THREE-PHASE MIXING CELL METHOD FOR GAS FLOODING

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ABSTRACT

CO$_2$ miscible gas flooding is a major source of oil production in the U.S., particularly in West Texas where natural sources of CO$_2$ can be obtained at reasonable cost. Low-temperature oil displacements by CO$_2$ involve complex phase behavior, where three hydrocarbon-phases can coexist.

Reliable design of miscible gas flooding requires knowledge of the minimum miscibility pressure (MMP), which is the required pressure for high displacement efficiency. A recent published study on MMP calculation by a new mixing cell method proved to be robust and reliable for two-phase flash calculations. Unlike previous two-phase “mixing cell” methods, this new method relies entirely on robust P-T EOS flash calculation.

Previous computational aspects of MMP estimation do not attempt to estimate the MMP for mixtures exhibiting three hydrocarbon-phases due to lack of robust algorithms for three-phase equilibrium. Further, computation of multicontact miscible gas flooding involves a large number of phase equilibrium calculations in a near-critical region, where the calculations are time-consuming and difficult.

Results from experiments and simulation show that more than 95% displacement efficiency can be achieved without the development of complete miscibility for three-phase flow for low-temperature oil displacements by CO$_2$. Recent investigation on the mechanism for high displacement efficiency improved our understanding of the effect of a third hydrocarbon-phase using the robust three-phase equilibrium algorithms developed. The mechanism for high displacement efficiency occurs when critical endpoints (CEP) are encountered at the leading and trailing edges of the three-phase region.
How miscibility is developed for three-phase displacements is not well known. A potential solution could be achieved by developing a new mixing cell model by using a similar methodology as the recently published two-phase mixing cell method.

We develop a three-phase mixing cell method involving two- and three-phase behavior, which is based on robust phase equilibrium calculation algorithm. By performing cell-to-cell contacts, the mixing-cell model determines the minimum tie-line lengths and minimum tie-triangle lengths developed at a certain pressure. These tie-line lengths are used to determine the MMP by extrapolation to an infinite number of contacts.

For three-hydrocarbon-phase displacement, an inaccurate prediction of injection pressure may have significant consequences. For example, if the injection pressure is relatively high, although the displacement efficiency may be satisfactory, leads to an unnecessarily large cost of pressurizing the injected gas. If the injection pressure is low, however, the miscible displacement process may become ineffective and less oil recovery would be achieved.

We demonstrate the importance of considering three-hydrocarbon phases, where the MMP assuming a two-phase approximation can result in unnecessary increase of injection pressure without a corresponding increment on oil recovery. The novel three-phase mixing cell method can be used to predict the pressure for an efficient displacement. We further show that there may be no MMP in some displacements where three hydrocarbon-phases exist.
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Chapter 1

Introduction

This chapter provides a brief introduction to the motivations of the present study, its objectives, and its results. The following chapters discuss these subjects in detail. An outline is also given in the last section.

1.1 Description of the Problem

Miscible gas flooding is a widely used method for enhanced oil recovery (EOR). In any gas injection design, one of the most important parameters is the minimum miscibility pressure (MMP). MMP is the lowest pressure at which gas and oil become miscible at a fixed temperature. MMP is an important parameter that determines the efficiency of the oil displacement by gas. The MMP is important because when gas and oil are miscible, the pore scale efficiency (or displacement efficiency) is 100% in the absence of dispersion. Hence, knowledge of MMP is essential in gas flooding designs.

Computational methods for estimation of MMP involving two hydrocarbon-phases have been developed. Several authors proposed multiple mixing cell methods to estimate MMP. Among those methods, a true mixing cell method was demonstrated to be simple, rapid, accurate and significant adverse effects of dispersion. This new mixing cell method can accurately determine all key tie lines of interest for a displacement of any displacement type, including combined condensing/vaporizing drives.

It is not trivial to understand the high displacement efficiency for low-temperature oil displacements by CO₂ because simulation of multicontact miscible gas flooding requires many phase equilibrium calculations in a near-critical region. Calculation of phase equilibrium is difficult and time-consuming for mixtures of reservoir oil and CO₂ at low temperature typically
below 120°F, where a third solvent-rich liquid phase can coexist with the oleic and gaseous phases.

Thanks to a benchmark contribution for constant-\(K\) flash calculation by Okuno et al. (2009), their robust and practical algorithm is guaranteed to converge to the correct solution for both positive and negative flash three-phase flash calculations. Based on the robust and efficient algorithms for three-phase equilibrium calculations, the mechanism for high displacement efficiency resulting from critical endpoints (CEPs) behavior when three hydrocarbon-phases are present has been explained for the first time.

There is no computational method to calculate the pressure of an efficient displacement and the thermodynamic MMP for three hydrocarbon-phases. The existing theory for the mixing cell method involves only two hydrocarbon-phases and the estimated MMP using two-phases mixing cell model for three-phases system could result in unnecessarily high injection pressure thus overestimating the optimal injection pressure. Development of a three-phase mixing cell method will make a contribution to improve our knowledge for enhanced oil recovery involving complex phase behavior for low-temperature CO\(_2\) flooding.

1.2 Research Objectives

Phase equilibrium calculations for three hydrocarbon phases become more difficult, complicated, and time-consuming than two-phase equilibrium calculations. Understanding the displacements exhibiting three hydrocarbon-phases requires robust and efficient three-phase flash calculation algorithms. Although the mechanism of a third hydrocarbon-phase on low-temperature oil displacement has been investigated recently, the pressure of an efficient displacement was not calculated in prior studies. In this thesis, we develop a mixing cell method for three hydrocarbon-phases using a robust reduced three-phase flash calculation method developed by Okuno et al. (2009). Using this three-phase mixing cell method, we calculate the
shortest tie-line and tie-triangle lengths with pressure in the displacement, and examine how the three-phase behavior affects these tie-line and tie-triangle lengths.

The objectives of the present study were to:

1. Develop a multiple mixing cell model, which is capable of handling two and three hydrocarbon-phases.
2. Demonstrate the importance of using three-phase mixing cell method for estimation of MMP or pressure for an efficient displacement.
3. Examine the oil recovery as a function of the minimum tie-line length / minimum tie-triangle length and injection pressure.
4. Understand the mechanism of high efficiency of oil displacements involving a third hydrocarbon-phase.

To achieve the first objective, we used a robust and efficient reduced method for stability analysis and flash calculations from Okuno et al. (2009). For the second objective, we calculate the minimum miscibility pressure using PennPVT (a two-phase mixing cell model) by assuming only two hydrocarbon phases. Also, we compared the results from our mixing cell model with 1-D compositional simulation in UTCOMP, a multiphase compositional reservoir simulator (Chang et al. 1990).

1.3 Outline of the Thesis

This thesis consists of seven chapters. Chapter 2 gives a literature review on a new mixing cell method for two phases. Algorithms of robust three-phase equilibrium calculations and negative flash calculations are then described. After that, the mechanism of low-temperature oil displacements by CO₂ is also reviewed.
In Chapter 3, we describe the new multiple mixing cell method developed which is not affected by dispersion for two-hydrocarbon phases. We calculate the MMP from PennPVT as an example of this method.

In Chapter 4, we demonstrate the importance of properly using a negative three-phase flash. The influence of initial $K$-values estimates on the convergence for stability analysis phase and flash calculations are investigated. We improve the three-phase equilibrium calculation by providing good initial estimates for $K$-values.

Chapter 5 extends the mixing cell method for two hydrocarbon-phases to three-phases to investigate the mechanism for high efficiency of low-temperature oil displacements by CO$_2$ where three hydrocarbon-phases coexist at equilibrium.

In Chapter 6, the same fluid models are used to study the complex three-phase behavior and its effects on displacement efficiency. Results from UTCOMP (a volume based IMPEC simulator) are used to calculate the oil recovery factor. Results from three-phase mixing cell method and the one-dimensional compositional simulation are then compared.

Finally, recommendations for future research are also presented in Chapter 7.
Chapter 2

Literature Review

This chapter provides a background on how to make positive and negative phase equilibrium calculation and computational methods of minimum miscibility pressure (MMP) estimation. Previous research on the characteristics and mechanism of low-temperature oil displacements by CO₂ is also reviewed.

2.1 MMP and Development of Miscibility in Gas Injection

During gas injection, miscibility can develop in one of two ways: first-contact miscibility (FCM) or multi-contact miscibility (MCM). If the oil and gas fluids form a single phase when mixed in any proportion when brought into contact, they are first-contact miscible. In most cases, oil and gas develop miscibility after exchanging components. The resulting miscibility is called multi-contact miscibility.

Multi-component miscibility can happen in three types of displacements: a vaporizing gas drive, a condensing gas drive, and a condensing/vaporizing (CV) drive. In vaporizing gas drives, the vaporization of the intermediate component from the oil into the vapor phase can lead to efficient displacement if enough of the intermediate component is present in the oil. The miscibility for this type develops at the oil tie line. The second type of condensing gas drive occurs when the transfer of intermediate component from the injected gas to the liquid phase. In this way, the miscibility develops at the gas tie line. The third type is called condensing/vaporizing gas drive, where the oil and gas become miscible through both the transfer of intermediate components from gas to oil and from oil to gas. For this type, the miscibility develops at neither the oil tie line nor the gas tie line, but one of the other key tie lines which are called crossover tie lines.
MMP can be estimated using several experimental methods: slim-tube experiments, mixing-cell experiments, rising bubble/falling drop experiments, and vanishing interfacial tension experiments. The experimental methods are both costly and time consuming and some of them fail for a condensing/vaporizing gas drive. Computational methods for MMP estimation have been developed: slim-tube compositional simulation, correlations, analytical calculations with method of characteristics (MOC), and multi-contact mixing cell methods. Slim-tube compositional simulation can be time-consuming and affected by numerical dispersion. Analytical calculations with MOC have some assumptions, which are not valid for complex fluid systems and the resulting MMP from analytical solutions are not valid for complex fluid systems. Ahmadi et al. (2011) showed an example where an incorrect MMP resulted from MOC calculation. Also there are limited MOC solutions for three-phase partially miscible flow could give reference.

The new mixing methods are fast and convenient alternatives to otherwise slow and expensive computational procedures. The next section reviews the shortcomings of the old mixing cell models and improvements of the MMP estimation from the new mixing cell method.

2.2 Mixing Cell Methods for Estimating MMP

The mixing cell method for estimating MMP is to mix analytically gas and oil in repeated contacts in one or a series of virtual PVT cells, and performing phase equilibrium calculations. In the section, we first review single-cell calculation and then multi-cell calculations.

2.2.1 MMP calculation with a single cell

MMP with a single mixing cell uses a single virtual PVT cell combined with an equation-of-state to estimate MMP. These published methods are based on the simplifying assumption that the oil or gas tie line controls miscibility (Hutchinson and Braun 1961). If miscibility is controlled
by either a condensing drive or vaporizing drive, single-cell mixing cell methods can accurately estimate the MMP. Miscibility is developed for condensing/vaporizing displacements in between the condensing and vaporizing portions, not at the leading edge or trailing edge in vaporizing or condensing drives. However, for most gas floods including CO₂ floods, the MMP estimates can be in error using a single mixing cell since the mechanism for miscibility development is the combined condensing/vaporizing drive.

2.2.2 MMP calculation with prior multiple cell method

Multiple mixing-cell methods consider only phase equilibrium calculations, and solving the flow equation is not carried out (Cook et al. 1969; Jaubert et al. 1998ab; Metcalfe et al. 1973; Zhao et al. 2006). Early multiple mixing cells methods were used to study the development of miscibility rather than calculating the MMP. Jaubert et al. (1998b) published the first algorithm for calculating MMP. Zhao et al. (2006a; 2006b) presented a more complex multiple mixing-cell method, where they included fractional flow to determine transfer amounts. The drawbacks relate to these previous mixing cell methods are derived from simplifying compositional simulators, and thus they inherit the drawbacks of simulations, including the effect of dispersion.

2.2.3 MMP calculation with a new multiple mixing cell method

This section presents a simple, practical, and robust multiple mixing-cell method to determine the MMP for displacements with any number of components proposed by Ahmadi et al. (2011). They developed a true mixing cell method that works for all displacements regardless of the displacement mechanism. Their mixing cell is not a simplified slim-tube simulation, and uses tie-line length as the criterion to estimate MMP.

Miscibility is achieved whenever one of the key tie lines becomes zero length where the length of a tie line is calculated by Eq. (2.1), in which x and y are equilibrium liquid and vapor compositions.
Tie-line Length \( = \| x - y \| = \sqrt{\sum_{i=1}^{Nc} (x_i - y_i)^2} \) (2.1)

The new mixing cell algorithm is based on finding the key tie-line lengths at each pressure. This procedure can be time consuming, depending on the tolerances specified for the convergence to each key tie line. In subsequent sections we review the key advantages and improvements. The faster approach for MMP calculation based on a novel extrapolation technique in their paper is not reviewed in this chapter but in Chapter 3.

The procedure of Ahmadi et al. (2011) is the following:

1. Specify the reservoir temperature, and an initial trial pressure that is below the MMP. The first trial pressure is based on the MMP of the purely condensing and purely vaporizing drives.

2. Start with two cells filled with injection gas, and reservoir oil as shown in Figure 2.1, where injection gas is located in the upstream cell and the reservoir fluid in the downstream cell. The reservoir oil and injection gas are then mixed and a flash or negative flash (Whitson and Michelsen 1989) with a cubic EOS is performed at this overall composition, resulting in two equilibrium compositions, one for liquid, and one for vapor.

3. Make additional contacts by mixing neighboring cells assuming gas moves ahead of the oil phase, until all \( Nc-1 \) key tie lines develop and converge to a specified tolerance. Once all the key tie lines are found, proceed to next step.

4. Calculate the tie-line length of each key tie line found and store the minimum tie-line length (TL).

5. Increase the pressure and repeat steps 1 through 4, and then determine an estimate of the MMP as the pressure at which the power-law extrapolation gives zero length.
The multiple mixing-cell method of Ahmadi et al. (2011) does not use a fixed number of cells, whereas all the previous methods do. In their mixing-cell method, cells do not have volume, while in other methods, cells do.

The mixing cell approach proposed here requires no input of petrophysical parameters or the solution of the flow equations. Their approach can also correct for dispersion by continuing cell-to-cell contacts until all the key tie lines are converged (or one of the tie lines approaches zero length), or by extrapolation of the results to an infinite number of contacts.

2.3 Three-Phase Flash Using a Reduced Method

This section explains the required basics for phase equilibrium calculations; the first part of this section derives fundamental equations to be satisfied at phase equilibrium, and reviews formulations and algorithms for flash calculations and stability analysis. Use of a robust multiphase Rachford-Rice equation extended to negative flash region is then reviewed.

2.3.1 Stability analysis

The total differential of the Gibbs free energy for a $N_p$-phase mixture consisting of $N_c$ components is

$$dG = (\partial G/\partial T)_{P,V} dT + (\partial G/\partial P)_{T,V} dP + \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \overline{G}_{ij} d n_{ij},$$

where $\overline{G}_{ij}$ is the partial molar Gibbs free energy of component $i$ in phase $j$ and $n_{ij}$ is the moles of component $i$ in phase $j$. At a fixed temperature and pressure, the above equation becomes

$$dG = \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \overline{G}_{ij} d n_{ij}.$$  

(2.3)

The molar Gibbs free energy of a multicomponent, multiphase system is given as

$$\overline{G} = \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \beta_{ij} x_i \overline{G}_{ij}$$

(2.4)
where $\beta_j$ is the mole fraction of phase $j$ and $x_{ij}$ is the mole fraction of component $i$ in phase $j$.

Stability analysis can detect whether a phase mixture is stable at a given temperature $T$, pressure $P$, and composition $z$. Stability analysis for two phases can provide a good estimate of $K$-values for the subsequent flash calculation for three phases.

Baker et al. (1982) demonstrated that a stable equilibrium state must be the global minimum of the Gibbs free energy. They also developed a necessary and sufficient condition for phase stability, that is, the tangent plane to the Gibbs free energy surface at a stable equilibrium state cannot lie above the Gibbs free energy surface at any composition. Based on the conclusion of Baker et al. (1982), Michelsen (1982a) developed a practical computational procedure for stability analysis by defining the tangent plane distance (TPD) function. The TPD function is the difference between the Gibbs free energy and the tangent plane to the Gibbs free energy at a phase composition. A phase is stable when the TPD function is positive or zero. The TPD function $D(x)$ is obtained in dimensionless form,

$$D_n(x) = D/RT = \ln \frac{\sum C_i x_i}{\sum \exp \left( -D/RT \right) x_i \ln x_i \varphi_i(z)}.$$  \hspace{1cm} (2.5)

Stability analysis searches for a composition at which the TPD function is negative. To identify phase stability, Michelsen (1982a) suggested to locate stationary points on the TPD function and checks the sign of the TPD function. This procedure is known as the stationary point method of. The stationary points are found at,

$$\ln X_i \varphi_i(x) - \ln z_i \varphi_i(z) = 0, \text{ where } X_i = x_i \exp(-D/RT) \text{ and } i = 1, ..., N_C.$$  \hspace{1cm} (2.6)

The stationary point method locates stationary points using equations (2.6) and checks to see if $\sum X_i > 1.0$ ($i = 1, ..., N_C$). If a stationary point at which $\sum X_i > 1.0$ is detected, then the current phase with a composition of $z$ is unstable. Otherwise, the current phase is assumed to be stable.
For multiphase mixtures, stability analysis is performed for a single-phase mixture or individual phases of a multiphase mixture. A test phase composition is the composition of one of the two known phases. However, it is difficult to ensure location of the global minimum of the TPD function from all stationary points using the stationary point method.

