqueous phase

β_x = phase fraction of the hydrocarbon-rich phase

β_y = phase fraction of the gas phase

φ_{iw} = fugacity coefficient of i^{th} component in the aqueous phase

φ_{ix} = fugacity coefficient of i^{th} component in the hydrocarbon-rich phase

φ_{iy} = fugacity coefficient of i^{th} component in the gas phase

ω = acentric factor

Subscripts

i = component index

j = phase index

k = phase index

w = water component index or aqueous phase index

x = hydrocarbon-rich phase index

y = gas phase index

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Appendix A: Flow Chart of the Augmented Free-Water Three-Phase Algorithm

Figure A-1 shows the flow chart of the augmented free-water three-phase algorithm.

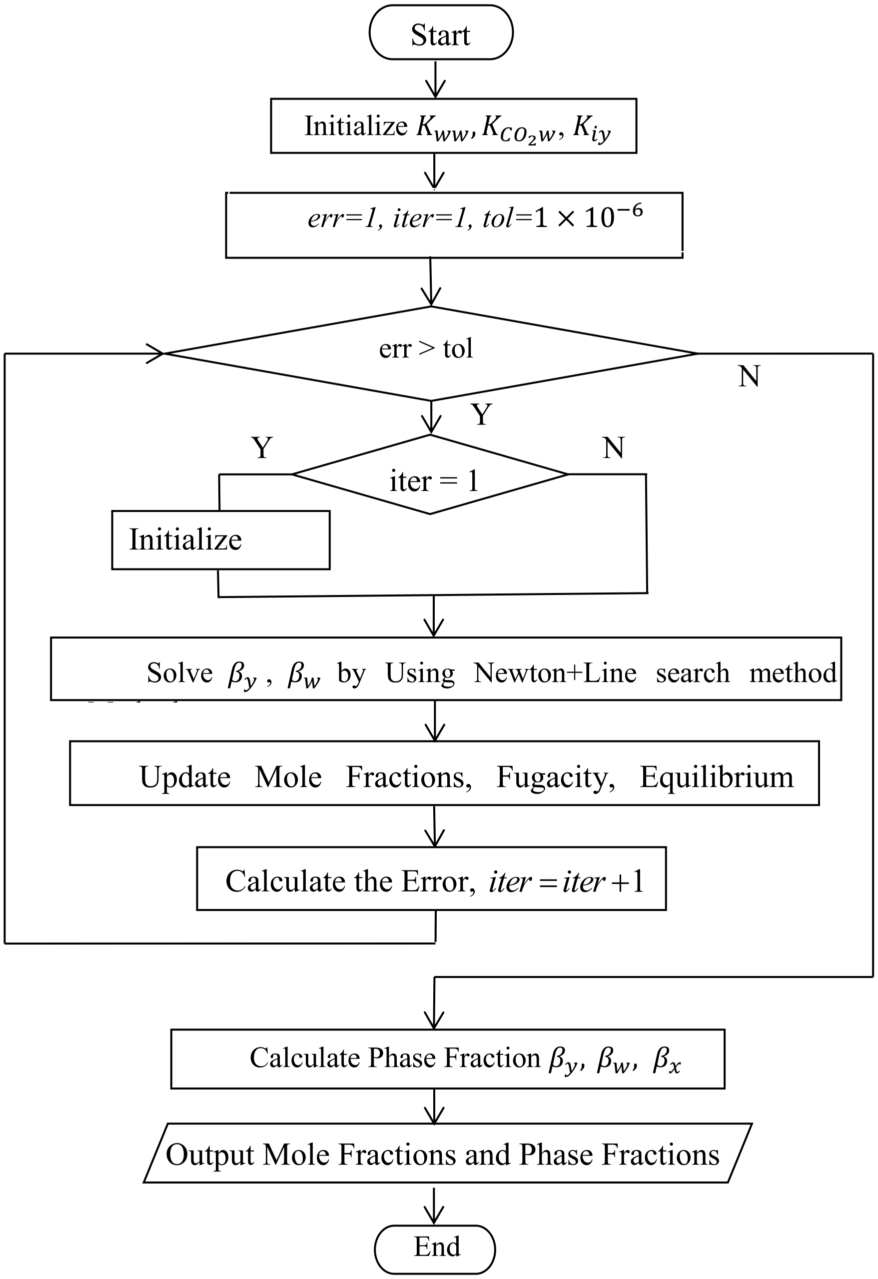


Figure A-1 Flow chart of the augmented free-water three-phase algorithm

Table 2.1 Fluid properties and BIPs for water/CO_2/C1/n-C16 mixture

Component	T_c (K)	P_c (bar)	ω	z (mol/mol)	$k_{H2O\text{-}j}$	$k_{CO2\text{-}j}$	$k_{C1\text{-}j}$	$k_{n\text{-}C16\text{-}j}$
H_2O	647.30	220.48	0.344	0.3	-	0.1896	0.4850	0.5000
CO_2	304.20	73.76	0.225	0.3	0.1896	-	0.1000	0.1250
C_1	190.60	45.96	0.008	0.1	0.4850	0.1000	-	0.0780
n-C_{16}	717.00	14.19	0.742	0.3	0.5000	0.1250	0.0780	-

Table 2.2 Fluid properties of NWE oil (Khan *et al.*, 1992)

Component	T_c (K)	P_c (bar)	ω	Mol%
CO_2	304.20	73.76	0.225	0.77
C_1	190.60	46.00	0.008	20.25
$C_{2,3}$	343.64	45.05	0.130	11.80
$C_{4\text{-}6}$	466.41	33.50	0.244	14.84
$C_{7\text{-}14}$	603.07	24.24	0.600	28.63
$C_{15\text{-}24}$	733.79	18.03	0.903	14.90
C_{25+}	923.20	17.26	1.229	8.81

Table 2.3 BIPs for water/CO_2/NWE oil mixture (Mohebbinia *et al.*, 2013)

Component	$k_{H2O\text{-}j}$	$k_{CO2\text{-}j}$
H_2O	-	0.1896
CO_2	0.1896	-
C_1	0.4850	0.1200
$C_{2,3}$	0.5000	0.1200
$C_{4\text{-}6}$	0.5000	0.1200
$C_{7\text{-}14}$	0.5000	0.0900
$C_{15\text{-}24}$	0.5000	0.0900
C_{25+}	0.5000	0.0900

Table 2.4 Comparison of phase compositions obtained by applying the augmented free-water three-phase flash method, and those obtained by applying the full three-phase flash method and free-water flash method for water/CO_2/NWE oil mixture at 400 bar and 600 K

Component	Full Three-Phase Flash			Augmented Free-Water Three-Phase Flash			Free-Water Three-Phase Flash		
	y_i (G)	x_i (O)	w_i (A)	y_i (G)	x_i (O)	w_i (A)	y_i (G)	x_i (O)	w_i (A)
H_2O	0.4504	0.3200	0.9604	0.4548	0.3208	0.9667	0.4892	0.3264	1.0000
CO_2	0.2937	0.2509	0.0361	0.2920	0.2491	0.0333	0.2801	0.2370	0.0000
C_1	0.0594	0.0526	0.0029	0.0593	0.0526	0.0000	0.0558	0.0497	0.0000
$C_{2,3}$	0.0338	0.0352	0.0005	0.0336	0.0351	0.0000	0.0314	0.0339	0.0000
$C_{4\text{-}6}$	0.0411	0.0514	0.0001	0.0407	0.0513	0.0000	0.0378	0.0506	0.0000
$C_{7\text{-}14}$	0.0745	0.1217	0.0000	0.0735	0.1219	0.0000	0.0670	0.1242	0.0000
$C_{15\text{-}24}$	0.0339	0.0858	0.0000	0.0333	0.0864	0.0000	0.0290	0.0911	0.0000
C_{25+}	0.0132	0.0823	0.0000	0.0127	0.0829	0.0000	0.0097	0.0872	0.0000

Table 2.5 Fluid properties of BSB oil (Khan *et al.*, 1992)

Component	T_c (K)	P_c (bar)	ω	Mol%
CO_2	304.22	73.77	0.225	3.37
C_1	160.00	46.00	0.008	8.61
$C_{2,3}$	344.22	45.00	0.131	15.03
C_{4-6}	463.22	34.00	0.240	16.71
C_{7-15}	605.78	21.75	0.618	33.04
C_{16-27}	751.00	16.54	0.957	16.11
C_{28+}	942.50	16.42	1.268	7.13

Table 2.6 BIPs for water/CO_2/BSB oil mixture (Mohebbinia *et al.*, 2013)

Component	k_{H2O-j}	k_{CO2-j}
H_2O	-	0.1896
CO_2	0.1896	-
C_1	0.4850	0.0550
$C_{2,3}$	0.5000	0.0550
C_{4-6}	0.5000	0.0550
C_{7-15}	0.5000	0.1050
C_{16-27}	0.5000	0.1050
C_{28+}	0.5000	0.1050

Table 2.7 Comparison of phase compositions obtained by applying the augmented free-water three-phase flash method, and those obtained by applying the full three-phase flash method and free-water flash method for water/CO_2/BSB oil mixture at 220 bar and 500 K

Component	Full Three-Phase Flash			Augmented Free-Water Three-Phase Flash			Free-Water Three-Phase Flash		
	y_i *(G)*	x_i *(O)*	w_i*(A)*	y_i *(G)*	x_i *(O)*	w_i *(A)*	y_i *(G)*	x_i *(O)*	w_i *(A)*
H_2O	0.1845	0.1145	0.9912	0.1846	0.1144	0.9916	0.1887	0.1150	1.0000
CO_2	0.4819	0.3275	0.0085	0.4812	0.3268	0.0084	0.4884	0.3292	0.0000
C_1	0.0671	0.0410	2.6709E-04	0.0680	0.0415	0.0000	0.0646	0.0391	0.0000
$C_{2,3}$	0.0882	0.0792	1.5757E-05	0.0882	0.0791	0.0000	0.0852	0.0764	0.0000
C_{4-6}	0.0749	0.0930	9.9031E-08	0.0748	0.0929	0.0000	0.0729	0.0912	0.0000
C_{7-15}	0.0868	0.1969	6.4232E-13	0.0867	0.1970	0.0000	0.0851	0.1975	0.0000
C_{16-27}	0.0517	0.1017	7.9533E-20	0.0157	0.1018	0.0000	0.0153	0.1039	0.0000
C_{28+}	9.4298E-04	0.0463	6.2682E-24	9.3589E-04	0.0464	0.0000	8.8136E-04	0.0477	0.0000

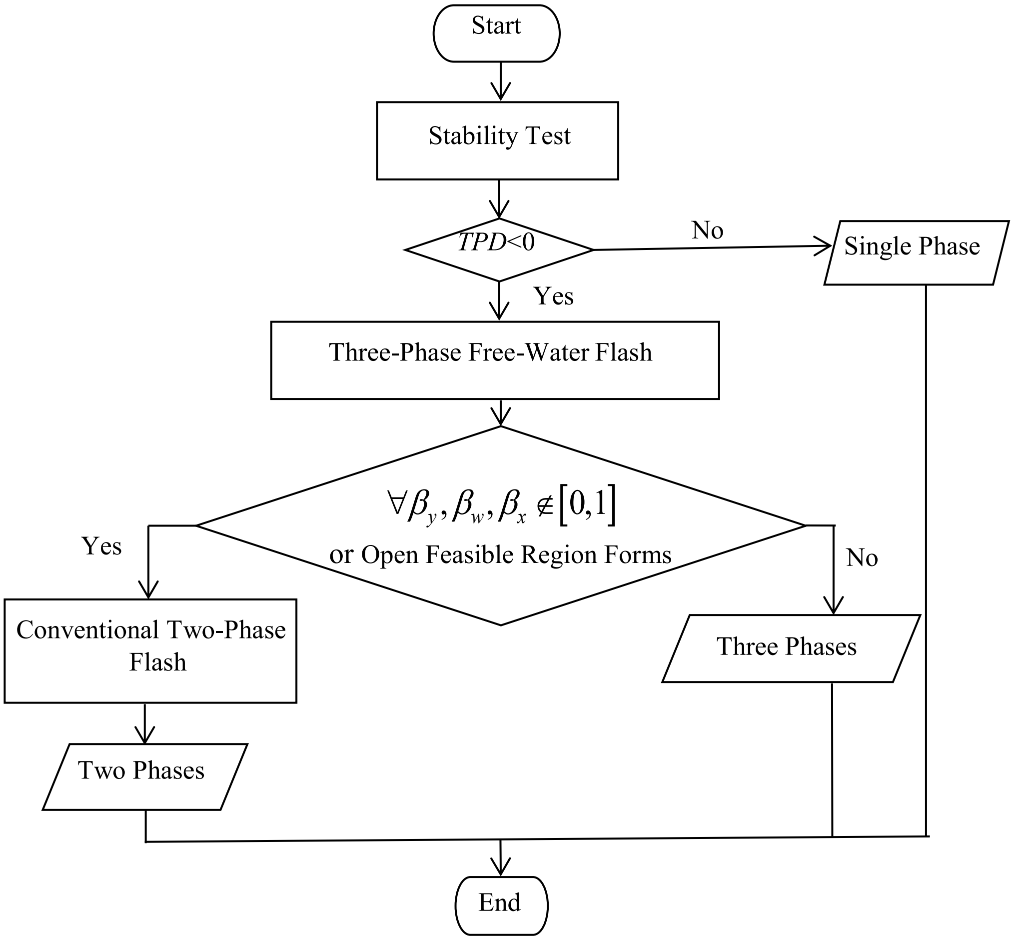
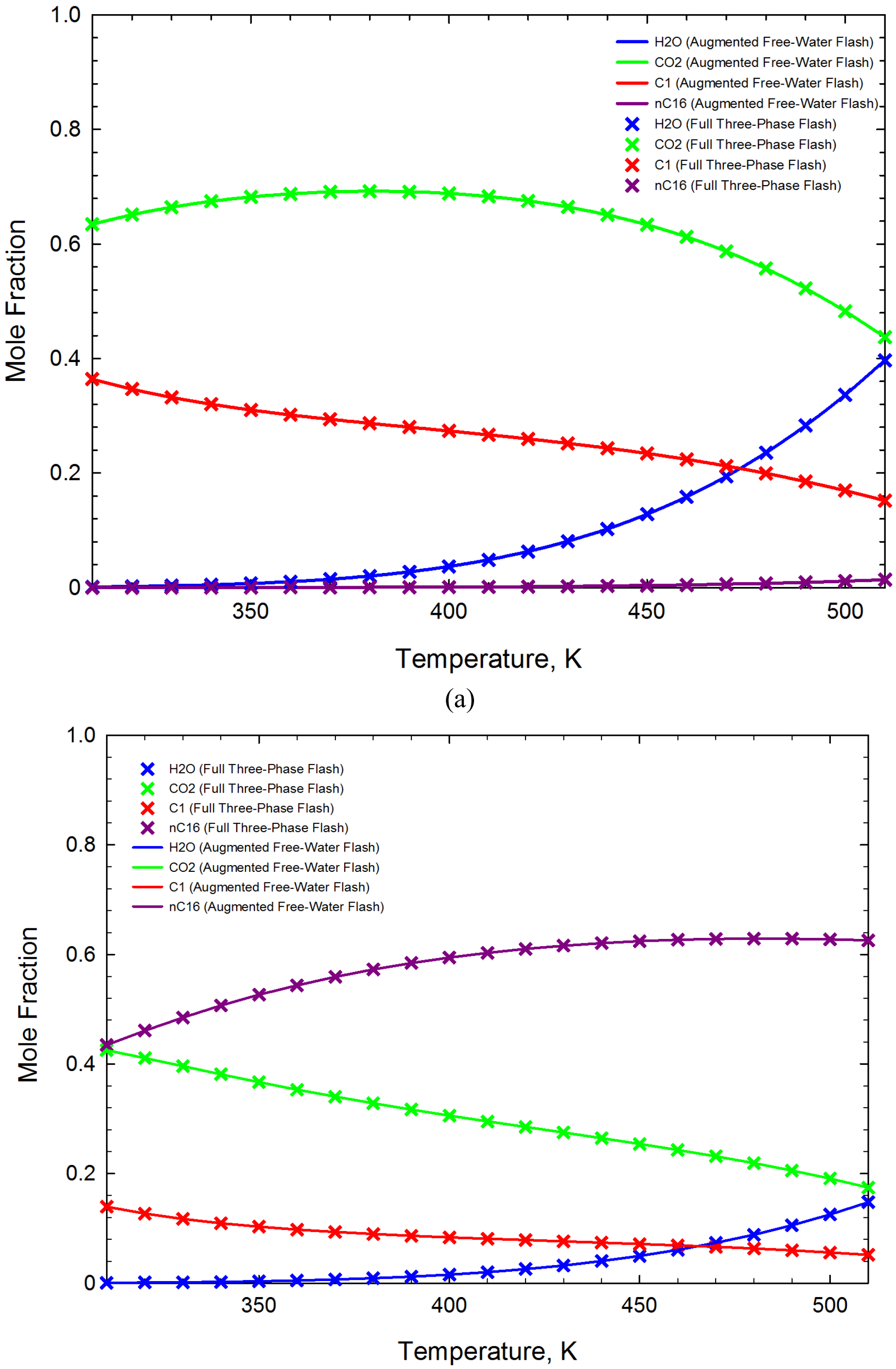


