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REDUCED PHASE EQUILIBRIUM CALCULATIONS: NEW REDUCED
PARAMETERS, CRITICAL ANALYSIS AND FLUID CHARACTERIZATION

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ABSTRACT

Phase equilibrium calculations constitute a significant percentage of computational time in compositional simulation, especially as the number of components and phases increases. Reduced methods address this problem by carrying out phase equilibrium calculations using a reduced number of independent parameters. Some researchers have found that reduced methods speed up flash calculations, decrease simulation times, and also improve robustness.

We propose new reduced parameters using the two-parameter binary interaction parameter (BIP) formula originally proposed by Li and Johns (2006). We implement the new reduced parameters to two- and three-phase equilibrium calculations. We compare the new reduced two-phase flash calculations with several reduced and conventional techniques in terms of robustness and speed. The new reduced two-phase flash calculations show improved robustness with similar speed as the fastest reduced flash calculations. The new algorithm is also shown to be significantly faster than the conventional methods. We further critically analyze several proposed reduced algorithms and explain why some of the reduced techniques are slower than others.

We further compare our new reduced multiphase equilibrium calculations with the reduced multiphase equilibrium calculations of Okuno et al. (2010a). Our results show that the improved robustness in our two-phase flash calculations becomes more significant in the three-phase region indicating a larger radius of convergence. We have also observed that our three-phase flash calculations converge to the correct solution more often than the other reduced technique.

Reduced methods may improve accuracy when many components and phases are used in phase equilibrium calculations. Reduced methods, however, may not be able to fit the exact BIPs determined from conventional cubic EOS characterizations. Therefore, one of the remaining
questions is accuracy. We carry out fluid characterization steps in a suitable manner for reduced phase equilibrium calculations. We show that for the fluids studied, reduced parameters estimate the experimental data well without compromising speed during phase behavior calculations.
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GLOSSARY

*Roman symbols*

\( a \)  
Attraction parameters

\( b \)  
Repulsion parameter

\( f \)  
Fugacity

\( f^o \)  
Ideal gas fugacity

\( h_i, g_i \)  
LJ two-parameter BIPs

\( k_{ij} \)  
Binary interaction parameter

\( n \)  
Component mole numbers, number of eigenvalues considered

\( q_i' \)  
Eigenvector

\( q_{ia} \)  
Vector of known parameters

\( x \)  
Liquid phase composition

\( y \)  
Vapor phase composition

\( w \)  
Acentric factor

\( z \)  
Overall composition

\( z_N \)  
Mole fraction

\( z_+ \)  
Plus fraction composition

\( A \)  
Dimensionless attraction parameter

\( B \)  
Dimensionless repulsion parameter

\( B_g \)  
Gas formation volume factor

\( B_o \)  
Oil formation volume factor

\( C_N \)  
Carbon number

\( C_+ \)  
Plus fraction carbon number

\( G \)  
Gibbs free energy

\( G_R \)  
Molar residual Gibbs free energy
\[H\] Hessian matrix
\[H^C\] Reduced Hessian matrix
\[J\] Jacobian matrix
\[L\] Liquid phase mole fraction
\[M\] Molecular weight
\[M_+\] Plus fraction molecular weight
\[N_C\] Number of components
\[N_P\] Number of phases
\[P\] Pressure
\[P_b\] Bubble point pressure
\[P_C\] Critical pressure
\[R\] Gas constant
\[R_{so}\] Solution gas/oil ration
\[Q\] Heat
\[S\] Entropy
\[T\] Temperature
\[T_C\] Critical temperature
\[U\] Internal energy
\[V\] Volume, vapor phase mole fraction
\[V_m\] Molar volume
\[V_P\] Partial volume
\[W\] Work, Transformation matrix
Greek letters

\( \beta \quad \) Phase mole fraction
\( \rho \quad \) Density
\( \delta_1, \delta_2 \quad \) Generalized EOS parameters
\( \phi \quad \) Fugacity coefficient
\( \Theta \quad \) LJ reduced parameters
\( \lambda \quad \) Eigenvalue
\( \mu \quad \) Chemical potential
\( \mu^o \quad \) Ideal gas chemical potential

Subscripts

\( i \quad \) Component index
\( j \quad \) Phase index

Abbreviations

BIP \quad \) Binary interaction parameter
CME \quad \) Constant mass expansion
CVD \quad \) Constant volume depletion
DD \quad \) Differential depletion
EOS \quad \) Equation of state
FG \quad \) Conventional method based on solution of nonlinear equations
ISD \quad \) Improved spectral decomposition
ILJ \quad \) Improved Li and Johns algorithm
LJ \quad \) Li and Johns algorithm
<table>
<thead>
<tr>
<th>Acronym</th>
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<tbody>
<tr>
<td>MG</td>
<td>Conventional method based on minimization of Gibbs Energy</td>
</tr>
<tr>
<td>MME</td>
<td>Minimum miscibility enrichment</td>
</tr>
<tr>
<td>MMP</td>
<td>Minimum miscibility pressure</td>
</tr>
<tr>
<td>OJS</td>
<td>Reduced algorithm based on (Okuno, Johns, &amp; Sepehrnoori, Application of a Reduced Method in Compositional Simulation, 2010a)</td>
</tr>
<tr>
<td>PNA</td>
<td>Paraffin-naphtene-aromatic</td>
</tr>
<tr>
<td>PR</td>
<td>Peng-Robinson</td>
</tr>
<tr>
<td>PV</td>
<td>Pore volume</td>
</tr>
<tr>
<td>PVT</td>
<td>Pressure-volume-temperature</td>
</tr>
<tr>
<td>RMG</td>
<td>Reduced minimization of Gibbs energy</td>
</tr>
<tr>
<td>SD</td>
<td>Improved spectral decomposition method (Hendriks &amp; Van Bergen, Application of a Reduction Method to Phase Equilibria Calculations, 1992)</td>
</tr>
<tr>
<td>SRK</td>
<td>Soave-Redlich-Kwong</td>
</tr>
<tr>
<td>SS</td>
<td>Successive substitution</td>
</tr>
<tr>
<td>TLL</td>
<td>Tie-line length</td>
</tr>
<tr>
<td>TPD</td>
<td>Tangent plane distance</td>
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First and foremost, I am grateful to my advisor, Dr. Russell Johns for allowing me to work on a very interesting topic. I would also like to thank the committee members, Dr. Christopher Griffin, Dr. Turgay Ertekin, and Dr. Yilin Wang for their participation and suggestions.

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Chapter 1

INTRODUCTION AND OBJECTIVES

Lean gas, flue gas, CO₂, N₂ and several other gases are injected in the reservoir as enhanced oil recovery techniques after primary recovery and water flooding. When the injected gas and reservoir oil come in contact, miscibility plays a very important role in enhancing the production of reservoir fluids. Miscibility occurs when the injected fluid and the reservoir oil form one phase at all mixture compositions. Miscibility avoids multiphase flow effects, reduces residual oil saturation significantly, and has a piston-like front displacement if dispersion is not severe. A miscible displacement has the slowest possible breakthrough time in one-dimension. Thus, only reservoir fluids are produced until breakthrough occurs.

Miscibility takes place upon first contact or is developed in multiple contacts in the reservoir. Miscibility occurs only at favorable temperature, pressure, and injected-fluid and reservoir-fluid compositions. These favorable conditions occur when the densities become similar near the minimum miscibility pressure (MMP). Miscibility is generally achieved at higher pressures, where the gas is supercritical.

Compositional reservoir simulators can be used to model the displacement behavior. By using compositional reservoir simulators, we can track the concentration of components throughout space and time. Hence, compositional reservoir simulators can be used to optimize the amount and the gases to inject in order to achieve better oil recovery. Simulating more components and phases improves the predictability of incremental oil recovery. Simulating more components and phases, however, slows down the phase equilibrium calculations.
Compositional reservoir simulators include phase behavior calculations. Phase behavior calculations are divided into stability analyses and flash calculations. In stability analysis, we calculate the number of phases that are stable at equilibrium. Flash calculations compute the chemical composition of each phase once the number of phases is determined. Several phases can occur at the reservoir conditions e.g., CO$_2$-rich oleic phase, gaseous phase, hydrocarbon-rich oleic phase, aqueous phase, and asphaltene-rich phase. As the number of phases increases, phase equilibrium calculations become more time consuming.

Moreover, a reservoir typically has hundreds of hydrocarbon components. These components are identified from sampling of the fluid at various locations within the reservoir. At laboratory conditions, the chemical compositions can be identified with several techniques. Generally, these techniques determine the composition up to a number of light and intermediate components. As such, components that have large number of carbon atoms are generally not identified in the laboratory. Instead, these heavier components are determined by correlations, where dozens of components are determined in this manner. At reservoir conditions, these components may be shared between different phases such as oil or gas. Flash calculations compute how components are distributed between different phases.

Flash calculations are solved iteratively and there are several solution techniques, the simplest of which is direct substitution known as successive substitution. Direct substitution suffers from excessive number of iterations as it has a linear convergence rate. The number of iterations required reaches infinity at the critical point. As most gas injections are carried out near critical conditions, direct substitutions are not preferred. Flash calculations conventionally start with direct substitution and continue with Newton’s minimization or the Newton-Raphson algorithm when a particular window of convergence is reached. The Hessian and Jacobian matrix in these algorithms are of rank $\left( N_P - 1 \right) \times N_C$ where $N_P$ is the number of phases and $N_C$ is the number of the components. For stability analysis, the rank is $N_C$. 
Phase equilibrium calculations become significantly slower when more components and more phases are considered in compositional simulation. Components with similar molecular weight and other properties are therefore lumped into a few pseudo-components to increase the computational speed. Lumping and delumping procedures use empirical correlations and other linear mixing rules that may decrease the accuracy of the fluid characterization and simulation results.

Reduced methods that are applicable to both stability analyses and flash calculations do not use the composition as independent parameters. The independent parameters required to construct the Jacobian matrix are called reduced parameters. That is, reduced methods decrease the number of independent parameters to be solved significantly in phase equilibrium calculations. Reduced methods do not neglect some of the components. Instead, they use reduced parameters that can be expressed as a function of composition. This way, reduced methods are able to carry out phase equilibrium calculations with many components. However, the binary interaction parameters may require adjustments to generate the reduced parameters because the inputs for the reduced method may not result in an exact match to the binary interaction parameters (BIP) characterized in the conventional approach.

In this research, our primary goal is to develop a new reduced two-phase flash calculation algorithm, and compare it with several reduced and conventional methods. We further implement our reduced parameters to stability analyses and three-phase flash calculations. We show that our reduced parameters improve the robustness of multiphase flash calculations in that the radius of convergence is larger for the fluids tested. Finally, we carry out fluid characterization for the reduced methods and show that these methods can reproduce well the fluid phase behavior.

Phase equilibrium calculations are based on thermodynamics laws and they are solved with optimization techniques. Therefore, Chapter 2 gives theoretical background on the derivation of phase equilibrium calculations, objective functions, and residual functions based on
thermodynamics laws. Moreover, it gives a brief introduction to optimization techniques, some of which are used in our phase equilibrium calculations. In addition, Chapter 2 explains the procedures in PVT data analysis, provides a critical literature review of phase equilibrium calculations, and provides the equations for several previously proposed and implemented algorithms. In Chapter 3, we introduce new reduced two-phase flash calculations. In chapter 4, we compare several two-phase flash calculation techniques in terms of accuracy, number of iterations, robustness and computational speed. Chapter 5 shows the implementation of our new reduced parameters to stability analyses and three-phase flash calculations and gives robustness comparisons with another reduced technique. In chapter 6, we carry out fluid characterization proper for reduced methods.
Chapter 2

LITERATURE REVIEW

In this chapter, we provide background information on the phase equilibrium calculations, optimization techniques, and pressure-volume-temperature (PVT) data analysis. We also give further literature review of various phase equilibrium calculations, and finally we provide the equations that are implemented in our research, but have been proposed by other researchers.

2.1. Phase Equilibrium Calculations

Phase equilibrium calculations consist of stability analyses and flash calculations. Figure 2.1 shows the flow chart for these phase equilibrium calculations. Stability analysis calculations start assuming there is only one phase. If the phase is unstable, then there are at least two phases.

Two-phase flash calculations are then carried out to compute the chemical compositions for each phase. After the two-phase flash calculations, a stability analysis can be carried out to search for an additional third phase. If an additional phase is found to be stable, three-phase flash calculations are carried out. This procedure can be extended to test for more phases.

Phase equilibrium calculations are based on the following three criteria (Baker et al., 1982).

1. Law of mass conservation.
2. Global minimum of Gibbs energy.
3. Equality of chemical potentials for all phases.

We explain the 2nd and 3rd criteria in the following sections.
2.1.1. Global Minimum of Gibbs Energy

In this section, we show that Gibbs energy is a minimum at equilibrium. The 2nd criterion described in chapter 2.1 satisfies the second law of thermodynamics. That is, entropy of an isolated macroscopic system never decreases. The implication for the phase equilibrium calculations is that the entropy of an isolated system is a maximum at equilibrium for a number of phases and compositions.