In stability analysis for two phases, Michelsen (1982a) recommended using the lightest and heaviest components as pure phases for initial estimates. Additionally, the following two sets of initial estimates have been used:

\[ X_i = z_i \varphi \left( \frac{z}{N} \right) \]  
\[ X_i = \sum_{j=1}^{N_P} \frac{y_{ij}}{N_P} \]  

(2.7)

(2.8)

### 2.3.2 Basics of phase equilibrium calculations

Flash calculations are used to determine equilibrium phase compositions and phase amounts for a given temperature \( T \), pressure \( P \), and overall composition \( z \). Robustness of flash calculations depends on the formulation and also the algorithm.

For a closed system at fixed temperature and pressure, the first-order necessary condition for a minimum of the Gibbs free energy in terms of fugacity is the following fugacity equations:

\[ \ln f_{ij} - \ln f_{i \varphi} = 0, \quad \text{where} \quad i = 1, \ldots, N_c \quad \text{and} \quad j = 1, \ldots, (N_P - 1) \].

(2.9)

In equations (2.9), \( f_{ij} \) is the fugacity of component \( i \) in phase \( j \). Phase \( N_P \) is the reference phase. The fugacity equations (2.9) are the working equations for flash calculations.

\[ F_{ij} = \ln \left( x_{ij} \varphi_{ij} \right) - \ln \left( x_{i \varphi} \varphi_{N_P} \right) = 0, \quad \text{where} \quad i = 1, \ldots, N_c \quad \text{and} \quad j = 1, \ldots, (N_P - 1) \]  

(2.10)

Fugacity equations are the first-order necessary conditions for a minimum of the Gibbs free energy, and solution of fugacity equations converges to a stationary point of the Gibbs free energy. The converged stationary point can be a minimum, or a saddle point, or a maximum.
However, robustness of flash calculations depends not only on the formulation but also on the algorithm used. The best way to avoid convergence to a false solution is to provide good initial estimates of $K$-values at the start of the flash. Good initial estimates are often available from the previous time step in compositional reservoir simulation except when the number of equilibrium phases changes over the time step (Okuno et al. 2010).

When the Hessian matrix is ill-conditioned, flash calculations are significantly affected by round-off errors due to the nearly singular Hessian matrix. The ill-conditioned Hessian matrix frequently occurs during simulation of multicontact miscible gas flooding because of a large number of flash calculations in near-critical regions (Trangenstein 1985).

Another issue in flash calculations is convergence to a false solution where multiple phases have the same composition and density. For two and three phases, this kind of false solution is called the trivial solution. There are also false solutions as well, not trivial ones.

Okuno et al. (2009) used the successive substitution algorithm to provide initial estimates for the independent variables. The subsequent algorithm is based on Newton’s method, and the convergence rate is quadratic in the vicinity of a solution.

### 2.3.3 Reduced method

Reduced methods for phase equilibrium calculations have been studied as a potential solution to improve the efficiency of compositional simulation. Number of independent variables or equations to be solved should be minimized because computational efforts rapidly increase with the number of equations to be solved.

Li and Johns (2006) introduced two sets of component-specific parameters $h_i$ and $g_i$ to replace binary interaction coefficients (BICs) during fluid characterization to accurately predict the phase behavior:

$$ k_{ij} = (h_i - h_j) g_i g_j, \quad \text{where } i, j = 1, ..., N_c. $$

(2.11)
The fugacity coefficient using a cubic EOS can be expressed using the following five reduced parameters, which are defined as

\[ \theta_j = \sum_{i=1}^{N_C} \eta_{ij} x_i, \]  

(2.12)

where \( \eta_i = \left( B_j, \sqrt{A_{ij} h_{ij}}, \sqrt{A_{ij}^2 g_{ij}}, \sqrt{A_{ij} g_{ij}} \right), j = 1,...,N_p, \) and \( k = 1,...,5. \)

For conventional formulations, the minimum number of independent variables or equations to be solved is \( N_C(N_p - 1) \) for a \( N_p \)-phase flash calculation using \( N_C \) components, while reduced flash algorithm solves for \( 6(N_p - 1) \) independent variables. The reduced method is initiated by the successive substitution (SS) method for flash calculation, and followed by Newton’s method.

### 2.3.4 Two-phase negative flash calculations

There are two types of flash calculations. Positive flash is an \( N_p \)-phase flash where the overall composition lies within the \( N_p \)-phase region, resulting in positive phase mole fractions. Negative flash is a flash where the overall composition is not within the \( N_p \)-phase region resulting in one or more negative phase mole fractions. Another type of negative flash, where the overall composition lies in negative composition space is not considered in this thesis. The feasible domain for phase mole fractions is wider than the physical region.

Whitson and Michelsen (1989) made a comprehensive discussion on the first type of two-phase negative flash. They calculate vapor-liquid equilibrium for systems that physically exist as a single phase, but still yield non-negative equilibrium compositions that satisfy the material balance and equal fugacity constraints for the P-T flash.

Allowing for a negative flash is important because of two reasons. First, to increase the robustness of the iterations, a few iterations may be outside of the multiphase region of interest, but with more iterations can move back into the multiphase region. Second, the mixing cell

...
method is entirely dependent on a negative flash, which offers information of tie line for MMP calculation.

Allowing for negative equilibrium phase fractions with

\[ L + V = 1 \] (2.13)

where \( L \) is liquid mole fraction, \( V \) is the vapor mole fraction. A component material balance must also be satisfied,

\[ z_i = x_i L + y_i V, \quad i = 1, \ldots, N_c \] (2.14)

The equilibrium mole fractions must also sum to unity,

\[ \sum_{i=1}^{N_c} x_i = \sum_{i=1}^{N_c} y_i = 1, \quad i = 1, \ldots, N_c. \] (2.15)

Equations (2.14) and (2.15) could be satisfied by solving the Rachford-Rice (1952) problem,

\[ f(V) = \sum_{i=1}^{N_c} (y_i - x_i) = 0. \] (2.16)

With constant \( K \)-values,

\[ K_i = y_i / x_i, \quad i = 1, \ldots, N_c, \] (2.17)

the objective function to be solved for the single unknown phase fraction, \( V \), is

\[ f(V) = \sum_{i=1}^{N_c} \left( \frac{z_i (K_i - 1)}{1 + V (K_i - 1)} \right) = 0, \quad i = 1, \ldots, N_c. \] (2.18)

Michelsen’s window for the problem is then derived as follows. From Eqs. (2.14) and (2.17), we write:

\[ z_i = x_i (1 + V(K_i - 1)) = x_i m_i(V), \quad i = 1, \ldots, N_c. \] (2.19)

The physical domain problem is defined by

\[ m_i(V) > 0 \] (2.20)
where \( f(V) \) is a monotonically decreasing function of \( V \), and there is only one unique solution existing between \( V_{\text{min}} \) and \( V_{\text{max}} \).

\( K \)-values are updated based on fugacity equations in the outer iteration loop. Iranshahr et al. (2010) noted that the physical domain is a bounded set of phase fractions if the \( K \)-values satisfy equation (2.22).

\[
\frac{\partial m_i}{\partial V} = g_i = K_i - 1, \ i = 1, \ldots, N_c
\]  

(2.21)

\[
\exists i, j \text{ such that } g_i g_j < 0.
\]  

(2.22)

### 2.3.5 Three-phase negative-flash calculations for constant-\( K \) values

Phase distribution calculation, or solution of Rachford–Rice (RR) equations, is an important step in phase equilibrium calculations. The multiphase algorithm to solve Rachford–Rice equations for negative flashes is reformulated as an unbounded linearly constrained minimization by Leibovici et al. (2008). The elegant minimization method first proposed by Michelsen (1994) solved for a convex objective function. Michelsen’s function was modified in such a way that the new function gradients are identical to the RR equations. Yan et al. (2012) showed that multiphase negative flash for ideal solutions can diverge if the feasible domain is not closed.

Large feasible regions contain zones near poles where the Hessian matrix is ill-conditioned. Okuno et al. (2009) developed a robust constant-\( K \)-flash algorithm with \( N_p \) phases as a minimization of a non-monotonic convex function with \( N_c \) linear constraints for multiphase RR equations that is guaranteed to converge to the correct solutions for both positive and negative flash calculations. The small feasible region defined by \( N_c \) linear constraints contains no poles. The initial guesses for phase molar fractions are ensured in the feasible region.
The minimization function $F$ in Okuno et al. (2009) is,

$$F(\beta) = \sum_{i=1}^{N_c} [-z_i \ln|t_i|]$$

where $t_i = 1 - \left[ \sum_{j=1}^{N_r-1} (1 - K_{ij}) \beta_j \right]$ for $i = 1, \ldots, N_c$ and $j, k = 1, \ldots, N_p - 1$.

A gradient vector of the function $F$ consists of the RR equations,

$$\nabla F = f = \{ f_i \} \in \mathbb{R}^{(N_r-1)}.$$  \hspace{1cm} (2.24)

The Hessian matrix consists of the derivatives of the RR equations with respect to the independent variables. That is,

$$\nabla^2 F = \{ H_{ij} \} = \{ \partial f_i / \partial \beta_j \} \in \mathbb{R}^{(N_r-1) \times (N_r-1)}.$$  \hspace{1cm} (2.25)

The smaller feasible domain is based on the non-negativity of phase component mole fractions, which requires the following inequalities:

$$0 \leq z_i \leq t_i = 1 - \left[ \sum_{j=1}^{N_r-1} (1 - K_{ij}) \beta_j \right]$$

$$0 \leq K_{ij} z_i \leq t_i = 1 - \left[ \sum_{j=1}^{N_r-1} (1 - K_{ij}) \beta_j \right].$$  \hspace{1cm} (2.26)

Opanness of the feasible domain is the criterion for judging divergence. Iranshahr et al. (2010) dealt essentially with the algorithms for phase distribution calculations at constant fugacity coefficients (i.e., ideal solutions). They derived the mathematical criterion to check the openness of the feasible domain in equation (2.28). Their constant $K$-flash calculation is then combined with the tie-simplex tabulation, where complete tie-simplex information is available in $P-T-x$ space of interest. That is,

$$g_{i,j} = \frac{(K_{j1} - 1)(K_{i2} - 1) - (K_{i1} - 1)(K_{j2} - 1)}{\sqrt{(K_{j1} - 1)^2 + (K_{j2} - 1)^2}},$$  \hspace{1cm} (2.27)

where $i$ and $j$ refer to the component indices, $i, j = 1, \ldots, N_c$.

The feasible domain is bounded if and only if
\exists j, k \text{ such that } g_{j,j}g_{k,k} < 0, \ i=1,...,N_c. \quad (2.28)

2.4 Low-Temperature Oil Displacement by CO₂

Multiple equilibrium-phases exist for mixtures of reservoir oil and CO₂ at temperatures typically below 120°F. Those phases include gaseous, oleic, CO₂-rich liquid, and asphaltenes. In this research, we consider at most three hydrocarbon-phases; gaseous (V), oleic (L₁), and CO₂-rich liquid (L₂) phases. This section first provides a review of the complex phase behavior of low-temperature CO₂ flooding, and then the displacement mechanism involving such complex phase behavior is reviewed.

2.4.1 Multiphase behavior of CO₂/reservoir-oil mixtures

The displacement efficiency can be significantly influenced by the phase behavior during the displacement of reservoir oil by CO₂. Phase behavior of CO₂/reservoir-oil mixtures involving L₁-L₂-V equilibrium has conventionally been studied on a P-x diagram. Figure 2.2 (Okuno, 2009) presents the phase behavior for the pseudo-binary system of a west Texas oil and CO₂ solvent.

Equilibrated two liquid-phases (L₁-L₂) can coexist above the three-phase region at higher pressures. Turek et al. (1998) reported that a L₂-V region exists at equilibrium at pressures above the three-phase region at very high CO₂ mole fractions (e.g., more than 99%) in their single-contact measurements for CO₂ and west Texas oils.

A P-x diagram for solvent/reservoir oil shows only a small part of actual phase behavior spanning P-T-x space. Use of a pseudo-binary phase diagram will lead to large error since it only represents phase behavior along the mixing line between the injection gas and reservoir oil at a fixed temperature. However, the observed composition path during an oil displacement is not the
mixing line between the oil and gas and the phase behavior along the composition path is more important to understand.

There are two types of critical endpoints (CEP) for CO$_2$/reservoir-oil system that form three-hydrocarbon-phases. The first type of CEP is where the two liquid phases $L_1$ and $L_2$ merge in the presence of the V phase ($L_1=L_2=V$). The second type of CEP is where the $L_2$ and V phases merge in the presence of the $L_1$ phase ($L_1=L_2=V$).

Representation of phase behavior by a ternary diagram does not have sufficient degrees of freedom to model critical points for more than two phases. CEPs only have one degree of freedom in $P-T-x$ space for three components, and the tricritical point has no degrees of freedom in $P-T-x$ space for three components.

2.4.2 Displacement characteristics and efficiency

The reported slim-tube measurements in the literature show that low-temperature oil displacement by CO$_2$ involving three hydrocarbon-phases can achieve more than 90% displacement efficiency (e.g., Yellig and Metcalfe 1980, Gardner et al. 1981 and Orr et al. 1983). Several authors reported simulation results involving three hydrocarbon-phases. The one-dimensional displacement simulations by Li and Nghiem (1986) showed high oil recovery without a miscible bank. Simulation results of west Texas oil displacements by CO$_2$ reported by Khan et al. (1992) stated that the high displacement efficiency of more than 90% can be achieved in the presence of immiscible three-hydrocarbon-phase flow.

Oil displacements by CO$_2$ involving $L_1$-$L_2$-$V$ equilibrium can achieve more than 95% displacement efficiency even if the two-phase regions are significantly immiscible. Okuno et al. (2010) explained the mechanism for high displacement efficiency as the composition path goes near the CEPs.
Figure 2.1 Illustration of repeated contacts in the new multiple mixing cell method. G: injecting gas composition; O: oil composition; Y: equilibrium gas composition; X: equilibrium liquid composition (Ahmadi et al. 2011).

Figure 2.2 $P-x$ diagram for the pseudo-binary mixture of a west Texas oil and CO$_2$ solvent.
Chapter 3

Multiple Two-Phase Mixing Cell Method

PennPVT is a phase behavior calculation toolkit developed in the Gas Flooding Joint Industry Project at the University of Texas at Austin. The toolkit incorporates phase equilibrium calculations (PT flash calculations) and minimum miscibility calculations (MMP calculations) for miscible gas flooding involving L-V equilibrium. The current two-phase mixing cell method is implemented in PennPVT.

CO₂ flooding at low temperatures often results in three hydrocarbon-phases, including a CO₂-rich liquid phase. However, computational methods for the calculation of MMP capable of handling three-phase equilibrium have not been developed. This is also true for the oil/solvent systems studied in this chapter. Based on the two-phase equilibrium assumptions for representation of real three-phase behavior, we give two examples of MMP calculations by PennPVT.

3.1 Multiphase Behavior of CO₂/Reservoir-Oil Mixtures

The four-component (quaternary) EOS fluid model developed by Okuno (2010) is referred to as the Bob Slaughter Block-Quaternary (BSB-Q) oil. The EOS parameters for the BSB-Q oil are given in Table 3.1. We consider gas injection (95% CO₂ and 5% C₁ injection) at the reservoir temperature of 105°F (Khan et al. 1992). The first quaternary fluid model is based on the original BSB oil that consists of seven components.

The second reservoir oil is the Bob Slaughter Block (BSB) west Texas oil and the fluid properties are summarized in Table 3.2. The reduced parameters $h_i$ and $g_i$ ($i = 1,...,N_C$) are also given together with conventional binary interaction coefficients BIC.
Figure 3.1 is the $P$-$x$ diagram for the pseudo-binary mixture of the BSB-Q oil and injection gas given in Table 3.1 (Okuno, 2009). The phase behavior is represented along the mixing line between the oil and injection gas instead of the actual composition path during displacements. Three-phase equilibrium region occurs in a different, wider pressure range during the displacements. Figure 3.2 represents the $P$-$x$ diagram for the BSB reservoir oil and injection gas at the reservoir temperature predicted by the EOS model (Okuno, 2009). Three hydrocarbon-phases occupies over a relatively small portion compared to the previous example with the BSB-Q oil.