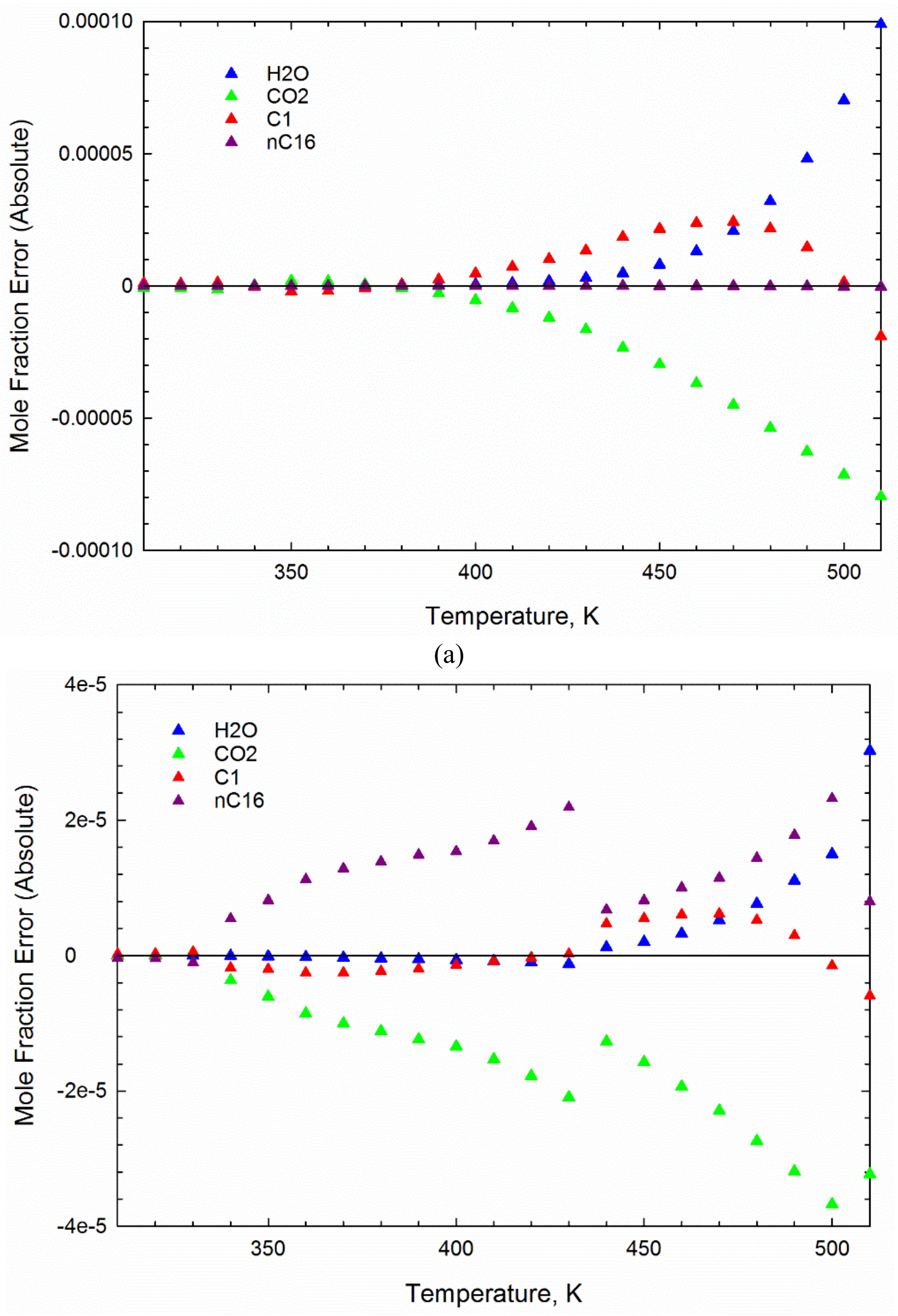
Figure 2.1 Flow chart of the new flash package for conducting augmented free-water three-phase flash and two-phase flash



(a)

(b)

Figure 2.2 Comparison of the compositions of the gas phase and the oleic phase that are calculated by the augmented free-water method and conventional full three-phase flash for water/CO_2/C_1/n-C_{16} mixture at *P*=100 bar: (a) comparison in the gas phase; and (b) comparison in the oleic phase.



(a)

(b)

Figure 2.3 Absolute deviations in the molar compositions of the gas phase and the oleic phase that are calculated by applying the augmented free-water three-phase method and those obtained by applying the full three-phase flash method for water/CO_2/C1/n-C_{16} mixture at *P*=100 bar: (a) absolute deviations in the gas phase; and (b) absolute deviations in the oleic phase.

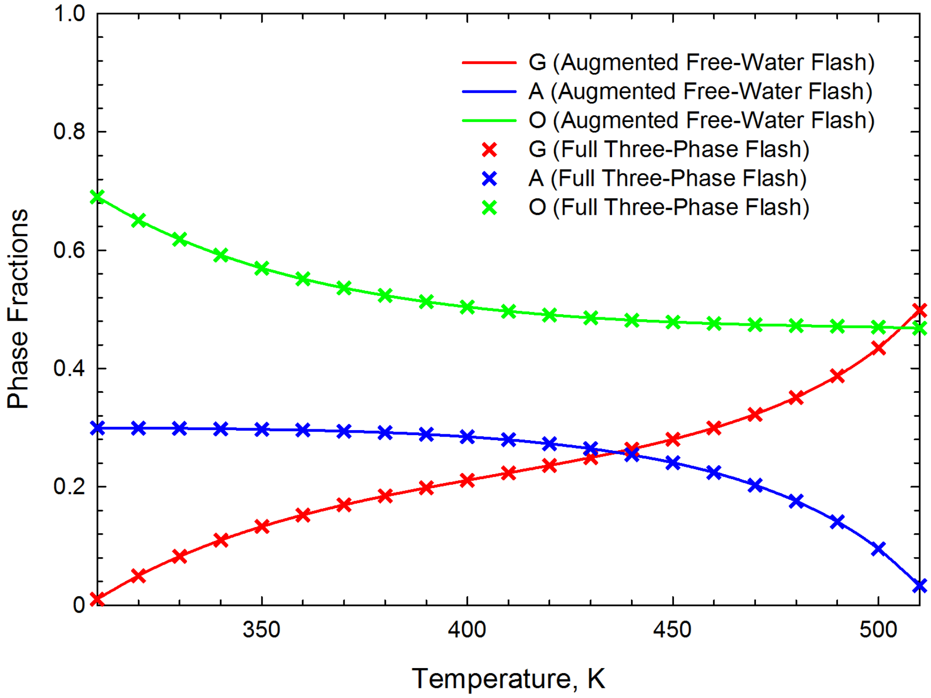


Figure 2.4 Comparison of phase fractions obtained by applying the augmented free-water three-phase method and those obtained by applying the full three-phase flash method for water/CO_2/C1/n-C_{16} mixture at P=100 bar.

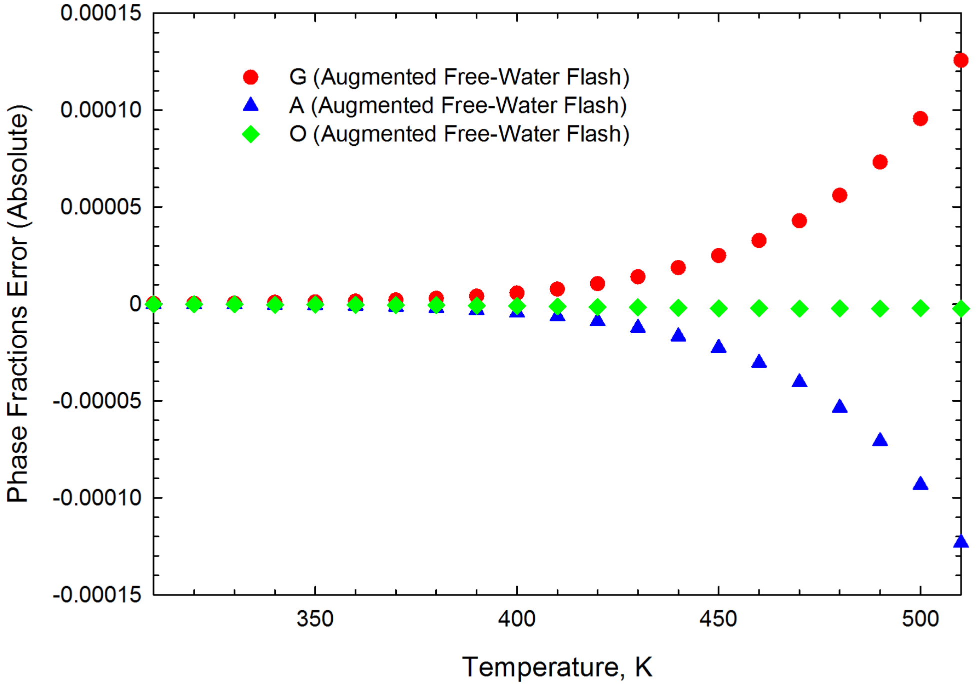


Figure 2.5 Absolute deviations of phase fractions in the three-phase zone obtained by applying the augmented free-water method and full three-phase flash method for water/CO_2/C1/n-C_{16} mixture at *P*=100 bar.

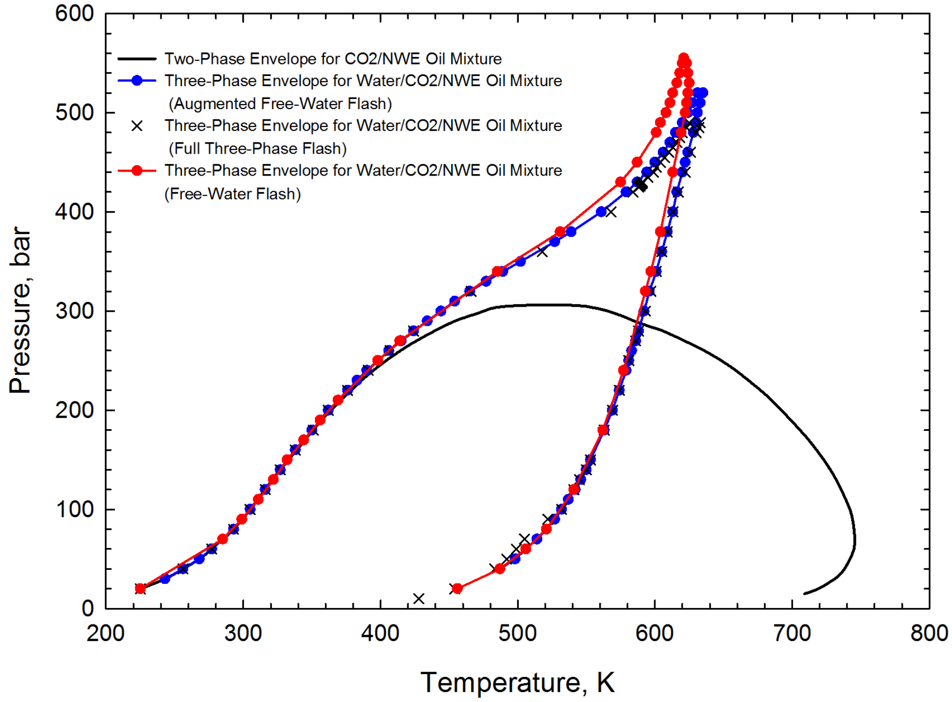


Figure 2.6 Calculated three-phase envelopes for the water/CO_2/NWE-oil mixture and two-phase envelope for the CO_2/NWE-oil mixture. The augmented free-water method, full three-phase flash method and free-water method have been used to calculate the three-phase envelopes.

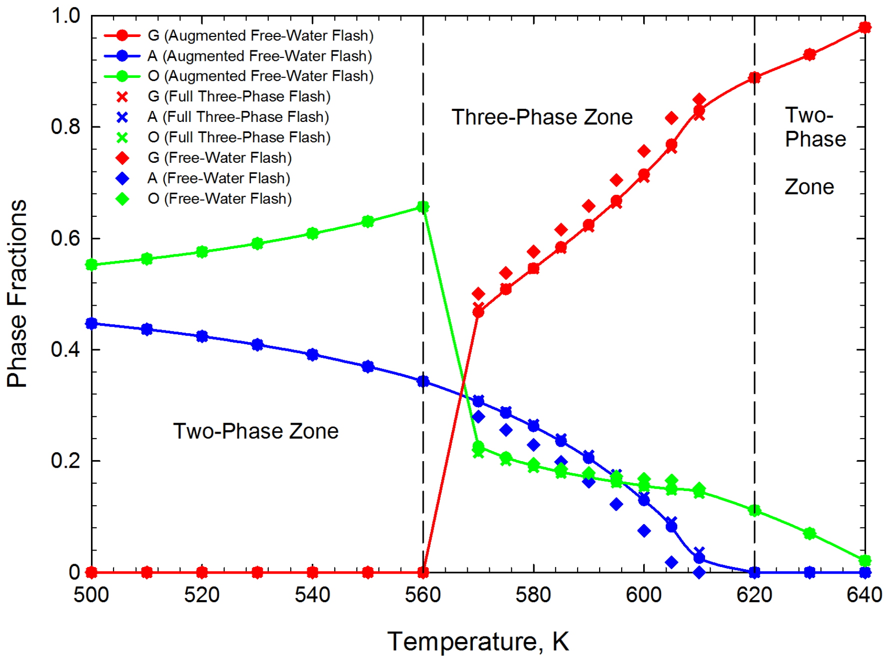


Figure 2.7 Comparison of phase fractions obtained by applying the augmented free-water three-phase method, the full three-phase flash method and the free-water method for water/CO_2/NWE-oil mixture at *P*=400 bar.

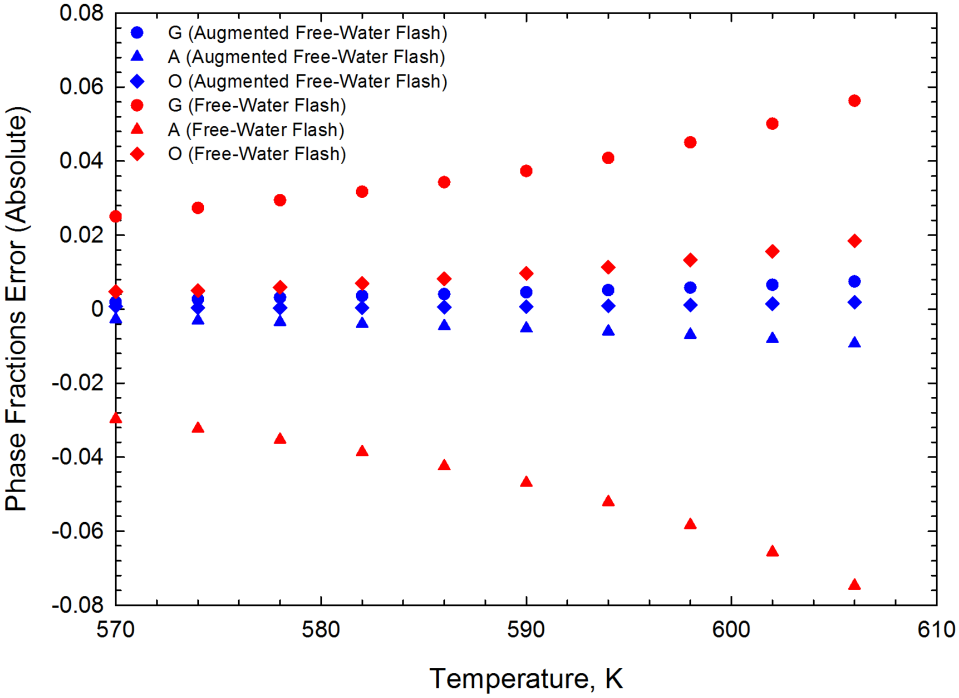


Figure 2.8 Comparison of absolute deviations of phase fractions in the three-phase zone obtained by applying the augmented free-water method, the free-water method and the full three-phase flash method for water/CO_2/NWE-oil mixture at *P*=400 bar.

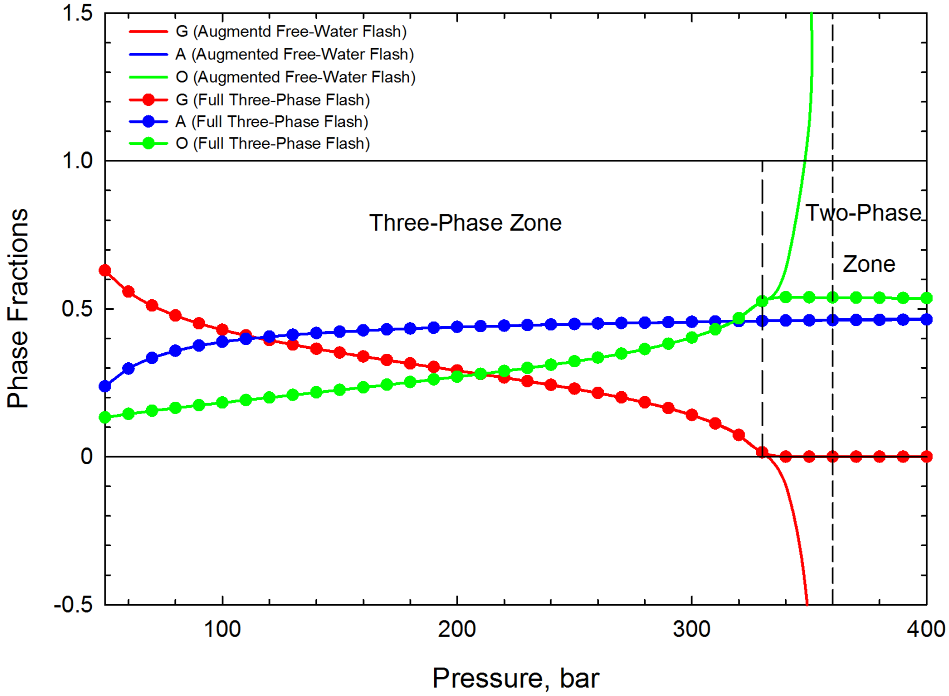


Figure 2.9 Comparison of phase fractions obtained by applying the standalone augmented free-water three-phase algorithm, the full three-phase flash method and the free-water method for the water/CO_2/NWE-oil mixture at *T*=480 K.