The 1st law of thermodynamics states that

\[ dU = dQ + dW. \]  

(2.1)
By using the 2nd law of thermodynamics, Clausius inequality states that

\[ dS \geq \frac{dQ}{T} . \]  \hspace{1cm} (2.2)

Combination of Eqs. (2.1) and (2.2) gives

\[ TdS - dU - PdV \geq 0 \]  \hspace{1cm} (2.3)

where \( U \) is internal energy, \( Q \) is heat, \( W \) is work done on the system, \( T \) is temperature, \( S \) is entropy, \( P \) is pressure and \( V \) is volume.

Gibbs energy can be expressed as

\[ G = U + PV - TS , \]  \hspace{1cm} (2.4)

or

\[ dG = dU + VdP + PdV -TdS -SdT . \]  \hspace{1cm} (2.5)

Substitution of Eq. (2.5) into Eq. (2.3) gives

\[ dG -VdP + SdT \leq 0 . \]  \hspace{1cm} (2.6)

At constant temperature and pressure, Eq. (2.6) becomes
where $G$ is Gibbs free energy. Equation (2.7) indicates that Gibbs energy of an isolated system must be a minimum (Firoozabadi, 1999; Okuno, 2009). That is, the correct number of phases and phase compositions give the lowest Gibbs energy. Phase equilibrium calculations often use Gibbs energy as they are computed at constant temperature and pressure.

2.1.2. Equality of Chemical Potentials

Equality of chemical potentials is a result of chemical equilibrium which can be derived from the 1st and 2nd law of thermodynamics. Consider two isolated systems separated by a partition. When we remove the partition, separating the two isolated systems, entropy after equilibrium becomes

\[ S = S^\prime + S'' \] (2.8)

\[ S^\prime = S'(U', V', n_1', \ldots, n_c') \] (2.9)

\[ S'' = S''(U'', V'', n_1'', \ldots, n_c'') \] (2.10)

where $n_i$ is mole number of component $i$.

Internal energy can be expressed as

\[ U = U(S, V, n_1, \ldots, n_c) \] (2.11)

Equation (2.11) can be written as
\[ dU = \left( \frac{\partial U}{\partial S} \right)_{V,n} dS + \left( \frac{\partial U}{\partial V} \right)_{S,n} dV + \sum_{i=1}^{N_c} \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_i} dn_i \]  \hspace{1cm} (2.12)

in differential form.

Chemical potential can be expressed as

\[ \mu_i = \sum_{i=1}^{N_c} \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_i} dn_i \]  \hspace{1cm} (2.13)

The \( U \) parameter in Eq. (2.13) can be replaced by other thermodynamic properties such as \( S \), Helmholtz energy (\( A \)) or \( G \). Moreover,

\[ \left( \frac{\partial U}{\partial S} \right)_{V,n} = T \hspace{1cm} \left( \frac{\partial U}{\partial V} \right)_{S,n} = -P \]  \hspace{1cm} (2.14)

Combination of Eqs. (2.12) through (2.14) results in:

\[ dS = \frac{dU}{T} + \frac{P}{T} dV - \sum_{i=1}^{N_c} \frac{\mu_i}{T} dn_i \]  \hspace{1cm} (2.15)

Therefore Eqs. (2.9) and (2.10) can be written as

\[ dS' = \frac{dU'}{T'} + \frac{P'}{T'} dV' - \sum_{i=1}^{N_c} \frac{\mu_i'}{T'} dn_i' \]  \hspace{1cm} (2.16)
respectively.

Considering \( d(U' + U'') = 0 \), \( d(V' + V'') = 0 \) and \( d(n'_i + n''_i) = 0 \), and \( dS = 0 \) at the maximum entropy condition, combination of Eqs. (2.8), (2.16) and (2.17) give

\[
dS = \left(\frac{1}{T'} - \frac{1}{T''}\right) dU' + \left(\frac{P'}{T'} - \frac{P''}{T''}\right) dV'' + \sum_{i=1}^{N_c} \left(\frac{\mu'_i}{T'} - \frac{\mu''_i}{T''}\right) dn''_i = 0 .
\]  

(2.18)

Nontrivial solution for this problem is

\[
T' = T'' \quad P' = P'' \quad \mu'_i = \mu''_i \quad i = 1, ..., N_c .
\]  

(2.19)

Equation (2.19) indicates that component chemical potentials are equal to each other for all phases. That is, chemical potentials of a component in different phases are equal in a closed system (Firoozabadi, 1999). Chemical potential can be expressed in terms of fugacity as

\[
\mu_i = \mu_i^o + RT \ln \frac{f_i}{f_i^o}
\]  

(2.20)
where \( \mu^o \) is ideal gas chemical potential, \( f \) is fugacity, and \( R \) is gas constant. As all the terms except \( f \) in the right hand side are constants at constant \( T \) and \( P \), equality of chemical potentials also results in

\[
f'_i = f''_i.
\] (2.21)

Equality of fugacities is taken as the convergence criterion in algorithms that are based on solution of nonlinear equations.

2.2. Residual Molar Gibbs Free Energy

In this section, we derive an expression for computing residual molar Gibbs free energy \((G_R)\), because \( G_R \) is used as the objective function in minimization algorithms. Molar Gibbs free energy can be expressed as follows:

\[
G = \sum_{i=1}^{N_c} z_i \mu_i(T, P, z_1, \ldots, z_{N_c})
\] (2.22)

where \( z_i \) is composition and \( N_c \) is the number of components. Substitution of Eq. (2.20) into Eq. (2.22) gives,

\[
G = \sum_{i=1}^{N_c} z_i \mu^o + \sum_{i=1}^{N_c} z_i RT \ln \frac{f_i}{f_i^o}
\] (2.23)

or,
\[ G = G^\circ + \sum_{i=1}^{N_c} z_i RT \ln \frac{f_i}{f_i^\circ}. \]  

(2.24)

where \( G^\circ \) is ideal gas mixture or any reference state molar Gibbs free energy. The equation can be manipulated as the following dimensionless quantity:

\[ \frac{G - G^\circ}{RT} + \sum_{i=1}^{N_c} z_i \ln f_i^\circ = \sum_{i=1}^{N_c} z_i \ln f_i. \]  

(2.25)

The dimensionless term defined in Eq. (2.25) can be used as the objective function in minimization algorithms. Considering

\[ f_i = \phi_i z_i p \]  

(2.26)

where \( \phi_i \) is the fugacity coefficient, the equation can further be manipulated into the following dimensionless term:

\[ G_R = \frac{G - G^\circ}{RT} + \sum_{i=1}^{N_c} z_i \ln \frac{f_i^\circ}{p} = \sum_{i=1}^{N_c} z_i \ln (\phi_i z_i) \]  

(2.27)

where \( G_R \) is residual molar Gibbs free energy. If multiple phases exist, then the dimensionless term becomes
where $\beta$ is phase mole fraction and $j$ is phase index. Eq. (2.28) is used as the objective function in minimization algorithms.

### 2.3. The Tangent Plane Criterion

Gibbs energy minimization could be used directly, but tangent plane distance (TPD) results in less calculations for stability analyses. Stability analysis is based on the sign of the TPD at its minimum (Michelsen, 1982a). TPD is the perpendicular distance between molar Gibbs energy surface and the tangent hyper-plane at that point. Stability analysis is initiated assuming only a single phase exists. If the TPD is negative at any minimum, the single phase is unstable and the phase splits into at least two phases. Flash calculations are then done.

We show an example of how to visualize the TPD. Figure 2.2 and Figure 2.3 show dimensionless Gibbs free energy at 1000 psi and 5000 psi, respectively. The fluid has two components namely CO$_2$ and C$_{25}^+$ (Li & Johns, 2006). Fugacities are calculated via Peng-Robinson (PR78) cubic equation of state (EOS) (Peng & Robinson, 1978).

When a tangent line is drawn between two points of the Gibbs free energy surface, and if the Gibbs free energy surface is above the tangent plane, there are multiple phases present. That is, concavity of the Gibbs energy surface indicates multiple phases. For example, there is a two-phase region for a large range of CO$_2$ compositions at 1000 psi. However, there is only one phase for all compositions at 5000 psi. Thus, CO$_2$ and C$_{25}^+$ are miscible for all compositions at 5000 psi.
2.4. Stability Analysis

In this section, we show the stability criteria based on TPD (Firoozabadi, 1999; Michelsen, 1982a) at constant temperature and pressure conditions. For a hypothetical single-phase mixture with \( n \) mole numbers, we obtain,

\[
G' = G^i(T, P, n_1, n_n) = \sum_{i=1}^{N_i} n_i \mu_i(T, P, z_1, z_n)
\]  

(2.29)

where \( n_i = n_{z_i} \), and \( n \) is the total number of moles. We split the single-phase mixture into two phases with \( n - \delta \) moles vapor phase and \( \delta \) moles liquid phase where \( \delta \) is infinitesimal. The Gibbs energy of the two-phase mixture is then,

\[
G'' = G(T, P, n - \delta) + G(T, P, \delta)
\]  

(2.30)
where $G(T, P, \tilde{\delta}) = \sum_{i=1}^{N_c} \delta_i \mu_i(T, P, \tilde{x})$. A first order Taylor series expansion of $G(\tilde{n} - \delta)$ around $G(\tilde{n})$ is

$$G(\tilde{n} - \delta) \approx G(\tilde{n}) - \sum_{i=1}^{N_c} \delta_i \mu_i(T, P, \tilde{n}) . \quad (2.31)$$

By combining Eqs. (2.29) through (2.31), the Gibbs energy difference between a two-phase mixture and a single-phase mixture is

$$\Delta G = G^u - G^i = G(T, P, \tilde{n} - \delta) + G(T, P, \tilde{\delta}) - \left( G(T, P, \tilde{n} - \delta) + \sum_{i=1}^{N_c} \mu_i(T, P, \tilde{n}) \delta_i \right)$$

$$= G(T, P, \tilde{\delta}) - \sum_{i=1}^{N_c} \mu_i(T, P, \tilde{n}) \delta_i$$

$$= \sum_{i=1}^{N_c} \delta_i \left( \mu_i(T, P, \tilde{\delta}) - \mu_i(T, P, \tilde{n}) \right)$$

$$= \delta \sum_{i=1}^{N_c} x_i \left( \mu_i(T, P, \tilde{\delta}) - \mu_i(T, P, \tilde{n}) \right) \quad (2.32)$$

where $x_i$ is the composition of the second infinitesimal phase. The following holds:

$$\Delta G / \delta = \sum_{i=1}^{N_c} x_i \left( \mu_i(T, P, \tilde{x}) - \mu_i(T, P, \tilde{z}) \right) . \quad (2.33)$$

Phase I is unstable when $\Delta G / \delta \leq 0$ for any possible value of $x_i$ where $\tilde{z}$ is fixed. If this value is positive at the global minimum, then it is positive at all points. The gradient at the minimum is zero:
\[
\frac{\partial}{\partial x_j} \left( TPD \right) = \frac{\partial}{\partial x_j} \left[ \sum_{i=1}^{N_c} x_i \left( \mu_i(T, P, \bar{x}) - \mu_i(T, P, \bar{z}) \right) \right] = 0
\]  
(2.34)

Equation (2.34) gives a minimum or maximum but not necessarily the global minimum.

The 1st term of Eq. (2.34) can be expressed as follows:

\[
\frac{\partial}{\partial x_j} \left( \sum_{i=1}^{N_c} x_i \mu_i(T, P, \bar{x}) \right) = \sum_{i=1}^{N_c} \frac{\partial x_i}{\partial x_j} \mu_i(T, P, \bar{x}) = \sum_{i=1}^{N_c} \frac{\partial x_i}{\partial x_j} \mu_i(T, P, \bar{x}) + \sum_{i=1}^{N_c} \frac{\partial \mu(T, P, \bar{x})}{\partial x_j} x_i
\]

\[= \mu_j(T, P, \bar{x}) - \mu_{N_c}(T, P, \bar{x}) + \sum_{i=1}^{N_c} \frac{\partial \mu(T, P, \bar{x})}{\partial x_j} x_i \]

(2.35)

where \( \sum_{i=1}^{N_c} \frac{\partial \mu(T, P, \bar{x})}{\partial x_j} x_i = 0 \) from the Gibbs-Duhem equation and we used that \( \frac{\partial x_i}{\partial x_j} = 1 \) for \( i=j \), \( \frac{\partial x_i}{\partial x_j} = 0 \) for \( i \neq j \) and \( \frac{\partial x_i}{\partial x_j} = -1 \) for \( i=N_c \).