### 3.2 MMP Calculation – Mixing Cell

This section gives a brief description of the fast MMP approximation procedure, which has been implemented in PennPVT with a two-phase mixing cell method.

1. At a fixed pressure, find the minimum tie-line length with each additional contact.
2. Plot the minimum tie-line length as a function of the power of the inverse of the number of contacts ($1/N^m$). Different values of $m$ are used to fit the data on a straight line. The sensitivity of the MMP to this value $m$ can also be estimated.
3. Find the minimum tie-line length at an infinite number of contacts by extrapolation.
4. Find the pressure at which the extrapolated tie-line length for an infinite number of contacts ($TL^\infty$) is exactly zero.

### 3.3 Examples of MMP Calculations with Two-phase Mixing Cell Method

This section presents example MMP calculation with the two-phase mixing cell method available in PennPVT. The MMP is the pressure at which the extrapolated minimum tie-line length becomes zero. The first MMP calculation example is for the BSB-Q oil quaternary displacement by a two-component injection gas (CO$_2$ 95% and C$_1$ 5%) at a temperature of 105°F.
MMP calculation is also performed for the second seven-component BSB oil displacement by a two-component injection gas at 105°F.

### 3.3.1 Input of parameters for MMP calculation

The MMP calculation has three steps in the excel PennPVT spreadsheet. First, add the compositions and PR 78 EOS parameters of the reservoir oil and injection gas from Table 3.1 manually to the sheet. Second, specify the binary interaction coefficients (BIC). Third, set the options of the calculation such as tolerance values. The screenshot of the Data sheet is shown in Figure 3. The screenshot of BIC sheet is shown in Figure 3.4.

The starting pressure is selected to be 500 psia in this case. It is important to choose an initial pressure that is below the MMP. After having all the prerequisite input parameters specified, we start the MMP calculation with the mixing cell method option. The number of contacts is typically set at 30, although more can be used if greater accuracy is desired.

### 3.3.2 CO₂ solvent displacement of BSB-Q oil

MMP values calculated from the mixing cell method for the BSB-Q oil at 105°F uses only the two-phase equilibrium assumption. That is, two-phase equilibrium is assumed to be stable. The result of the MMP calculation is presented in a sheet as shown in Figure 3.5. The top part of the sheet shows the setup of the problem. In Figure 3.5, the minimum tie-line lengths are given as a function of the number of contacts \( (1/N^m) \) for a four-component oil displaced by injection gas described in Table 3.1, where \( N \) is the number of contacts, \( m \) is the exponent used in power-law extrapolation for data fitting.

Here, different values of \( m \) are used so that the data fall on straight line. In this example, PennPVT reports a range of MMPs for \( m=0.2, 0.25, \) and 0.3. The estimation of MMP with this approach is less than a minute when using 30 contacts, compared to the typical slim-tube
experiment, which will take about one month for one MMP estimation. The sensitivity of the MMP is obtained by using \( m = 0.2 \) and \( m = 0.3 \) to estimate a lower and upper MMP value.

Based on the two-phase assumption for the fluid model in Table 3.1, the MMP using the mixing cell method is estimated to be 1454 +/- 60.7 psia. The predicted MMP calculated during the BSB-Q oil displacement by CO\(_2\)-rich gas takes more effort than the usual MMP calculations, which are based on true two-phase behavior. For the real three-phase behavior, the two-phase mixing cell may detect the wrong tie-lines during its flash calculation process.

### 3.3.3 CO\(_2\) solvent displacement of BSB oil

For the second MMP calculation example, we consider the seven-component BSB oil displacement by injection gas assuming only two phases exist during CO\(_2\) solvent flooding. Figure 3.6 shows the output sheet by PennPVT. The estimated MMP using two-phase mixing cell method is reported to be 1370+/- 69.9 psia using the same extrapolation method as discussed in the previous section.

Both the BSB-Q and BSB oil have large three-phase regions. The reliability of the two-phase mixing cell model on prediction of reservoir fluids displacements by injection gas involving actual three-phase will be discussed in the later chapters.
### Table 3.1 Fluid properties for BSB-Q oil (a quaternary model for the BSB oil)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Properties</th>
<th>Oil (Mol %)</th>
<th>Gas (Mol %)</th>
<th>Tc (°F)</th>
<th>Pc (psia)</th>
<th>Acentric factor</th>
<th>Molecular weight</th>
<th>Vc (ft³/lb·mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td>3.37</td>
<td>95.0</td>
<td>87.89</td>
<td>1069.87</td>
<td>0.225</td>
<td>44.01</td>
<td>1.51</td>
</tr>
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<td>C₁</td>
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<td>667.20</td>
<td>0.008</td>
<td>16.04</td>
<td>1.59</td>
</tr>
<tr>
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<td>64.78</td>
<td>0.0</td>
<td>492.58</td>
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<td>98.45</td>
<td>6.60</td>
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<tr>
<td>C₇₋₁₅</td>
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<td>23.24</td>
<td>0.0</td>
<td>971.92</td>
<td>251.05</td>
<td>1.042</td>
<td>354.20</td>
<td>20.55</td>
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</table>

<table>
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<tr>
<th>Binary Interaction Parameters</th>
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<th>C₁</th>
<th>C₄₋₆</th>
<th>C₇₋₁₅</th>
<th>C₂₈+</th>
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<tbody>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>g</td>
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<td>0.055</td>
<td>0.055</td>
<td>0.081</td>
<td>0.105</td>
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</table>

### Table 3.2 Fluid properties for BSB oil (from Khan et al. 1992)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Properties</th>
<th>Oil (Mol %)</th>
<th>Gas (Mol %)</th>
<th>Tc (°F)</th>
<th>Pc (psia)</th>
<th>Acentric factor</th>
<th>Molecular weight</th>
<th>Vc (ft³/lb·mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td>3.37</td>
<td>95.0</td>
<td>87.90</td>
<td>1069.87</td>
<td>0.225</td>
<td>44.01</td>
<td>1.51</td>
</tr>
<tr>
<td>C₁</td>
<td></td>
<td>8.61</td>
<td>5.0</td>
<td>-116.59</td>
<td>667.20</td>
<td>0.008</td>
<td>16.04</td>
<td>1.59</td>
</tr>
<tr>
<td>C₂₋₃</td>
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<td>15.03</td>
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<td>2.90</td>
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<td>9.00</td>
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<td>1236.79</td>
<td>238.12</td>
<td>1.268</td>
<td>519.62</td>
<td>32.5</td>
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<table>
<thead>
<tr>
<th>Binary Interaction Parameters</th>
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<th>C₂₋₃</th>
<th>C₄₋₆</th>
<th>C₇₋₁₅</th>
<th>C₁₆₋₂₇</th>
<th>C₂₈+</th>
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<td>h</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>g</td>
<td>1.000</td>
<td>0.055</td>
<td>0.055</td>
<td>0.055</td>
<td>0.105</td>
<td>0.105</td>
<td>0.105</td>
</tr>
</tbody>
</table>
Figure 3.1 $P$-$x$ diagram for the pseudo-binary mixture of the BSB-Q oil and injection gas given in Table 3.1 (Okuno, 2009).

Figure 3.2 $P$-$x$ diagram for the pseudo-binary mixture of the BSB oil and injection gas given in Table 3.2 (Okuno, 2009).
Figure 3.3 Data sheet for MMP calculation of BSB-Q oil displacement by injection gas shown in Table 3.1

<table>
<thead>
<tr>
<th>Component</th>
<th>Oil z\textsubscript{i}</th>
<th>Gas z\textsubscript{i}</th>
<th>T\textsubscript{e} (\textdegree F)</th>
<th>P\textsubscript{e} (psia)</th>
<th>φ</th>
<th>Vol Shift</th>
<th>M\textsubscript{w}</th>
<th>Ω\textsubscript{d}</th>
<th>Ω\textsubscript{h}</th>
<th>V\textsubscript{e} (ft\textsuperscript{3}/lb-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CO\textsubscript{2}</td>
<td>0.0337</td>
<td>0.95</td>
<td>87.89</td>
<td>1069.67</td>
<td>0.225</td>
<td>-0.03</td>
<td>44.01</td>
<td>0.45724</td>
<td>0.0778</td>
<td>1.5100</td>
</tr>
<tr>
<td>2 C\textsubscript{1}</td>
<td>0.0081</td>
<td>0.95</td>
<td>-116.59</td>
<td>667.2</td>
<td>0.008</td>
<td>-0.0833</td>
<td>16.043</td>
<td>0.45724</td>
<td>0.0778</td>
<td>1.5900</td>
</tr>
<tr>
<td>3 CH\textsubscript{1}</td>
<td>0.0479</td>
<td>0</td>
<td>452.58</td>
<td>596.21</td>
<td>0.401</td>
<td>0</td>
<td>90.45</td>
<td>0.45724</td>
<td>0.0778</td>
<td>6.6000</td>
</tr>
<tr>
<td>4 CH\textsubscript{2}</td>
<td>0.2324</td>
<td>0</td>
<td>871.2</td>
<td>251.05</td>
<td>1.042</td>
<td>0</td>
<td>354.2</td>
<td>0.45724</td>
<td>0.0778</td>
<td>20.5500</td>
</tr>
</tbody>
</table>

Figure 3.4 BIC sheet for MMP calculation of BSB-Q oil displacement by injection gas shown in Table 3.1
Figure 3.5 Result for MMP calculation of BSB-Q oil displacement by injection gas shown in Table 3.1

Figure 3.6 Result sheet for MMP calculation of BSB oil displacement by injection gas shown in Table 3.2
Chapter 4

Three-Phase Flash Calculations

In this chapter, we examine the application of three-phase stability analysis and flash calculations in our three-phase mixing cell method. First, we study a robust and efficient algorithm developed by Okuno et al. (2009) for the multiphase Rachford-Rice (RR) equations that is guaranteed to converge to the correct solutions for both positive and negative flash based on a bounded feasible domain. Second, we demonstrate with a ternary fluid example an improvement on the selection of initial $K$-values estimates to locate the correct non-trivial minimum solution.

4.1 Convergence of Three-Phase Flash

The method proposed by Michelsen (1994) for solving multiphase Rachford-Rice (RR) equations as a bound constrained minimization is extended to the negative flash region and reformulated as a bounded linearly constrained minimization by Okuno et al. (2009). In this section, we first calculate the iteration path for the bounded feasible region using constant $K$-values. After that, the procedure for valid $K$-values as suggested by Iranshahr et al. (2010) is also investigated in this section.

4.1.1 Solution domain for bounded three-phase systems

For three-phase constant-$K$ values, the function becomes monotonic if the feasible region is unbounded. That is, the function does not have a minimum, and there is no solution to the constant-$K$ flash with $Np$ phases. This section gives examples for bounded feasible regions, and
also examines the conditions that must be satisfied by the $K$-values to guarantee a bounded feasible region.

Figure 4.1 describes the construction of the feasible domain for a seven-component system with an admissible set of $K$-values presented in Table 4.1. The overall composition and $K$-values are from Okuno et al. (2009). In Figure 4.1, the shaded region is the feasible domain, which is determined by the constraints defined in equation (2.26). The feasible domain is derived based on non-negativity of phase component mole fractions, which is of smaller size without poles (Okuno et al. 2009). A feasible initial estimate of $\beta$ (phase mole fraction) is then calculated by an equally weighted mean of the vertices of the bounded feasible region.

The minimization function is convex and non-monotonic if the region is bounded (Okuno et al. 2009). The minimum of the convex function is found using search directions and step sizes based on Newton’s method with a line search along that direction. The curve represents the iteration path, which starts at the initial estimate point, and then ends at the converged solution point.

Mathematically, the feasible region is proved to be bound since the inequality in equation (2.28) is satisfied. Table 4.2 shows the calculated $g_{i,j}$ from equation (2.27). The inequality (2.28) means that there should be at least one positive and at least one negative number in each column of $g_{i,j}$ calculated in Table 4.2.

4.1.2 Solution domain for unbounded three-phase systems

Figure 4.2 describes the construction of a feasible domain for a three-component example with a set of $K$-values presented in Table 4.3. The overall composition and the $K$-values are chosen based on Iranshahr et al. (2010).

In Figure 4.2, the region shaded in grey is the unbounded feasible domain, which is determined by the constraints defined in equation (2.26). A feasible initial estimate of the $\beta$ is
calculated by an equally weighted mean of the vertices of the unbounded feasible region. The line in the unbounded region shows Newton’s direction in the first iteration step in RR formulation. The function does not have a minimum, and there is no solution to the constant-$K$ flash with $N_p$ phases. The reason is that the minimization function becomes monotonic when the region is unbounded.

The unbounded region for Iranshahr’s case could be observed in a mathematical way since the relationship defined in inequality (2.28) cannot be satisfied in the example in Table 4.4. In this table, the condition, $\exists j, k$ such that $g_{i,j}, g_{k,i} < 0$ is not satisfied for $i=1, \ldots, N_c$.

### 4.2 Influence of Initial $K$-value Estimates on Stability Analysis and Flash

In this section, the effect of initial $K$-value estimates on convergence for stability analysis and flash calculation is discussed. We describe first the improvement on the reduced three-phase flash and illustrated it with an example. Then the three-phase equilibrium flowchart is given. The Peng-Robinson equation of state (Peng and Robinson 1976a) is used with the van der Waals mixing rules throughout this research as given in Appendix B.

Stability analysis can fail in two ways. First, it can fail to predict the existence of an additional phase since it may converge to a trivial solution. Second, it locates the local minima instead of global minima because stability analysis cannot guarantee location of the global minimum of the TPD function when multiple local minima of the TPD function occur for multiple phases.

The potential existence of a trivial solution is particularly pronounced near the critical region and calculations in this region are more likely to converge to the trivial solution unless initial estimates close to the final solution are used. Use of multiple sets of judiciously selected
initial estimates is suggested in order to improve the reliability of stability analysis. The solution to be converged depends significantly upon on the initial estimate used.

In multiphase compositional simulation, such as with UTCOMP (Chang et al. 1990), a good initial estimate may be available from the previous time step or from the previous iteration step in the flash calculation based on the observation that the overall composition in a grid block does not change significantly between time steps. Based on a similar methodology, for our three-phase mixing cell model, a better initial estimate for stability analysis and flash is obtained from the nearest cell in the previous contact level. In the mixing cell method, whenever an initial estimate does not result in an ill-conditioned Hessian matrix during the stability analysis and flash calculation, that initial estimate is used. Nonetheless, the initial estimate is switched to the second nearest cell in previous contact level and Wilson’s approximation for $K$-factors is employed as initial estimates when no other $K$-values are available.

The three-phase equilibrium calculation in this chapter begins with a positive/negative two-phase flash calculation. The single phase stability test is skipped because the overall composition lies on the extension of a tie-line even in the single phase region (unless it is FCM). By skipping the stability analysis, we can capture the information for tie-line lengths in the previous developed two-phase mixing cell method to calculate the MMP. After a positive or negative two-phase flash, a three-phase flash is performed only when the existence of a three-phase solution is ensured by stability tests.

The influence of initial $K$-values on flash calculations is demonstrated using a ternary diagram. Consider the three-component three-phase example in Table 4.5 at 70°F and 790 psia. The tie triangle observed for the overall composition is shown in the ternary diagram. See Table 4.6 for phase compositions of the three-phase region. Based on Gibbs phase rule, the compositions of the tie triangle are invariant.
Figure 4.3 is a ternary representation for the fluid example in Table 4.5 with an overall composition and initial $K$-value distribution shown in Table 4.7. The diamond denotes the overall composition, which is outside of the three-phase region. The three-phase region is represented by a stationary tie triangle. Table 4.7 gives the results of the two-phase flash calculation using the corresponding initial $K$-values. The liquid and vapor phase compositions are represented by squares in Figure 4.3. The tie line connects these two points, which is shown by a dashed line shown in Figure 4.3. The tie line can traverse (intersect) the tie triangle due to a poor set of initial $K$-value estimates.

Based on this false two-phase flash calculation, the two-phase stability analysis detects an unstable phase. A subsequent three-phase flash calculation is performed by finding three-phase compositions only if one phase has a negative phase mole fraction. The converged negative three-phase results are described in Table 4.8.

Reevaluation of the two-phase flash calculation at the current overall composition is further investigated. To obtain reliable initial $K$-values, we select one side of the tie triangle as compositions for calculation of the initial $K$-values. In this case, the two phases with a positive phase mole fraction are chosen to generate a new set of initial $K$-value estimates, which is given in Table 4.9. Stability analysis in this case only detects two phases and the compositions of the two phases are circles in Figure 4.3. A tie line connecting these two points is also plotted as a solid line.