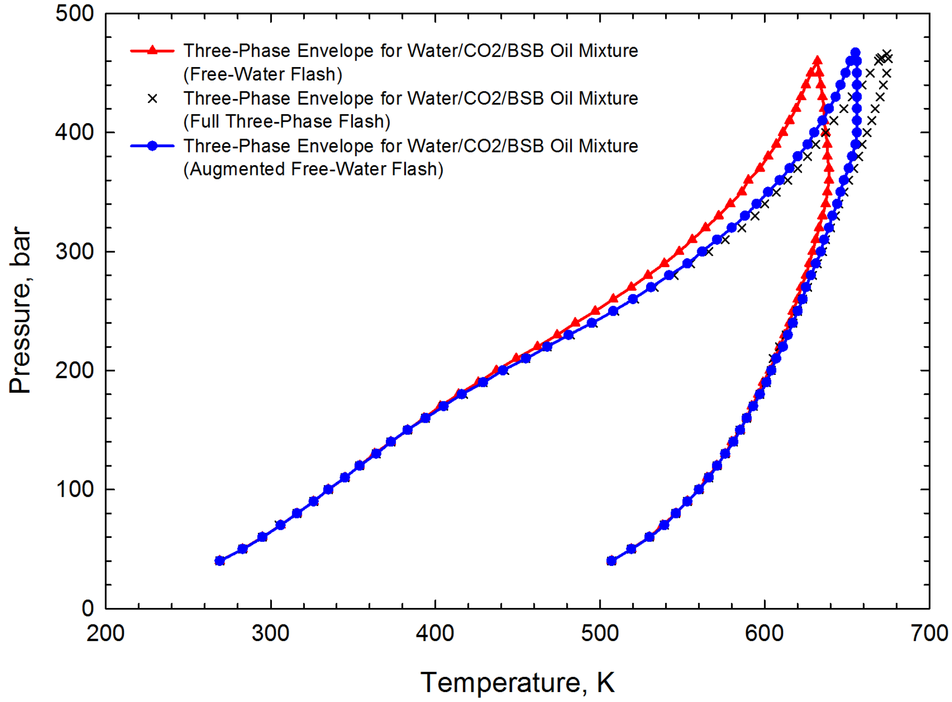


Figure 2.10 Calculated three-phase envelopes for the water/CO_2/BSB-oil mixture with the augmented free-water method, the full three-phase flash method and the free-water method.

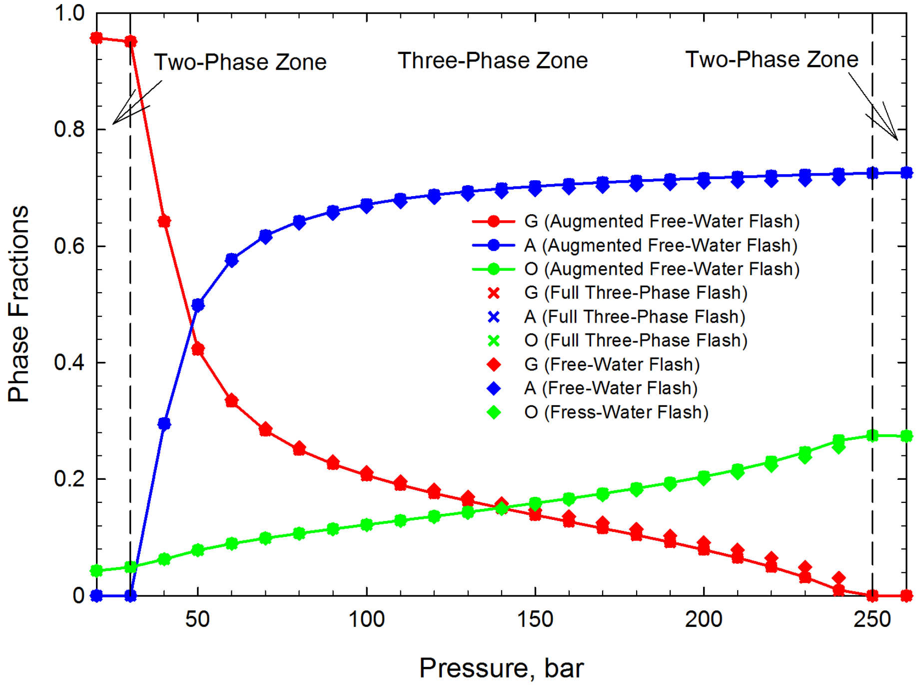


Figure 2.11 Comparison of phase fractions obtained by applying the augmented free-water three-phase method, the full three-phase flash method and the free-water method for water/CO_2/BSB-oil mixture at *T*=500 K.

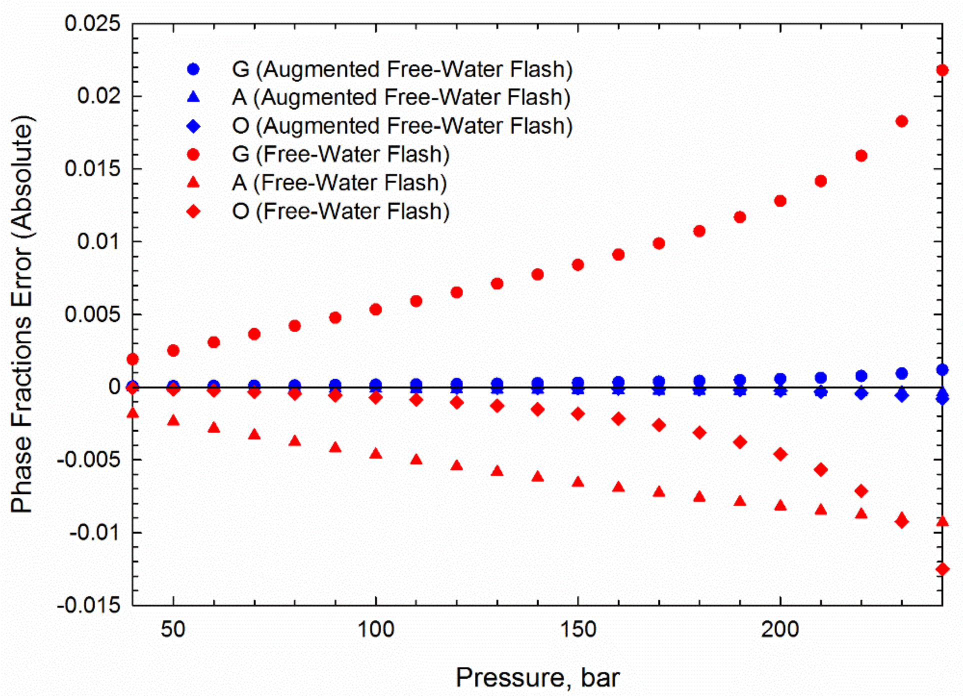


Figure 2.12 Comparison of absolute deviations of phase fractions obtained by applying the augmented free-water method, the free-water method and the full three-phase flash method in the three-phase zone for water/CO_2/BSB-oil at *T*=500 K.

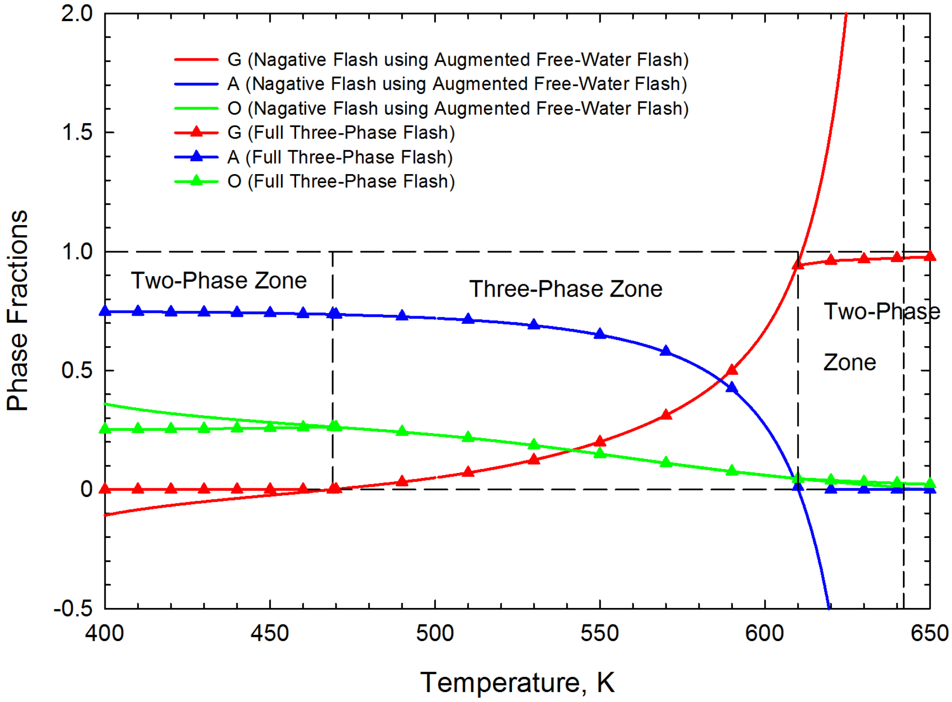
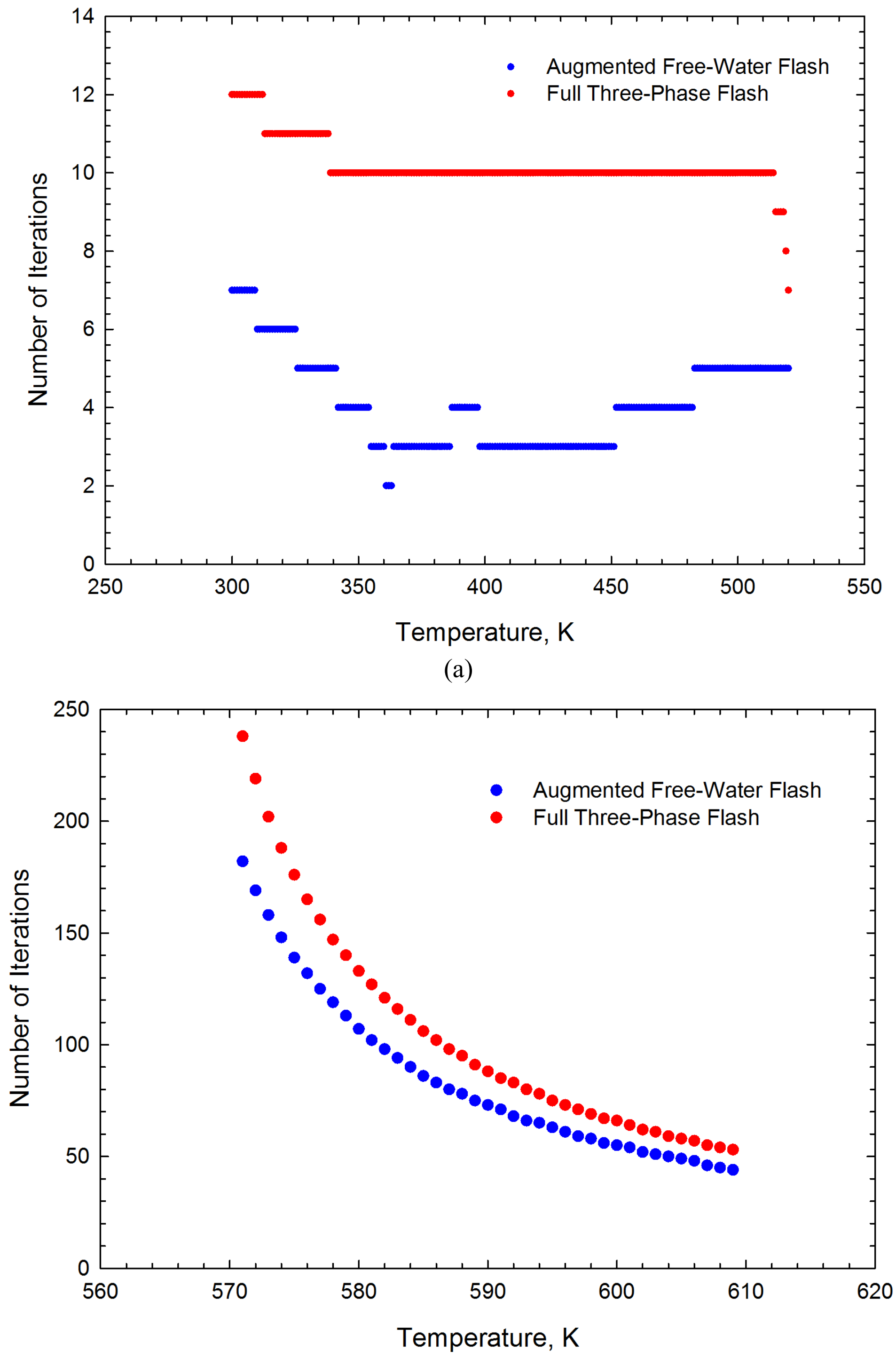


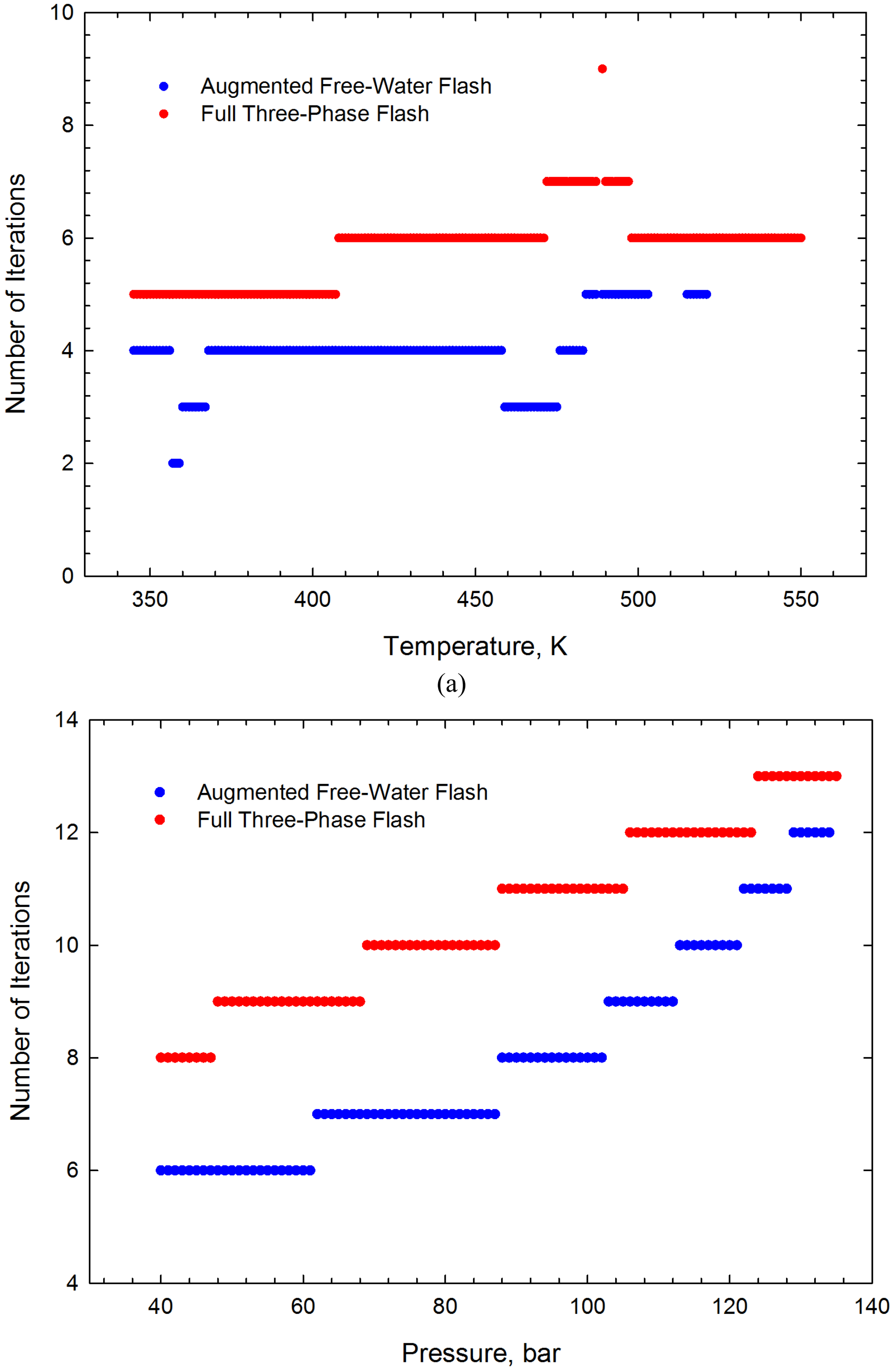
Figure 2.13 Comparison of phase fractions obtained by applying the standalone augmented free-water three-phase algorithm, the full three-phase flash method and the free-water method for the water/CO_2/BSB-oil mixture at *P*=220 bar.



(a)

(b)

Figure 2.14 Comparison between the number of iterations in the three-phase zone required by the augmented free-water three-phase algorithm and those by the full three-phase flash method for water/CO_2/NWE-oil mixture (a) at *P*=80 bar (b) at *P*=400 bar



(a)

(b)

Figure 2.15 Comparison between the number of iterations required by the augmented free-water three-phase algorithm and those by applying the full three-phase flash method for water/CO_2/BSB-oil mixture in the three-phase zone: (a) at *P*=100 bar (b) at *T*=400 K.