The 2nd term of the Eq. (2.34) can be expressed as follows:

\[- \sum_{i=1}^{N_c} \frac{\partial \left( x_i \mu_i(T, P, \bar{z}) \right)}{\partial x_j} = - \sum_{i=1}^{N_c} \left( \frac{\partial x_i}{\partial x_j} \right) \mu_i(T, P, \bar{z}) = - \mu_j(T, P, \bar{z}) + \mu_{N_c}(T, P, \bar{z}) \]

(2.36)

Substitution of Eqs. (2.35) and (2.36) into Eq. (2.34) gives,

\[\frac{\partial TPD}{\partial x_j} = \mu_j(T, P, \bar{x}) - \mu_{N_c}(T, P, \bar{x}) - \mu_j(T, P, \bar{z}) + \mu_{N_c}(T, P, \bar{z}) = 0\]

(2.37)
or,

\[ \mu_j(T, P, x) - \mu_j(T, P, z) = \mu_{N_c}(T, P, x) - \mu_{N_c}(T, P, z) = K \quad \text{for } j = 1, \ldots, N_c - 1. \] (2.38)

Eqs. (2.38) give the stationary points. Substitution of Eq. (2.38) into Eq. (2.33) gives,

\[ TPD(x) = \sum_{i=1}^{N_c} x_i K = K. \] (2.39)

By using Eqs. (2.20) and (2.26), TPD can be expressed in terms of fugacity coefficients as

\[ \mu^\circ_i(T, P) + RT \ln \frac{f_i(T, P, x)}{f^\circ_i(T, P)} - (\mu^\circ_i(T, P) + RT \ln \frac{f_i(T, P, z)}{f^\circ_i(T, P)}) = K \] (2.40)

Eventually the expression becomes,

\[ \ln \frac{f_i(T, P, x)}{f^\circ_i(T, P)} - \ln \frac{f_i(T, P, z)}{f^\circ_i(T, P)} = k \] (2.41)

where \( k = K / RT \). Eq. (2.41) can be written in terms of fugacity coefficients as

\[ \ln \frac{f_i(T, P, x)}{f^\circ_i(T, P)} - \ln \frac{f_i(T, P, z)}{f^\circ_i(T, P)} = k. \] (2.42)

Insertion of Eq. (2.26) into Eq. (2.42) gives
\[
\ln x_i + \ln \phi(T, P, \tilde{x}) - \ln \left( z_i \phi(T, P, \tilde{z}) \right) = k .
\]  
(2.43)

If \( k \) is smaller than zero, the single-phase is unstable and a phase split occurs. The stability criteria can be written in the following way considering constant \( T \) and \( P \). By further manipulation of Eq. (2.43),

\[
S_i = \ln X_i + \ln \phi(x) - \ln \left( z_i \phi(z) \right) = 0
\]  
(2.44)

where

\[
\ln X_i = \ln x_i - k \quad \text{or} \quad X_i = x_i e^{-k} .
\]  
(2.45)

If we take the sum of both sides:

\[
\sum_{i=1}^{N_c} X_i = \sum_{i=1}^{N_c} x_i e^{-k} \quad \text{or} \quad \sum_{i=1}^{N_c} X_i = e^{-k} .
\]  
(2.46)

Substitution of the definition of \( e^{-k} \) in Eq. (2.46) into Eq. (2.45):

\[
x_i = \frac{X_i}{\sum_j X_j}
\]  
(2.47)
where \( X_i \) is at a stationary point. The stability analysis can be solved by successive substitution (SS) or Newton-Raphson (NR). Convergence could occur at the local minimum in Gibbs free energy instead of the global minimum in Gibbs free energy. A global search is very expensive for use in compositional simulation. Instead, several initial guesses of compositions are made to search for a negative TPD, which means the single-phase mixture is unstable. Moreover, the solution might converge to the trivial solution, where \( z_i^{test} = x_i \). For a nontrivial solution, if

\[
\sum_i X_i \geq 1 ,
\]

(2.48)

then the solution is unstable and a phase split occurs.

Stability analysis can be solved either by minimizing the TPD with respect to phase mole numbers (Perschke, 1988) or by solution of nonlinear equations (Michelsen, 1982b; Okuno, 1999). Techniques to solve for nonlinear equations take \( X_i \) as independent parameters.

### 2.5. Flash Calculations

This section presents the equations to be solved in two-phase flash calculations. As shown before, there are two types of flash calculations:

1. The equilibrium solution is at the minimum of Gibbs energy.

2. Component fugacities for the same component are equal in different phases.

The former criterion can be solved by minimization algorithms and the latter criterion can be solved by solution of nonlinear equations using fugacities.

Equation (2.28) can be written as,
\[ g^* = \sum_{j=1}^{N_c} \sum_{i=1}^{N_c} n_{ij} \ln f_{ij} \] (2.49)

The function \( g^* \) is the dimensionless Gibbs free energy and the objective function to be minimized. For a two-phase system, the independent variables are mole numbers of the reference phase. The mole numbers of the other phase can be found from

\[ n_i^T = n_i^L + n_i^V. \] (2.50)

Moreover, phase mole fractions are calculated as

\[ \beta_j = \frac{\sum_{j=1}^{N_c} n_{ij}}{n_T}. \] (2.51)

To solve the flash calculations by using the equality of component fugacities criteria, then the residual functions are

\[ R_i = \ln f_i^L - \ln f_i^V \quad i = 1, \ldots, N_c \] (2.52)

The roots of the residual functions are found by solution of the nonlinear equations. The independent parameters are reference phase composition, reference phase mole number, or K-values.
2.6. **Cubic Equations of State**

Cubic equations of state (EOS) models are often used to compute the fluid behavior. These models are important in flash calculations as they are used to calculate several thermodynamic properties such as fugacity and Gibbs free energy and they are relatively computationally inexpensive. The cubic equations are modified from the ideal gas law,

\[
V_m = \frac{RT}{p}
\]  

(2.53)

where \(V_m\) is molar volume and \(R\) is the gas constant. However, this model does not take into account two important effects. First, the equation assumes that volume goes to zero as pressure goes to infinity. In reality, as pressure increases, the volume converges to a finite value because of the repulsive forces between molecules. Second, the ideal gas equation does not take into account the attraction forces between the molecules. These attraction forces decrease the volumetric expansion as pressure decreases (Pedersen & Christensen, 2006).

These two observations lead to attraction parameter \(a\), and repulsion parameter \(b\). Van der Waals proposed

\[
p = \frac{RT}{V_m} - b - \frac{a}{V_m^2}.
\]  

(2.54)

Other cubic EOS models have been proposed such as Redlich-Kwong (RK) (Redlich & Kwong, 1949), Soave-Redlich-Kwong (SRK) (Soave, 1972), and Peng-Robinson (PR) (Peng & Robinson, 1976). We use PR78 (Peng & Robinson, 1978) in our calculations. The expression for PR EOS is as follows:
The same equation can be written in terms of the compressibility factor as

\[ Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^3 - B^2) = 0 \]  \hspace{1cm} (2.56)

where \( Z \) is compressibility factor, \( A \) is dimensionless \( a \) parameter, and \( B \) is dimensionless \( b \) parameter. The equation is a cubic equation and hence it has three roots. If there is more than one positive real root, the compressibility factor that gives the lowest Gibbs free energy is generally used. If there are three real positive roots, only the maximum and minimum roots should be considered as the middle root is always unstable.

For a mixture, the \( B \) parameter is

\[ B = \sum_{i=1}^{N_c} x_i B_i \]  \hspace{1cm} (2.57)

and the \( A \) parameter is

\[ A = \sum_{i=1}^{N_c} \sum_{j \neq i} A_{ij} x_i x_j \]  \hspace{1cm} (2.58)

where

\[ A_{ij} = \sqrt{A_i A_j} \left( 1 - k_{ij} \right) \]  \hspace{1cm} (2.59)
and \( k_{ij} \) is the binary interaction parameter (BIP). Furthermore,

\[
A_i = \frac{p}{(RT)^2}a_i, \quad (2.60)
\]

\[
B_i = \frac{b_ip}{RT}, \quad (2.61)
\]

\[
a_i = \frac{0.45723529R^2T_{ci}^{1.5}\alpha_i}{p_{ci}}, \quad (2.62)
\]

\[
b_i = \frac{0.077796074RT_{ci}}{p_{ci}}, \quad (2.63)
\]

\[
\alpha_i = \left[1 + m_i \left[1 - \left(\frac{T}{T_{ci}}\right)^{1/2}\right]\right]^2. \quad (2.64)
\]

\[
m_i = \begin{cases} 
0.37464 + 1.54226w_i - 0.26992w_i^2 & \text{for } w_i \leq 0.49 \\
0.379642 + 1.48503w_i - 0.164423w_i^2 + 0.016666w_i^3 & \text{for } w_i > 0.49 
\end{cases} \quad (2.65)
\]

Equation (2.65) is only applicable for PR78 EOS. In phase equilibrium calculations, the above equations are carried out to compute the compressibility factor. Dimensionless Gibbs free energy can be calculated with Eq. (2.27). The fugacity coefficient is calculated as

\[
\ln \phi_i = \frac{B_i}{B}(Z - 1) - \ln(Z - B) - \frac{A_i}{2\sqrt{2}B} \left[2\sum_j x_j A_j - \frac{B_i}{A_i} - \frac{B}{B} \right] \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right). \quad (2.66)
\]

Fugacity is calculated with Eq. (2.26). Peneloux volume shift parameters are introduced to estimate the density (Jhaveri & Youngren, 1988).
\[ P = \frac{RT}{V-b} - \frac{a(T)}{(V+c)(V+2c+b)+(b+c)(V-b)} \]  

(2.67)

where \( c \) is the volume shift parameter. With this expression, phase equilibrium compositions are not affected but the densities are adjusted.

### 2.7. Mathematical Methods

Phase equilibrium calculations are solved either by minimization or solution of nonlinear equations. We first consider minimization.

#### 2.7.1. Minimization of an Objective Function

In this section, we present the methods to find the minimum of an objective function. An objective function \( g \) can be expressed by Taylor’s expansion around the point \( g^* \) as,

\[ g^* = g^* + \sum_{i=1}^{n} \Delta \alpha_i \left. \frac{\partial g}{\partial \alpha_i} \right|_{g^*} + \frac{1}{2} \sum_{j=1}^{n} \sum_{i=1}^{n} \Delta \alpha_i \Delta \alpha_j \left. \frac{\partial^2 g}{\partial \alpha_i \partial \alpha_j} \right|_{g^*} + \ldots \]  

(2.68)

where \( \alpha \) represents the vector of independent parameters (Bertsekas, 1999; Nocedalm & Wright, 2006). At a stationary point, the gradient equals zero.
\[
\frac{\partial g}{\partial \alpha_i} = 0 \text{ for } i = 1, n \tag{2.69}
\]

Equation (2.68) can also be expressed as,

\[
g^* = g^0 + \Delta \bar{\alpha} \cdot \bar{d}_o + \frac{1}{2} \Delta \bar{\alpha}^T H_o \Delta \bar{\alpha} \tag{2.70}
\]

where \( d \) is the gradient vector and \( H \) is the Hessian matrix. Note that \( \partial \Delta \alpha_k = \partial \alpha_k \) because \( \Delta \alpha_k = \alpha_k - \alpha_o \). The gradient of \( g \) is,

\[
\frac{\partial g^*}{\partial \Delta \alpha_k} = d_k^o + \sum_{i=1}^{n} \Delta \alpha_i H_{ki}^o = 0 \quad \text{or} \quad 0 = \bar{d}_o + H_o \Delta \bar{\alpha} \tag{2.71}
\]

Therefore, the step direction for the next update can be expressed as,

\[
\Delta \bar{\alpha} = \left( H_o \right)^{-1} \bar{d}_o \tag{2.72}
\]

The method for finding the minimum is called Newton’s method when the full Hessian matrix, which describes curvature through second order partial differentials, is kept. Newton’s method converges quadratically near a stationary point. If it is away from the solution, Newton’s method may not converge. Other methods that can be used to compute the Hessian matrix are shown in Appendix A. Appendix A also shows an example for minimization of the sum of the square of errors.
The Hessian matrix has to be positive definite so that the step is in a descent direction. There are many methods to force the Hessian matrix to be positive definite, some of which are explained in the next section.

2.7.1.1. **Positive Definite Hessian Matrix**

There are two criteria to satisfy the convergence to a minimum of an objective function.

1. The gradient vector is zero.
2. The Hessian matrix is positive definite.

If the Hessian matrix is not positive definite, the step direction will not be a descent direction. Therefore, it is important to have a positive definite Hessian matrix.

There are several ways to force the Hessian matrix to be positive definite. If all of the eigenvalues of the Hessian matrix are positive then the Hessian matrix is positive definite. The eigenvalues of a Hessian matrix can be computed by eigenvalue decomposition methods e.g. QR algorithm, or inverse iteration.

With spectral decomposition, once the eigenvalues are computed they can be changed in various ways. One approach is to replace all the negative eigenvalues, if present, with positive ones. Another approach is to replace the negative eigenvalues with unity as in the steepest descent method. Eigenvalues can also be made positive by adding \( \lambda I \) to the Hessian matrix. The parameter \( \lambda \) is a scalar that makes the minimum eigenvalue a positive one.

There are other methods that make the Hessian matrix positive definite without having to calculate the eigenvalues. One method is to start with a very small \( \lambda \) and calculate the objective function \( g^* = f(n_i + \alpha d) \). The parameter \( \lambda \) is then increased until the objective function at the new step becomes less than the previous step.
All of the above methods are costly. There are two methods that can be practical for the minimization of Gibbs free energy. One is modified Cholesky decomposition. The other is using a line search.