Based on the discussion in the previous section, the algorithm for the three-phase flash calculation is given in Figure 4.4.
Table 4.1 Example overall compositions and constant-\(K\) values for flash calculation (Okuno, 2009)

<table>
<thead>
<tr>
<th>Component</th>
<th>(Z)</th>
<th>(K_1)</th>
<th>(K_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20432</td>
<td>1.2347</td>
<td>1.5271</td>
</tr>
<tr>
<td>2</td>
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<td>0.02456</td>
</tr>
<tr>
<td>3</td>
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<td>2.2953</td>
<td>1.4635</td>
</tr>
<tr>
<td>4</td>
<td>0.29629</td>
<td>1.5895</td>
<td>1.1609</td>
</tr>
<tr>
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<tr>
<td>6</td>
<td>0.06249</td>
<td>0.02038</td>
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<td>0.03169</td>
<td>1.40715</td>
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</tr>
</tbody>
</table>

Table 4.2 Calculation of \(g_{ij}\) from Eq. (2.27)

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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</thead>
<tbody>
<tr>
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</table>

Table 4.3 Example overall composition and constant \(K\)-values for ternary flash calculations

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<th>Component</th>
<th>(z)</th>
<th>(K_1)</th>
<th>(K_2)</th>
</tr>
</thead>
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<td>0.30</td>
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<tr>
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<td>0.35</td>
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<td>1.3</td>
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Table 4.4 Calculation of \(g_{ij}\) from Eq.(2.27)

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<th>-0.23</th>
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<tr>
<td></td>
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<td>0.29</td>
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<tr>
<td>(g_{ji}^*)</td>
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Table 4.5 Properties of the ternary mixture

<table>
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<th>Component</th>
<th>Mole fraction (Mol %)</th>
<th>Tc (°F)</th>
<th>Pc (psia)</th>
<th>Acentric factor</th>
</tr>
</thead>
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<tr>
<td>CO₂</td>
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<td>1069.87</td>
<td>0.225</td>
</tr>
<tr>
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<td>0.152</td>
</tr>
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<table>
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</tr>
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</tr>
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<td>C₁₆</td>
<td>0.570104</td>
<td>1.131639</td>
<td>0.149997</td>
</tr>
</tbody>
</table>

Table 4.6 Tie triangle for three-phase region

<table>
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<th>Phase2</th>
<th>Phase3</th>
</tr>
</thead>
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<td>0.492927</td>
<td>0.905347</td>
<td>0.845271</td>
</tr>
<tr>
<td>2</td>
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<td>0.214173</td>
<td>0.094644</td>
<td>0.149800</td>
</tr>
<tr>
<td>3</td>
<td>0.064111</td>
<td>0.292900</td>
<td>0.000008</td>
<td>0.004930</td>
</tr>
<tr>
<td>Mole fraction (Mol%)</td>
<td>0.211199</td>
<td>0.332760</td>
<td>0.456040</td>
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</tbody>
</table>

Table 4.7 Incorrect two-phase flash calculation

<table>
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<tr>
<th>Component</th>
<th>$z$</th>
<th>Initial $K$</th>
<th>Converged two-phase flash</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>L</td>
</tr>
<tr>
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<tr>
<td>3</td>
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<td>0.000028</td>
<td>0.222177</td>
</tr>
<tr>
<td>Mole fraction (Mol%)</td>
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<td>0.675150</td>
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Table 4.8 Negative three-phase flash calculation

<table>
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<th>Component</th>
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<th>Phase3</th>
<th>Converged K1</th>
<th>Converged K2</th>
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<tbody>
<tr>
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<tr>
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<td>0.0000087</td>
<td>0.004929</td>
<td>59.4146</td>
<td>0.0017555</td>
</tr>
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<td>Mole fraction (Mol%)</td>
<td>0.493631</td>
<td>-0.594470</td>
<td>1.10084</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.9 Correct two-phase flash calculation

<table>
<thead>
<tr>
<th>Component</th>
<th>Initial K-values</th>
<th>L</th>
<th>V</th>
<th>Converged K-values</th>
</tr>
</thead>
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<tr>
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<td>3</td>
<td>0.016831</td>
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<td>Mole fraction (Mol%)</td>
<td>0.557422</td>
<td>0.442578</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.1 Iteration path for Example in Table 4.1
Figure 4.2 Unbounded solution domain for Example in Table 4.3

Figure 4.3 Ternary representations for two- and three- phase flash calculation
Figure 4.4 Flow chart of multiphase flash calculations in the multiple mixing-cell method
Chapter 5

Three-Phase Mixing Cell Method

In this chapter, we propose the first multiple three-phase mixing cell method for oil fluid systems with an arbitrary number of components in either oil or gas. This efficient, robust, and novel three-phase mixing cell method is presented to understand miscibility development by considering the sizes of the tie lines and tie triangles. The mixing cell method is proposed to predict the displacement pressure at which gas can efficiently recover the original oil.

The first section describes in detail the basic steps in constructing our three-phase mixing cell algorithm. Special effort is made to identify the feasible mixing scheme and a robust three-phase flash calculation algorithm is implemented in the three-phase mixing cell model. In subsequent sections, the applications of the newly proposed mixing cell model are demonstrated based on two multicomponent oil examples with three-phase behavior.

5.1 Multiple three-phase mixing cell model

The two-phase multiple mixing cell method has been used to explore the mechanism of multiple-contact miscibility by tracing the key tie lines. The MMP is the lowest pressure at which any of the key tie lines is a critical tie line based on the analytical theory of gas displacement processes. Tie lines are important parameters to indicate miscibility development. In general, there exist \( Nc-1 \) key tie lines for \( Nc \) component displacements when only two hydrocarbon phases are encountered. These key tie lines include the injection (gas) tie line, initial (oil) tie line, and \( Nc-3 \) cross-over tie lines. For a quaternary system, miscibility occurs when a key tie line becomes a critical tie line of zero length based on the MOC theory of two-phase gas injection.
MOC estimates of MMP are not available for three hydrocarbon phases and a two-phase approximation at these pressures could lead to wrong results in the predicted pressure for efficient displacement. No analytical solution has been developed for a multicomponent oil displacement by gas injection involving three-hydrocarbon phases. Our three-phase mixing cell method serves as a computational method to understand the complex displacement involving three hydrocarbon-phases. When evaluating the three-phase mixing cell model for MMP estimation, it is required to trace the sizes of the tie-line and tie-triangle regions.

5.1.1 Contacts in three-phase mixing cell model

Based on the experience from the previous two-phase mixing cell method, the effect of several important parameters are considered, including the number of cells, the fractions of equilibrium gas and second liquid phases moved from one cell to the next, which are defined as fluid mobility factors. The goal of this section is to introduce the development of a three-phase mixing cell model with multicell equilibrium pressure-temperature (PT) flash calculations.

The previous two-phase mixing cell model is based on the observation that neither the ratio between injected gas and oil nor the fluid mobility affects the MMP. Based on a similar methodology, the three-phase mixing cell method does not calculate recovery factor or transfer specific amounts of fluid based on cell volumes; it relies on performing pressure-temperature (PT) flash calculations using PR EOS (Peng and Robinson 1976a), and on mixing the equilibrium vapor, equilibrium second liquid, and equilibrium oil in each cell in a particular way. It is not obvious how this should be done so this section examines several possibilities. The following steps describe the algorithm of the three-phase mixing cell method for calculating tie-line lengths in two- and three-phase regions based on three different mixing schemes.

In the first mixing scheme, two cells are mixed at fixed temperature and pressure, where the injection gas is located in the upstream cell and the reservoir fluid in the downstream cell (See
Figure 5.1). The reservoir oil ($x^o$) and injection gas ($y^G$) mixture results from the mass balance equation $z = x^o + \alpha(y^G - x^o)$ with $0 < \alpha < 1$. The resulting overall composition $z$ will be either in the two-phase region, the two-phase tie-line extension region, or the three-phase region. Thus, a positive/negative two- or three-phase flash with a cubic EOS can be performed at this overall composition, resulting in two or three equilibrium compositions. For a three-phase flash, equilibrium phases are labeled as oleic ($L_1$), gaseous ($V$), and CO$_2$-rich liquid ($L_2$). The equilibrated vapor is labeled as the phase that contains the greatest mole fraction of injected gas component. The equilibrated liquid is determined to be the phase with the lowest gas component mole fraction, and the third phase is the equilibrated second liquid. Since gas is injected we assume that the equilibrium vapor moves ahead of the equilibrium second liquid and the equilibrium second liquid moves ahead of the equilibrium liquid. For a two-phase flash, equilibrated liquid ($L_1$), and vapor ($V$) form. This is the first contact.

The second series of contacts contains both an upstream and downstream contact (see Fig. 5.1). Zhao et al. (2006a) demonstrated that MMP is independent on fractional flow, which is, the amount of vapor and liquid phases moving from cell to cell, in a multiple two-phase mixing cell method. This finding is further extended when applied in our three-phase mixing cell model for the first proposed mixing scheme. Assuming the equilibrium vapor phase and equilibrium second liquid phase are moving side by side, a combined vapor phase $y^G$ can be obtained by using the material balance equation $y^G = L_2 + \alpha(V - L_2)$. When performing the upstream contact, the combined liquid phase $x^o$ can be obtained by mixing equilibrium liquid phase ($L_1$), equilibrium vapor ($V$) and second liquid phases ($L_2$). Therefore another assumption in the first mixing scheme is that only a proportion of equilibrium vapor and second liquid phases is moved from the upstream cell to downstream cell.
The downstream contact mixes the combined vapor phase with fresh oil, and the upstream contact mixes the combined liquid phase with the fresh injection gas. When mixing combined vapor and liquid, we always use the same material balance equation \( z = x^o + \alpha(y^G - x^o) \). Two new sets of equilibrium liquid and vapor phases result from these flash calculations. This completes the second contact.

For the third series of contacts, combined liquid and vapor phases are generated from equilibrium liquid, second liquid and vapor phases from the previous contact to determine the overall composition for phase equilibrium calculations. When forward and backward mixing occurs for \( x^o \) with \( y^G \), \( z = x^o + \alpha(y^G - x^o) \) is used as the material balance equation. Besides mixing with \( L_2 \) from the second contact, the equilibrium oil mixes with injection gas and equilibrium gas mixes with the fresh oil. This is the third contact.

We continue with additional contacts by mixing neighboring cells, as shown in Figure 5.1. The number of cells is \( 2M+2 \), where \( M \) is the contact level. At each contact level, the tie-line lengths are calculated for cells forming two- and three-phases. Then we model the development of tie-line length both in time and space formed in each cell.

The second mixing scheme (See Figure 5.2) is similar to the scheme in the traditional two-phase mixing cell method (Ahmadi, et al. 2011). The main difference in the illustrated second mixing scheme with the first one (See Figure 5.1) is that the equilibrium \( L_2 \) phase is discarded if the flash calculation results in three equilibrium compositions. In this way, only equilibrium vapor (V) and equilibrium liquid (\( L_1 \)) are mixed using the material balance equation, \( z = x^o + \alpha(y^G - x^o) \). After \( M \) contacts, a total of \( 2M+2 \) cells are generated.

The difference in the third mixing scheme and the first one described above is the consideration in how the equilibrated \( L_2 \) phase is mixed (See Figure 5.3). For the second mixing scheme, the \( L_2 \) phase in the current contact level is not involved in mixing with any phases in or
not in equilibrium. For the third mixing scheme, only the $L_2$ phase in the current contact level is not involved in any mixing with phases in equilibrium. This assumes the $L_2$ phase is not always surrounded by equilibrium $L_1$ and $V$ phases. The number of cells cannot be predicted in advance as a function of the contact level in the third scheme. In this research, we mainly discuss the results from the first mixing scheme (See Figure 5.1) though the second mixing scheme (See Figure 5.2) may also be feasible. We also briefly compare the three proposed mixing schemes.

A plot of the minimum tie-line length versus $(1/N)^p$, where $N$ is the number of cells, gives the estimated minimum tie-line/tie-triangle length at infinite contact for that pressure. A graph of the estimated minimum tie-line/tie-triangle length is then made for different trial pressures to understand the development of miscibility.

### 5.1.2 Tie-triangle

The three-phase region consists of an infinite number of tie triangles with sides as shown in Figure 5.4. Tie-line lengths between $L_1$ and $V$ phases, $L_2$ and $V$ phases, $L_1$ and $L_2$ phases are calculated by equations (5.1), (5.2) and (5.3), respectively.

\[
TL_{L_1-V} = \left\| x_{L_1}^L - x_{V}^V \right\| = \sqrt{\sum_{i=1}^{N_c} (x_{L_1}^{L_i} - x_{V}^{V_i})^2} 
\]

\[
TL_{L_2-V} = \left\| x_{L_2}^L - x_{V}^V \right\| = \sqrt{\sum_{i=1}^{N_c} (x_{L_2}^{L_i} - x_{V}^{V_i})^2} 
\]

\[
TL_{L_1-L_2} = \left\| x_{L_1}^L - x_{L_2}^L \right\| = \sqrt{\sum_{i=1}^{N_c} (x_{L_1}^{L_i} - x_{L_2}^{L_i})^2} 
\]

Here, $x_{L_1}^{L_i}$, $x_{L_2}^{L_i}$, $x_{V}^{V_i}$ represent equilibrium $L_1$, $L_2$ and $V$ compositions, respectively.

The tie-line lengths (TLL) represent the distances between the two phase-compositions in composition space and the level of criticality at a fixed pressure and temperature, since the tie-line length between two phases is zero at a critical point. Critical endpoints (CEPs) are critical
states where the two of the three coexisting phases become identical. There are two types of CEPs, the first CEP is where the \( L_1 \) and \( L_2 \) phases merge in the presence of the \( V \) phase, and the other CEP is where the \( L_2 \) and \( V \) phases merge in the presence of the \( L_1 \) phase. A CEP is not a point but a tie line in composition space. A tricritical point is where three phases simultaneously become identical (Widom 1973, Griffiths 1974). This is a true critical point.

Knowledge of both the tie-line length and the tie-triangle length are required to understand the size of the tie triangle. The tie-triangle length (TTL) is used because at a CEP the tie-triangle length will approach the length of the remaining tie line as it should. In this thesis, the definition of the tie-triangle length includes the tie line in a two-phase region.

We also examined the use of the area of a tie triangle as a measure of the closeness to miscibility. This approach was discarded because the tie-line lengths for a two-phase region would not be continuous with a disappearing three-phase region. That is, the area of a tie-triangle at a CEP is zero, but a tie line still exists there.

5.2 Results

Applications of our newly developed three-phase mixing cell method for a four-component gas flood are discussed in this section and later extended to a fluid with seven components. First, the displacement mechanism is discussed considering the tie triangles and tie lines that form in the mixing cell. Second, prediction of the pressure for an efficient displacement is estimated by extrapolation of the minimum tie-line lengths and tie-triangle lengths for any cell at a growing contact number.

5.2.1 \( \text{CO}_2 \) solvent displacement of BSB-Q oil

In this section, the three-phase mixing cell model based on the previously proposed methodology is tested for the four-component oil displacement by a two-component injection gas
as shown in Table 3.1. We first demonstrate how to make the tie-line length plots at different trial pressures. Factors responsible for development of tie-line lengths are discussed together with possible ways to improve the tie-line length development. Second we examine the effect of pressure on development of miscibility in the context of phase behavior of CO₂/hydrocarbon mixtures.

5.2.1.1 Lengths of tie lines and tie triangles

At reservoir pressure and temperature, there are two ways to estimate the lengths of the tie triangles and tie lines in the three-phase mixing cell. The first approach is through the static profile of tie-line length at fixed number of contacts. The second approach is to see how the tie triangles and tie lines evolve by increasing the number of contacts. The first way provides important knowledge on the size of tie triangles and tie lines in composition space, and thus, provides knowledge of miscibility development. The second way presents how tie triangles and tie lines change with contacts, and how their lengths can be used to extrapolate to an infinite number of contacts.

We first generate the tie-line lengths profile predicted by the second mixing scheme (See Figure 5.2). The tie-line lengths are developed after 1000 contacts as shown in Figure 5.5 at 1300 psia and 105 °F. In this figure, \( TL_{L_1-V} \) represents the distance between the \( L_1 \) phase composition and the \( V \) phase composition. Similarly, \( TL_{L_1-L_2} \), \( TL_{L_2-V} \) represent the distance between the \( L_1 \) and \( L_2 \) phase compositions and between the \( L_2 \) and \( V \) phase compositions. Figure 5.6 shows the tie-line lengths profile using the third mixing scheme (See Figure 5.3). The two- and three-phase regions alternate after 6 contacts.