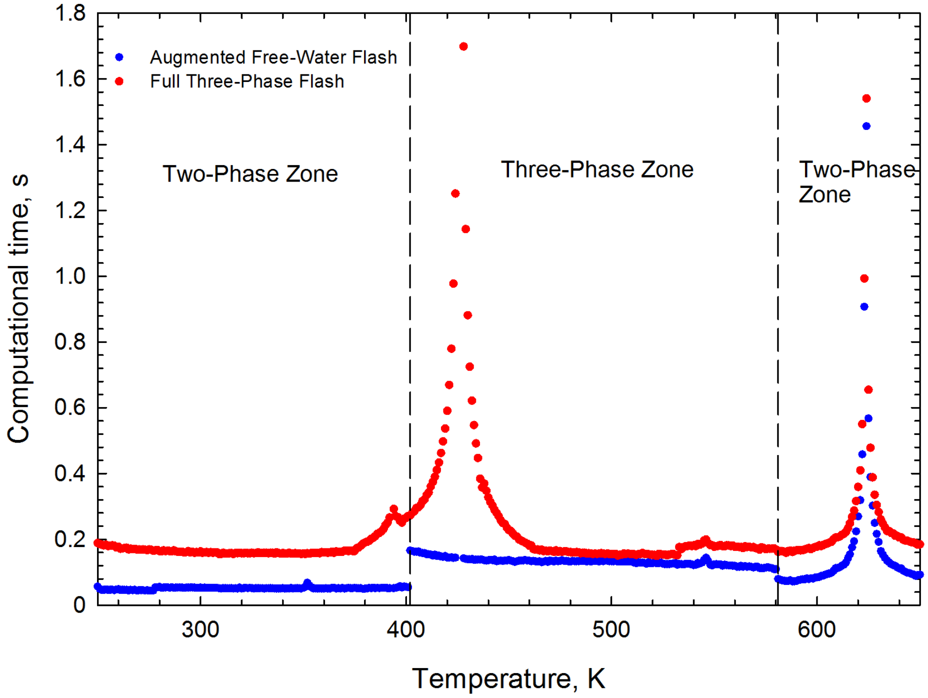


Figure 2.16 Comparison between the computational time required by the augmented free-water method and those required by the full three-phase flash method for water/CO_2/NWE-oil mixture at *P*=250 bar.

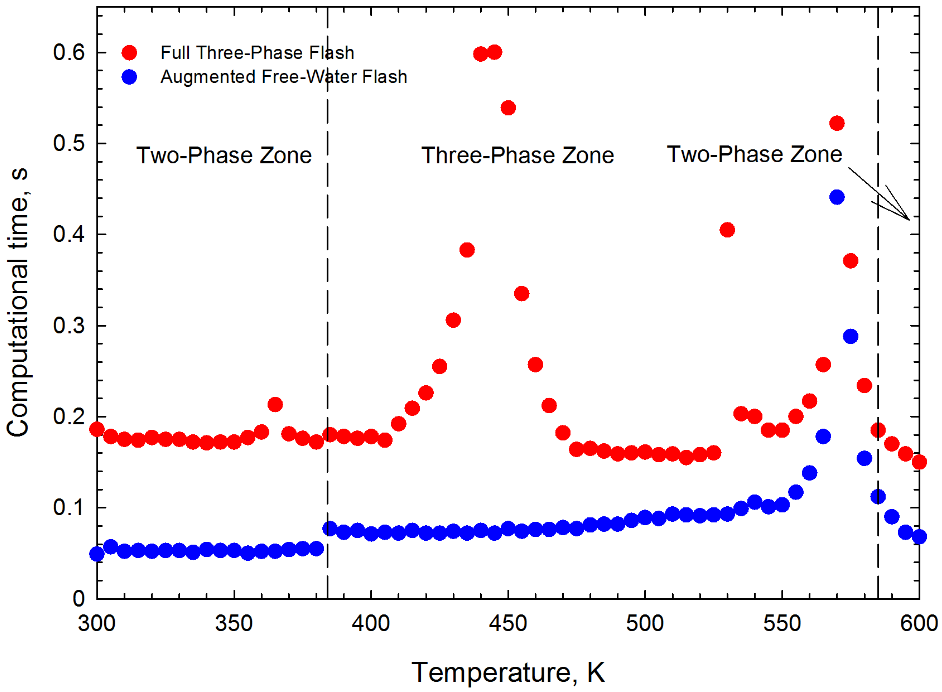


Figure 2.17 Comparison between the computational time required by the augmented free-water method and those by applying the full three-phase flash method for water/CO_2/BSB-oil mixture at P=150 bar.

CHAPTER 3 APPLICATION OF AUGMENTED FREE-WATER RACHFORD-RICE ALGORITHM TO WATER/HYDROCARBONS MIXTURES CONSIDERING THE DISSOLUTION OF METHANE IN THE AQUEOUS PHASE

A version of this chapter will be submitted to *Fluid Phase Equilibria*.

Abstract

Multiphase equilibria for water/hydrocarbon mixtures are frequently encountered in hydrocarbon reservoirs. The presence of water in these mixtures can lead to a higher number of equilibrating phases, increasing the complexity of the multiphase split calculations. It is a common approach to treating water as the bulk free phase and performing only two-phase split calculations on the hydrocarbon-rich liquid phase and vapor phase. The free-water flash algorithm uses a different approach; it considers the effect of water presence on the overall phase equilibrium of water/hydrocarbon mixtures, albeit also assuming the aqueous phase to be pure water. The free-water algorithm might be less accurate in some cases where the solubility of methane in the aqueous phase cannot be neglected. In this study, a modified version of the free-water flash method previously developed by our research group, the so-called augmented free-water flash, is extended to perform three-phase vapor-liquid-aqueous (VLA) flash calculations for methane-containing water/hydrocarbons mixtures on the basis of the assumption that only the existence of water and methane is considered in the aqueous phase. Moreover, we develop a flash package incorporating this augmented free-water method; this flash package can handle the single-phase, two-phase, or three-phase equilibrium calculations. Example calculations made on two methane-containing water/hydrocarbons mixtures demonstrate that the phase compositions and phase mole fractions calculated by augmented free-water method provide better predictions compared with the traditional free-water method since the solubility of methane is considered in the aqueous phase. Use of our new algorithm is also shown to be computationally more efficient than the conventional full three-phase flash algorithm. Therefore, our augmented free-water approach strikes a good balance between computational efficiency and prediction accuracy.

Keywords: Augmented free-water flash, Methane, Negative flash, Three-phase flash, Water/hydrocarbons mixtures

3.1. Introduction

Water is an inevitable substance in hydrocarbon reservoirs, resulting in that multiphase equilibria for water/hydrocarbons mixtures are frequently encountered in hydrocarbon reservoirs (e.g., vapor-liquid-aqueous three-phase equilibria). The higher number of equilibrating phases increases the complexity of the multiphase split calculations. One common approach used to replace the three-phase split calculations for the water/hydrocarbon mixtures is to treat water as the bulk free phase and perform only two-phase split calculations on the hydrocarbon-rich liquid phase and vapor phase [1]. To simulate thermal recovery processes (e.g., steam injection), two-phase split calculations coupled with a steam table is commonly used to replace the three-phase flashes [2-5]. However, it is recognized that the simplification of three-phase equilibrium calculations can lead to convergence issues in the compositional simulations, and the oil-recovery simulation results based on two-phase equilibrium calculations can be significantly different from those based on three-phase equilibrium calculations [6-9].

Phase equilibrium calculations should be robust as they are the prerequisite for performing accurate compositional reservoir simulations [10]. Phase equilibrium calculations should be also efficient since the computation time spent on the phase equilibrium calculations during reservoir simulations can be substantial [2, 10-13]. To lower the computational cost of three-phase split calculations, Lapene *et al.* [2] developed a revised flash algorithm based on the free-water concept that only water is present in the aqueous phase [14]. In their algorithm, they modified the Rachford-Rice equations and transformed the three-phase flash calculation into a pseudo-two-phase flash calculation. The convergence of this modified RR equations is guaranteed with the use of a monotonic objective function [2], while the previous objective function proposed by Iranshahr *et al.* [15] is not monotonic and the water dissolution in the hydrocarbon-rich phase is ignored. It is noted that, however, the free-water algorithm might be less accurate for some methane-containing water/hydrocarbons mixtures where the solubility of methane in the aqueous phase cannot be neglected. Further modification to the original free-water flash algorithm is needed to ensure that the presence of methane in the aqueous phase is well captured in the split calculations.

Recently, based on the fact that the solubility of CO_2 in the aqueous phase cannot be negligible, Pang and Li [16] proposed an augmented free-water algorithm for CO_2/water/hydrocarbons mixtures that assumes only CO_2 coexists with water in the aqueous phase. Example calculations show that their method is proven to be more accurate in describing the actual three-phase and two-phase equilibria of the CO_2/water/hydrocarbons mixtures than the free-water method. In this work, this augmented free-water algorithm is further extended to model the water/hydrocarbons mixtures by taking into account the dissolution of methane in the aqueous phase. In the revised algorithm, we develop new correlations for initializing the *K*-values used in the augmented free-water flash algorithm; the Rachford-Rice equations are also modified by considering only water and methane in the aqueous phase. Then, example calculations made on two methane-containing water/hydrocarbons mixtures are carried out using both the augmented free-water flash algorithm and the free-water flash algorithm; comparisons are then made between the flash results calculated using these two approaches.

3.2. Mathematical Formulation

3.2.1. Phase Stability Testing

Phase stability testing, which detects whether the phase of interest is stable or not, plays a fundamental role in the realm of phase equilibrium calculations. It is based on the method of finding if there is any trial phase with a less Gibbs free energy than the feed. The function of tangent plane distance (*TPD*) is given below [17]:

$$TPD\left(\left\{Y_i\right\}\right) = 1 + \sum_{i=1}^{N_c} Y_i \left[\ln\phi_i\left(\overrightarrow{Y_i}\right) + \ln Y_i - \ln\phi_i\left(\vec{z}\right) - \ln z_i - 1\right] \tag{1}$$

$$y_i = \frac{Y_i}{\sum_{i=1}^{N_c} Y_i} \tag{2}$$

where N_c is the number of components, z_i is the mole fraction of the i^{th} component in the feed, Y_i and y_i represents the mole number and mole fraction of the i^{th} component in the trail phase, respectively. If the minimum value of *TPDs* is found to be less than 0, the instability of the feed is detected; otherwise, the phase is stable. The initial estimates of the trail phase can be given as,

$$Y_i = K_i^{stab} z_i \tag{3}$$

where $\left\{K_i^{stab}\right\}$ refer to the equilibrium ratios. Li and Firoozabadi [10] summarized the works by Michelsen [17] and Cañas-Marín *et al.* [18] and proposed a set of initializations of equilibrium ratios for stability testing:

$$\left\{K_i^{stab}\right\} = \left[\left\{K_i^{Wilson}\right\}, \left\{\frac{1}{K_i^{Wilson}}\right\}, \left\{\sqrt[3]{K_i^{Wilson}}\right\}, \left\{\frac{1}{\sqrt[3]{K_i^{Wilson}}}\right\}, \left\{K_i^{New}\right\}\right] \tag{4}$$

where K_i^{Wilson} are the equilibrium ratios initialized by the Wilson correlation [19], and $\left\{K_i^{New}\right\}$ are the new initializations of *K*-values proposed by Li and Firoozabadi [10, 17]. The expressions for K_i^{Wilson} and $\left\{K_i^{New}\right\}$ are given as follows:

$$K_i^{Wilson} = \frac{P_{ci}}{P}\exp\left[5.37\left(1+w_i\right)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{5}$$

$$\begin{cases} K_i^{New} = \dfrac{0.9}{z_i} \\ K_{j\neq i}^{New} = \dfrac{\dfrac{0.1}{N_c-1}}{z_j} \end{cases} \tag{6}$$

where T_{ci}, P_{ci} and w_i represent the critical temperature, critical pressure and acentric factor of the the i^{th} component. In our case, in order to effectively test the stability of methane-containing water/hydrocarbons mixtures, we introduce one more set of initial estimates of equilibrium ratios for water containing mixtures as shown in Eq. [7]:

$$\begin{cases} K_i^{Water} = \dfrac{1-10^{-6}}{z_i} \\ K_{j\neq i}^{Water} = \dfrac{\dfrac{10^{-6}}{N_c-1}}{z_j} \end{cases} \tag{7}$$

This new set of equilibrium ratios considers the case where the fraction of a given component in the trial phase is 99.9999 mol%, while the other components equally share 0.0001 mol%. An extensive testing of Eq. 7 indicates that this set of equilibrium ratios works effectively for water-containing mixtures. As such, the following $2N_c$+4 sets of initial equilibrium ratios can be used for performing *TPD* analysis:

$$\left\{K_i^{stab}\right\} = \left[\left\{K_i^{Wilson}\right\}, \left\{\frac{1}{K_i^{Wilson}}\right\}, \left\{\sqrt[3]{K_i^{Wilson}}\right\}, \left\{\frac{1}{\sqrt[3]{K_i^{Wilson}}}\right\}, \left\{K_i^{New}\right\}, \left\{K_i^{water}\right\}\right] \tag{8}$$

3.2.2. Three-phase Flash Calculation

At a three-phase equilibrium, the following iso-fugacity relation holds:

$$f_i(x) = f_i(y) = f_i(w) \tag{9}$$

where $f_i(x)$, $f_i(y)$ and $f_i(w)$ are the fugacity of the i^{th} component in phase *x*, phase *y* and phase *w*, respectively. *x*, *y* and *w* represent the oleic phase, vapor phase and aqueous phase, respectively. The oleic phase (i.e., hydrocarbon-rich liquid phase) has been chosen to be the reference phase in this work to define the equilibrium ratios as follows:

$$\begin{cases} K_{iy} = \dfrac{y_i}{x_i} = \dfrac{\varphi_{ix}}{\varphi_{iy}} \\ K_{iw} = \dfrac{w_i}{x_i} = \dfrac{\varphi_{ix}}{\varphi_{iw}} \end{cases} \tag{10}$$

where K_{iy} is the equilibrium ratio of component *i* in the vapor phase with respect to the oleic phase, and K_{iw} is the equilibrium ratio of component *i* in the aqueous phase with respect to the oleic phase. x_i, y_i and w_i are molar compositions of component *i* in the oleic phase, vapor phase and aqueous phase, respectively, φ_{ix}, φ_{iy} and φ_{iw} are the fugacity coefficients of the i^{th} component in the oleic phase, vapor phase and aqueous phase, respectively.

As mentioned by Pang and Li [16] in their augmented free-water assumption, when there are only two components including water and methane are considered in the aqueous phase, the equilibrium ratios of the components in the aqueous phase can be reduced to only two *K* values, i.e., K_{ww} and K_{CH_4w}. The material balance equations can be described as:

$$\begin{cases} z_i = \beta_x x_i + \beta_y y_i + \beta_w w_i,\ i = \text{water, CH}_4 \\ z_i = \beta_x x_i + \beta_y y_i,\ i \neq \text{water, CH}_4 \end{cases} \tag{11}$$

$$\beta_x + \beta_y + \beta_w = 1 \tag{12}$$

where β_x, β_y and β_w are the fractions of the oleic phase, vapor phase and aqueous phase, respectively. By combing Eqs. (8), (9) and (10), the mole fraction of component *i* in the oleic phase can be obtained:

$$\begin{cases} x_i = \dfrac{z_i}{1+\beta_y\left(K_{iy}-1\right)-\beta_w},\ i \neq \text{water, CH}_4 \\ x_i = \dfrac{z_i}{1+\beta_y\left(K_{iy}-1\right)+\beta_w\left(K_{iw}-1\right)},\ i = \text{water, CH}_4 \end{cases} \tag{13}$$

The RR equations used in the augmented free-water method are:

$$\begin{cases} \sum_{i=1}^{N_c} \left(x_i - y_i \right) = 0 \\ \sum_{i=1}^{N_c} \left(x_i \right) - w_w - w_{CH_4} = 0 \end{cases} \tag{14}$$

Here we substitute Eq. (11) to Eq. (12) to obtain the new RR equations containing only phase fractions and *K* values as the variables:

$$\begin{cases} RR_y : \dfrac{z_w \left(1 - K_{wy}\right)}{1 + \beta_y \left(K_{wy} - 1\right) + \beta_w \left(K_{ww} - 1\right)} + \dfrac{z_{\mathrm{CH}_4} \left(1 - K_{\mathrm{CH}_4 y}\right)}{1 + \beta_y \left(K_{\mathrm{CH}_4 y} - 1\right) + \beta_w \left(K_{\mathrm{CH}_4 w} - 1\right)} \\ + \sum_{\substack{i \neq \text{water} \\ i \neq \mathrm{CH}_4}}^{N_c} \dfrac{z_i \left(1 - K_{iy}\right)}{1 + \beta_y \left(K_{iy} - 1\right) - \beta_w} = 0 \\ RR_w : \dfrac{z_w \left(1 - K_{ww}\right)}{1 + \beta_y \left(K_{wy} - 1\right) + \beta_w \left(K_{ww} - 1\right)} + \dfrac{z_{\mathrm{CH}_4} \left(1 - K_{\mathrm{CH}_4 w}\right)}{1 + \beta_y \left(K_{\mathrm{CH}_4 y} - 1\right) + \beta_w \left(K_{\mathrm{CH}_4 w} - 1\right)} \\ + \sum_{\substack{i \neq \text{water} \\ i \neq \mathrm{CH}_4}}^{N_c} \dfrac{z_i}{1 + \beta_y \left(K_{iy} - 1\right) - \beta_w} = 0 \end{cases} \tag{15}$$

The two RR equations are solved using the minimization method that is developed based on the works by Michelsen [20] and Okuno *et al.* [21]. Michelsen [20] firstly presented the objective function by integrating RR equations; Leibovici and Nichita [22] then used the feasible region developed by Leibovici and Neoschil [23] as the constraints to minimize the objective function. Okuno et *al.* [21] proposed a set of new constraints based on the fact that the phase fractions should lie within [0, 1], which leads to a smaller feasible region. The following objective function and constraints can be derived based on the work by Okuno *et al.* [21]:

$$\begin{cases} \min F(\beta) = \sum_{i=1}^{N_c} -z_i \ln\left[1 - \beta_y \left(1 - K_{iy}\right) - \beta_w \left(1 - K_{iw}\right)\right] \\ \text{subject to: } \beta_y \left(1 - K_{iy}\right) + \beta_w \left(1 - K_{iw}\right) \le \min\left\{1 - z_i, 1 - K_{iy} z_i, 1 - K_{iw} z_i\right\}, i = 1, \ldots, N_c \end{cases} \tag{16}$$

Base on the assumption that only water and methane are taken into account in the aqueous phase, the objective function and constraints can be modified to:

$$\begin{cases} \min F(\beta) = \sum_{i=1}^{N_c} -z_i \ln\left[1-\beta_y\left(1-K_{iy}\right)-\beta_w\right] \\ +\left(-z_w\right)\ln\left|1-\beta_y\left(1-K_{wy}\right)-\beta_w\left(1-K_{ww}\right)\right|+\left(-z_{CH_4}\right)\ln\left|1-\beta_y\left(1-K_{CH_4y}\right)-\beta_w\left(1-K_{CH_4w}\right)\right| \quad (17) \\ \text{subject to: } \begin{cases} \beta_y\left(1-K_{iy}\right)+\beta_w \leq \min\left\{1-z_i, 1-K_{iy}z_i\right\}, i \neq \text{water,CH}_4 \\ \beta_y\left(1-K_{wy}\right)+\beta_w\left(1-K_{ww}\right) \leq \min\left\{1-z_w, 1-K_{wy}, 1-K_{ww}z_w\right\} \\ \beta_y\left(1-K_{CH_4y}\right)+\beta_w\left(1-K_{CH_4w}\right) \leq \min\left\{1-z_{CH_4}, 1-K_{CH_4y}, 1-K_{CH_4w}z_{CH_4}\right\} \end{cases} \end{cases}$$

In the augmented free-water RR algorithm, the number of variables appearing in the revised objective function are N_c+4, including $\{K_{iy}\}$, K_{ww}, K_{CH_4w}, β_y and β_w, while the conventional three-phase RR algorithm has $2N_c$+2 variables to be solved. The revised objective function is convex. The proof of its convexity is similar to the one presented by Michelsen [20].