**Modified Cholesky Factorization**

Modified Cholesky factorization decomposes the Hessian matrix into,

\[
LDL^T = H
\]

(2.73)

where \( L \) is the lower triangular matrix, \( D \) is the diagonal matrix consisting of the eigenvalues of \( H \), and \( H \) is the Hessian matrix. The eigenvalues are checked during factorization to see if they are smaller than a very small positive number. If so they are corrected so that all the diagonal terms become positive. Once \( L \) and \( D \) are determined, LU decomposition can be used to solve for the step direction.

**Line Search**

Line search optimizes the function \( f(\alpha_1 + \alpha d) \) with respect to \( \alpha \), which is a scalar that is multiplied by the step direction. The new step direction finds the minimum Gibbs energy with respect to \( \alpha \) at the surroundings. Therefore, line search is a 1-D minimization problem. If an explicit expression can be found for the derivative terms, Newton’s method can be applied. Otherwise, cubic interpolation can be used.
2.7.2. Solution of Nonlinear Equations Using Fugacities

In this section, we derive the Newton-Raphson techniques that are used to find roots of equations. That is,

\[ f(x) = 0 \]  \hspace{1cm} (2.74)

where \( x \) is a set of independent parameters. Taylor’s first order approximation of the function \( f \) near point \( a \) is expressed as

\[ f(x) = f(a) + \frac{\partial f(x)}{\partial x} \bigg|_a (x - a) \]  \hspace{1cm} (2.75)

Because roots are at \( f = 0 \), the above equation becomes

\[ f(a) + \frac{\partial f(x)}{\partial x} \bigg|_a (x - a) = 0 \quad \text{or} \quad J\Delta x = -R \]  \hspace{1cm} (2.76)

where \( J \) is the Jacobian matrix, and \( R \) is the residual function. At a particular point, the residual function and Jacobian matrix are calculated, and then the vector \( \Delta x \) is solved for. Independent parameters are updated with \( x^{k+1} = x^k + \Delta x \). The iterations are repeated until the residual functions converge to zero.
2.8. PVT Data Analysis

In the previous sections, we have covered the theory behind phase equilibrium calculations and its solution techniques. We have explained that cubic equations are used to estimate hydrocarbon liquid-vapor phase behavior. The cubic EOS’s require fluid data as input. The fluid data are overall composition, acentric values, critical temperature and pressure. Moreover, molecular weight and volume shift parameters are input for use in density estimations.

A typical reservoir has hundreds of hydrocarbon components. Identification of all of these components correctly is experimentally and computationally impractical. Moreover, cubic EOS’s do not exactly calculate the fluid properties, but they are rather generalized formulas. Several experiments are carried out to mimic the behavior of the fluid during reservoir depletion or for other reservoir processes. These experiments give information about the light and intermediate hydrocarbon components. For all these reasons, a fair amount of uncertainty comes into play in phase behavior characterization. However, several procedures and correlations are made in order to represent the fluid behavior in the best manner. All of these analyses use pressure-volume-temperature (PVT) data. In the following sections, we explain the experiments, simulations, and the regression techniques.

2.8.1. Component Identification

Hydrocarbon components are well known for molecules that have up to six carbon atoms. That is, the fluid properties e.g. critical temperature, critical pressure, and acentric value of the hydrocarbon components and their isomers are known. The parameters of these defined components are fixed and should not be changed in any fluid characterization procedure. Undefined components (C$_7^+$) have more than six carbon atoms. When the number of components
is large, there are many more isomers that must be identified in a fluid analysis, which is not possible. Therefore, C$_7^+$ fluid properties can be modified for fluid characterization since the specific components are uncertain.

Hydrocarbons can be divided into homologous groups based on the type and shape of their bonds between carbon atoms. Hydrocarbons can be divided into three groups as paraffins, naphthenes, and aromatics (Pedersen & Christensen, 2006). As the number of atoms increases, the same molecular formula can be achieved with different bonding. Therefore, the number of isomers increases rapidly as the number of carbon atoms increases. There are two isomers for butane, three isomers for pentane, five isomers for hexane, 75 isomers for decane, and 366,319 isomers for the general formula C$_{20}$H$_{42}$.

Paraffins have single bonds, naphthenes have single cyclic bonds, and aromatics have double cyclic bonds between the carbon atoms. An oil reservoir can be identified according to its PNA (Paraffin-Naphthene-Aromatic) distribution. Density increases from paraffins to aromatics for the same carbon number.

A typical reservoir includes thousands of hydrocarbon components and hence it is impossible to identify every single component. Instead, they are identified according to their boiling point cuts. As the carbon number increases, the boiling point temperature generally increases. A hydrocarbon component within a particular boiling point cut is assumed to belong to the same carbon number group, e.g. C$_7$, C$_8$. For example, benzene has six carbon atoms but it falls into the C$_7$ boiling cut category because of its high boiling point.

Gas chromatography (GC) and true boiling point (TBP) analysis are used for component identification. GC is more applicable for gas samples and a TBP analysis is applicable for oil samples. For GC analyses, a gas sample is injected into a GC column and every component can be identified by its peak. Oil samples are not suitable for GC analysis because the number of components increases rapidly as the carbon number increases. TBP analysis is based on
increasing the temperature of an oil sample. The components that evaporate within a temperature cut are assumed to belong to a particular carbon number. GC provides fluid data for C_1-C_5 and TBP provides fluid data above C_6 usually until C_{20} (the last fraction). Components that are heavier than the last fraction are lumped into one heavy fraction component, which is called the plus fraction. Plus fraction molecular weight has an error up to ±20% (Pedersen & Christensen, 2006). Table 2.1 shows composition, molecular weight (M), and density of a condensate gas. Generally, there is no information for components that have more than twenty carbon atoms.
Laboratory analyses do not give fluid data for a larger number of carbon components. Therefore, fluid data for the plus fraction is extrapolated based on generalized correlations. Below, we carry out splitting of the plus fraction as described in Pedersen and Christensen (2006). For $C_7^+$ components, mole fraction and carbon mole number show the following behavior:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>M</th>
<th>Density (g/cm$^3$) 15 °C, 1.01 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO_2$</td>
<td>2.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1$</td>
<td>76.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2$</td>
<td>7.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_3$</td>
<td>3.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$iC_3$</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$nC_4$</td>
<td>1.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$iC_5$</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$nC_5$</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_6$</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_7$</td>
<td>0.95</td>
<td>95</td>
<td>0.726</td>
</tr>
<tr>
<td>$C_8$</td>
<td>1.08</td>
<td>106</td>
<td>0.747</td>
</tr>
<tr>
<td>$C_9$</td>
<td>0.78</td>
<td>116</td>
<td>0.769</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>0.592</td>
<td>133</td>
<td>0.781</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>0.467</td>
<td>152</td>
<td>0.778</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>0.345</td>
<td>164</td>
<td>0.785</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>0.375</td>
<td>179</td>
<td>0.802</td>
</tr>
<tr>
<td>$C_{14}$</td>
<td>0.304</td>
<td>193</td>
<td>0.815</td>
</tr>
<tr>
<td>$C_{15}$</td>
<td>0.237</td>
<td>209</td>
<td>0.817</td>
</tr>
<tr>
<td>$C_{16}$</td>
<td>0.208</td>
<td>218</td>
<td>0.824</td>
</tr>
<tr>
<td>$C_{17}$</td>
<td>0.22</td>
<td>239</td>
<td>0.825</td>
</tr>
<tr>
<td>$C_{18}$</td>
<td>0.169</td>
<td>250</td>
<td>0.831</td>
</tr>
<tr>
<td>$C_{19}$</td>
<td>0.14</td>
<td>264</td>
<td>0.841</td>
</tr>
<tr>
<td>$C_{20}^+$</td>
<td>0.833</td>
<td>377</td>
<td>0.873</td>
</tr>
</tbody>
</table>

**2.8.2. Splitting**

Table 2.1. Molar composition of a gas condensate mixture (of Pedersen and Christensen (2006)).
\[ C_N = A + B \ln z_N \]  

(2.77)

where \( C_N \) is carbon number and \( z_N \) is its corresponding mole fraction. \( A \) and \( B \) are best fit constants to this trend. This equation is constrained by the following material balance.

\[ z_+ = \sum_{i=C_+}^{C_{eq}^\text{max}} z_i \]  

(2.78)

where \( z_i \) is mole fraction, \( i \) is component index, \( C_+ \) is the carbon number of the smallest carbon number component in the plus fraction, and \( z_+ \) is the total mole fraction of the plus fraction. Moreover, the average molecular weight of the plus fraction has to match the laboratory data.

\[ M_+ = \sum_{i=C_+}^{C_{eq}^\text{max}} z_i M_i / \sum_{i=C_+}^{C_{eq}^\text{max}} z_i. \]  

(2.79)

The molecular weight can be calculated from

\[ M_i = 14C_N - 4. \]  

(2.80)

The density can be correlated to the carbon number as follows.

\[ \rho_N = C + D \ln C_N. \]  

(2.81)

The following constraint has to be satisfied.
\[
\rho_i = \frac{\sum_{i=C_i}^{C_{max}} z_i M_i}{\sum_{i=C_i}^{C_{max}} \rho_i}.
\] (2.82)

Pedersen and Christensen (2006) take \(C_{max}\) as 80 in their examples. Other fluid properties for each split component can be calculated with the following correlations:

\[
T_C = c_1\rho + c_2\ln M + c_3 M + \frac{c_4}{M}
\] (2.83)

\[
\ln P_C = d_1 + d_2\rho^{d_3} + \frac{d_4}{M} + \frac{d_5}{M^2}
\] (2.84)

\[
m = e_1 + e_2 M + e_3\rho + e_4 M^2
\] (2.85)

where \(m\) is used to calculate the acentric factor. The \(c, d,\) and \(e\) parameters are constants. \(T_C\) is in Kelvin and \(P_C\) is in atm. Table 2.2 gives \(c, d,\) and \(e\) coefficients for the PR cubic equation of state. These correlations are based on various fluids and assume a certain PNA distribution.

<table>
<thead>
<tr>
<th>Subindex/Coefficient</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>7.34043×10^7</td>
<td>9.73562×10^9</td>
<td>6.18744×10^4</td>
<td>-2.05932×10^8</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>7.28462×10^-2</td>
<td>2.18811</td>
<td>1.63910×10^2</td>
<td>-4.04323×10^3</td>
<td>1/4</td>
</tr>
<tr>
<td>e</td>
<td>3.73765×10^-1</td>
<td>5.49269×10^-3</td>
<td>1.17934×10^-2</td>
<td>-4.93049×10^-6</td>
<td>-</td>
</tr>
</tbody>
</table>

Once \(m\) is determined, acentric factor can be calculated from Eq. (2.86).
\[ m = 0.37363 + 1.54226w - 0.26992w^2 \]  

(2.86)

where \( w \) is the acentric factor. Khan (1992) and Khan et al. (1992) solve these set of equations with Newton-Raphson iterations. However, their equations are based on the correlations given by Pedersen et al. (1988). We rewrite the equations according to Pedersen and Christensen (2006) where \( T_C, P_C, \) and \( m \) values can be solved once density and molecular weight are determined.

Density, molecular weight and fluid composition are solved together to satisfy all material balance and mass constraints. The unknown parameters are \( C_{\text{max}} - C_+ + 1 \) compositions, density, and molecular weight values in addition to \( A, B, C, \) and \( D \). Therefore, there are \( 3(C_{\text{max}} - C_+ + 1) + 4 \) unknown parameters. We use the equation of Khan (1992) in order to solve the splitting equations provided by Pedersen and Christensen (2006). Khan (1992) solves for \( A \) and \( B \) first and \( C \) and \( D \) second, and hence two separate steps are required. The necessary equations required for the first step are given in Table 2.3.

The number of equations and the number of unknowns are equal to \( 2 \times (C_{\text{max}} - C_+) + 4 \). When the definitions of \( z_i \) and \( M_i \) in Eqs. (2.78) and (2.79) are substituted, the equations in Table 2.3 reduce to those in Table 2.4. After substitution, the number of equations reduces to two. \( C_{\text{max}} \) and \( C_+ \) can be taken as 80 and 20, respectively. The equations are solved iteratively with Newton-Raphson iterations. The Jacobian matrix is

\[
J_{ik} = \begin{bmatrix} \frac{\partial f_1}{\partial A} & \frac{\partial f_1}{\partial B} \\ \frac{\partial f_2}{\partial A} & \frac{\partial f_2}{\partial B} \end{bmatrix} = \begin{bmatrix} \sum_{i=C_+}^{C_{\text{max}}} e^{A_i B C_{N_i}} (14C_{N_i} - 4) \sum_{i=C_+}^{C_{\text{max}}} e^{A_i B C_{N_i}} (14C_{N_i} - 4) C_{N_i} \\ \sum_{i=C_+}^{C_{\text{max}}} e^{A_i B C_{N_i}} C_{N_i} \end{bmatrix}. \tag{2.87}
\]
A and B values can be initialized as -2 and -0.1, respectively. After solving for A and B, C and D are solved by using the equations in Table 2.5. By substitution of \( z_i, M_i, \rho_i \) and \( \rho_{c^{*-1}} \), the equations in Table 2.5 reduce to two as shown in Table 2.6. Equation (2.88) shows the Jacobian matrix equations. The following values are obtained from Table 2.1. \( \rho_{c^{*-1}} = \rho_{y} \) is 0.841, \( z_{c^{*}} \) is 0.833, \( M_{c^{*}} \) is 377 and \( \rho_{c^{*}} \) is 0.873. These values are used to solve the equations in Table 2.6.