For the first mixing scheme, we outline how the tie-line lengths evolve using the newly developed three-phase mixing cell method. Then profiles of tie-line lengths and tie-triangle lengths are presented after 1000 contacts in the following discussion.
The profiles of tie-line lengths at 1200 psia and 105 °F are shown in Figures 5.7, 5.8, 5.9, 5.10, and 5.11 after 50, 100, 200, 500 and 1000 contacts, respectively. Use of a small value of gas-oil mixing ratio $\alpha$ (see equation $z = x^o + \alpha(y^G - x^o)$) leads to an insufficiently developed gas tie line, which appears at the tail of a three-phase region. The reason is less gas is mixed with the next cell, leaving a large region of initial oil.

As the contacts increase, the tie-line lengths develop and approach a constant value. Figure 5.11 is a profile of tie-line lengths at 1000 contacts. The tie-triangle length (sum of the shortest two sides) is also given as shown in Figure 5.12 after 1000 contacts, where the minimum length is in front of the three-phase region inside the two-phase region at 1200 psia.

We increase the injection pressure to 1250 and 1300 psia as shown in Figures 5.13 and 5.15. These figures give the profiles of two-phase tie-line lengths after 1000 contacts while Figures 5.14 and 5.16 show the tie-triangle lengths. The minimum tie-line length for $TL_{L_2-V}$ in Figure 5.13 at 1250 psia decreases compared to the minimum tie-line length in Figure 5.11 at a pressure of 1200 psia. This decrease in minimum tie-line length continues at a higher pressure of 1300 psia as shown in Figure 5.15. The minimum tie-line length is the tie-line length between the $L_2$ and $V$ phases, indicating that the compositions of these two phases are approaching each other as the pressure is increased. Therefore, tie-triangle approaches a CEP.

### 5.2.1.2 Effect of pressure on three-phase behavior

At each pressure, the minimum tie-line length and the tie-triangle length are calculated by power-law extrapolation using the tie-line lengths resulting from the 991$^{th}$ to 1000$^{th}$ contacts. As the number of contacts increase, the tie lines develop as was discussed above.

Figures 5.17, 5.18, and 5.19 show the extrapolation of the tie-line lengths from the last 100 contact levels where the filled circles show the actual data at pressures of 1200, 1250, and
1300 psia. The solver in Excel is used to optimize the exponent $m$ to give the best fit as shown in Figures 5.17 to 5.19 for the last 100 data points.

It is important to track the smallest tie-line length between the phases to obtain the pressure for an efficient displacement. Figure 5.20 presents the fitted curves of the smallest tie-line lengths versus pressure at pressures of 1200, 1250, and 1300 psia. The curve of minimum tie-line lengths with pressure is monotonically decreasing. As is shown in Figure 5.20, the smallest tie line at 1333 psia approaches zero length so that the MMP is approximately 1333 psia when estimated this way.

Although tracking the smallest tie-line length may give a prediction of the pressure for an efficient displacement, it may result in a wrong MMP. Figures 5.21, 5.22, and 5.23 present the extrapolated values of minimum tie-triangle lengths. The extrapolation of the tie-triangle length is shown in Figures 5.21, 5.22, and 5.23 by outputting data from the last 100 contacts, i.e. 991$^{th}$ to 1000$^{th}$. As shown in Figures 5.21 to 5.23 at pressures of 1200 to 1300 psia, the extrapolated smallest tie-triangle lengths are larger than 0.3 and do not come close to zero, indicating that miscibility is not obtained. The MMP is not obtained at 1300 psia on the basis of minimum tie-triangle length.

The pressure of 1333 psia is the pressure where one of the tie lines obtains zero length as indicated in Figure 5.20. Figure 5.24 shows the development of tie-line length at 1333 psia after 1000 contacts. The minimum tie-line length as shown in Figure 5.24 increases as compared to the minimum tie-line length as shown in Figure 5.15 instead of becoming zero. A corresponding profile of the tie-triangle length is represented in Figure 5.25.

The tie-line length and tie-triangle length at a pressure of 1350 psia are shown in Figures 5.26 and 5.27, respectively. The minimum tie-line length does not become zero and the tie-triangle length remains large showing that the MMP predicted by the trend of tie-line length in Figure 5.20 is not correct. That is, tie lines of significant length remain at these pressures.
Miscibility development predicted only by the minimum tie-line length may lead to wrong results for CO$_2$-solvent flooding process involving three-hydrocarbon-phase flow.

We also calculated the extrapolated values of the minimum tie-line and tie-triangle lengths at pressures of 1333 and 1350 psia as shown in Figures 5.28, 5.29, 5.30, and 5.31. In conclusion, the extrapolated minimum tie-line lengths and extrapolated tie-triangle lengths are compared for the five trial pressures as shown in Figures 5.32, and 5.33. For the quaternary displacement, the minimum tie-line length decreases to a value close to zero from 1200 psia to 1300 psia, and then increases again from 1300 psia to 1350 psia. The trend of the tie-triangle lengths, however, decreases as shown in Figure 5.33, but remains larger than 0.3 for all pressures examined.

5.2.2 CO$_2$ solvent displacement of BSB oil

In order to further prove the reliability of our newly developed three-phase mixing cell method, a seven-component displacement by injection gas as shown in Table 3.2 is examined next. For this liquid-liquid-vapor displacement, the effect of pressure on the three-phase behavior is illustrated using tie-triangle and tie-line lengths by mixing cells at different pressures.

5.2.2.1 Lengths of tie lines and tie triangles

Figure 5.34 shows the profile of tie-line lengths from the two- and three-phase regions after 1000 contacts. The number of equilibrated groups is shown by the x-axis. For a series of pressures (1200, 1250, 1300, 1350, 1400, and 1450 psia), as shown in Figures 5.34, 5.36, 5.38, 5.40, 5.42, and 5.44, the development of tie-line lengths after 1000 contacts are given. The profiles of tie-triangle length after 1000 contacts are presented in Figures 5.35, 5.37, 5.39, 5.41, 5.43, and 5.45 at pressures of 1200, 1250, 1300, 1350, 1400, and 1450 psia.
As shown in Figure 5.34, the three-phase region is bounded by two two-phase regions. No single phase region exists because the negative two-phase flash calculation is implemented in our three-phase mixing cell model. The gas tie line occurs at the injection composition while the oil tie line develops at the initial composition. The minimum tie-line length is developed at the tie line between L_2 and V phases as shown by the continuous solid line in Figure 5.34. A similar plot is given in Figure 5.36 at 1250 psia and the minimum tie-line length TL_{L_2-V} further decreases compared with Figure 5.34 inside the three-phase region.

Figure 5.38 shows a sharp decrease in TL_{L_2-V}, which appears at the tail of the three-phase region. The three-phase region shrinks as the pressure increases from 1250 to 1300 psia. As indicated by TL_{L_2-V} in Figure 5.38, the distance between L_2 and V phase compositions becomes very small near the tail of the three-phase region, which represents the upper critical endpoint (CEP) behavior. However, the distance between the L_2 and V phases does not exhibit an asymptotic reduction near the tail of the three-phase region at higher pressures, which are shown in Figures 5.40, 5.42, and 5.44.

### 5.2.2.2 Effect of pressure on three-phase behavior

The minimum tie-line lengths are plotted as a function of the power of the inverse of the number of contacts. The exponent \(m\), used in the extrapolation, is used to linearly fit the data from 991\textsuperscript{st} to 1000\textsuperscript{th} contacts. The extrapolated minimum tie-line length at infinite contact number is shown in Figures 5.46, 5.47, 5.48, 5.49, 5.50, and 5.51 at pressures of 1200, 1250, 1300, 1350, 1400 and 1450 psia.

The tie-triangle length is a better representation of miscibility. The results of the extrapolated minimum tie-triangle length at infinite number of contacts are shown in Figures 5.52 to 5.56, which are at the same corresponding pressures as Figures 5.46 to 5.50.
Figure 5.58 gives the extrapolated minimum tie-line length at infinite contact number for different pressures. The extrapolated minimum tie-line length does not exhibit an asymptotic decrease with pressures just like for the BSB-Q oil. It decreases up to 1300 psia and then increases for higher pressures. Figure 5.59 shows the development of the extrapolated minimum tie-triangle length with changing pressure. The result shows that the extrapolated tie-triangle length decreases with pressure, similar to the quaternary BSB-Q displacement.
Figure 5.1 Illustration of repeated contacts in the multiple three-phase mixing cell method by the first mixing scheme. G: injecting gas composition, O: oil composition, L₁: equilibrium oleic phase, L₂: equilibrium CO₂-rich liquid phase, V: equilibrium gaseous phase. X: combined liquid phase, Y: combined vapor phase.

Figure 5.2 Illustration of repeated contacts in the multiple three-phase mixing cell method by the second mixing scheme. G: injecting gas composition, O: oil composition, L₁: equilibrium oleic phase, L₂: equilibrium CO₂-rich liquid phase, V: equilibrium gaseous phase.
Figure 5.3 Illustration of repeated contacts in the multiple three-phase mixing cell method by the third mixing scheme. G: injecting gas composition, O: oil composition, L₁: equilibrium oleic phase, L₂: equilibrium CO₂-rich liquid phase, V: equilibrium gaseous phase.

Figure 5.4 Schematic of a tie-triangle
Figure 5.5 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.2 for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 and after 1000 contacts.

Figure 5.6 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.3 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 and after 6 contacts.
Figure 5.7 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 and after 50 contacts.

Figure 5.8 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 100 contacts.
Figure 5.9 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 200 contacts.

Figure 5.10 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 500 contacts.
Figure 5.11 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 1000 contacts.

Figure 5.12 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Figure 5.13 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 after 1000 contacts.

Figure 5.14 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105 °F and 1250 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Figure 5.15 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 after 1000 contacts.

Figure 5.16 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Figure 5.17 Extrapolation of the minimum tie-line length at a pressure of 1200 psia to determine $TLL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-line length $TLL^\infty$ for $m=0.908$ is 0.079.

Figure 5.18 Extrapolation of the minimum tie-line length at a pressure of 1250 psia to determine $TLL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-line length $TLL^\infty$ for $m=0.923$ is 0.033.
Figure 5.19  Extrapolation of the minimum tie-line length at a pressure of 1300 psia to determine \( T_{\text{LL}}^{\infty} \) for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-line length \( T_{\text{LL}}^{\infty} \) for \( m=0.911 \) is 0.00482.

Figure 5.20 Extrapolation of the minimum tie-line lengths for BSB-Q oil displacement by injection gas as shown in Table 3.1
Figure 5.21 Extrapolation of the minimum tie-triangle length at a pressure of 1200 psia to determine $TTL^\infty$ for BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ for $m=0.97$ is 0.369.

Figure 5.22 Extrapolation of the minimum tie-triangle length at a pressure of 1250 psia to determine $TTL^\infty$ for BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ for $m=0.967$ is 0.36.
Figure 5.23  Extrapolation of the minimum tie-triangle length at a pressure of 1300 psia to determine TTL\(^x\) for BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length TTL\(^x\) for m=1.35 is 0.353.

Figure 5.24  Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1333 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Figure 5.25 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105°F and 1333 psia by the injection gas shown in Table 3.1 after 1000 contacts.

Figure 5.26 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105 °F and 1350 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Figure 5.27 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB-Q oil displacement at 105 °F and 1350 psia by the injection gas shown in Table 3.1 after 1000 contacts.

Figure 5.28 Extrapolation of the minimum tie-line length at a pressure of 1333 psia to determine $TLL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-line length $TLL^\infty$ for $m=1.9$ is $0.0074$. 
Figure 5.29 Extrapolation of the minimum tie-line length at a pressure of 1350 psia to determine $TLL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-line length $TLL^\infty$ for $m=0.903$ is 0.0115.

Figure 5.30 Extrapolation of the minimum tie-triangle length at a pressure of 1333 psia to determine $TTL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ for $m=1.7$ is 0.35.
Figure 5.31 Extrapolation of the minimum tie-triangle length at a pressure of 1350 psia to determine TTL\(^m\) for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length TTL\(^m\) for m=0.902 is 0.348.

Figure 5.32 Illustration of minimum tie-line lengths at different trial pressures for BSB-Q oil displacement by injection gas as shown in Table 3.1.
Figure 5.33 Illustration of minimum tie-triangles lengths at different trial pressures for BSB-Q oil displacement by injection gas as shown in Table 3.1

Figure 5.34 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.2 after 1000 contacts
Figure 5.35 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.2 after 1000 contacts

Figure 5.36 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.2 after 1000 contacts
Figure 5.37 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.2 after 1000 contacts

Figure 5.38 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.2 after 1000 contacts
Figure 5.39 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.2 after 1000 contacts.

Figure 5.40 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105 °F and 1350 psia by the injection gas shown in Table 3.2 after 1000 contacts.
Figure 5.41 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1350 psia by the injection gas shown in Table 3.2 after 1000 contacts.

Figure 5.42 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1400 psia by the injection gas shown in Table 3.2 after 1000 contacts.
Figure 5.43 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1400 psia by the injection gas shown in Table 3.2 after 1000 contacts.

Figure 5.44 Development of tie-line lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1450 psia by the injection gas shown in Table 3.2 after 1000 contacts.
Figure 5.45 Development of tie-triangle lengths using our mixing cell model with the mixing scheme shown in Figure 5.1 for the BSB oil displacement at 105°F and 1450 psia by the injection gas shown in Table 3.2 after 1000 contacts.

Figure 5.46 Extrapolation of the minimum tie-line length at a pressure of 1200 psia to determine $TLL^\infty$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length $TLL^\infty$ for $m=0.514$ is 0.0199.
Figure 5.47  Extrapolation of the minimum tie-line length at a pressure of 1250 psia to determine $TLL^{\infty}$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length $TLL^{\infty}$ for $m=0.855$ is 0.0097.

Figure 5.48  Extrapolation of the minimum tie-line length at a pressure of 1300 psia to determine $TLL^{\infty}$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length $TLL^{\infty}$ for $m=0.798$ is 0.00439.
Figure 5.49 Extrapolation of the minimum tie-line length at a pressure of 1350 psia to determine $TLL_\infty$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length $TLL_\infty$ for $m=0.922$ is 0.0523.

Figure 5.50 Extrapolation of the minimum tie-line length at a pressure of 1400 psia to determine $TLL_\infty$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length $TLL_\infty$ for $m=0.768$ is 0.0619.
Figure 5.51 Extrapolation of the minimum tie-line length at a pressure of 1450 psia to determine TLL° for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-line length TLL° for m=0.641 is 0.0677.

Figure 5.52 Extrapolation of the minimum tie-triangle length at a pressure of 1200 psia to determine TTL° for the BSB oil displacement by the injection gas shown in Table 3.2 Minimum tie-triangle length TTL° for m=0.627 is 0.289.
Figure 5.53 Extrapolation of the minimum tie-triangle length at a pressure of 1250 psia to determine TTL for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-triangle length TTL for m=0.642 is 0.288.

Figure 5.54 Extrapolation of the minimum tie-triangle length at a pressure of 1300 psia to determine TTL for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-triangle length TTL for m=0.956 is 0.29.
Figure 5.55 Extrapolation of the minimum tie-triangle length at a pressure of 1350 psia to determine $TTL^*$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-triangle length $TTL^*$ for $m=0.756$ is 0.287.

Figure 5.56 Extrapolation of the minimum tie-triangle length at a pressure of 1400 psia to determine $TTL^*$ for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-triangle $TTL^*$ for $m=0.72$ is 0.212.
Figure 5.57 Extrapolation of the minimum tie-triangle length at a pressure of 1450 psia to determine TTL\(^*\) for the BSB oil displacement by the injection gas shown in Table 3.2. Minimum tie-triangle length TTL\(^*\) for m=0.895 is 0.181.

Figure 5.58 Illustration of minimum tie-line lengths at different trial pressures for the BSB oil displacement by injection gas as shown in Table 3.2.
Figure 5.59 Illustration of minimum tie-triangle lengths at different trial pressures for the BSB oil displacement by injection gas as shown in Table 3.2
Chapter 6

1-D Compositional Simulation and Comparisons

In this chapter, we perform one-dimensional compositional simulations and compare them to the three-phase mixing cell results in Chapter 5 at a series of pressures. Displacements of multicomponent oils by injection gas are examined to calculate tie-line and tie-triangle lengths, together with oil recoveries. Results of compositional simulations are sensitive to the grid block size. One-dimensional compositional simulations are conducted with a varying number of grid blocks. This is used to quantify the impact of numerical dispersion on results.

6.1 1-D Compositional Simulation

The first case is a displacement of a four-component oil by a two-component injection gas at a fixed temperature of 105°F, reported in Okuno (2009). In this section, tie-line lengths, tie-triangle lengths, and oil recoveries are modeled using a compositional simulator (UTCOMP). These are then plot as a functions of pressure.

6.1.1 CO₂ solvent displacement of BSB-Q oil

The profiles of the tie-line lengths indicate two critical endpoints (CEPs) in composition space, where two of the three equilibrated phases become critical. There exist two types of CEPs at the operating temperature and pressures. The first CEP is where the L₁ and L₂ phases become identical in the presence of the V phase. This is the lower critical endpoint. The second CEP is where the L₂ and V phases merge in the presence of the L₁ phase. This is also referred to as the upper critical endpoint.