3.2.3. Initial Estimates of the Augmented Free-water Three-phase Flash Calculation

Appendix A shows the flow chart of the augmented free-water three-phase flash algorithm for methane-containing water/hydrocarbons mixtures. The three-phase flash algorithm consists of two iteration loops: the inner iteration loop and outer iteration loop. In the inner iteration loop, the objective function is solved by Newton and line search method as suggested by Okuno *et al.* [21], so that both phase fractions and phase compositions can be calculated. In the outer loop, the equilibrium ratios are updated based on the ratio of the fugacity between two phases. In this work, Peng-Robinson equation of state (PR-EOS) is used [24].

Hereafter, we explain how we initialize and update the equilibrium rations of the vapor phase and the aqueous phase. We firstly run 4 outer loops of the conventional free-water three-phase flash algorithm, which provides the initial estimates of $\{ K_{iy} \}$ and K_{ww} to be used in the augmented free-water three-phase flash. Although there are additional outer loops appearing in the augmented free-water flash, we find the number of iterations needed by our augmented free-water flash is still fewer than that needed by the full three-phase flash. The initializations of $\{ K_{iy} \}$ and K_{ww} for conventional free-water method we introduce herein are originated from the method proposed by Lapene *et al.* [4].

In each of the 4 outer loops, we adopt the following equation proposed by Lapene *et al.* [2] to initialize the equilibrium ratio of the water component in vapor phase with respect to the oleic phase, which performs better for the water/hydrocarbons mixtures than the original form developed by Peng and Robinson [25]:

$$K_{wy} = \frac{p}{p_{cw}} \frac{T_{cw}}{T} \tag{18}$$

The initial guess of mole fraction of water in the vapor phase is proposed by Lapene *et al.* [2]:

$$y_w = \frac{p_{sat}^w}{p} \tag{19}$$

where p_{sat}^w is the saturation pressure of pure water that can be obtained by the correlation given by Bridgeman and Aldrich [26]. Based on the definition of the equilibrium ratios, the expression of K_{ww} can be written as:

$$K_{ww} = \frac{K_{wy}}{y_w} w_w \tag{20}$$

Since the initializations of $\{K_{iy}\}$ and K_{ww} should be identical to those for conventional free-water method, w_w is set to 1 in our case. In the 5th loop, the empirical correlation proposed by Pang and Li [16] is used to initialize the equilibrium ratio of methane in the aqueous phase with respect to the oleic phase:

$$K_{\mathrm{CH_4}w} = \frac{0.5}{K_{ww}} \tag{21}$$

This correlation still works well in guaranteeing the convergence when methane is considered in the aqueous phase.

3.2.4. Augmented Free-water Flash Package

In the conventional full three-phase flash, the phase stability testing, which is always performed prior to the phase split calculation, determines the necessity of conducting a further phase split calculation. **Appendix B** shows the flow chart that shows the procedure for conducting the conventional three-phase flash.

However, in some cases, the use of such exhaustive approach leads to an undesirable computational cost for multiphase equilibrium calculations (e.g., a three-phase equilibrium calculation), hampering its wide use in compositional simulators. In order to increase the computation efficiency without losing the robustness, both negative flash and regular flash are applied in the augmented free-water flash algorithm. Pang and Li [16] incorporated the augmented free-water algorithm to a flash package that could handle single-phase, two-phase and three-phase flash calculation. The following gives a brief introduction of the procedures employed in the flash package:

(1) Perform phase stability testing for the feed by checking the value of *TPD*. If *TPD*<0, the feed is unstable; otherwise, the feed is stable and the calculation terminates.

(2) When the instability of the feed is detected, the augmented free-water three-phase flash is conducted.

(3) If the results of phase fractions are shown to be physical (i.e., within [0,1]), the system is at a three-phase equilibrium. Other situations will happen when the phase fractions calculated by augmented free-water three-phase algorithm is unphysical (e.g., beyond [0,1]) or an open feasible region appears in successive substitution iterations; in these cases, we switch to a two-phase flash calculation. Pang and Li [1] gave more details about how to properly switch from a three-phase split to a two-phase split.

As for the augmented three-phase flash, if the feed is actually at a three-phase equilibrium, one will only perform one run of phase stability testing and one run of augmented three-phase flash. But, as for the conventional three-phase flash, one needs to perform two runs of phase stability testing, i.e., one run of two-phase flash and one run of three-phase flash.

3.3. Example Calculations

Two fluid mixtures are used in the example calculations; one synthetic mixture and one quaternary mixture are tested to validate the accuracy, robustness and computational efficiency of the augmented free-water flash method. The results calculated by conventional full-phase flash and free-water flash are used as benchmarks to be compared against those calculated by the augmented free-water flash.

3.3.1. Case 1: Quaternary Mixture Containing Water

In Case 2, the quaternary mixture consists of pure water, C_1, C_7 and C_D (Athabasca bitumen). A single pseudo-component C_D is used to characterize the bitumen [27-28]. This mixture was also used to perform isenthalpic flash calculations by Zhu and Okuno [29]. The critical properties of components in the quaternary mixture and the binary interaction parameters (BIPs) used are listed in **Table 3.1**.

Figure 3.1(a), Figure 3.1(b) and Figure 3.1(c) show the phase moles fractions of the oleic phase, aqueous phase and vapor phase within the three-phase zone over a wide range of temperatures and pressures, respectively. It can be seen from Figure 3 that all the data points (including those near the critical region) can be solved successfully, which is manifested by the smooth surfaces of the calculated results. This validates the robustness of our proposed augmented free-water flash algorithm. **Figure 3.2(a)** and **Figure 3.2(b)** show the compositions of the vapor phase and the oleic phase that are calculated by the augmented free-water method, free-water method and conventional full three-phase flash at P=110 bar. Both two figures demonstrate that a good agreement can be achieved between the phase compositions calculated by the augmented free-water method and those calculated by the conventional full-phase flash method, while the phase compositions calculated by the free-water three-phase flash deviate from those calculated by the conventional full three-phase flash. Figure 3.2 proves that our augmented free-water method gives a better prediction of the phase compositions compared with free-water method.

Figure 3.3 compares the phase mole fractions calculated by these three methods, while **Figure 3.4** shows the absolute deviations between the phase mole fractions calculated by the augmented free-water flash (or the free-water flash) and those calculated by the full three-phase flash. The absolute error is calculated by subtracting the phase fractions obtained by the augmented free-water flash (or the free-water flash) from the phase fraction obtained by the conventional three-phase flash. The largest absolute deviation obtained with the augmented free-water three-phase flash is found to be 8.22×10^{-6}, demonstrating that the augmented approach can accurately reproduce the phase equilibria of the water-containing quaternary mixture as given by the conventional flash.

3.3.2. Case 2: Water/Reservoir Fluid Mixture

This synthetic mixture consists of water and a synthetic reservoir fluid. The critical properties of the components in the reservoir fluid and the BIP used are listed in **Table 3.2**. **Figure 3.5** presents the multiphase boundaries of the water/reservoir fluid mixture with different molar water cuts which are calculated using the augmented free-water three-phase flash. These multiphase envelopes are similar to the ones given for water/gas condensate mixtures by Lindeloff and Michelsen [30]. As depicted by Figure 3.5, the water content can significantly affect the multiphase boundaries of the water/reservoir fluid mixtures, which is consistent with the findings by Lindeloff and Michelsen [30]. **Figure 3.6** shows the calculated phase fractions of vapor phase, oleic phase and aqueous phase at different water cuts at T=598 K, P=330 bar; the calculations are done with the augmented free-water three-phase flash. The feed equilibrates as a vapor phase until the water content reaches up to 0.3; at water content larger than 0.3, a vapor-liquid equilibrium (VLE) occurs. When water content is higher than 0.5, a VLA three-phase equilibrium appears. The mole fraction of the aqueous phase increases with an increase in the water cut, accompanied with a decrease in the vapor-phase fraction. **Figure 3.7** compares the three-phase envelopes for the water/reservoir fluid mixture at 0.75 water content; these phase envelopes are calculated by the conventional three-phase flash method, the free-water method and the augmented free-water method, respectively. It can be seen from Figure 3.7 that the three-phase envelope calculated by the augmented free-water method agrees relatively well with that calculated by the conventional three-phase flash method, while the free-water method yields a three-phase envelope that is deviating from the one calculated by the conventional flash.

Figure 3.8 compares the phase fractions calculated by the above three different methods at P=400 bar. Again, the augmented free-water method provides phase-fraction predictions that are close to those by the conventional three-phase flash method. It can be seen from Figure 3.8 that the augmented free-water approach provides a better match of the phase fractions calculated by the conventional full three-phase flash than the free-water approach. **Figure 3.9** compares the absolute deviations in the phase-fraction predictions in the three-phase zone yielded by the augmented free-water method and by the free-water method at P=400 bar. The maximum absolute error given by the augmented free-water method is found to be 8.7×10^{-4}, which is much smaller than 2.4×10^{-2} yielded by the free-water method. **Figure 3.10** plots the mole fractions of methane in the aqueous phase under different pressures and temperatures calculated by the three different algorithms. It can be seen from **Figure 3.10** that the solubility of methane in the aqueous phase is increasing with the increase of pressure or temperature. The mole fractions of methane in the aqueous phase obtained by augmented free-water flash are found to be underestimated especially at pressures higher than 300 bar, while they are assumed to be zero in the free-water flash method. The underestimation of the amount of methane in water by the augmented free-water flash will result in an overestimation in the vapor phase fraction. This is probably the reason leading to that the three-phase envelopes at high pressure/temperature conditions predicted by the augmented free-water flash tend to deviate more from those predicted by the conventional three-phase flash (See Figure 3.7)

Table 3.3 compares the phase compositions calculations by applying the three flash method for the water/reservoir fluid mixture at 400 bar and 638 K. It can be observed from Table 3.3 that the compositions of the components in the aqueous phase, calculated by the conventional three-phase flash, are nearly zero except for water and CH_4. This is a further validation of the underlying assumption adopted in the new algorithm that only water and CH_4 are considered to be present in the aqueous phase. Moreover, in comparison to the free-water three-phase flash method, the augmented free-water three-phase flash is able to provide predictions of the vapor-phase compositions that are much closer to those predicted by the conventional three-phase flash method; similar conclusion can be also made for the oleic phase.

Figure 3.11 compares the phase fractions calculated by performing the standalone augmented algorithm that is not coupled into the flash package and those calculated by performing the conventional three-phase flash at T=470 K. Note that the phase fractions obtained by the augmented free-water three-phase flash agree well with the results calculated by the conventional full three-phase flash when the system is at a three-phase equilibrium. As shown in Figure 3.11, a two-phase equilibrium occurs when pressure is higher than 460 bar.

Figure 3.12 plots the number of iterations required by the augmented free-water flash and by the conventional full three-phase flash at P=400 bar; the number of iterations needed by both methods are tested within the three-phase zone. As seen from Figure 3.12, a fewer number of iterations is required in our augmented method compared with the conventional approach, although an additional 4 runs of conventional free-water iterations are conducted in our method to obtain the initial estimates of equilibrium ratios. **Figure 3.13** compares the computational time consumed by the augmented free-water three-phase method and that consumed by the full three-phase flash method for the water/reservoir fluid mixture at P=400 bar. It can be obviously observed from Figure 3.13 that our augmented flash consumes much less computational time than the conventional flash.

3.4. Conclusions

The augmented free-water method has been applied to simulate the phase behavior of water/hydrocarbon mixtures based on the assumption that only water and methane coexist in the aqueous phase. Moreover, the augmented free-water algorithm is incorporated into a flash package where single-phase, two phase and three-phase equilibrium can be handled. The switching criteria proposed in our previous work [16] are proven to be robust and efficient for performing the three-phase flash computations for the water/hydrocarbon mixtures. Example calculations made on two fluid mixtures demonstrate that the augmented free-water algorithm provides a more accurate representation of both phase compositions and phase fractions of the three-phase equilibria than the free-water flash algorithm.

Nomenclature

err = error

f_{iw} = fugacity of i^{th} component in the aqueous phase

f_{ix} = fugacity of i^{th} component in the hydrocarbon-rich phase

f_{iy} = fugacity of i^{th} component in the vapor phase

F = objective function

$iter$ = number of iterations

K_{CH_4w} = equilibrium ratio of CH_4 component in the aqueous phase with respect to the reference phase

K_{CH_4y} = equilibrium ratio of CH_4 component in the vapor phase with respect to the reference phase

K_{iw} = equilibrium ratio of the i^{th} component in the aqueous phase with respect to the reference phase

K_{iy} = equilibrium ratio of the i^{th} component in the vapor phase with respect to the reference phase

K_{ww} = equilibrium ratio of water component in the aqueous phase with respect to the reference phase

K_{wy} = equilibrium ratio of water component in the vapor phase with respect to the reference phase

N_c = number of components

P = pressure, bar

P_c = critical pressure, bar

T = temperature, K

T_c = critical temperature, K

w_i = mole fraction of i^{th} component in the aqueous phase

x_i = mole fraction of i^{th} component in the hydrocarbon-rich phase

y_i = mole fraction of i^{th} component in the vapor phase

z_i = mole fraction of i^{th} component in the feed

β_w = phase fraction of the aqueous phase

β_x = phase fraction of the hydrocarbon-rich phase

β_y = phase fraction of the vapor phase

φ_{iw} = fugacity coefficient of i^{th} component in the aqueous phase

φ_{ix} = fugacity coefficient of i^{th} component in the hydrocarbon-rich phase

φ_{iy} = fugacity coefficient of i^{th} component in the vapor phase

ω = acentric factor

Subscripts

i = component index

j = phase index

k = phase index

w = water component index or aqueous phase index

x = hydrocarbon-rich phase index

y = vapor phase index

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Appendix A: Flow Chart of the Augmented Free-Water Three-Phase Algorithm

Figure A-1 shows the flow chart of the augmented free-water three-phase algorithm.

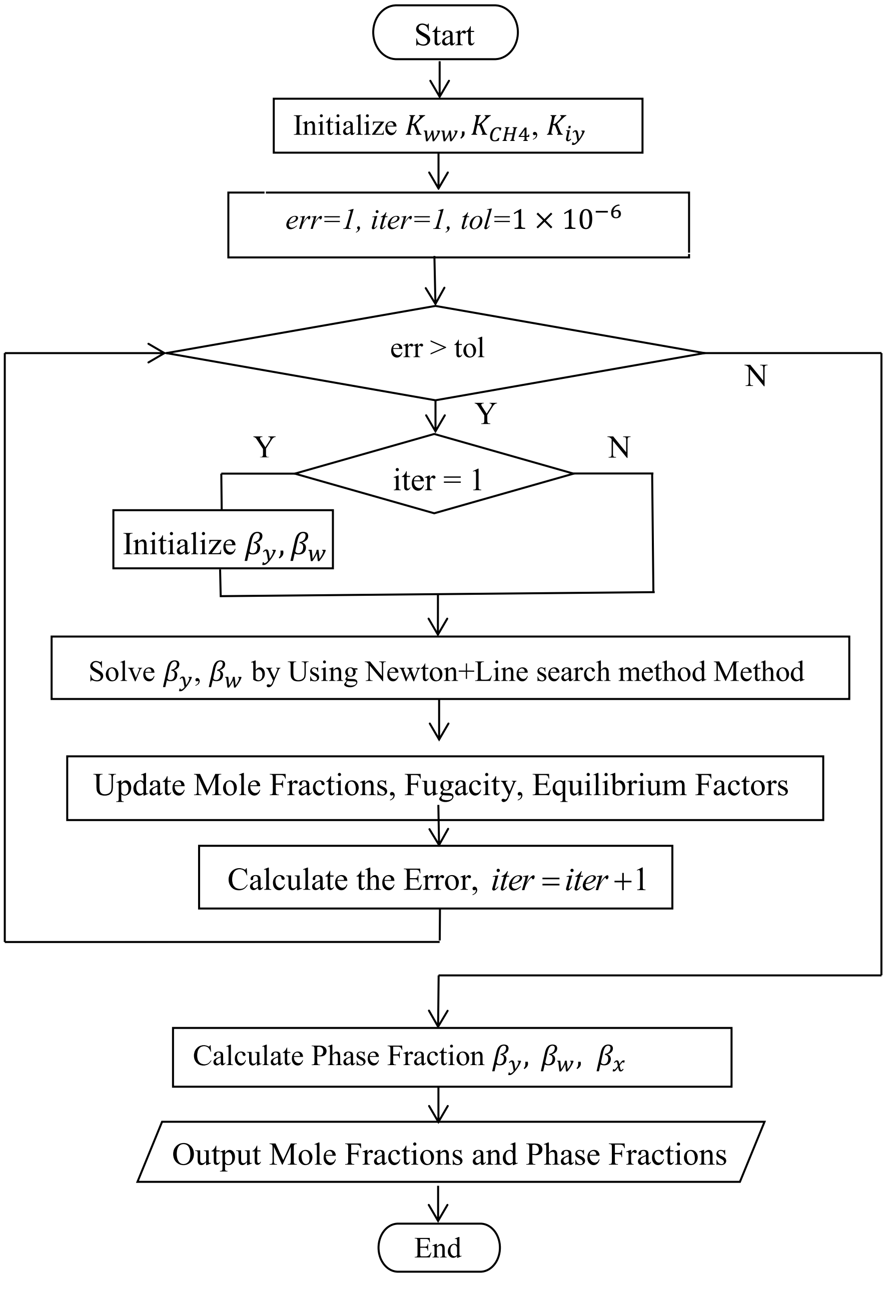


Figure A-1 Flow chart of the augmented free-water three-phase flash algorithm [16]

Appendix B: Flow Chart of the Conventional Full Three-Phase Flash Algorithm

Figure B-1 shows the procedures of the conventional full three-phase flash algorithm.