### Table 2.3. Set of equations to solve for A and B parameters.

<table>
<thead>
<tr>
<th>Equation</th>
<th>No. of Equations</th>
<th>No. of Unknowns</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sum_{i=0}^{C_{\text{max}}} z_i M_i = z_c M_{c^*} )</td>
<td>1</td>
<td>2((C_{\text{max}}-C_c+1))</td>
</tr>
<tr>
<td>( \sum_{i=0}^{C_{\text{max}}} z_i = z_c )</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( \ln z_i = A + BC_{N_i} )</td>
<td>( C_{\text{max}}-C_c+1 )</td>
<td>2</td>
</tr>
<tr>
<td>( M_i = 14C_{N_i} - 4 )</td>
<td>( C_{\text{max}}-C_c+1 )</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2.4. Reduced set of equations to solve for A and B parameters.

<table>
<thead>
<tr>
<th>Equation</th>
<th>No. of Equations</th>
<th>No. of Unknowns</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_1 = \sum_{i=0}^{C_{\text{max}}} e^{A + BC_{N_i}} (14C_{N_i} - 4) - z_c M_{c^*} = 0 )</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>( f_2 = \sum_{i=0}^{C_{\text{max}}} e^{A + BC_{N_i}} - z_c = 0 )</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
The Jacobian matrix for the equations in Table 2.6 is shown in Eq. (2.88).

\[
J^T = \begin{bmatrix}
\frac{\partial f_1}{\partial C} & \frac{\partial f_1}{\partial D} \\
\frac{\partial f_2}{\partial C} & \frac{\partial f_2}{\partial D}
\end{bmatrix} = \begin{bmatrix}
\sum_{i=C}^{\text{max}} e^{A+iBC_{N_i}}(14C_{N_i} - 4) \\
\sum_{i=C}^{\text{max}} e^{A+iBC_{N_i}}(14C_{N_i} - 4)\ln C_{N_i} \\
1 & \ln C_{N_{C-1}}
\end{bmatrix}.
\]
By using the equations mentioned above, we do splitting for the North Sea gas condensate from Pedersen and Christensen (2006). The fluid properties are shown in Table 2.1.

By solving the equations in Table 2.4 and Table 2.6 separately, we obtain A, B, C, and D. Finally, we compute the fluid properties, shown in Table 2.7, by using Eqs. (2.83)-(2.85). Our results match with Pedersen and Christensen (2006) within 1% error. The slight difference is due to the fact that only a few digits were available in their data.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>M</th>
<th>Density</th>
<th>Tc (°C)</th>
<th>Pc (bar)</th>
<th>w</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.10117</td>
<td>276</td>
<td>0.85</td>
<td>461.55</td>
<td>14.83</td>
<td>0.934</td>
</tr>
<tr>
<td>21</td>
<td>0.08885</td>
<td>290</td>
<td>0.85</td>
<td>472.87</td>
<td>14.51</td>
<td>0.964</td>
</tr>
<tr>
<td>22</td>
<td>0.078094</td>
<td>304</td>
<td>0.85</td>
<td>483.92</td>
<td>14.23</td>
<td>0.994</td>
</tr>
<tr>
<td>23</td>
<td>0.068613</td>
<td>318</td>
<td>0.86</td>
<td>494.74</td>
<td>13.99</td>
<td>1.023</td>
</tr>
<tr>
<td>24</td>
<td>0.060283</td>
<td>332</td>
<td>0.86</td>
<td>505.35</td>
<td>13.77</td>
<td>1.050</td>
</tr>
<tr>
<td>25</td>
<td>0.052965</td>
<td>346</td>
<td>0.86</td>
<td>515.76</td>
<td>13.57</td>
<td>1.077</td>
</tr>
<tr>
<td>26</td>
<td>0.046534</td>
<td>360</td>
<td>0.87</td>
<td>525.99</td>
<td>13.40</td>
<td>1.103</td>
</tr>
<tr>
<td>27</td>
<td>0.040885</td>
<td>374</td>
<td>0.87</td>
<td>536.05</td>
<td>13.24</td>
<td>1.128</td>
</tr>
<tr>
<td>28</td>
<td>0.035921</td>
<td>388</td>
<td>0.87</td>
<td>545.96</td>
<td>13.10</td>
<td>1.151</td>
</tr>
<tr>
<td>29</td>
<td>0.031560</td>
<td>402</td>
<td>0.88</td>
<td>555.73</td>
<td>12.97</td>
<td>1.174</td>
</tr>
<tr>
<td>30</td>
<td>0.027729</td>
<td>416</td>
<td>0.88</td>
<td>565.37</td>
<td>12.86</td>
<td>1.195</td>
</tr>
<tr>
<td>31</td>
<td>0.024363</td>
<td>430</td>
<td>0.88</td>
<td>574.88</td>
<td>12.75</td>
<td>1.216</td>
</tr>
<tr>
<td>32</td>
<td>0.021405</td>
<td>444</td>
<td>0.88</td>
<td>584.28</td>
<td>12.66</td>
<td>1.235</td>
</tr>
<tr>
<td>33</td>
<td>0.018806</td>
<td>458</td>
<td>0.89</td>
<td>593.58</td>
<td>12.57</td>
<td>1.253</td>
</tr>
<tr>
<td>34</td>
<td>0.016523</td>
<td>472</td>
<td>0.89</td>
<td>602.77</td>
<td>12.49</td>
<td>1.270</td>
</tr>
<tr>
<td>35</td>
<td>0.014517</td>
<td>486</td>
<td>0.89</td>
<td>611.87</td>
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<td>0.95</td>
<td>911.03</td>
<td>11.67</td>
<td>0.965</td>
</tr>
</tbody>
</table>

2.8.3. **Lumping**

After splitting, more than 80 components are present. Simulating 80 components is computationally too expensive with the conventional methods. Therefore, the components are lumped back into pseudo-components that preserve the nature of the C7 fraction. C7+ fractions are divided based on equal weight criteria. The number of required pseudo-components are arbitrarily set as shown in Table 2.8.
Once the components are lumped, the fluid parameters for the lumped pseudocomponents are determined as shown in Eqs. (2.89) to (2.91) (Pedersen et al., 1985).

\[
T_{ik} = \frac{\sum_{i=0}^{n} z_i M_i T_{ci}}{\sum_{i=0}^{n} z_i M_i} \quad (2.89)
\]

\[
P_{ik} = \frac{\sum_{i=0}^{n} z_i M_i P_{ci}}{\sum_{i=0}^{n} z_i M_i} \quad (2.90)
\]

\[
w_{ik} = \frac{\sum_{i=0}^{n} z_i M_i w_i}{\sum_{i=0}^{n} z_i M_i} \quad (2.91)
\]

We lump the heavy fractions of the fluid shown in Table 2.1 into three plus fraction pseudo-components. Non-hydrocarbons and defined components are not lumped. Pseudo-component properties are shown in Table 2.9. The values in Table 2.9 match the results of Pedersen and Christensen (2006).
**Binary Interaction Parameters**

Binary interaction parameters (BIP-\(k_{ij}\)) are used to compute the attraction parameter \(A\) as given in Eq. (2.58). The BIP matrix, a matrix that contains the BIP values between all components, is used in Eq. (2.59). All binaries have BIPs, that may be positive, negative or zero. A positive BIP between two components shows the polarity between the corresponding components. The BIP matrix diagonal elements are always zero since they correspond to interaction between the same component. BIPs between hydrocarbon components are very small or zero. Generally, BIPs are non-zero between non-hydrocarbons/non-hydrocarbons and non-hydrocarbons/hydrocarbons. \(\text{CO}_2\), \(\text{H}_2\text{S}\) and \(\text{N}_2\) are the common non-hydrocarbons found in a petroleum reservoir. Therefore, we usually do not need to have more than three non-zero columns in a BIP. If a BIP coefficient is positive, the \(A\) value decreases. The magnitude of the decline in the \(A\) value captures the effect of the polarity on the attraction parameter. BIP parameters between \(\text{CO}_2\), \(\text{N}_2\) and \(\text{H}_2\text{S}\) with hydrocarbons are positive. BIP parameters between \(\text{CO}_2/\text{N}_2\) and \(\text{CO}_2/\text{H}_2\text{S}\) are typically negative. Appendix C shows the BIP matrices for several fluids.

The BIPs can be determined by a best fit to saturation pressure of binary systems between predicted and experimental data (Danesh, 2007). BIPs should be seen as a tuning parameter rather than a physical parameter since compositions are not usually binary for oils.
Several correlations have been proposed for BIP values (Deo et al., 1992; Elliott & Daubert, 1985; Kato et al., 1981; Nishiumi & Arai, 1988; Slot-Petersen, 1989; Varotsis et al., 1986). Slot-Petersen (1989) proposed a correlation for BIPs applicable for PR EOS. The correlation is tested for six different fluids from Jacobi et al. (1959). The fluids are labeled from S-1 to S-6 where S-1 is black oil, S-6 is the lightest fluid. S-3 is a near-critical fluid. All of the fluids have nitrogen, carbon dioxide, light, intermediate and heavy hydrocarbons. Jacobi et al. explains that binary interaction parameters are a function of $M_i$, $M_j$, $M_*$, $k_{ij}$ where $M$ is the molecular weight, $i$ and $j$ are the binary coefficient index, the ‘+’ symbol represents the heaviest fraction. The expression is as follows:

$$ k_{ij} = m_i (M_j)^n + d_i $$  \hspace{1cm} (2.92)

where

$$ m_i = \frac{k_{ij}}{(M_*)^n - (M_j)^n} $$  \hspace{1cm} (2.93)

and

$$ d_i = -(M_i)^n \times m_i $$  \hspace{1cm} (2.94)

where $n$ is a constant. Slot-Petersen (1989) does trial and error by varying $n$, the number of nonzero coefficients and $R_i$ where
\[ k_{(i+1)} = R k_i. \] (2.95)

The objective function is the error in saturation pressures between the numerical estimation and the laboratory data. Moreover, Slot-Petersen (1989) confirms the goodness of fit using correlation with other laboratory data.

Slot-Petersen (1989) conclude that the BIPs are very sensitive to the composition of the fluid, and somewhat sensitive to the temperature. Slot-Petersen (1989) states the new correlation is able to make correct estimations for near-critical mixtures. Laboratory measured expansion data is crucial to determine the BIPs for near critical mixtures. Tuning the EOS only to saturation pressures does not give sufficient accuracy. For black oil and lean-gas condensates, BIPs are required only for the methane binaries. However, for near-critical fluids, more columns are necessary to give correct estimations of saturation pressures. Slot-Petersen (1989) adds that this correlation is not suitable for compositional reservoir simulations as the BIPs are sensitive to compositional variations.

Deo et al. (1993) and Nishiumi and Arai (1988) calculate BIPs separately for different hydrocarbon groups e.g. paraffins, aromatics based on varying temperature for binary systems. Kato et al. (1981) proposed a BIP correlation as a function of the acentric factor generalized for CO₂-hydrocarbon mixtures for PR-EOS. The BIPs are only applicable between CO₂ and another hydrocarbon component and they change with temperature. BIPs are regressed to the bubble-point pressure. An objective function is developed to minimize the error between the calculated and experimental values. Kao et al. (1981) take derivatives of this objective function with respect to BIP parameters in order to see how sensitive the objective function is to the changes in compositions and temperature. They show that the results are sensitive to different composition
and temperatures. Therefore, they take an average at various compositions for a binary system to compute the BIP as follows:

\[
\bar{\delta}_y = \frac{\sum_n \delta_y^* F(\delta_y^*)}{\sum_n F(\delta_y^*)}
\]  

(2.96)

where \( n \) denotes the data point, \( \delta_y^* \) is the best fit BIP for that data point and

\[
F(\delta_y^*) = \left[ \frac{\partial (P_{\text{exp}} - P_{\text{calc}})}{\partial \delta_y^*} \right]_{P,T} .
\]  

(2.97)

Kato et al. (1981) note that there are two important challenges in determining the BIPs: 1) The selection of the objective function and 2) The choice of the convergence criterion, which affects the quality of regression. Katz and Firoozabadi (1978) calculate the BIPs between methane and heavy hydrocarbons by doing a best fit to the bubble-point curve. A common correlation for BIP parameters between hydrocarbon-hydrocarbon components is given by Oellrich et al. (1981) as

\[
k_{ij} = 1 - \left( \frac{2v_i^{1/6}v_j^{1/6}}{v_i^{1/6} + v_j^{1/6}} \right) ^\theta
\]  

(2.98)

where \( v_i \) is the critical volume and \( \theta \) is hydrocarbon-hydrocarbon interaction coefficient exponent.
2.8.5. Minimum Miscibility Pressure

Minimum miscibility pressure (MMP) calculations are required for fluid characterization to determine the best conditions for gas injection. MMP is a very important physical property in solvent injection. Miscibility occurs when the injectant and the oil in place become similar and eventually form one phase. Well above the MMP, oil moves in a piston like behavior. Miscibility increases the displacement efficiency by decreasing the residual oil saturation. Miscibility can occur by first contact miscibility or by developing miscibility in situ in a multicontact process. If the injectant and the oil form only a single hydrocarbon phase when mixed in any proportion, then they are first contact miscible (Ahmadi, 2011; Jarrell et al., 2002; Lake, 1989; Orr, 2007).