We conduct sensitivity runs by altering the number of grid blocks in the x-direction at 1200 psia as shown in Figures 6.1, 6.2, 6.3, 6.4 and 6.5. Progressively more grid blocks are used
in Figures 6.1 to 6.5. The UTCOMP simulations are performed at 1200 psia using 50, 100, 200, 500 and 1000 grid blocks to decrease numerical dispersion. Tie-line lengths at 0.3 pore-volumes injected (PVI) are plotted versus dimensionless distance in Figures 6.1 to 6.5. In these displacements, 0.3 PVI is equal to 0.5 hydrocarbon-pore-volumes injected (HCPVI). The larger number of grid blocks, the better these tie-lines develop and the more accurate the extrapolations would be.

A three-phase hydrocarbon region exists in between the two-hydrocarbon phase regions at a low injection pressure of 1200 psia. Large $TL_{L_1-L_2-V}$, $TL_{L_2-V}$ and $TL_{L_1-L_2}$ indicate the composition path does not go near to the critical end-point at 1200 psia. Therefore, the L$_1$, L$_2$ and V phases are immiscible with each other. Figure 6.6 provides the profile of the tie-triangle lengths at the same pressure of 1200 psia using 1000 grid blocks, and further provides information about the tri-critical point. In Figure 6.6, the smallest value is at the front of the three-phase region. The smallest value does not tend towards zero.

As stated above, the profiles of the tie-line and tie-triangle lengths are also considered for the other pressures to understand miscibility development. Figures 6.7, 6.9, 6.11, and 6.13 show these lengths at 1250, 1300, 1333, 1350 psia using 1000 grid blocks, respectively. As shown in Figures 6.5, 6.7, 6.9, 6.11, and 6.13, the displacements exhibit three-hydrocarbon-phase flow while the length of the three-phase region shrinks as pressure increases. The smallest tie-line length occurs for $TL_{L_2-V}$ in the BSB-Q oil displacements by injection gas. $TL_{L_2-V}$ exhibits the most significant sensitivity to displacement pressure.

As shown by the minimum value of $TL_{L_2-V}$, the L$_2$ and V phase compositions approach one another at the tail of the three-phase regions at 1300, 1333, and 1350 psia. The L$_2$ phase is vaporized into the V phase at the tail of the three-phase region as shown in Figure 6.9 when $TL_{L_2-V}$ decreases dramatically. The $TL_{L_1-L_2}$ also shows a tendency to decrease, although not as
much as $TL_{1-v}$. Development of CEPs occurs when composition paths go through critical endpoints at relatively high pressures, 1300, 1333, and 1350 psia.

Figures 6.8, 6.10, 6.12, and 6.14 show profiles of tie-triangle length for the UTCOMP simulations at 1250, 1300, 1333, 1350 psia using 1000 grid blocks. In none of these cases, the minimum value of the tie-triangle length approaches zero. Development of miscibility has not been observed for composition paths that go through a three-phase region in this set of simulations with increasing pressure. The smallest tie-triangle length occurs at the front of the three-phase region as shown in Figure 6.8 or at the neighboring downstream two-phase region.

In Figure 6.15, oil recovery factors are plotted versus pore-volume injected for the displacements of the BSB-Q oil at different pressures using 1000 grid blocks. The oil recoveries above 1300 psia are overlapping at 1.2 pore volumes injected (PVI).

Extrapolations are applied to obtain an accurate solution while limiting the required computational costs to understand the effect of pressure on three-phase behavior by introducing Peclet number. A Peclet number of zero means that dispersive transport completely dominates over convection, and an infinite Peclet number implies convective-dominated flow. The Peclet number of a 1-D displacement was estimated by Lantz (1971) as,

$$Pe = \frac{2L}{\Delta x}$$

(6.1)

where $L$ is the distance between wells and $\Delta x$ is the size of a grid block. The distribution of wells in our reservoir only includes one injection and production well.

To calculate the minimum tie-line length with zero numerical dispersion, the tie-line length is extrapolated to the infinite value of the Peclet number (infinite number of grid blocks). The Peclet number is calculated as the value of twice the number of grid blocks approximately for the one-dimensional simulations. In order to decrease the effect of dispersion, we investigate two extrapolations to compare the predicted tie-line/tie-triangle lengths and oil recoveries with respect to number of grid blocks. One way is to perform extrapolation by employing the 200, 500, and
1000 grid blocks. The second way uses a varying number of grid blocks of 50, 100, 200, 500 and 1000.

Figures 6.16 to 6.20 show the power-law extrapolation of the minimum tie-line length to the infinite Peclet number of exponent $m$ by using all five sets of number of grid blocks. The extrapolated values of the minimum tie-line length are also calculated by using the last three sets of number of grid blocks, i.e., 200, 500, and 1000. Similar to the mixing cell, the tie-triangle lengths are used to measure miscibility development. The results of the extrapolated minimums of the tie-triangle lengths are shown in Figures 6.21 to 6.25 using the second extrapolation method. We also calculate the extrapolated minimums of the tie-line lengths using the first extrapolation method.

Oil recoveries at 2.0 hydrocarbon pore volumes injected (HCPVI) with different Peclet numbers and pressures for the BSB-Q oil displacements by the injection gas are shown in Figures 6.26 to 6.30 at 1200, 1250, 1300, 1333, and 1350 psia. Figures 6.26 to 6.30 show the extrapolation of the oil recovery for each BSB-Q oil displacement case to estimate the recovery factor with no numerical dispersion using all five points. The extrapolated oil recoveries using the last three points are also calculated although the plots are not given.

The extrapolated minimum tie-line lengths coupled with extrapolated oil recoveries are shown in Figure 6.31 using larger numbers of grid blocks, i.e., 200, 500, and 1000. As shown in Figure 6.31, there is a small “knee” in the recovery curve, indicating a pressure of 1300 psia for an efficient displacement. The pressure at the “knee” is in good agreement with the mixing cell-calculated minimum tie-line length of 1300 psia.

The minimum tie-line length is misleading at 1300 psia, as it is predicting the occurrence of MMP values close to zero (0.0027 using second extrapolation method). However, based on these simulation case studies using UTCOMP, at pressure of 1333 psia, the minimum tie-line length increases after 1300 psia.
A similar plot is given for the extrapolated minimum tie-triangle lengths coupled with extrapolated oil recoveries in Figure 6.32. The minimum tie-triangle length is decreasing as pressure increases while still larger than 0.2.

Likewise, Figure 6.33 shows the extrapolated minimum tie-line lengths and oil recoveries with respect to pressure using all the full range of number of grid blocks. The result of extrapolated minimum tie-triangle lengths and oil recoveries is shown in Figure 6.34. There is a good agreement between the proposed extrapolation methods considering the extrapolated minimum tie-line/tie-triangle lengths, and oil recoveries.

### 6.1.2 CO₂ solvent displacement of seven-component oil

In this section, the low-temperature seven-component BSB oil displacement presented in section 5.2.2 is investigated using one-dimensional simulation in this section. We first examine the effect of pressure on tie-line and tie-triangle lengths. Then, the effect of the three-phase region on displacement efficiency is examined. We are interested in the qualitative trend of the tie-line lengths and oil recoveries by extrapolations to the infinite Peclet number with pressures.

The reservoir properties are given in Table 6.1. The displacement pressures are 1200, 1250, 1300, 1350, 1400, and 1450 psia, and the reservoir temperature is constant at 105 °F. Figure 6.36 shows the tie-line lengths at 1200 psia and operating temperature after 0.3 pore volumes injected (PVI). The L₁-V two-phase regions flow ahead of and behind the L₁-L₂-V three-phase region in the context of CO₂/hydrocarbon mixtures. The single-phase L₁ region exists at the front of the two-phase region since the injected gas does not displace the oil. At 1200 psia, the smallest phase composition distance as shown by TL₁-L₂-V, is inside the three-phase region. TL₁-L₁₂ is smaller at the front of three-phase region compared with other points in the three-phase region. The TL₁-V is large along the entire dimensionless distance including the two- and three-phase regions, exhibiting significant immiscibility between L₁ and V phases.
Similar plots for tie-line lengths are given in Figure 6.37 at 1250 psia, Figure 6.39 at 1300 psia, Figure 6.41 at 1350 psia, Figure 6.43 at 1400 psia, and Figure 6.45 at 1450 psia. As pressure increases, the three-phase region becomes narrower. In Figure 6.37 at 1250 psia, L_2 and V phases are highly immiscible in the three-phase region according to the values of $TL_{L_2-V}$ even though $TL_{L_2-V}$ represents the smallest tie-line length. At 1300 psia as shown in Figure 6.39, $TL_{L_2-V}$ decreases and becomes the smallest tie-line at the tail of three-phase region, indicating the existence of an elongated tie-triangle encountered during the composition path at this pressure and a CEP where L_2 and V phases become miscible. However, at the tail of three-phase region, phase L_1 is immiscible with the L_2 and V phases as indicated by $TL_{L_1-L_2}$ and $TL_{L_1-V}$.

The tie-triangle length plots are presented in Figures 6.36, 6.38, 6.40, 6.42, 6.44, and 6.46 at different pressures 1200, 1250, 1300, 1350, 1400 and 1450 psia and the characteristics of the profiles are similar. The tie-triangle length remains large along the entire displaced distance including two- and three-phase regions, and the smallest value occurs at the front of three-phase region inside the three- or two-phase region as shown in these figures.

Figure 6.47 shows the oil recoveries at 1.2 PVI predicted by simulations taken with 1000 grid blocks at five different pressures 1200, 1250, 1300, 1350, 1400 and 1450 psia. All the displacements involve three-hydrocarbon-phase flow. The displacement at 1300 psia results in 95.18% oil recovery at 1.2 pore-volumes injected (PVI) and the increment in oil recovery becomes insignificant above 1300 psia as shown in Figure 6.47. The displacement efficiency is 95.94% at 1350 psia, which is only improved by 0.79% compared to 1300 psia. As pressure increases to 1400 psia, the displacement recovers 95.71% of the original oil, which is only 0.55% greater compared to 1300 psia. This value is actually smaller by 0.48% compared to 1350 psia.

The significant difference between displacement efficiency for two- and three-phase flow and two-phase can be interpreted as described below. In the BSB oil displacement, the high displacement efficiency is achieved when the composition path geos near the CEPs, especially the
UCEP where L$_2$ and V phases become miscible in the presence of immiscible L$_1$ and V phases coexisting at the entire displaced distance. For gas flooding only involving two-phase flow, the displacement efficiency becomes greater when two phases become miscible. However, this condition is not necessary for resulting in high displacement efficiency for three-hydrocarbon-phase flow.

One task in compositional simulation (UTCOMP) is to define the threshold phase density to identify the phases since the relative permeability model depends on it. We use a trial-and-error approach. Phase mislabeling could occur when the unique threshold density fails to label correctly the phases. Phase labeling is important for the reliability of simulation results since it affects the relative permeability model. Density inversion happens between the vapor phase and CO$_2$-rich second liquid phase at the regions near the injection well during the rich gas flooding process as shown in Figures 6.41, 6.43, and 6.45.

To address the problem of numerical dispersion, tie-line and tie-triangle lengths, and oil recovery are extrapolated to the infinite Peclet number by using different numbers of grid blocks at pressures as discussed above, i.e., 1200, 1250, 1300, 1350, 1400 and 1450 psia. The effect of dispersion using a smaller number of grid blocks is not negligible. For example, the oil recovery factor is 88% when Npe is 2000, while it decreases to 67% when Npe is 100 at a pressure of 1200 psia. The effect of numerical dispersion on the reliability of tie-line length, tie-triangle length, and oil recovery is considered in this section for the other pressures.

Based on the discussion above, the first extrapolation technique is used during one-dimensional simulations performed by varying the grid-block size, i.e., 200, 500, and 1000. The second extrapolation technique uses the entire series of varying number of grid blocks, i.e., 50, 100, 200, 500, and 1000. As indicated in Figures 6.48, 6.49, 6.50, 6.51, 6.52, and 6.53, the minimum tie-line lengths are shown by black solid points at six different pressures (1200, 1250,
1300, 1350, 1400 and 1450 psia). The extrapolated values are given in these figures using the entire series of varying grid block cases.

Similar plots are presented for the tie-triangle length as shown in Figures 6.54, 6.55, 6.56, 6.57, 6.58, and 6.59 at pressures of 1200, 1250, 1300, 1350, 1400, and 1450 psia. In Figure 6.56 at 1300 psia, we observe a smaller tie-triangle length using 50 grid blocks. In Figure 6.58, the tie-triangle length using 200 grid blocks is significantly higher since the two-phase region at the front of three-phase region disappears due to numerical dispersion. The resulting extrapolation value of the minimum tie-triangle length using all cases with varying number of grid blocks becomes less reliable due to numerical dispersion, when compared to the extrapolation method using the last three values. Oil recoveries at 1.2 PVI are extrapolated as given in Figures 6.61, 6.62, 6.63, 6.64, and 6.65.

Figure 6.66 represents the extrapolated values of the minimum tie-line lengths and oil recoveries at 1.2 PVI as pressure increases using more grid blocks. The minimum lengths of the tie lines decrease from 1200 to 1300 psia and increase from 1300 to 1450 psia. The slope for oil recovery becomes significantly smaller after 1300 psia. By the same extrapolation method, Figure 6.67 gives the extrapolated values of the minimum tie-triangle length. The minimum tie-triangle length has a tendency to decrease as pressure increases.

Similarly, Figure 6.68 represents the extrapolated values of the minimum tie-line length and oil recoveries as a function of pressure, and Figure 6.69 shows the extrapolated minimum tie-triangle length and oil recoveries versus pressure. Both Figures 6.68 and 6.69 comprise data from all five cases. The extrapolated minimum tie-triangle length using all the five cases (number of grid blocks) is less accurate than using the last three cases due to numerical dispersion. The effect of different extrapolation methods can be observed in Figures 6.67 and 6.69. This confirms that we are able to achieve an improved accuracy using the last three values (number of grid blocks).
6.2 Comparisons of Mixing Cell Method and Compositional Simulation

In order to validate the new three-phase mixing cell method, we compare the profiles of tie-line lengths from our three-phase mixing cell method with one-dimensional compositional simulation by two oil fluid examples as discussed in Chapter 5 and section 6.1. In this section, comparisons of the calculated minimum tie-line lengths with changing pressures are also presented together with the tie-triangle lengths for a series of increasing pressures at the constant reservoir temperature of 105°F. Then, the development of miscibility is compared under each of the methods based on information from tie triangles and tie lines with knowledge of oil recovery. Equilibrium ratios are also considered to examine the mass transfer of components between phases.

6.2.1 CO₂ solvent displacement of four-component oil

In this section, we compare the results from our mixing cell method and 1-D UTCOMP simulation for the four-component BSB-Q oil displacement by injection gas as shown in Table 3.1. First miscibility development during the gas flooding processes is compared based on the development of tie-line lengths and equilibrium ratios. Second, the extrapolated minimum tie-line lengths and tie-triangle lengths are compared from both the mixing cell method and 1-D simulation with the oil recoveries from compositional simulations.

6.2.1.1 Comparison of miscibility development

Tie-line lengths represent the distance between phase compositions in compositional space. Profiles of tie-line lengths are compared from our mixing cell method with one-dimensional UTCOMP simulation for BSB-Q oil displacement by injection gas as shown in Table 3.1. The profiles generated from the three-phase mixing cell model are after 1000 contacts,
while the profiles generated from UTCOMP simulations use 1000 grid cells as shown in Figures 6.70, 6.74, 6.78, 6.82, 6.86 for several increasing pressures. The left figure shows the tie-line lengths from our three-phase mixing cell method, while the plot on the right shows the tie-line lengths from one-dimensional simulation at 0.5 HCPVI. In Figures 6.70, 6.74, 6.78, 6.82, the y-axis is comparable but the x-axis is not since the velocities are not compared by the mixing cell method.

We start from the lowest pressure shown in Figure 6.70. The oil tie-line from the mixing cell model shown on the left develops near the 1000th cell while the gas tie-line is not well developed because the mixing ratio used is near zero. The oil tie-line from one-dimensional simulation, which develops at a dimensionless distance approximately equals to 0.45. This is consistent with the oil tie-line from our three-phase mixing cell method. The minimum tie-line between the L_2 and V phases is calculated via simulation and the mixing cell model. The results are shown in Figure 6.70. The calculated minimum tie-line lengths also match.