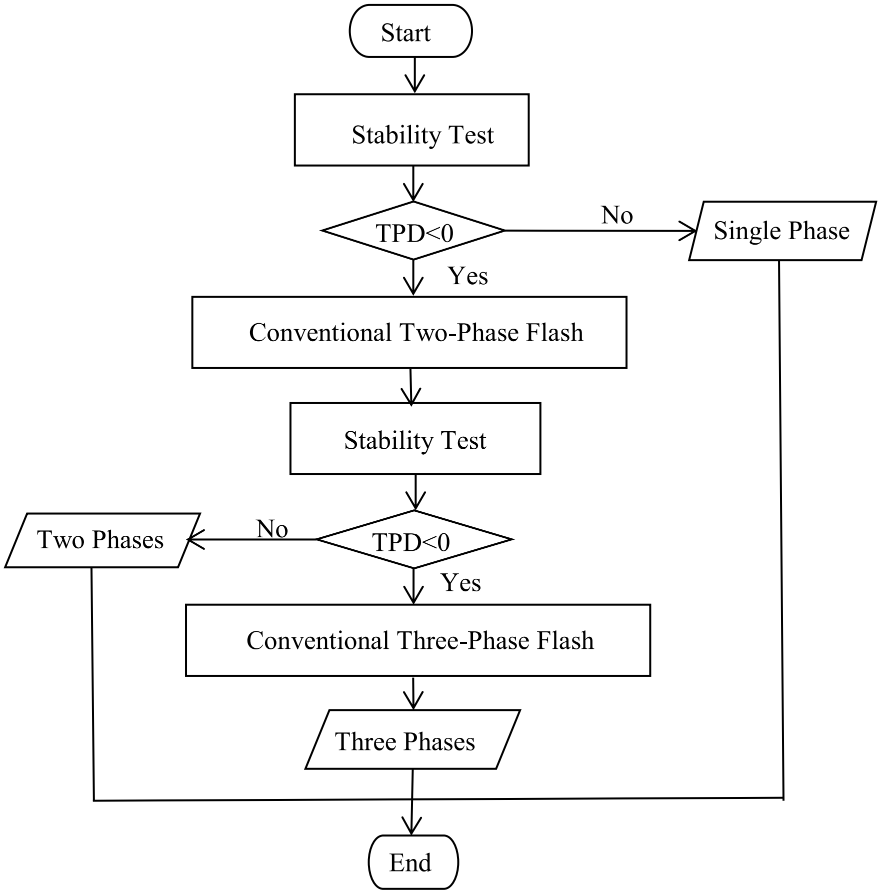


Figure B-1 Flow chart of the conventional three-phase flash calculation

Table 3.1 Properties of the components in the quaternary mixtures used in this study

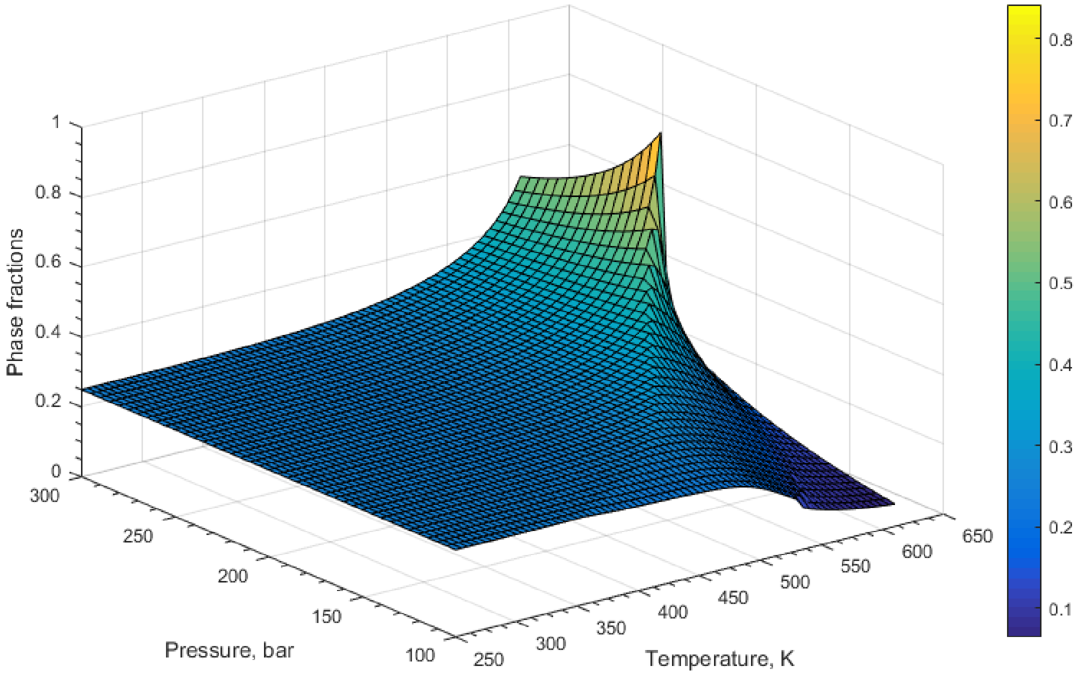
Component	T_c (K)	P_c (bar)	ω	z (mol/mol)	k_{H2O-j}	k_{C1-j}
H_2O	647.30	220.89	0.344	0.75	-	0.7560
C_1	190.6	46	0.008	0.08	0.7560	-
C_7	540.2	27.36	0.351	0.15	0.5610	0.0352
C_D	1090.9	7.86	1.361	0.02	0.1000	0.0000

Table 3.2 Properties of the components in the reservoir fluid mixture used in this study

Component	T_c (K)	P_c (bar)	ω	Mol%	k_{H2O-j}
C_1	190.58	46.04	0.011	0.75	0.4850
C_2	305.42	48.8	0.099	0.05	0.5000
C_3	369.82	42.49	0.152	0.02	0.5000
C_4	408.14	36.48	0.177	0.02	0.5000
C_5	464.78	35.29	0.233	0.02	0.5000
C_6	507.43	30.12	0.305	0.01	0.5000
C_7	540.26	27.36	0.351	0.02	0.5000
C_{16}	717.00	14.19	0.742	0.06	0.5000
C_{29}	816.55	14.51	1.129	0.05	0.5000

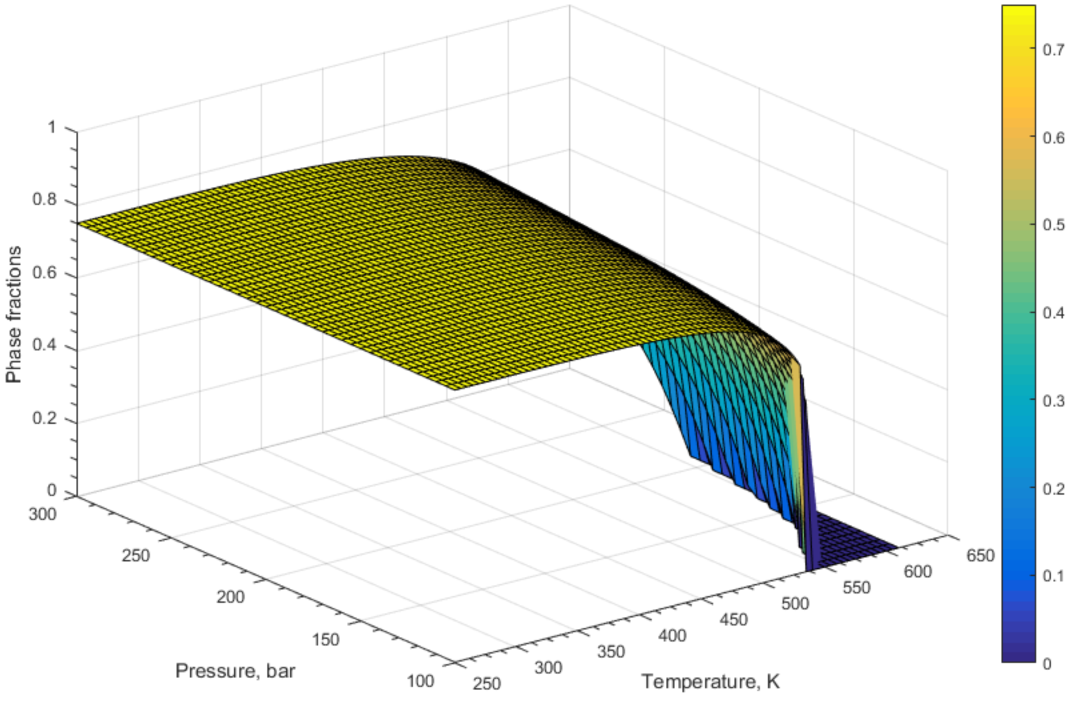
Table 3.3 Comparison of the phase compositions computed by applying the augmented free-water three-phase flash method, the conventional full three-phase flash method and the free-water three-phase flash method for the water/reservoir fluid mixture at 400 bar and 638 K

Component	Full Three-Phase Flash			Augmented Free-Water Three-Phase Flash			Free-Water Three-Phase Flash		
	y_i (V)	x_i (O)	w_i(A)	y_i (V)	x_i (O)	w_i (A)	y_i (V)	x_i (O)	w_i (A)
H_2O	0.654931	0.477154	0.968369	0.661044	0.476651	0.973372	0.746506	0.477337	1.0000
C_1	0.258043	0.266163	0.029533	0.254018	0.263601	0.026628	0.202317	0.244681	0
C_2	0.017436	0.020277	0.001371	0.017622	0.020692	0	0.01327	0.018948	0
C_3	0.007057	0.009027	0.000336	0.007032	0.00911	0	0.005224	0.008591	0
C_4	0.007109	0.009838	0.000195	0.007017	0.009863	0	0.005143	0.009569	0
C_5	0.007122	0.010813	0.000135	0.006997	0.010822	0	0.005048	0.010714	0
C_6	0.003569	0.00602	2.92E-05	0.003486	0.006014	0	0.002456	0.006179	0
C_7	0.007135	0.013141	3.05E-05	0.00695	0.013134	0	0.004788	0.013853	0
C_{16}	0.020808	0.082166	5.99E-08	0.019958	0.083371	0	0.009511	0.100183	0
C_{29}	0.01679	0.1054	2.58E-08	0.015875	0.106743	0	0.005736	0.109944	0



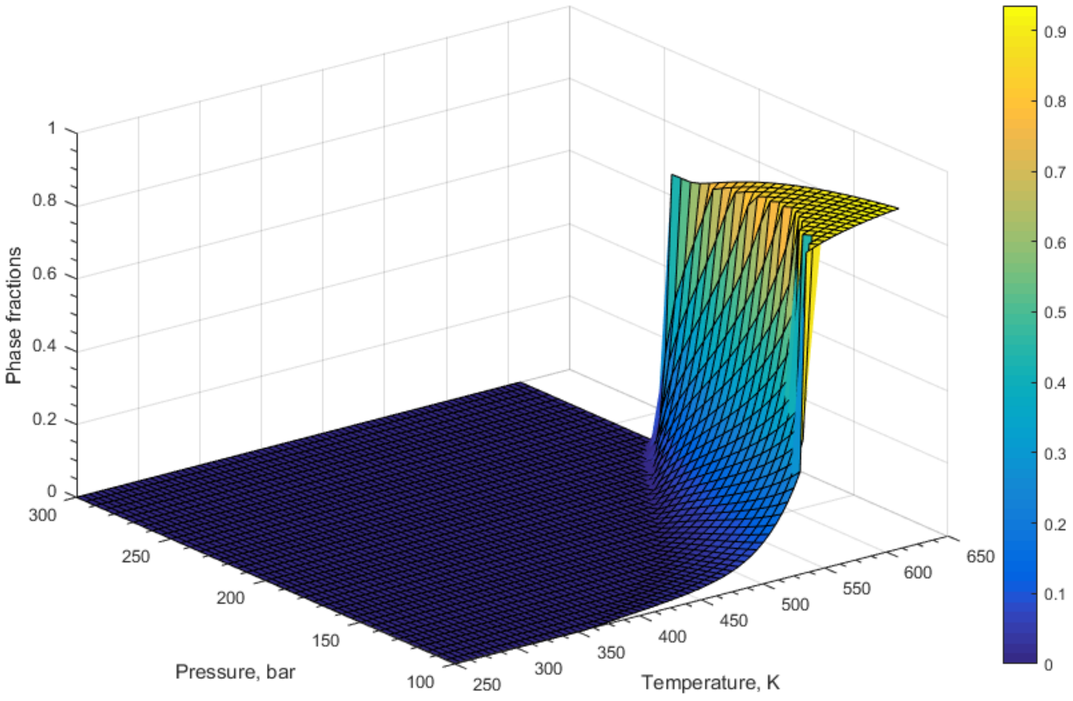
Phase fractions
1
0.8
0.6
0.4
0.2
0
Pressure, bar
300
250
200
150
100
Temperature, K
250
300
350
400
450
500
550
600
650
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

(a)



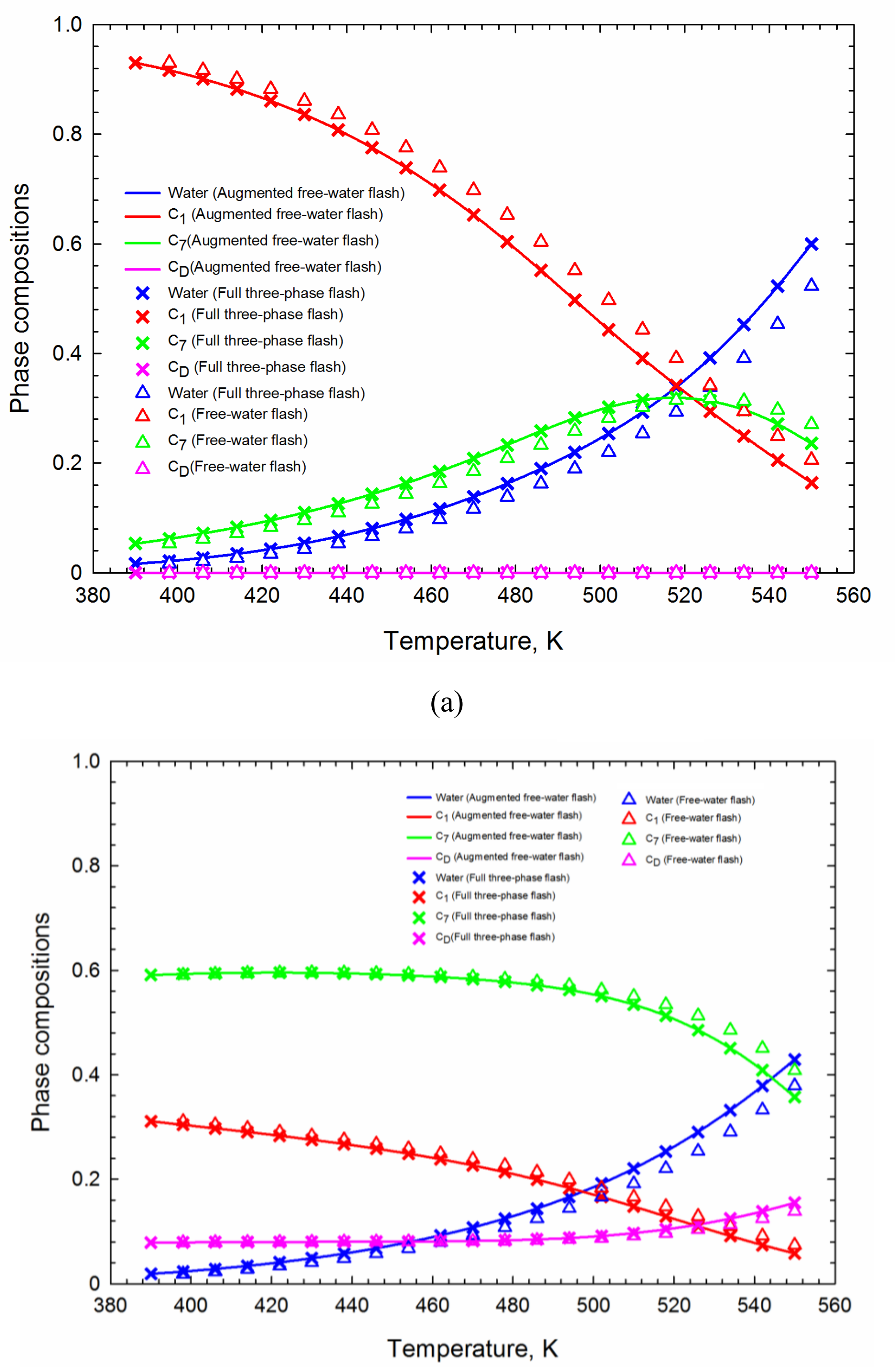
Phase fractions
1
0.8
0.6
0.4
0.2
0
Pressure, bar
300
250
200
150
100
Temperature, K
250
300
350
400
450
500
550
600
650
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

(b)



(c)

Figure 3.1 Phase fractions of the three individual phases calculated by the augmented free-water three-phase flash method: (a) phase fraction of the oleic (O) phase; (b) phase fraction of the aqueous (A) phase; and (c) phase fractions of the vapor (V) phase. The calculations are done for the quaternary mixtures.