Multi-contact miscibility occurs through multiple mixing steps of oil and injection gas. There are three miscibility drive mechanisms: condensing gas drive, vaporizing gas drive, and condensing/vaporizing gas drive. The vaporizing gas drive process is as described below:

1. Gas and oil form two equilibrium phases as they mix.
2. Equilibrium liquid phase becomes lighter as it contacts more injectant. Intermediate components in the oil are vaporized into the gas phase.
3. Miscibility occurs when oil lies on a tie-line extension thru the critical point.

Miscibility with a vaporizing gas drive mechanism occurs at the front edge of the displacement. For vaporizing gas drives, the composition of the injectant is not an important factor to determine MMP as the liquid phase becomes lighter after multiple contacts. The condensing gas drive process is as follows:

1. Gas and oil form two equilibrium phases as they mix.
2. Intermediate components in the injection gas are condensed into the equilibrium oil.
3. Miscibility occurs when the injection gas lies on a tie-line extension thru a critical point.

Miscibility in a condensing gas drive process occurs at the tail end of the displacement, closer to the injection fluid. For condensing gas drives, the equilibrium liquid becomes lighter until it reaches the tie-line extension thru the gas composition.

Miscibility may not occur at the front or at the tail but somewhere in the middle as the two-phase region changes its composition. This process is called a combined condensing/vaporizing gas drive. Condensing/vaporizing gas drives occur in most injection processes, such as for CO₂ and rich gas injection.

Multiple contact miscibility may never occur. Miscibility will not occur when the key tie-lines do not reach a critical point. At higher pressures, it is easier to achieve miscibility because the key tie-lines become shorter.

If the oil is very heavy and gas is very light, miscibility is more difficult. Light injectants are nitrogen, methane, and flue gas. They achieve miscibility at very high pressures in a vaporizing gas drive process. CO₂, hydrocarbons (C₂-C₆), and H₂S are intermediate components. Condensing/vaporizing gas drives occur when the intermediate components are injected. There are several methods to calculate MMP such as slimtube experiments, slimtube simulations, analytical methods (method of characteristics), and multiple mixing cells.

2.8.6. Laboratory Experiments

Several laboratory experiments are made to mimic reservoir depletion processes and other processes, i.e. EOR. Coefficients in EOS equations can be fit to the laboratory data to mimic the fluid phase behavior during depletion. The experiments include constant volume depletion, constant mass expansion, differential liberation, slimtube displacement, and swelling
tests. Swelling tests, slintube displacements and multi-contact tests are carried out for gas injection purposes. Constant volume depletion is applicable for condensate gas and volatile oil. Constant mass expansion is applied both for oil and gas mixtures. Differential liberation is only applicable for oil mixtures.

2.8.6.1. **Constant Mass Expansion**

Constant mass (constant composition) expansion (CME) experiments are applicable for both oil and gas reservoirs. CME experiments give saturation pressure, under-saturated oil density, isothermal oil compressibility, and two-phase volumetric behavior at pressures below the saturation point (Whitson & Brule, 2000). The procedure is as follows. A fixed amount of oil is transferred to an isothermal closed cell. The experiment starts at a small volume and at a high pressure above the saturation point. Gradually, the volume is increased and hence the pressure is decreased. We can measure the saturation pressure when a second phase starts to form. For a gas condensate, relative volume, liquid volume and Z-factor are measured. Relative volume is the volume of the reservoir fluid divided by the volume of the reservoir fluid at the saturation pressure (see Eq. (2.101)). Liquid volume is measured below the saturation pressure and compressibility factor is measured above the saturation pressure. For oil, compressibility and Y-factor are measured. Compressibility is

\[
C_o = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T.
\]  

(2.99)

Y-factor is
\[ Y \text{-factor} = \frac{P^{\text{tot}} - P}{\frac{P}{V^{\text{tot}} - V^{\text{sat}}} - V^{\text{sat}}} \]. \tag{2.100}

Y-factor gives the extent of gas that is released as the pressure drops. Y-factor increases for oil that releases less gas as the pressure drops (Pedersen & Christensen, 2006).

An example of CME laboratory data for oil F1 from Jaubert et al. (2002) can be found in Table 2.10. The experiment is carried out at 374.85°K and saturation pressure is found to be 96.9 bar.

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>( V_{\text{rel}} )</th>
<th>Density (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>356</td>
<td>0.959</td>
<td>776.40</td>
</tr>
<tr>
<td>257</td>
<td>0.971</td>
<td>766.87</td>
</tr>
<tr>
<td>160</td>
<td>0.987</td>
<td>754.15</td>
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<tr>
<td>118.5</td>
<td>0.995</td>
<td>747.94</td>
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<tr>
<td>96.9</td>
<td>1.000</td>
<td>744.60</td>
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<td>716.33</td>
</tr>
<tr>
<td>84</td>
<td>1.060</td>
<td>702.74</td>
</tr>
</tbody>
</table>

The \( V_{\text{rel}} \) term in Table 2.10 can be found by Eq. (2.101).

\[ V^{\text{rel}} = \frac{V^{\text{tot}}}{V^{\text{sat}}} \]. \tag{2.101}
2.8.6.2. **Constant Volume Depletion**

During depletion, gas condensates and volatile oils form a second phase below the saturation point. As the gas is produced, it expands to fill the pore volume of the reservoir. With constant volume depletion (CVD), we obtain information about the composition and PVT behavior of the gas during depletion. The experiment is very similar to CME except the gas is removed step by step. A CVD experiment gives liquid volume as a percentage of dew point volume, gas Z-factor, two phase Z-factor, and viscosity of gas and gas compositions. CVD laboratory data for a condensate gas (Test B) from PVTSim database is given in Table 2.11. PVTSim is a commercial PVT simulation package.

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>Liq Vol % of V_b</th>
<th>% Produced Mole</th>
<th>Gas Phase Z-Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>28100</td>
<td>0</td>
<td>0</td>
<td>0.893</td>
</tr>
<tr>
<td>23500</td>
<td>1.3</td>
<td>11.91</td>
<td>0.852</td>
</tr>
<tr>
<td>18000</td>
<td>3.4</td>
<td>30.77</td>
<td>0.836</td>
</tr>
<tr>
<td>12500</td>
<td>4.6</td>
<td>52.05</td>
<td>0.858</td>
</tr>
<tr>
<td>8400</td>
<td>4.7</td>
<td>68.41</td>
<td>0.893</td>
</tr>
<tr>
<td>4900</td>
<td>4.4</td>
<td>81.21</td>
<td>0.932</td>
</tr>
</tbody>
</table>

In Table 2.11, the second column gives the volume of the liquid compared to the bubble-point volume as the pressure drops. The third column gives the percentage of moles produced compared to the mole numbers of the initial solution.
2.8.6.3. Differential Liberation

The differential liberation (differential depletion) experiment (DD) is only applicable for oil mixtures. DD not only gives information about the reservoir fluid, but it also gives information about the well stream conditions. Initially, the pressure is at or above the saturation pressure and the temperature is at the reservoir conditions. Similar to CVD, the volume is increased. Hence, gas forms. This newly formed equilibrium gas is removed at constant pressure. This step is carried out many times. The last step is carried out at standard conditions. DDE measures oil formation volume factor ($B_o$), gas formation volume factor ($B_g$), solution gas/oil ratio ($R_{so}$), gas gravity and compressibility factor of gas. Differential liberation laboratory data for an oil mixture (Test A) from PVTSim database is shown in Table 2.12.

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>$B_o$</th>
<th>$R_{so}$</th>
<th>Oil density (kg/m$^3$)</th>
<th>Gas Phase Z-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>26790</td>
<td>1.396</td>
<td>132.9</td>
<td>718</td>
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</tr>
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<td>23960</td>
<td>1.365</td>
<td>119.4</td>
<td>726</td>
<td>0.889</td>
</tr>
<tr>
<td>20940</td>
<td>1.329</td>
<td>103.7</td>
<td>735</td>
<td>0.888</td>
</tr>
<tr>
<td>17980</td>
<td>1.297</td>
<td>89.6</td>
<td>744</td>
<td>0.876</td>
</tr>
<tr>
<td>15000</td>
<td>1.265</td>
<td>75.7</td>
<td>753</td>
<td>0.88</td>
</tr>
<tr>
<td>11290</td>
<td>1.227</td>
<td>58.6</td>
<td>765</td>
<td>0.894</td>
</tr>
<tr>
<td>7240</td>
<td>1.186</td>
<td>40.4</td>
<td>778</td>
<td>0.904</td>
</tr>
<tr>
<td>3310</td>
<td>1.144</td>
<td>21.9</td>
<td>791</td>
<td>0.949</td>
</tr>
<tr>
<td>100</td>
<td>1.067</td>
<td>0</td>
<td>816</td>
<td></td>
</tr>
</tbody>
</table>

The formulas for the terms obtained from differential liberation experiments can be found below:
\[ B_o = \frac{\text{Oil volume at cell (reservoir conditions)}}{\text{Oil volume at standard conditions}} \]  
\[ B_g = \frac{\text{Gas volume at cell (reservoir) conditions}}{\text{Gas volume at standard conditions}} \]

Solution gas-oil ratio gives how much gas releases from an oil mixture at standard conditions. The equation is as follows,

\[ R_{so} = \frac{\text{Volume of gas dissolved at standard conditions}}{\text{Volume of liquid phase at standard conditions}} \]

The gas gravity is

\[ \text{Gas gravity} = \frac{\text{Molecular weight of gas}}{\text{Molecular weight of atmospheric air}} \]

2.8.6.4. Swelling Test

During a swelling test, the injection gas is injected into an undersaturated oil mixture in a PVT cell. The pressure is increased to attain the saturation pressure. At the saturation pressure, the volume of the cell is measured. More gas is injected and the pressure is increased to attain the saturation pressure. This step is repeated a couple of times. Swelling tests are carried out in order to investigate how oil swells when it contacts gas in a condensing drive process. The swelling test gives saturation pressure, saturated oil density, swollen volume, and injected gas (Jaubert et al., 2002). Table 2.13 gives the swelling test results for oil F3 at 387.45 °K from Jaubert et al. (2002).
The terms in Table 2.13 are as follows,

\[ X_{\text{gas}} = \frac{\text{Mole number of gas added in the cell since the beginning of the experiment}}{\text{Mole number of gas added} + \text{mole number of oil initially introduced in the cell}} \]  

and

\[ V_{\text{swell}} = \frac{V_{\text{sat}}}{V_{\text{sat}}(\text{initial})} . \]

### 2.8.6.5. Multi-Contact Test

In this test, a small amount of gas is injected into the oil at constant temperature and pressure. At equilibrium, two phases occur. Either the oil phase is contacted with more injection gas or the gas phase is mixed with the initial oil mixture in repeated contacts. Multi-contact tests are able to identify the MMP for a condensing drive (backward contacts) and for a vaporizing drive (forward contacts). However, these tests cannot identify the MMP for condensing/vaporizing drives (Ahmadi, 2011). At every step, the following are recorded: composition, phase mole numbers,
phase compositions, phase densities and molecular weights, gas phase compressibility factor, and partial volume (VP). From Jaubert et al. (2002), VP is

\[ VP = \frac{\text{Liquid phase volume}}{\text{Total cell volume}} \times 100. \quad (2.108) \]

2.8.6.6. **Slim-tube Test**

The slim-tube test is carried out to determine MMP. Slim-tubes are 5-120 ft. long and their diameter is 0.12-0.63 inches (Ahmadi, 2011). Therefore, multidimensional effects such as gravity override are lessened. The experiment is carried out at constant temperature and pressure. 1.2 PV of solvent is usually injected. The experiment is repeated several times with increasing pressure. The pressure at which the recovery is 90% may be taken as the MMP although determination of MMP from slim-tube experiments is not exact. The value of 90% is arbitrary but indicates high displacement efficiency.

2.8.7. **PVT Simulations**

Gas chromatography and true boiling point analyses give compositional information about the reservoir fluid. Moreover, other fluid properties such as saturation pressure, MMP, or density can be measured with other laboratory experiments explained in section 2.8.6. Equations of state compute the fluid properties with mathematical models. PVT simulations use these models to compare with laboratory results and are matched with fluid characterization. Most of the fluid parameters such as formation volume factor, gas-oil ratio or other volumetric properties can be
calculated easily once the equilibrium compositions are calculated. For MMP calculations, slim-tube simulations can be carried out.