Profiles of equilibrium ratios can also be used to examine the mass transfer between phases. For three-hydrocarbon systems, K-values can be represented in three ways to understand the composition distribution between two of the three phases as shown in Figures 6.71, 6.72, 6.73 at 1200 psia. K-values are calculated based on the component mole fractions. There are three sets of K-values, \( K_{N/L_1}, K_{N/L_2}, \) and \( K_{L_2/L_1} \) \( (i = 1, \ldots, N_C) \), which are defined as

\[
K_{i/L_1} = \frac{x_{N_i}}{x_{L_1}}
\]

\[
K_{i/L_2} = \frac{x_{N_i}}{x_{L_2}}
\]

\[
K_{L_2/L_1} = \frac{x_{L_2}}{x_{L_1}}.
\]

Also, in each figure, the left-hand side plot shows the result from the mixing cell method and the right-hand side plot shows the UTCOMP simulation results. In Figures 6.71 and 6.72, CO_2 is extracted from the V and L_1 phases into the L_2 phase as indicated by \( K_{L_2/L_1} \) and \( K_{V/L_2} \) at the front and at the tail of three-phase region. As \( K_{V/L_1} \) indicates in Figure 6.73, CO_2 is condensed
from the V into the L₁ phase in the two-phase region ahead of the three-phase region, while CO₂ is vaporized from the L₁ into V phase in the two-phase region behind the three-phase region.

Figures 6.74 compares the tie-line length profile for simulation and the mixing cell method at 1250 psia. The development of tie-lines are consistent from the mixing cell model and 1-D simulation while the gas tie-line still does not develop due to the mixing ratio used from the mixing cell method. The tendency of CO₂ to be extracted from the V and L₁ phases into the L₂ phase becomes greater as indicated by \( K_{L_2/L_1} \) and \( K_{V/L_2} \) at the front and at the tail of the three-phase region as shown in Figures 6.75, and 6.76. Figure 6.76 shows good agreement from our mixing cell method and 1-D simulation. Also, Figure 6.77 shows the immiscible L₁ and V phases for the entire displacement.

The tie-line length profiles for various pressures are shown in Figures 6.78, 6.82, and 6.86 at pressures of 1300, 1333 and 1350 psia. The minimum value of tie-line length between L₂ and V decreases dramatically from 1250 psia to 1300 psia for both the mixing cell and 1-D simulation methods as shown in Figure 6.78. \( K_{L_2/L_1} \) becomes 1.0 for the 1-D simulation in Figure 6.79, indicating that L₂ and L₁ are miscible even though the \( K_{L_2/L_1} \) from the mixing cell model is not 1.0 for the BSB-Q oil displacement by injection gas. \( K_{V/L_2} \) values from both methods are becoming 1.0 at the tail of the three-phase region as shown in Figure 6.80. As we further increase the pressure, the development of miscibility based on profiles of tie-line length are similar at the pressure of 1300 psia as shown in Figures 6.82 and 6.86 for 1333 and 1350 psia. The \( K \)-values profiles in Figures 6.83 to 6.85 are for 1333 psia and the \( K \)-values profiles in Figures 6.87 to 6.89 are for 1350 psia. The behavior of \( K \)-values at 1333 and 1350 psia have the same trend as discussed for 1300 psia.
6.2.1.2 Comparison of minimum tie-line length

MMP can be interpreted as the pressure where the curve shows a distinct bend on a plot of recovery versus pressure for a vapor-liquid displacement or for that matter for a $L_1$-$L_2$-$V$ displacement. Figure 6.90 shows the comparison of minimum tie-line lengths. Both methods, the mixing cell method and the one-dimensional simulations use extrapolated minimum tie-line lengths. The simulation uses the last three values to perform extrapolations in Figure 6.90 since a higher accuracy is achieved as discussed in section 6.1. The extrapolated oil recoveries are used for simulation. The minimum tie-line length, which is also the tie-line length between the $L_2$ and $V$ phases approaches zero at the pressure of 1300 psia for the two plots in Figure 6.90. The mixing cell method shows a CEP as in 1-D simulation.

Figure 6.91 compares the minimum tie-triangle length for the mixing cell and simulations. Same extrapolation techniques as in Figure 6.90 are used to calculate the minimum lengths and oil recoveries. Complete miscibility, defined as a single phase displacement, is not achieved at CEP since the values of the minimum tie-triangle length are not close to zero. A sharp bend on the minimum tie-triangle length curve is not seen. A smooth transition occurs from pressures with small values to pressures with larger values of tie-triangle length. A sharp increase in oil recovery is observed at first. Once increases in pressure leads to a CEP a smooth change in recovery takes place. The displacement for recoveries approaching 98% is therefore a liquid-liquid-vapor displacement instead of a classical single phase miscible displacement.

6.2.2 CO$_2$ solvent displacement of seven-component oil

The second case for comparison is for displacement of a seven-component BSB oil by injection CO$_2$ as shown in Table 3.2. We first examine miscibility development based on profiles
of tie-line lengths and $K$-values. Then the extrapolated minimum tie-line lengths and tie-triangle lengths are compared from both the mixing cell method and 1-D UTCOMP simulations.

### 6.2.2.1 Comparison of miscibility development

Miscibility development involving three-hydrocarbon phases is considered for the seven-component BSB oil displacement by CO$_2$ solvent. In Figure 6.92, the smallest tie-line lengths develop inside the three-phase region at similar values for the mixing cell and simulation. The oil and gas tie-lines also show good agreement from the mixing cell method and 1-D simulation.

Figures 6.93, 6.94, and 6.95 show the $K$-values of the two methods. Figure 6.93 shows the development of miscibility between L$_2$ and L$_1$ phases at the front of the three-phase region. The development of miscibility between V and L$_2$ phases occurs at the smallest tie-line length shown in Figure 6.92 both in our mixing cell method and 1-D simulation. At the same time, immiscible two-phase flow exists at a pressure of 1200 psia as shown in Figure 6.95. Obtaining three-phase flow with a modest increase in pressure is key to achieving good oil recovery.

Figure 6.96 shows the profile of tie-line lengths at a higher pressure of 1250 psia. The smallest tie-line length at 1250 psia decreases when compared to the smallest tie-line length in Figure 6.92, which is at a pressure of 1200 psia. The L$_2$ and L$_1$ phases become increasingly miscible at the front of the three-phase region while the V and L$_2$ phases become more miscible at the smallest tie-line length region as shown in Figures 6.97 and 6.98. The L$_1$ and V phases are still immiscible as indicated in Figure 6.99.

The tie-line length between the L$_2$ and V phases is sensitive to the pressure change from 1250 to 1300 psia according to the profile of tie-line lengths in Figure 6.100 both from our mixing cell method and 1-D simulations. The three-phase region shrinks dramatically when pressure is increased from 1250 to 1300 psia. The smallest tie-line length occurs between the L$_2$ and V phases, at the tail of the three-phase region. From Figures 6.101 and 6.102, the
development of miscibility between the L\(_1\) and L\(_2\) phases occurs at the front of three-phase region, and development of miscibility between V and L\(_2\) phases occurs at the tail of the three-phase region. Figures 6.101 and 6.102 show that the composition path is near a CEP.

Figure 6.104 shows the tie-line length profile at a pressure of 1350 psia, which is higher using the pressure near the CEP. The tie-line length between L\(_2\) and V phases generated from the three-phase mixing cell method after 1000 contacts decreases similarly to the 1-D simulation using 1000 grid blocks. For three-phase mixing cell, the compositions are not dependent on fractional flow as they are in simulation. As the pressure increases, the three-phase region becomes smaller, and the compositions pass further from the CEP area. This problem could potentially be addressed by changing the mixing ratio used or continuing to perform more contacts in the mixing cell model. The level of dispersion in the mixing cell and simulations are not the same.

The plot on the right of Figure 6.104 shows the drawback of using UTCOMP simulations: phase labeling is necessary to generate physical phase compositions. The threshold phase densities between the vapor phase and CO\(_2\)-rich second liquid phase must be changed by trial-and-error. This explains the injection of the L\(_2\) phase at the pressure of 1350 psia for UTCOMP simulation. Due to this phase labeling problem, the profile of K-values between L\(_2\) and L\(_1\) phases from UTCOMP simulation should be compared with the profile of K-values between V and L\(_1\) phases from the mixing cell model as shown in Figure 6.105. Similar plots are also shown for a pressure of 1400 psia in Figures 6.108 to 6.111.

Figure 6.112 shows the tie-line length profile at 1450 psia for both methods. The minimum tie-line length in the mixing cell method and simulations show good agreement. The oil tie lines in simulation are strongly affected by numerical dispersion and almost disappear at the front of three-phase region. Figures 6.113 to 6.115 show K-values profiles at 1450 psia, which have similar trend as for the K-values at 1350 and 1400 psia.
6.2.2.2 Minimum tie-line length comparison

We compare the mixing cell with the simulation results, which use extrapolations from 200, 500, and 1000 grid blocks. A distinct bend occurs on the recovery curve as shown in Figure 6.116 using one-dimensional compositional simulation at 1300 psia. There is a good agreement on the trend of the minimum tie-line length from mixing cell method and UTCOMP simulation. A sharp increase on the minimum tie-line length curve occurs at 1350 psia for mixing cell, and 1450 psia for simulation. Figure 6.117 shows that the tie-triangle length decreases as pressure increases. The displacement results in high oil recovery and the CEP behavior is the reason for good displacement efficiency.
Table 6.1 Reservoir properties for simulations of one-dimensional oil displacements by CO₂

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>1000 ft × 10 ft × 10 ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of grid cells</td>
<td>N_GB^x × 1 × 1</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.20</td>
</tr>
<tr>
<td>Permeability</td>
<td>1000 mD</td>
</tr>
<tr>
<td>Relative permeability model</td>
<td>Corey</td>
</tr>
<tr>
<td>Residual saturation</td>
<td>0.40 / 0.20 / 0.05 / 0.05</td>
</tr>
<tr>
<td>Endpoint relative permeability</td>
<td>0.35 / 0.50 / 0.65 / 0.65</td>
</tr>
<tr>
<td>Exponent</td>
<td>3.0 / 3.0 / 3.0 / 3.0</td>
</tr>
<tr>
<td>Initial saturation</td>
<td>0.4 / 0.6 / 0.0 / 0.0</td>
</tr>
</tbody>
</table>

* W: Aqueous phase, L₁: Oleic phase, G: Gaseous phase, L₂: CO₂-rich liquid phase

N_GB: Number of grid blocks for x dimension

Figure 6.1 Development of tie-line lengths at 0.5 HPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 50 grid blocks
Figure 6.2 Development of tie-line lengths at 0.5 HPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 100 grid blocks

Figure 6.3 Development of tie-line lengths at 0.5 HPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 200 grid blocks
Figure 6.4 Development of tie-line lengths at 0.5 HPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 500 grid blocks.

Figure 6.5 Development of tie-line lengths at 0.5 HPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 1000 grid blocks.
Figure 6.6 Development of tie-triangle lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 using 1000 grid blocks.

Figure 6.7 Development of tie-line lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 using 1000 grid blocks.
Figure 6.8 Development of tie-triangle lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 using 1000 grid blocks.

Figure 6.9 Development of tie-line lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 using 1000 grid blocks.
Figure 6.10 Development of tie-triangle lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 using 1000 grid blocks

Figure 6.11 Development of tie-line lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1333 psia by the injection gas shown in Table 3.1 using 1000 grid blocks
Figure 6.12 Development of tie-triangle lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1333 psia by the injection gas shown in Table 3.1 using 1000 grid blocks

Figure 6.13 Development of tie-line lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1350 psia by the injection gas shown in Table 3.1 using 1000 grid blocks
Figure 6.14 Development of tie-triangle lengths at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1350 psia by the injection gas shown in Table 3.1 using 1000 grid blocks

Figure 6.15 Oil recoveries for the displacements of the BSB-Q oil (105°F) at different pressures by the injection gas shown in Table 3.1
Figure 6.16 Extrapolation of the minimum tie-line length to estimate $TLL^\infty$ with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1200 psia. Extrapolated minimum tie-line length $TLL^\infty$ is 0.0874 for $m=0.932$ by last 3 points and 0.0875 for $m=0.803$ by all 5 points.

Figure 6.17 Extrapolation of the minimum tie-line length to estimate $TLL^\infty$ with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1250 psia. Extrapolated minimum tie-line length $TLL^\infty$ is 0.0407 for $m=0.584$ by last 3 points and 0.0395 for $m=0.356$ by all 5 points.
Extrapolation of the minimum tie-line length to estimate $TLL^\infty$ with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1300 psia. Extrapolated minimum tie-line length $TLL^\infty$ is 0.000379 for $m=0.445$ by last 3 points and 0.00271 for $m=0.957$ by all 5 points.

Extrapolation of the minimum tie-line length to estimate $TLL^\infty$ with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1333 psia. Extrapolated minimum tie-line length $TLL^\infty$ is 0.0000359 for $m=0.851$ by last 3 points and 0.00467 for $m=0.679$ by all 5 points.
Figure 6.20 Extrapolation of the minimum tie-line length to estimate $TLL^\infty$ with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1350 psia. Extrapolated minimum tie-line length $TLL^\infty$ is 0.00427 for $m=0.716$ by last 3 points and 0.00546 for $m=0.934$ by all 5 points.

Figure 6.21 Extrapolation of the minimum tie-triangle length at a pressure of 1200 psia to determine $TTL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ is 0.359 for $m=0.514$ by last 3 points and 0.361 for $m=0.849$ by all 5 points.
Figure 6.22 Extrapolation of the minimum tie-triangle length at a pressure of 1250 psia to determine $TTL^\infty$ for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ is 0.304 for $m=0.987$ by last 3 points and 0.301 for $m=0.99$ by all 5 points.

Figure 6.23 Extrapolation of the minimum tie-triangle length at a pressure of 1300 psia to determine $TTL^\infty$ for the BS-B-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length $TTL^\infty$ is 0.259 for $m=0.911$ by last 3 points and 0.257 for $m=0.652$ by all 5 points.
Figure 6.24 Extrapolation of the minimum tie-triangle length at a pressure of 1333 psia to determine TTL_{T} for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length TTL_{T} is 0.233 for m=0.595 by last 3 points and 0.238 for m=0.676 by all 5 points.

Figure 6.25 Extrapolation of the minimum tie-triangle length at a pressure of 1350 psia to determine TTL_{T} for the BSB-Q oil displacement by the injection gas shown in Table 3.1. Minimum tie-triangle length TTL_{T} is 0.219 for m=0.445 by last 3 points and 0.233 for m=0.428 by all 5 points.
Figure 6.26 Extrapolation of the oil recovery at 1.2 PVI to estimate the recovery factor with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1200 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.805 for $m=0.924$ by last 3 points and 0.802 for $m=0.898$ by all 5 points.

Figure 6.27 Extrapolation of the oil recovery at 1.2 PVI to estimate the recovery factor with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1250 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.931 for $m=0.653$ by last 3 points and 0.921 for $m=1.02$ by all 5 points.
Extrapolation of the oil recovery at 1.2 PVI to estimate the recovery factor with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1300 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.991 for $m=0.881$ by last 3 points and 0.989 for $m=0.801$ by all 5 points.

Extrapolation of the oil recovery at 1.2 PVI to estimate the recovery factor with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1333 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.991 for $m=0.875$ by last 3 points and 0.988 for $m=0.836$ by all 5 points.
Figure 6.30 Extrapolation of the oil recovery at 1.2 PVI to estimate the recovery factor with no dispersion for the BSB-Q oil displacement by the injection gas shown in Table 3.1 at a pressure of 1350 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.991 for $m=0.858$ by last 3 points and 0.984 for $m=0.941$ by all 5 points.

Figure 6.31 Oil recoveries at 1.2 PVI and minimum values of TLL along the composition path for the BSB-Q oil displacements at 105°F by the injection gas shown in Table 3.1 using last 3 points
Figure 6.32 Oil recoveries at 1.2 PVI and minimum values of TTL along the composition path for the BSB-Q oil displacements at 105°F by the injection gas shown in Table 3.1 using last 3 points.

Figure 6.33 Oil recoveries at 1.2 PVI and minimum values of TLL along the composition path for the BSB-Q oil displacements at 105°F by the injection gas shown in Table 3.1 using all 5 points.
Figure 6.34 Oil recoveries at 1.2 PVI and minimum values of TTL along the composition path for the BSB-Q oil displacements at 105°F by the injection gas shown in Table 3.1 using all 5 points

Figure 6.35 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.2 using 1000 grid blocks
Figure 6.36 Development of the tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.

Figure 6.37 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.
Figure 6.38 Development of tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.

Figure 6.39 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.
Figure 6.40 Development of tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.

Figure 6.41 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1350 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.
Figure 6.42 Development of tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1350 psia by the injection gas shown in Table 3.2 using 1000 grid blocks

Figure 6.43 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1400 psia by the injection gas shown in Table 3.2 using 1000 grid blocks
Figure 6.44 Development of tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1400 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.

Figure 6.45 Development of the tie-line lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1450 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.
Figure 6.46 Development of tie-triangle lengths at 0.5 HCPVI for the BSB oil displacement at 105°F and 1450 psia by the injection gas shown in Table 3.2 using 1000 grid blocks.