(a)

(b)

Figure 3.2 Comparison of phase compositions calculated by the augmented free-water three-phase flash, the conventional three-phase flash and the free-water three-phase flash: (a) phase compositions in the vapor phase; and (b) phase compositions in the oleic phase. These calculations are done for the quaternary mixtures at *P*=110 bar.

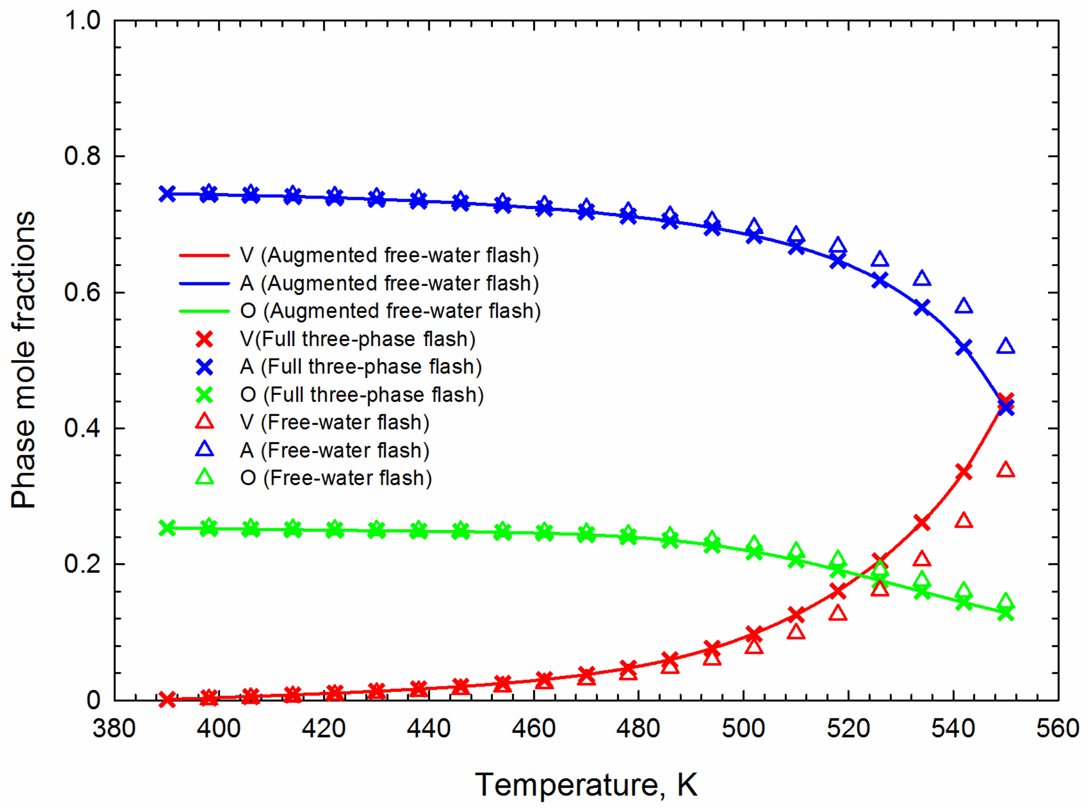


Figure 3.3 Comparison of phase fractions obtained by applying the augmented free-water three-phase method, the full three-phase flash method and the free-water three-phase flash method. These calculations are done for the quaternary mixture at *P*=110 bar.

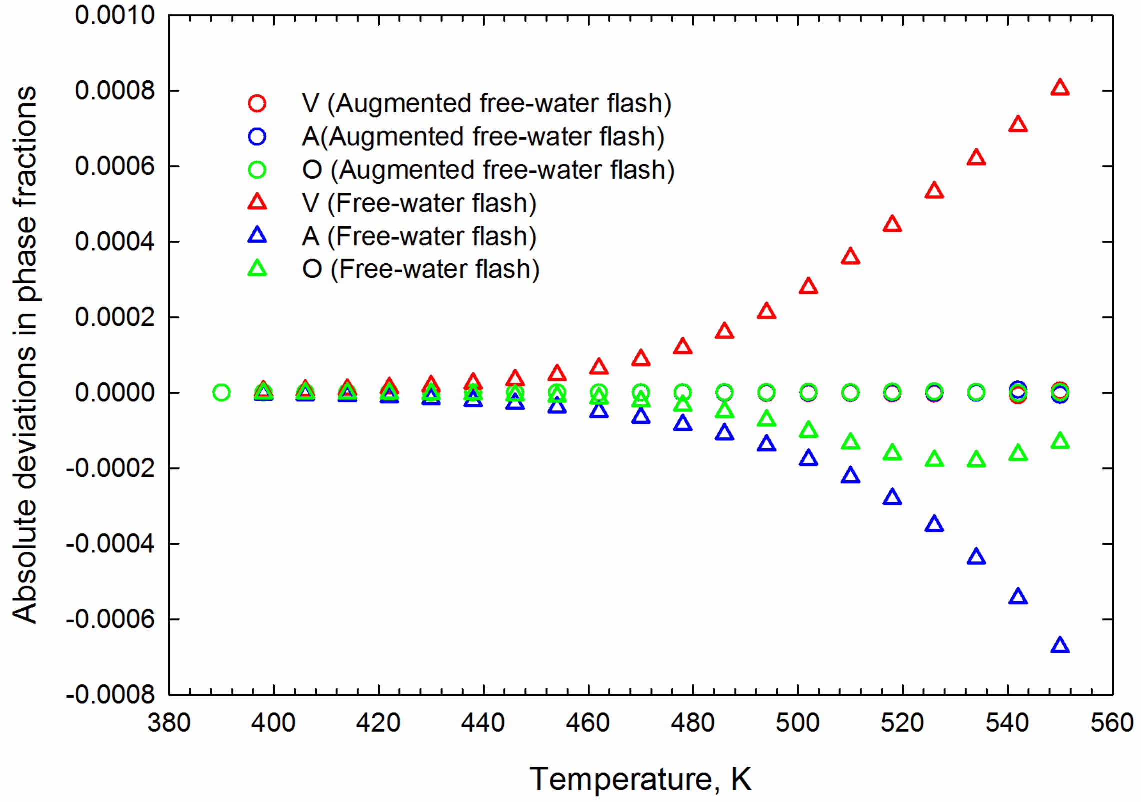
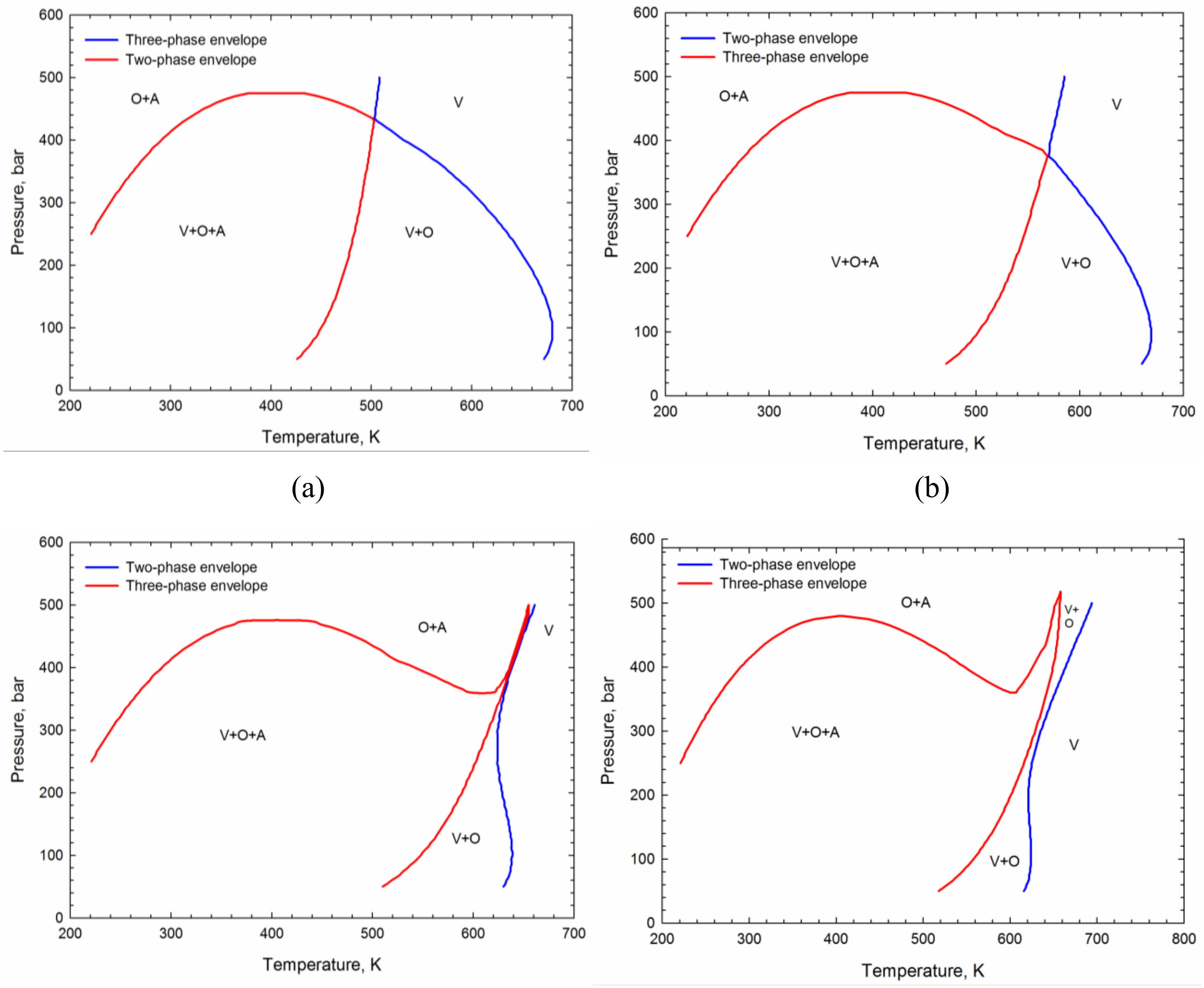


Figure 3.4 Comparison of absolute deviations of phase fractions in the three-phase zone yielded by applying the augmented free-water three-phase flash method and the free-water three-phase flash method. The calculations are done for the quaternary mixture at *P*=110 bar.



(a)

(b)

(c)

(d)

Figure 3.5 Phase envelopes for the water/reservoir fluid mixtures with different water contents calculated using the augmented free-water flash: (a) 0.10 water cut; (b) 0.30 water cut; (c) 0.65 water cut; (d) 0.75 water cut.

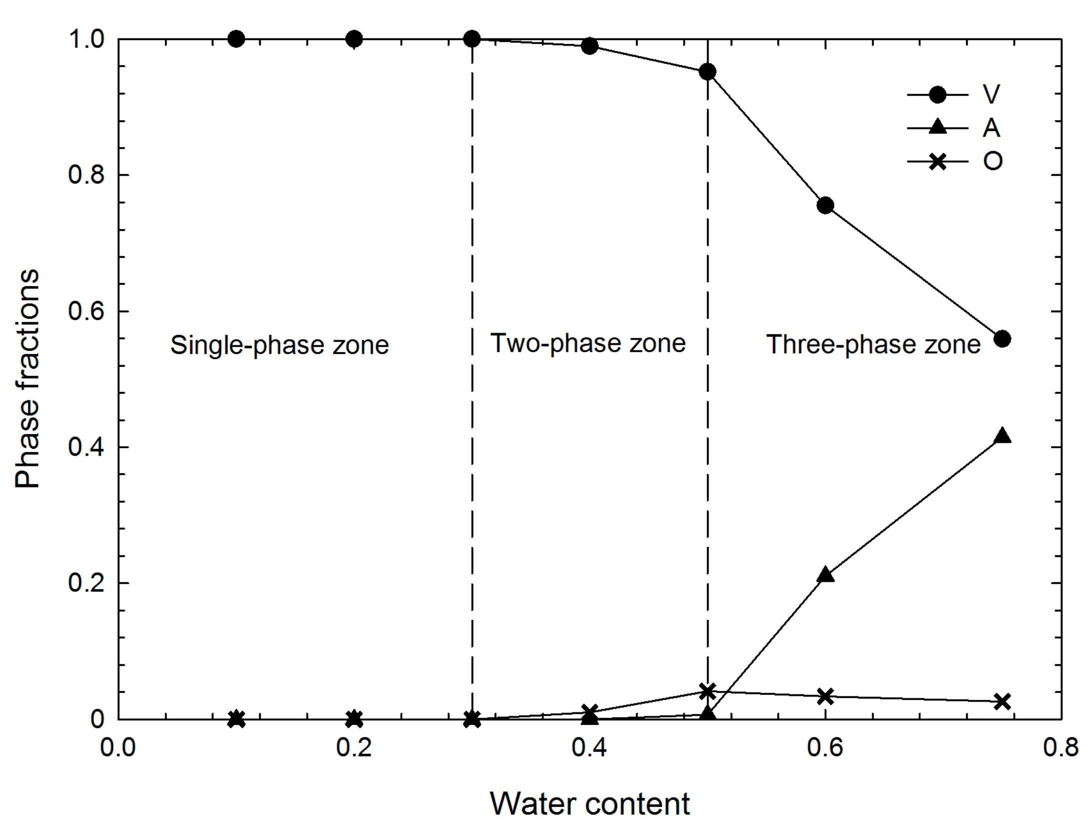


Figure 3.6 Calculated phase fractions for the water/reservoir fluid mixtures by the augmented free-water flash at different water contents at *T*=598 K and *P*=330 bar.

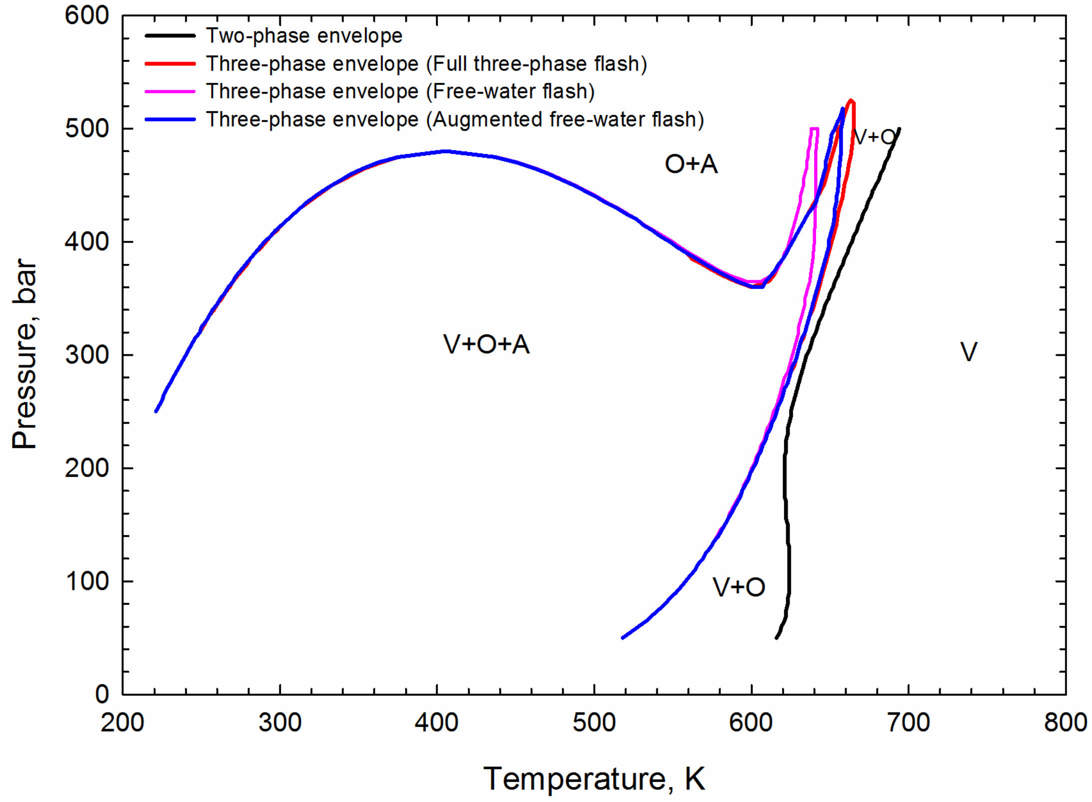


Figure 3.7 Calculated three-phase envelopes for the water/reservoir fluid mixture. The augmented free-water method, full three-phase flash method and free-water method have been used to calculate the three-phase envelopes.