2.8.8. Fluid Characterization

Cubic EOS correlations are only approximations to fluid behavior. Regression to laboratory data is carried out to better estimate the fluid behavior. The independent parameters are those required for the phase equilibrium calculations and the regressed data is experimental data, e.g., liquid volume, saturation point. Regressed parameters might vary according to the fluid type, for example, near critical fluid, multiphase fluid, etc. There are several regression procedures in the literature (Coats & Smart, 1986; Khan, 1992, Pedersen & Christensen, 2006; Whitson & Brule, 2000).

Binary interaction parameters, volume shift parameter, critical temperature, critical pressure, acentric factor of C\textsubscript{7+} components; plus fraction molecular weight can be used as independent parameters. As hydrocarbons that have lower than seven carbon atoms are defined, they can’t be used for regression. All of these regression parameters are initialized by correlations. In fact, it is better to vary the coefficients used in these correlations rather than the fluid parameter itself so that the expected trends are preserved. Equations (2.83) to (2.85) are used to estimate the fluid parameters. (Christensen, 1999) provides the following regression procedure.

1. Do regression to the experimental saturation points. Allow the plus molecular weight to be adjusted by up to ±10%, keeping the weight composition constant.

2. Evaluate whether the deviations between experimental and calculated data suggest deficiencies in density predictions. If that is the case, allow the volume translation
parameter of the C$_7^+$ components to be adjusted by ±50% (same percent for all C$_7^+$ components).

3. Determine the two or three most sensitive coefficients in Eqs. (2.83) to (2.85). These coefficients are those with the largest impact on the calculation results for a given percentage change.

4. Perform parameter regression using the most sensitive coefficients determined in the preceding step with a maximum adjustment of ±20%.

The advantage of varying the coefficients is that critical properties are changed simultaneously by varying two or three coefficients. Therefore, the resulting critical properties will have a rational correlation. Varying the critical temperature, critical pressure, and acentric factor themselves can result in unphysical critical properties. This will result in incorrect estimations. For a near-critical fluid, estimation of the critical temperature is important because that determines whether 100% liquid or vapor exists right below the phase envelope.

Coats and Smart (1986) do regression for twelve different fluids. There are two steps:

1. Adjust one binary parameter—generally methane/plus fraction binary—to match exactly the same bubble-point or dew-point pressure.

2. Regress on $\Omega_a$ and $\Omega_b$ of methane and the plus fraction, and methane-plus fraction binary unless otherwise stated.

The regressed parameters may be saturation pressure; density; K-values; constant composition expansion (CCE) data including relative volume, volume fraction liquid, and gas and liquid gravities; constant-volume expansion (CVE) data including volume fraction liquid, cumulative gas removed, gas z factor, and oil and gas gravities etc.
The regression is based on least-squares minimization. Coats and Smart (1986) vary the independent parameters by 3% initially. However, they start to increase that percentage step by step to fit the data. This way the dependent parameters are kept within acceptable limits.

Egwuenu et al. (2008) do fluid characterization where MME/MMP data are regressed in addition to other laboratory data. As MMP/MME data are important for gas flood recovery efficiency, fluid characterization that matches the MMP/MME gives better recovery estimates. Two injection fluids CO$_2$ and enriched gas are tested in their research. The injection and reservoir fluid are lumped from eleven and twelve components to four and five pseudo-components. The lumping is based on similarity of K-values. The original fluid that is not lumped is already tuned to PVT data. The challenge here is to tune data when the fluid is lumped to fewer components.

EOS tuning for the lumped fluid has two steps. Initially, the PVT data is matched. Secondly, MMP/MME and/or swelling data are matched. Molecular weights, critical properties, acentric factors and the BIPs between the lightest and heaviest components are regressed. Critical properties are varied no more than 10% from their initial values. However, BIPs are adjusted more than 10% if needed. PVT data that is regressed on are $B_o$, $R_s$, liquid viscosity and density, saturation pressures, and relative volume.

Each fluid was tuned in four different ways. They are tuned only to 1) PVT 2) PVT and swelling data 3) PVT and MMP/MME 4) PVT, swelling data and MMP/MME. Egwuenu et al. (2008) compare the tuning techniques with 1-D numerical simulations. The results show that MMP/MME tuning improves the results, particularly the recovery and front shape. However, saturation pressure shows a worse match using MMP/MME data as would be expected.

Khan et al. (1992) and Khan (1992) do fluid characterization of Texas oils. As Texas reservoirs form three phases at high CO$_2$ concentrations and low temperature, fluid characterization needs to be done accordingly. Generally, they use the techniques and
correlations of Christensen (1999) for fluid characterization. These correlations give initial guesses for several fluid properties. They split the heavy components using the correlations of Christensen (1999) and then lump them into pseudo-components by mass averaging. They validate their results with four low temperature injection cases. They compare P-T plots where three experimental and calculated three-phase regions are shown.

2.9. Literature Review of Phase Equilibrium Calculations

The following sections give a literature review of solution techniques for stability analyses and flash calculations. All reduced and conventional methods are reviewed.

Phase equilibrium calculations can be solved through several solution techniques such as successive substitution (SS), Newton’s minimization, Newton-Raphson (NR), Quasi-Newton, or non-iterative methods. All phase equilibrium calculations start with SS, or accelerated SS (Crowe & Nishio, 1975). Other techniques have faster convergence rates. However, SS methods have a larger region of convergence. Therefore, SS methods are used to reduce solution divergence. As SS iterations have a linear convergence rate (Michelsen & Mollerup, 2007), other methods take over when a particular switch criterion is met. The switching criterion in compositional simulator is generally

\[
\left\| \ln \left( f'^{i^L} \right) - \ln \left( f'^{i^V} \right) \right\|_{\infty} < 0.0001.
\]  

(2.109)

SS iterations are particularly slow near the critical region. Exactly at the critical region, the iterations will not converge (Michelsen, 1982a).
2.9.1. Stability Analysis

Stability analysis searches for whether another phase should form. If the tangent plane distance is negative, then a new phase is found. Therefore, stability analysis is based on minimization of the tangent plane distance (TPD) (Baker et al., 1982). We show two different solution techniques from the literature review. One uses Newton’s method as a minimization technique (Michelsen, 1982a; Perschke, 1985), the other uses solution of nonlinear equations with Newton-Raphson.

2.9.1.1. Successive Substitution

Both techniques that use minimization and solution of nonlinear equations start with successive substitution. Wilson’s correlation (Wilson, 1969) can be used to initiate K-values for a two-phase flash. Three possible guesses for a one-phase stability analysis are

\[ K_i(1\phi) = \left[ K_{i}^{\text{Wilson}}, \frac{1}{K_{i}^{\text{Wilson}}}, \sqrt{K_{i}^{\text{Wilson}}} \right]. \] (2.110)

from Li and Firoozabadi (2010). When two phases are present, we use several K-value guesses from the prior stability analysis and flash calculations (Li & Firoozabadi, 2010; Li & Firoozabadi, 2012; Michelsen, 1982a) to see if a third phase should form. The following can be used as estimated for the initial K-values:

\[ K_i(2\phi) = \left[ K_{i}^{1\phi - \text{stab}}, \frac{1}{K_{i}^{1\phi - \text{stab}}}, K_{i}^{1\phi - \text{flash}}, \frac{1}{K_{i}^{1\phi - \text{flash}}} \right]. \] (2.111)

Stationary point (the minimum of the objective function) is calculated as follows:
\[ X_i = K_i z_i \]  \hspace{1cm} (2.112)

Once the stationary point is calculated with Eq.(2.112), the fugacity coefficient is updated and the convergence criterion is checked by Eq. (2.44). With successive substitution (SS), the convergence criterion used here is generally \( \| S \|_\infty < 0.001 \). If convergence is not achieved, \( X_i \) is updated by \( X_i = \phi \left( \tilde{x} \right) / \left( z, \phi \left( \tilde{z} \right) \right) \). If convergence is achieved, we switch to Newton’s method.

2.9.1.2. Minimization of Tangent Plane Distance

Michelsen and Mollerup (2007) develop a stability analysis algorithm that is both robust and efficient. The objective function to minimize is the same as Eq. (2.33). We show it below for simplicity.

\[
g^* = \frac{\Delta G}{\delta} = \sum_{i=1}^{N_i} x_i \left( \mu_i(T, P, \tilde{x}) - \mu_i(T, P, \tilde{z}) \right) . \tag{2.113}
\]

If \( \Delta G < 0 \), the one phase assumption is unstable and there is a phase split. The gradient is

\[
g = \frac{\partial g^*}{x_i} = \left( \mu_i(\tilde{x}) - \mu_i(\tilde{z}) \right) - \left( \mu_i(\tilde{x}) - \mu_i(\tilde{z}) \right) \tag{2.114}
\]

at constant \( T \), and \( P \). The variable \( g \) in Eq. (2.114) is zero at a stationary point. Therefore, it can be used as a residual function in a Newton-Raphson algorithm. Michelsen and Mollerup (2007) propose the following objective function:
The gradient vector is

\[ \frac{\partial tm}{\partial X_j} = \ln \left( X_i \varphi \left( \frac{X}{X} \right) \right) - \ln \left( z_i \varphi \left( \frac{z}{z} \right) \right) . \] (2.116)

The Hessian matrix is

\[ H_j = \frac{1}{X_i} \delta_j + \frac{\partial \ln \phi}{\partial W_j} . \] (2.117)

The Hessian matrix is a symmetric matrix where first order differentials of the gradient are taken with respect to \( X_j \). Michelsen and Mollerup (2007) further simplify the Hessian matrix by canceling the terms that converge to zero at the solution. They calculate the step direction with Newton’s method. Moreover, the trust region modification is applied to the Hessian matrix to achieve an optimum step size.

\[ (H + \eta S) \Delta x_i + g = 0 \] (2.118)

where \( S \) is a diagonal matrix with positive elements. The parameter \( \eta \) is chosen in such a way that the Hessian matrix is made positive definite, the magnitude of the correction is smaller than a

2.9.1.3. Solution of Nonlinear Equations

Another solution technique for stability analysis uses the NR algorithm. The residual functions to be solved are shown in Eq. (2.44). The Jacobian matrix is

\[
J = \frac{\partial S}{\partial X_j}.
\]  

(2.119)

The equations are solved as

\[
J \Delta X_j = -S_i.
\]  

(2.120)

2.9.1.4. Quasi-Newton

The Quasi-Newton method is another solution technique where the Hessian matrix is approximated so that constructing the Hessian matrix is not as time consuming. Michelsen (1982a) recommends the Quasi-Newton method for stability analysis. Hoteit and Firoozabadi (2006) apply the Quasi-Newton method to stability analysis and conclude that the Quasi-Newton method is faster than the Newton’s method even though the Quasi-Newton method converges in a larger number of iterations due to super linear convergence.
2.9.2. Two Phase Flash Calculations

In this section, we cover the solution techniques for flash calculations. Similar to stability analysis, flash calculations can be solved with successive substitution, NR, Newton’s method or Quasi-Newton.

2.9.2.1. Successive Substitution

Initial K-value estimates for two-phase flash calculations start with Wilson’s correlation (Wilson, 1969). K-values can also be started from the stability analysis or a prior time step in simulation. However, the latter causes convergence problems near the critical region (Okuno, 2009).