Figure 6.47 Oil recoveries for the displacements of the BSB oil (105°F) at different pressures by the injection gas shown in Table 3.2.
Figure 6.48 Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1200 psia. Extrapolated minimum tie-line length $TLL_\infty$ is 0.0239 for $m=0.839$ by last 3 points and 0.0282 for $m=0.75$ by all 5 points.

Figure 6.49 Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1250 psia. Extrapolated minimum tie-line length $TLL_\infty$ is 0.0124 for $m=0.33$ by last 3 points and 0.1 for $m=0.33$ by all 5 points.
Figure 6.50  Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for
the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of
1300 psia. Extrapolated minimum tie-line length TLL\(^\infty\) is 0.000352 for m=0.485 by
last 3 points and 0.00259 for m=0.909 by all 5 points.

Figure 6.51  Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for
the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of
1350 psia. Extrapolated minimum tie-line length TLL\(^\infty\) is 0.00565 for m=0.945 by
last 3 points and 0.00263 for m=1.2 by all 5 points.
Figure 6.52 Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1400 psia. Extrapolated minimum tie-line length $T_{LL\infty}$ is 0.00949 for $m=0.798$ by last 3 points and 0.00558 for $m=0.878$ by all 5 points.

Figure 6.53 Extrapolation of the minimum tie-line length to estimate TLL with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1450 psia. Extrapolated minimum tie-line length $T_{LL\infty}$ is 0.0611 for $m=1.22$ by last 3 points and 0.0561 for $m=1.791$ by all 5 points.
Figure 6.54 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1200 psia to determine TTL. Minimum tie-triangle length $TTL^\infty$ is 0.272 for $m=0.849$ by last 3 points and 0.258 for $m=0.311$ by all 5 points.

Figure 6.55 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1250 psia to determine TTL. Minimum tie-triangle length $TTL^\infty$ is 0.269 for $m=0.891$ by last 3 points and 0.264 for $m=0.844$ by all 5 points.
Figure 6.56 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1300 psia to determine TTL. Minimum tie-triangle length TTL is 0.231 for m=0.739 by last 3 points and 0.19 for m=0.175 by all 5 points.

Figure 6.57 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1350 psia to determine TTL. Minimum tie-triangle length TTL is 0.208 for m=0.403 by last 3 points and 0.244 for m=0.557 by all 5 points.
Figure 6.58 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1400 psia to determine TTL. Minimum tie-triangle length TTL is 0.211 for m=1.013 by last 3 points and 0.251 for m=0.591 by all 5 points.

Figure 6.59 Extrapolation of the minimum tie-triangle length for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1450 psia to determine TTL. Minimum tie-triangle length TTL is 0.194 for m=0.108 by last 3 points and 0.281 for m=1.5 by all 5 points.
Figure 6.60 Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1200 psia. Extrapolated oil recovery factor $R_F^\infty$ is 0.924 for $m=0.697$ by last 3 points and 0.906 for $m=0.624$ by all 5 points.

Figure 6.61 Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1250 psia. Extrapolated oil recovery factor $R_F^\infty$ is 0.94 for $m=0.721$ by last 3 points and 0.935 for $m=0.7$ by all 5 points.
Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1300 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.981 for $m=0.688$ by last 3 points and 0.98 for $m=0.604$ by all 5 points.

Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1350 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.979 for $m=0.808$ by last 3 points and 0.98 for $m=0.641$ by all 5 points.
Figure 6.64 Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1400 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.97 for $m=0.842$ by last 3 points and 0.97 for $m=0.764$ by all 5 points.

Figure 6.65 Extrapolation of the oil recovery at 1.2 HCPVI to estimate the recovery factor with no dispersion for the BSB oil displacement by the injection gas shown in Table 3.2 at a pressure of 1450 psia. Extrapolated oil recovery factor $RF^\infty$ is 0.97 for $m=1.09$ by last 3 points and 0.957 for $m=0.9$ by all 5 points.
Figure 6.66  Oil recoveries at 1.2 PVI and minimum values of TLL along the composition path for the BSB oil displacements at 105°F by the injection gas shown in Table 3.2 using last 3 points

Figure 6.67  Oil recoveries at 1.2 PVI and minimum values of TTL along the composition path for the BSB oil displacements at 105°F by the injection gas shown in Table 3.2 using last 3 points
Figure 6.68  Oil recoveries at 1.2 PVI and minimum values of TLL along the composition path for the BSB oil displacements at 105°F by the injection gas shown in Table 3.2 using all 5 points

Figure 6.69  Oil recoveries at 1.2 PVI and minimum values of TTL along the composition path for the BSB oil displacements at 105°F by the injection gas shown in Table 3.2 using all 5 points
Figure 6.70 Tie-line lengths for BSB-Q oil displacement at 1200 psia, 105°F. Left: mixing-cell model, Right: 1-D simulation.

Figure 6.71 $K_{2/L_1}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.
Figure 6.72 $K_{vL2}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.

Figure 6.73 $K_{vL1}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1200 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.
Figure 6.74 Tie-line lengths for BSB-Q oil displacement at 1250 psia, 105°F. Left: mixing-cell model, Right: 1-D simulation.

Figure 6.75 $K_i/l_1$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.
Figure 6.76 $Kv/V_{L2}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.

Figure 6.77 $Kv/V_{L1}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1250 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.
Figure 6.78 Tie-line lengths for BSB-Q oil displacement at 1300 psia, 105°F
Left: mixing-cell model, Right: 1-D simulation.

Figure 6.79 $K_{L2/L1}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Left: mixing-cell model, Right: 1-D simulation.
Figure 6.80 \( K\upsilon_{12} \) profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.

Figure 6.81 \( K\upsilon_{13} \) profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1300 psia by the injection gas shown in Table 3.1 after 1000 contacts. Left: mixing-cell model, Right: 1-D simulation.
Figure 6.82 Tie-line lengths for BSB-Q oil displacement at 1333 psia, 105°F.
Left: mixing-cell model, Right: 1-D simulation.

Figure 6.83 $K_{1.2/L_1}$ profiles at 0.5 HCPVI for the BSB-Q oil displacement at 105°F and 1333 psia by the injection gas shown in Table 3.1 after 1000 contacts.
Left: mixing-cell model, Right: 1-D simulation.
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Chapter 7

Summary, Conclusions, and Recommendations for Future Research

7.1 Summary and conclusions

We developed a multiple three-phase mixing cell method based on a robust three-phase flash calculation algorithm. The mixing cell method, as the name applies, is to achieve dynamic miscibility by mixing the injected gas with oil in place through multiple contacts at a given reservoir temperature condition. The design of the new three-phase mixing scheme is based on the simplification that the mixing cell model is not dependent on fractional flow, i.e. there is no required relative permeability model.

Phase equilibrium calculations become more difficult when multicontact miscibility is approached and/or when the number of phases increases. A more reliable initial estimate approach for three-phase flash calculation has been implemented in the three-phase mixing cell method. Tie-triangle information is obtained for the purpose of calculation of minimum tie-line length and minimum tie-triangle length.

Understanding the impact of the third CO₂-rich second liquid phase on the miscibility development is essential to optimal design of injection pressure management. Determining the injection pressure by compositional simulation for each possible variation is impractical and time-consuming. This study gives an easy and robust way to determine the pressure for an efficient displacement qualitatively on the basis of extrapolated tie-line lengths at a series of pressures.

As stated before, optimization of the injection pressure is important for economic consideration as a tradeoff between the cost of pressurizing the injected gas and satisfactory oil recoveries. The three-phase mixing cell method can provide useful information for the optimal
injection pressure as a robust and fast alternative method when compared to traditional compositional simulation.

This research focuses on the mixing cell method to investigate the three-hydrocarbon-phase system. The oil displacement by low-temperature CO$_2$ flooding exhibits immiscible three-hydrocarbon-phase flow for all pressures of interest. The results of tie-line lengths from three-phase mixing cell method are obtained at certain contact levels for a series of different pressures. The behavior of tie-line length between L$_2$ and V phases changes significantly with pressure. The minimum tie-line length doesn't decrease monotonically with the increase of pressure. The reason is that immiscible liquid-phase flow still exists when pressure goes up. Thus, complete miscibility could not be achieved when just one of the tie-line lengths approaches zero. A better representation for the development of miscibility is the minimum tie-triangle length. The extrapolated minimum tie-triangle length at infinite contact number decreases asymptotically with increasing pressures, but does not become zero.

One-dimensional simulation results are also performed as comparisons for three-phase mixing cell methods. Compositional simulation finds composition paths as the method proceeds, which the location depends on fractional flow. Tie-line length is extrapolated to infinite Peclet number to calculate the minimum tie-line length with no numerical dispersion. The same extrapolation technique is then applied for calculating the minimum tie-triangle length and oil recoveries at different pressures. The extrapolated oil recovery factor does not increase significantly with pressure after the minimum tie-line length bends up while a more than 96% high displacement efficiency is obtained. The advantages of mixing cell method against compositional simulation become significant in the near-critical region, which is important in gas flooding simulation where no phase mislabeling problem is needed.

The tie-line lengths at different pressures are consistent in the three-phase mixing cell method and the one-dimensional simulation. The three-phase mixing cell method and one-
dimensional compositional simulation both indicate that the minimum tie-triangle length does not decrease asymptotically with increasing pressures. Also the critical endpoint behavior can be observed by the minimum tie-line length between L_2 and V phases, in both mixing cell method and simulation for the two oil fluid systems. Comparing to the three-phase mixing cell method, one-dimensional compositional simulation is more time-consuming, since the extrapolations to zero numerical dispersion require the simulation being performed at different number of grid blocks.

The MMPs for the same fluid systems are calculated based on the assumption that only two-hydrocarbon phases existing during contacts. The MMP, which represents the pressure for 100% displacement efficiency, is about 150 psia or 70 psia higher than the pressure leads to 98% or 96% oil recovery when taking three-phase conditions into consideration. Thus, optimization of injection pressure could be achieved by the new three-phase mixing cell method.

**7.2 Recommendations for future research**

The increasing interest and complexity of the presence of a second liquid phase during low-temperature oil displacement by injection gas, leads to the need to understand the miscibility development involving three hydrocarbon-phases. A potential solution could be a three-phase mixing cell method.

The three-phase mixing cell method relies on a robust positive/negative two- or three-phase flash calculation. Three-phase flash calculations become more difficult when multicontact miscibility is approached. Reliable initial K-estimates are important to guarantee the correct convergence of flash calculations. The three-phase mixing cell method could be further improved by only performing positive/negative three-phase flash calculations to obtain tie-triangles. The tie-simplex tabulation would also be a possibility for reliable initial estimates.
A robust and fast three-phase mixing cell method could be developed to extrapolate the tie-line lengths to zero with increasing pressures. The critical endpoint behavior can be observed when one of the tie-line lengths approaches zero. The existence of the thermodynamic minimum miscibility pressure (MMP) could be further investigated.

Different mixing schemes for equilibrated phases contacting with neighboring cells may be further developed based on theoretical three-phase method of characteristics (MOC) solution. The independence of the mixing ratio, which is used in material balance equation to determine the overall composition for each cell, could be verified. The independence of the exponent used in the power-law extrapolation to calculate the minimum tie-line length at infinite contacts could be demonstrated also.

Oil examples with more components can be used for the study on miscibility development for three-phase flow.
Glossary

Roman symbols

\(d_{L_1,V}\) Phase composition distance between the \(L_1\) and \(V\) phases
\(d_{L_2,V}\) Phase composition distance between the \(L_2\) and \(V\) phases
\(d_{L_1,L_2}\) Phase composition distance between the \(L_1\) and \(L_2\) phases
\(f_{ij}\) Fugacity of component \(i\) in phase \(j\)
\(G\) Gibbs free energy
\(\bar{G}\) Molar Gibbs free energy
\(\bar{G}_{ij}\) Partial molar Gibbs free energy of component \(i\) in phase \(j\)
\(h_i\) Parameter for component \(i\) for the reduced method
\(H\) Hessian matrix
\(J\) Jacobian matrix
\(k_{ij}\) Binary interaction coefficient between components \(i\) and \(j\)
\(K\) \(K\)-values
\(L\) Liquid phase or liquid phase mole fraction
\(L_1\) Oleic phase
\(L_2\) Solvent-rich liquid phase
\(N_C\) Number of components
\(N_P\) Number of phases
\(P\) Pressure
\(T_C\) Critical temperature
\(TL_{L_1,V}\) Tie-line length between the \(L_1\) and \(V\) phases
\(TL_{L_2,V}\) Tie-line length between the \(L_2\) and \(V\) phases
\(TL_{L_1,L_2}\) Tie-line length between between the \(L_1\) and \(L_2\) phases
\(TL^*\) Minimum tie line length at infinite number of contacts (in mixing cell)
\(V\) Vapor phase mole fraction, or gaseous phase
\(x_{ij}\) Mole fraction of component \(i\) in phase \(j\)
\(X_i\) Independent variable for component \(i\) used for stability analysis
\(y_i\) Mole fraction of component \(i\) in a vapor phase
\(z_i\) Mole fraction of component \(i\) in a mixture
Greek letters
\[ \alpha \] Mixing-ratio parameter (in mixing cell)
\[ \beta \] Mole fraction of phase \( j \)
\[ \theta_i \] \( i^{th} \) reduced parameter
\[ \theta_{ij} \] \( i^{th} \) reduced parameter in phase \( j \)
\[ \phi_{ij} \] Fugacity coefficient of component \( i \) in phase \( j \)

Superscripts
\[ G \] Gas
\[ O \] Oil
\[ L_1 \] Liquid phase
\[ L_2 \] CO\(_2\)-rich liquid phase
\[ V \] Vapor phase
\[ m \] Linearizing exponent used in \( 1/ N^m \) (mixing cell)

Subscripts
\[ C \] Critical property
\[ m \] Mixture
\[ R \] Reduced quantity
\[ u \] Upper bound
\[ max \] Maximum

Abbreviations
BIC Binary interaction coefficient
BSB-Q Bob Slaughter Block quaternary oil
CEP Critical endpoint
EOS Equation of state
HCPVI Hydrocarbon-pore-volume injected
LCEP Lower critical endpoint
MMP Minimum miscibility pressure
PVI Pore-volume injected
RR Rachford-Rice equations
<table>
<thead>
<tr>
<th>SS</th>
<th>Successive substitution algorithm</th>
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<tbody>
<tr>
<td>TPD</td>
<td>Tangent plane distance function</td>
</tr>
<tr>
<td>UCEP</td>
<td>Upper critical endpoint</td>
</tr>
<tr>
<td>TTL</td>
<td>Tie-triangle length</td>
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<tr>
<td>TLL</td>
<td>Tie-line length</td>
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References

Ahmadi, K. 2011. Advances in Calculation of Minimum Miscibility Pressure. PhD dissertation, the University of Texas at Austin, Austin, Texas.


UTCOMP version 3.8. 2003. The University of Texas at Austin, Austin, Texas.


Appendix A

Flow Chart of Multiphase Equilibrium Calculations in UTCOMP (from Chang 1990) is given in appendix A.
Appendix B

Three-Phase mixing cell uses the Peng-Robinson EOS:
\[ P = \frac{RT}{(V - b) - a(T)} / \left[ V(V + b) + b(V - b) \right], \]
where
\[ a(T) = 0.45724R^2T_c^2 \alpha(T)/P_c \]
\[ b = 0.07780RT_c/P_c \]
\[ \alpha(T) = 1 + m(\omega)\left(1 - \sqrt{T/T_c}\right) \]
\[ m(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \text{ for } \omega < 0.49 \]
\[ m(\omega) = 0.37964 + \omega(1.48503 + \omega(-0.16442 + 0.01667\omega)) \text{ for } \omega > 0.49. \]

For phase behavior modeling in mixing cell model, van der Waals mixing rule is used for a mixture with \(N_c\) components,
\[ a_m = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij} \text{ and } b_m = \sum_{i=1}^{N_c} x_i b_i, \]
The combing rule for \(a_{ij}\) is
\[ a_{ij} = \sqrt{a_i a_j (1 - k_{ij})} = a_{ji}. \]

\(k_{ij}\) are binary interaction parameter.

Defining
\[ B = b_mP/RT, \]
\[ A = a_mP(RT)^2, \]
\[ A_{ij} = a_{ij}P(RT)^2, \]
the fugacity coefficient is calculated by
\[ \ln \phi_i = (Z - 1)\frac{B}{B} - \ln (Z - B) - \frac{A}{(\delta_1 - \delta_2)B} \left( \frac{2\sum_{j=1}^{N_c} x_j A_{ij}}{A} - \frac{B}{B} \right) \ln \left[ \frac{Z + \delta_1 B}{Z + \delta_2 B} \right], \]
where \(\delta_1 = 1 + \sqrt{2}\), and \(\delta_2 = 1 - \sqrt{2}\).