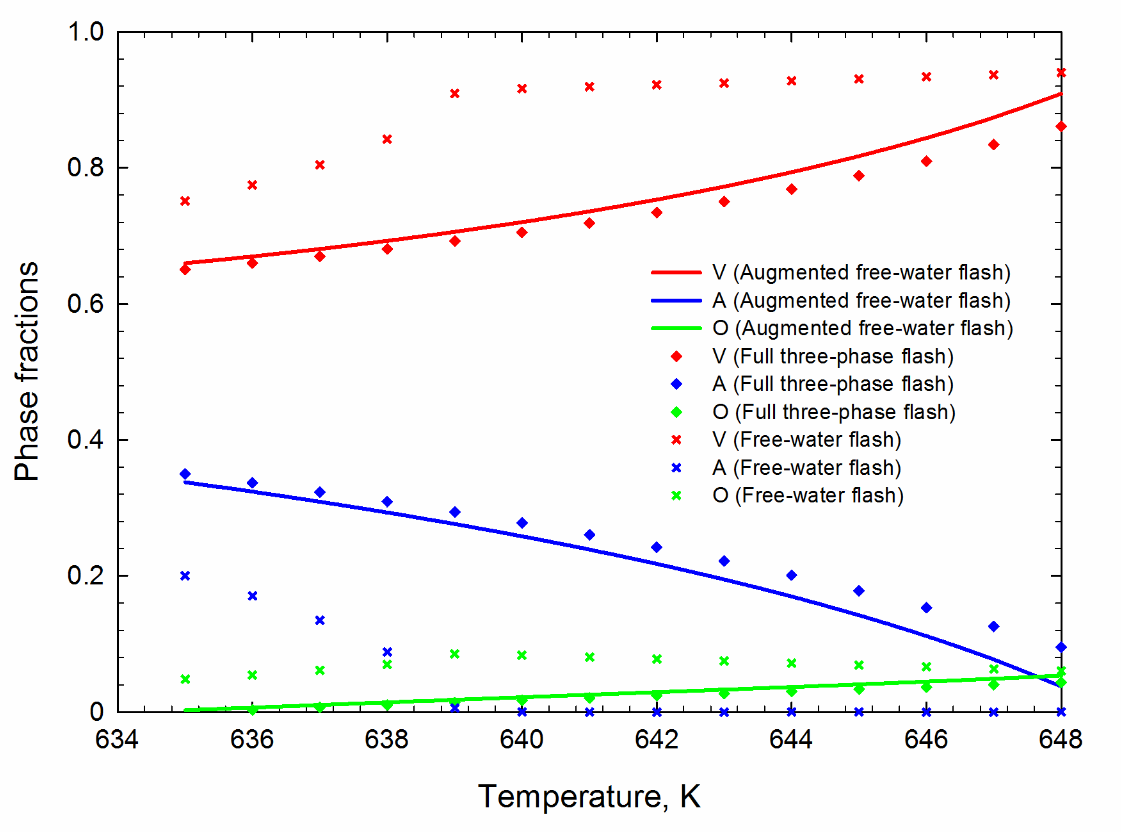


Figure 3.8 Comparison of phase fractions obtained by applying the augmented free-water three-phase flash method, the full three-phase flash method and the free-water three-phase flash method. These calculations are done for the water/reservoir fluid mixture at *P*=400 bar.

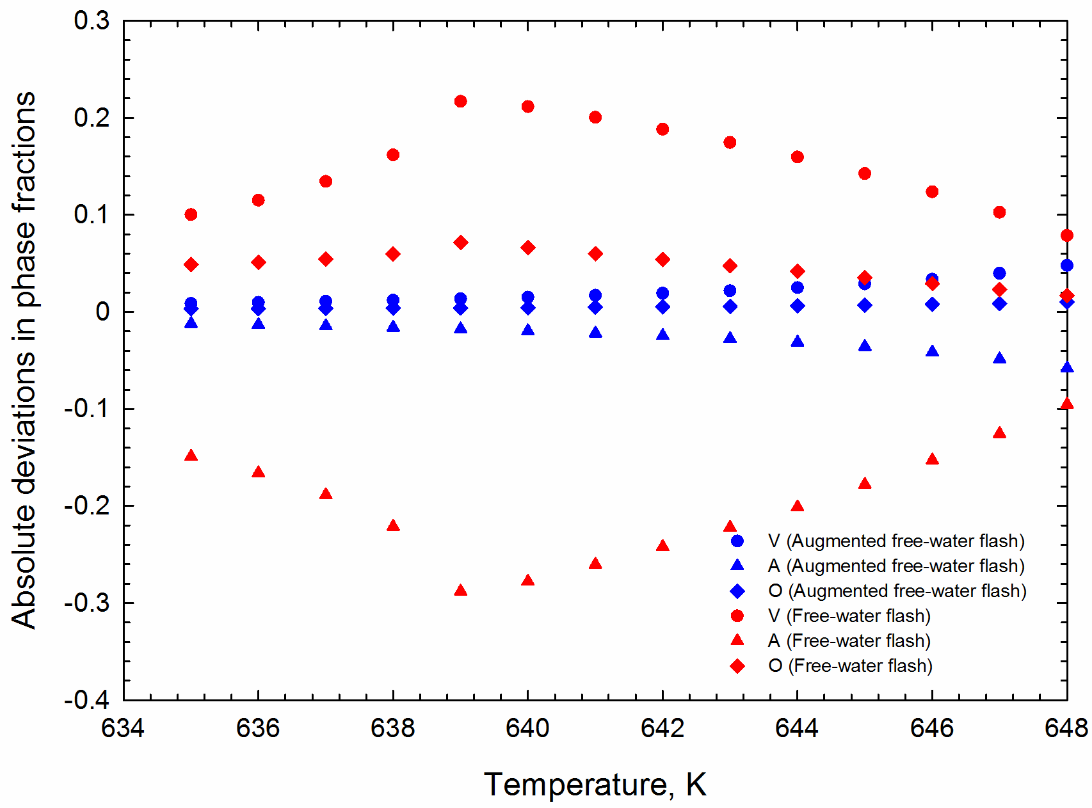


Figure 3.9 Comparison of absolute deviations of phase fractions in the three-phase zone yielded by applying the augmented free-water flash method and the free-water flash method. These calculations are done for the water/reservoir fluid mixture at *P*=400 bar.

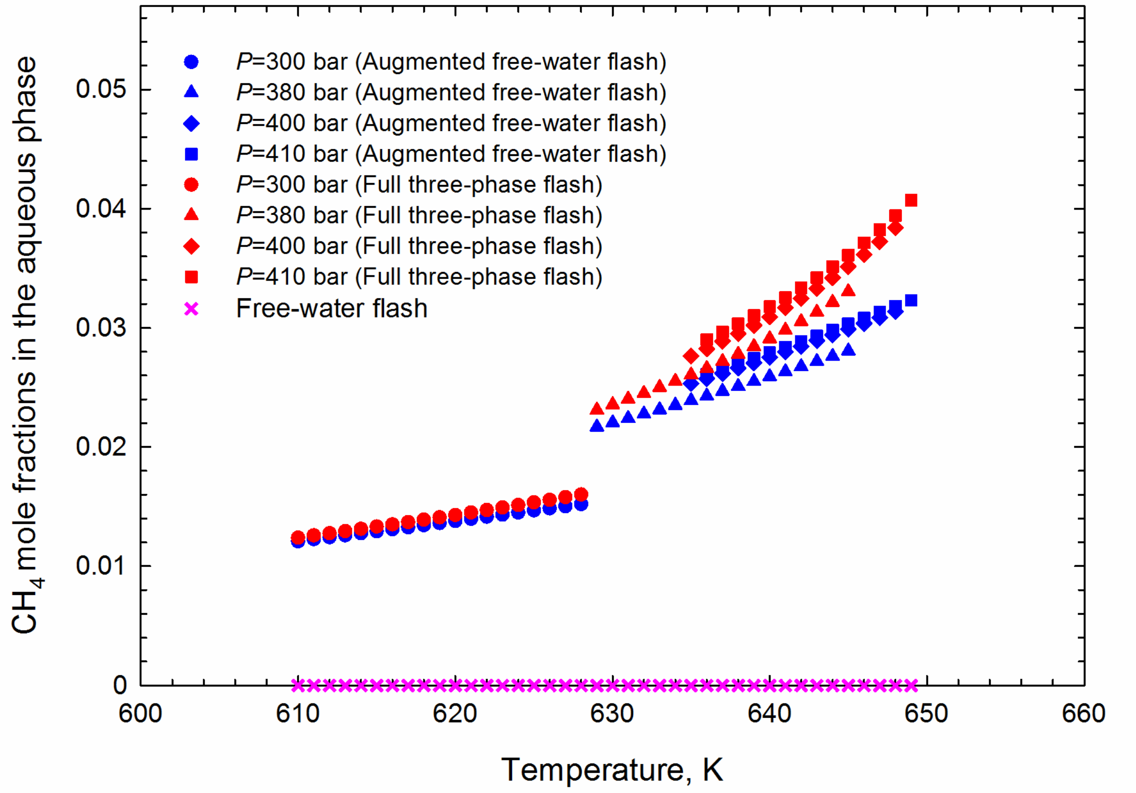


Figure 3.10 Mole fractions of methane in the aqueous phase under different pressures and temperatures obtained by the augmented free-water flash, the full three-phase flash and the free-water three-phase flash. These calculations are done for the water/reservoir fluid mixture.

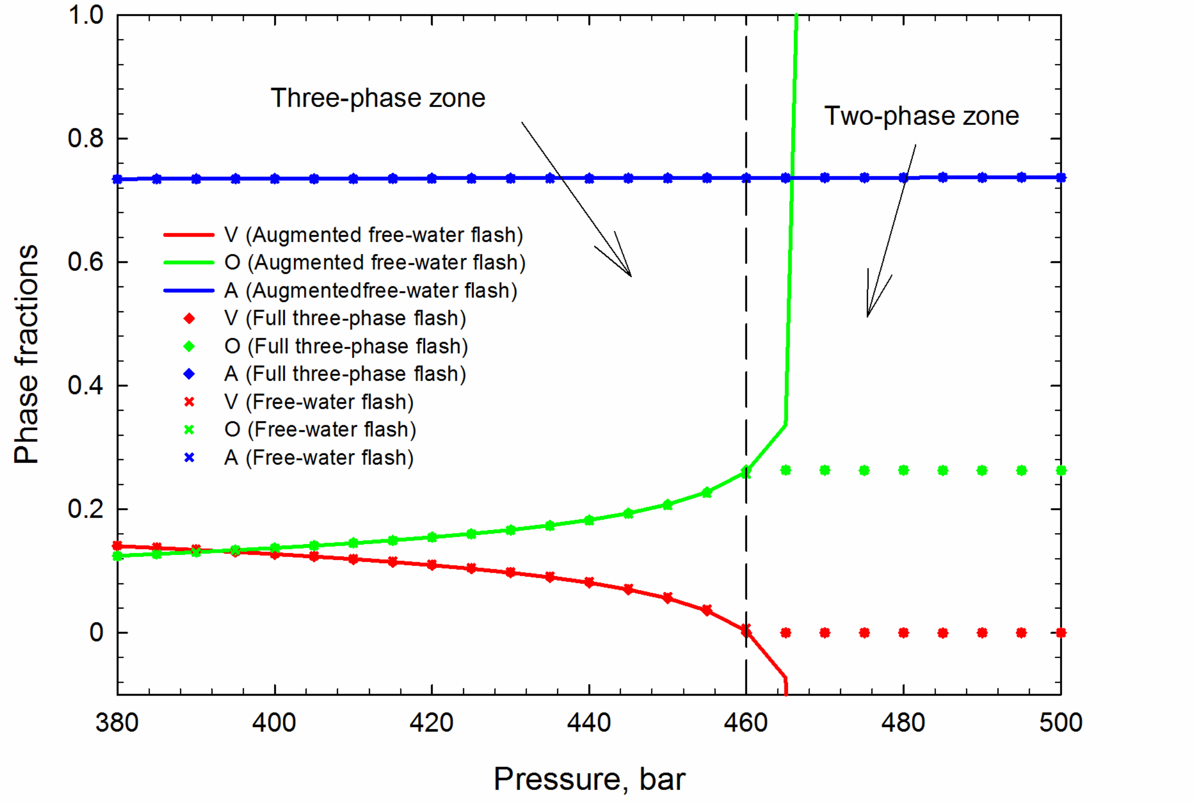


Figure 3.11 Comparison of the phase fractions obtained by applying the standalone augmented free-water three-phase flash algorithm, the full three-phase flash algorithm and the free-water three-phase flash algorithm. These calculations are done for the water/reservoir fluid mixture at *T*=470 K.

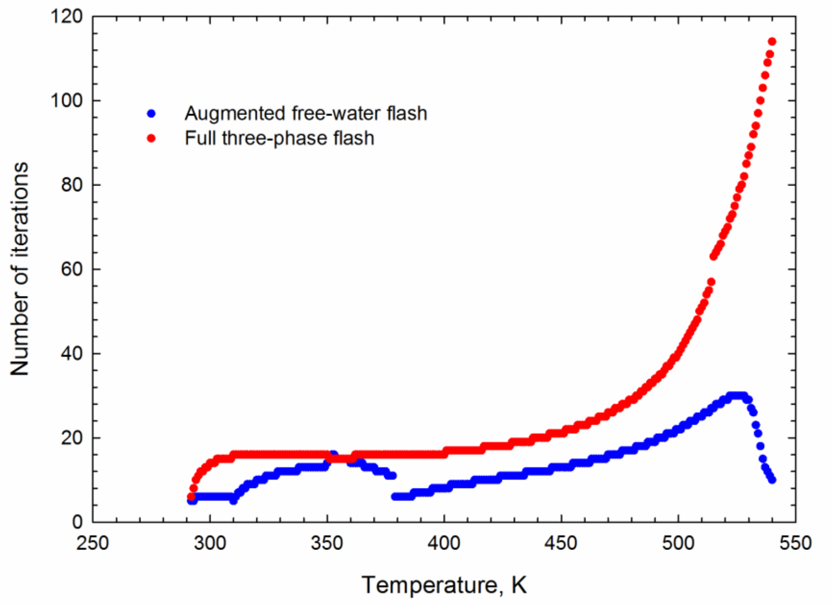


Figure 3.12 Comparison between the number of iterations required by the augmented free-water three-phase algorithm and those by the full three-phase flash method. These three-phase flash calculations are done for the water/reservoir fluid mixture at *P*=400bar.

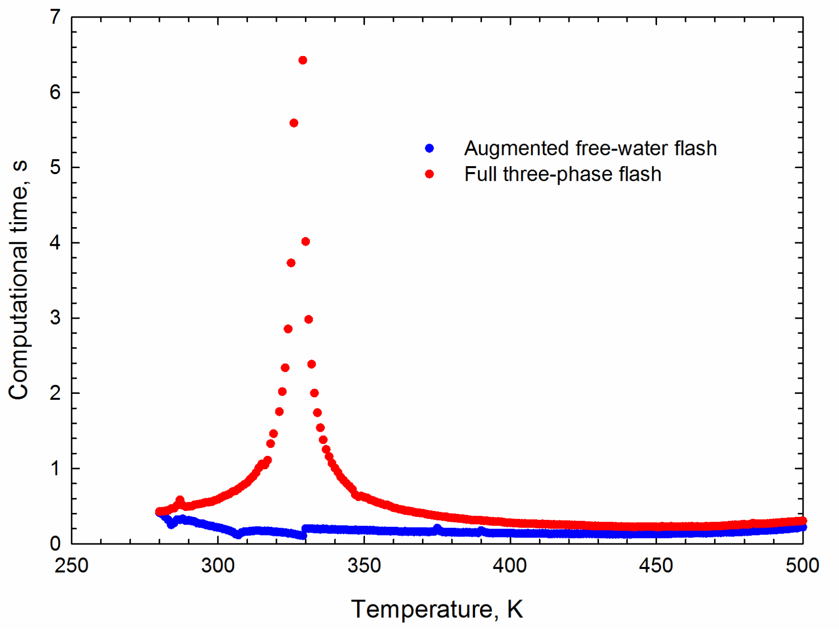


Figure 3.13 Comparison between the computational time consumed by the augmented free-water three-phase flash method and that consumed by the full three-phase flash method. These calculations are done for the water/reservoir fluid at *P*=400 bar.

CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

In this study, a new algorithm is proposed based on the assumption that only the presence of water and one soluble gas is taken into account in the aqueous phase. A flash package, coupling with the new augmented free-water three-phase flash algorithm, is developed to deal with single-phase, two-phase, and three-phase equilibria calculations. The stability of the feed is firstly tested when executing the flash package. If the feed is found to be stable, a single-phase equilibrium can be concluded. If the instability of the feed is detected, the augmented free-water three-phase algorithm is initiated. Switching criteria have been proposed to switch between two-phase and three-phase flashes. If the phase fractions calculated by this augmented free-water three-phase algorithm are beyond [0, 1] or if an open feasible region occurs during the successive substitution iterations, two-phase flash will be initiated. Moreover, effective methods for initializing *K* values are proposed in the augmented flash routine, resulting in that a fewer number of iterations is required to conduct the augmented free-water three-phase flash calculations.

The algorithm has been used firstly to simulate the phase behavior for CO_2/water/hydrocarbons mixtures; then a further application to water/hydrocarbon mixtures considering the methane dissolution in water further validates the robustness and efficiency of this augmented free-water algorithm. The results obtained by example calculations show that the augmented free-water three-phase flash algorithm can provide flash results that are in good agreement with those given by the full three-phase flash algorithm since the solubility of gas (i.e., CO_2/CH_4) in the aqueous phase has been taken into account. The computational time and number of iterations are significantly decreased with the use of the new flash package incorporating the augmented algorithm. In summary, the augmented free-water three-phase flash algorithm provides a more accurate representation of three-phase behavior than the free-water flash algorithm. The flash package coupling this proposed algorithm is computationally more efficient than the conventional full-phase flash algorithm.

4.2. Recommendations

In this work, the thermodynamic model selected for performing conventional full-phase flash is PR-EOS [1]. However, the phase density cannot be accurately predicted with PR-EOS due to the constant compressibility factor embedded in PR-EOS. Thus, in order to obtain a more accurate prediction of the molar volume and phase equilibria especially for the mixtures containing water, cubic-plus-association equation of state (CPA EOS) can be used to calculate the above thermodynamic properties as it is more appropriate for aqueous systems [2].

Moreover, as for the CO_2/hydrocarbons/water mixtures, in addition to three-phase equilibria, four-phase vapor-liquid-liquid-aqueous (VLLA) equilibria can be present under reservoir conditions. This augmented free-water flash algorithm can be extended to simulate such four-phase equilibria. Developing such four-phase free-water flash algorithm is a more challenging task, requiring us to invest on the following two aspects: 1) more work is needed to properly initialize the *K*-values used in the four-phase flash; 2) extensive efforts need to be made to properly determine the number of co-existing phases under given pressure/temperature conditions.

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