Once the K-values are initialized, constant-K flash calculations are carried out to compute the phase compositions (Rachford & Rice, 1952). Then, fugacity coefficients are computed. Residual functions are

\[ R_i = \ln f_i^L - \ln f_i^V = 0 \quad (2.121) \]

The switch criterion is \[ \| \mathbf{R} \|_\infty < 0.001 \]. If convergence is achieved, we switch to NR or Newton’s minimization. Otherwise, K-values are updated with

\[ K = \frac{\phi_i^L}{\phi_i^V} \quad (2.122) \]

Once the K-values are updated, constant-K flash calculations are conducted and the step is repeated until convergence.
2.9.2.2. Minimization of Gibbs Energy

Flash calculations follow the stability analysis calculations if the fluid is multiphase. There are
two convergence criteria for flash calculations, namely minimization of Gibbs energy (Michelsen,
1982b; Perschke et al., 1989; Trangenstein, 1985) and equality of component fugacities at
different phases (Michelsen, 1986). Minimization of Gibbs energy can be solved with Newton or
Quasi-Newton method. The objective function is

\[ g^* = \sum_{j=1}^{N_L} \sum_{i=1}^{N} n_j \ln f_{ij}. \]  

Several algorithms have been used (Mehra et al., 1982; Michelsen, 1982b) to minimize
the objective function. Michelsen proposes a robust and efficient algorithm that has advantages
over the solution of nonlinear equations technique. The proposed algorithm uses Newton’s
method to update the independent parameters.

\[ n_{ij}^{k+1} = n_{ij}^k - H_{ij}^{-1} d_i \]  

where \( H \) is the Hessian matrix, \( d \) is the gradient vector and \( n \) is a vector that contains the
reference phase mole numbers. The gradient is a vector that contains the first order partial
derivatives of Gibbs energy with respect to phase mole numbers. That is,

\[ d_i = \frac{\partial g^*}{\partial n_{i1}} = \sum_{k=1}^{N} \left( \frac{\partial n_{i2}}{\partial n_{k1}} \ln f_{k2} + \frac{\partial \ln f_{i2}}{\partial n_{k1}} n_{k2} + \frac{\partial n_{i1}}{\partial n_{k1}} \ln f_{k1} + \frac{\partial \ln f_{i1}}{\partial n_{k1}} n_{k1} \right) \]
for a two-phase mixture. The subscript $l$ is the reference phase index. Gibbs-Duhem equation states

$$
\sum_{i=1}^{N_c} \frac{\partial \ln f_{ij}}{\partial n_{ki}} n_{ij} = 0 .
$$

(2.126)

Finally, the gradient can be expressed as

$$
d_i = \ln f_{ij} - \ln f_{il} .
$$

(2.127)

This simple expression is identical to the error function in the solution of nonlinear fugacity equations for a flash calculation. This convergence criterion holds for the minimization technique as well and the first order partial derivative is zero at a local minimum. The Hessian matrix is

$$
H = \frac{\partial d_i}{\partial n_{ki}} = \frac{\partial^2 g^*}{\partial n_{ki} \partial n_{ki}} = \frac{\partial \ln f_{ij}}{\partial n_{ki}} - \frac{\partial \ln f_{il}}{\partial n_{ki}} .
$$

(2.128)

As the Hessian matrix is symmetric, the number of calculations required is reduced by half. Similar to stability analysis, Michelsen (1982b) uses a trust region, and Perschke (1988) uses line search to optimize the step size.

Modified Cholesky decomposition is one approach used to force the Hessian matrix to be positive definite so the solution is at a local minimum. Modified Cholesky decomposition gives
\[ LDL^T = H \]  \hspace{1cm} (2.129)

where \( L \) is a lower triangular matrix, \( D \) is a diagonal matrix consisting of eigenvalues. If any of the eigenvalues are negative, modified Cholesky decomposition corrects it to be positive. Finally, LU decomposition can be easily applied to solve for the step direction.

Independent parameters are phase mole numbers rather than phase composition to avoid Rachford-Rice iterations. Summation of the updated reference phase mole numbers gives the total number of moles in the reference phase. As the total number of moles in the fluid is constant, total mole numbers of the other phase can easily be computed. This way, phase mole fractions and phase compositions are updated. Okuno et al. (2010a) showed that Gibbs energy minimization is faster and more robust than the solution of nonlinear equations technique.

2.9.2.3. Solution of Fugacity Equations

Equality of component fugacities at different phases is a criterion for flash calculations. This criterion can be used as a residual function to be solved (Michelsen 1982b; Nghiem et al. 1983).

\[ f_i^L - f_i^V = 0. \]  \hspace{1cm} (2.130)

By using Eq. (2.26), residual equations can be written as

\[ R_i = \phi_i^L x_i - \phi_i^V y_i = 0 \]  \hspace{1cm} (2.131)

where \( x_i \) is liquid phase composition and \( y_i \) is vapor phase composition. The Jacobian matrix is
The Newton-Raphson equations are as follows:

\[ J \Delta x = -R . \]  \hspace{2cm} (2.133)

### 2.9.3. Reduced Two-Phase Flash Calculations

The conventional phase equilibrium calculations take phase composition as independent parameters. The reservoir fluid can have hundreds of components so that it is computationally impractical to include all the components in a simulation. Therefore, fluid components with similar molecular weight are lumped into pseudo-components. This technique increases the computational speed but reduces the accuracy since not only are the compositions lumped but also the fluid properties are lumped such as critical temperature, acentric factor, and so forth.

Reduced methods are one approach to speed up flash and stability calculations so that more components and phases can be used. In order to understand reduced methods, we rewrite the fugacity coefficient expression below:

\[ \phi = \exp \left( \frac{B}{B}(Z - 1) - \ln(Z - B) \right) - \frac{A}{2\sqrt{2}B} \left( \frac{\sum_j x_j A_j}{A} - \frac{B}{B} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \]  \hspace{2cm} (2.134)

The partial derivatives to construct the Jacobian matrix include the term \( \partial \phi / \partial x_j \). This term is actually a function of the following parameters,
\[ \phi_i = f(A, B, \sum_j x_j A_j) \]  

(2.135)

because \( B_i \) is constant during the iterations and \( Z = f(A, B) \). If we can express these three parameters in terms of reduced parameters as

\[ A, B, \sum_j x_j A_j = f(\Theta) , \]  

(2.136)

we can have the following expression:

\[ \frac{\partial \phi_i}{\partial x_j} = \sum_k \frac{\partial \phi_i}{\partial \Theta_k} \frac{\partial \Theta_k}{\partial x_j} . \]  

(2.137)

This expression is helpful if the number of reduced parameters is small and fixed. We cannot take \( A, B, \) and \( \sum_j x_j A_j \) as independent parameters for the following reasons: \( \sum_j x_j A_j \) is vector of length \( N_C \) and it wouldn’t be practical to use a vector as independent parameters. Secondly, once we solve for the reduced parameters, the solution has to be able to express phase compositions. Even if these parameters can be expressed in terms of phase composition, they cannot explicitly calculate the phase composition. Therefore, we cannot use \( A, B, \) and \( \sum_j x_j A_j \) as a series of independent parameters. Michelsen (1986) realized that the parameter \( A \) and \( \sum_j x_j A_j \) can be expressed in the following way. Conventionally,
If BIP-’s are zero,

\[ A = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \sqrt{A_i A_j} x_i x_j (1 - k_{ij}) \quad \text{and} \quad \sum_j x_j A_{ij} = \sum_{j=1}^{N_c} \sqrt{A_i A_j} x_j (1 - k_{ij}). \]  \hspace{1cm} (2.138)

and

\[ \sum_j x_j A_{ij} = \sqrt{A_i} \sum_{j=1}^{N_c} \sqrt{A_j} x_j . \]  \hspace{1cm} (2.139)

Therefore, we can express both \( \sum_j x_j A_{ij} \) and \( A \) as a function of \( \sum_{j=1}^{N_c} \sqrt{A_j} x_j \), which is a scalar. Fugacity is also a function of \( B \). Moreover, reference phase mole fraction has to be taken as an independent parameter in order to be able to express the reduced parameters of the other phase with the following equations,

\[ x_i L + y_i V = z_i \]

\[ \sum_i A_i x_i L + \sum_i A_i y_i V = \sum_i A_i z_i \]  \hspace{1cm} (2.141)

where \( L \) is liquid phase mole fraction and \( V \) is vapor phase mole fraction. Finally, the reduced parameters of the other phase can be computed as
The reduced method of Michelsen (1988) needs only three independent parameters with no dependency on the number of components. The independent parameters are updated with Newton Raphson’s iterations with the following residual functions:

\[ e_1 = \sum_{i=1}^{N_c} (y_i - x_i) \]
\[ e_2 = \sum_{i=1}^{N_c} x_i \sqrt{A_i} - \sqrt{A} \]  \hspace{1cm} (2.143)
\[ e_3 = \sum_{i=1}^{N_c} x_i B_i - B \ . \]

At the next iteration, the fugacity coefficients can be computed only with these three updated reduced parameters. At convergence, the residual functions in Eq. (2.143) should be less than a small specified tolerance. Alternatively, one could calculate the fugacities from the reduced parameters and use a component fugacity convergence criterion. Phase compositions are updated after the fugacity coefficients are computed. The necessary equations are as follows:

\[ K_i = \frac{\phi_i^L}{\phi_i^V} \]  \hspace{1cm} (2.144)
\[ x_i = \frac{z_i}{1 + V(K_i - 1)} \]  \hspace{1cm} (2.145)
\[ y_j = K_i x_i. \] (2.146)

The disadvantage of this technique is that it assumes zero BIPs. This is the only way of expressing parameter \( A \) as a function of a scalar.

Several authors proposed new reduced parameters that take into account nonzero BIPs (Hendriks & Van Bergen, 1992; Jensen & Fredenslund, 1987; Li & Johns, 2006). Jensen and Fredenslund (1987) proposed a new reduced algorithm with five independent parameters that is applicable up to one nonzero BIP column only. Nichita and Minescu (2004) introduced a reduction method with \( 2m+3 \) reduction parameters where \( m \) is the number of components with non-zero BIPs. Hendriks (1987) showed mathematically how the reduction method can be applied to minimization of Gibbs energy by using Newton Raphson’s algorithm under certain criteria. Hendriks and Van Bergen (1992) analyzed the BIP matrix. Considering the BIP is symmetric, it can be expressed by spectral decomposition as

\[ (1-k_q) = \sum_{k=1}^{N_c} \lambda_k q^k_i q^k_j. \] (2.147)

The parameter \( q^k \) is the eigenvector corresponding to the \( k^{th} \) eigenvalue, and \( \lambda_k \) is the \( k^{th} \) eigenvalue. For \( n \) non-zero (or very small) eigenvalues, new reduced parameters are defined as

\[ \Theta_{\alpha} = \sum_{i=1}^{N_c} q^\alpha_i \sqrt{\lambda_i} x_i, \quad \alpha = 1, \ldots, n. \] (2.148)
These reduced parameters are able to express both $\sum j_i A_j$ and $A$ (From Eqs. (2.138))

$$A \approx \sum_{a=1}^{n} \lambda_a \Theta_a^2$$  \hspace{1cm} (2.149)

and

$$\sum_{j=1}^{N_c} A_j x_j \approx \sum_{a=1}^{n} \lambda_a \Theta_a \sqrt{A_i q_{ia}}.$$ \hspace{1cm} (2.150)

Equation (2.149) is derived from

$$A = \sum_{i=1}^{N_c} N_c \sqrt{A_i} \sqrt{A_j} x_i x_j (1 - k_j).$$ \hspace{1cm} (2.151)

Substitution of Eq. (2.147) gives

$$A = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} \sqrt{A_i} \sqrt{A_j} x_i x_j \sum_{k=1}^{N_c} \lambda_i q_i^k q_j^k = \sum_{k=1}^{N_c} \lambda_k \sum_{i=1}^{N_c} \sqrt{A_i} x_i q_i^k \sum_{j=1}^{N_c} \sqrt{A_j} x_j q_j^k.$$ \hspace{1cm} (2.152)

Substitution of Eq. (2.148) gives

$$A = \sum_{k=1}^{N_c} \lambda_k Q_k^2.$$ \hspace{1cm} (2.153)
When the zero eigenvalues are excluded, Eq. (2.153) becomes the same as (2.149). Note that $\lambda_\alpha$, $A_i$ and $q_{i\alpha}$ are constant during the phase equilibrium calculations. Therefore, the only independent parameters are the reduced parameters. The number of the reduced parameters equals the number of non-zero eigenvalues. The number of non-zero eigenvalues increases as the number of nonzero columns in the BIP matrix increases.

Eqs. (2.149) and (2.150) are only approximate since small eigenvalues are set to zero, which change the BIP values. This method is referred to as spectral decomposition (SD), where the number of reduced parameters depends on the number of eigenvalues ($n$) retained. In total, there are $n+2$ reduced parameters when $B$ and the mole fraction of liquid are also included. The Newton-Raphson iterations then solve $n+2$ error functions:

$$e_\alpha = \sum_{i=1}^{N_c} x_i \sqrt{A_i} q_{i\alpha} - Q_{i\alpha} \quad \alpha = 1, \ldots, n$$

$$e_{n+1} = \sum_{i=1}^{N_c} x_i B_i - B$$

$$e_{n+2} = \sum_{i=1}^{N_c} (y_i - x_i)$$

Li and Johns (2006) took a different approach to develop new reduced parameters when BIPs are nonzero. They expressed the BIP matrix using two parameters through the function

$$k_{ij} = (h_i - h_j)^2 g_i g_j$$
where \( h_i \) and \( g_i \) are component tuning parameters determined from a best fit to PVT data (or in some cases by doing a best fit of the BIPs from prior tuned characterizations). Using Eq. (2.155) they derived the following expressions:

\[
A = \Theta_1^2 + 2\Theta_2^2 - 2\Theta_3\Theta_4
\]

(2.156)

\[
\sum_{j=1}^{N_c} A_j x_j = \sum_{a=1}^{4} \Theta_a q_{ia}
\]

(2.157)

where the four reduced parameters are

\[
\Theta_a = \left\{ \sum_{i=1}^{N_c} x_i \sqrt{A_i}, \sum_{i=1}^{N_c} x_i \sqrt{h_i g_i}, \sum_{i=1}^{N_c} x_i h_i^2 g_i, \sum_{i=1}^{N_c} x_i \sqrt{g_i} \right\}
\]

(2.158)

and the vector of known parameters are

\[
q_{ia} = \left\{ \sqrt{A_i}, 2\sqrt{A_i h_i g_i}, -\sqrt{A_i g_i}, -\sqrt{A_i h_i^2 g_i} \right\}
\]

(2.159)

Together with the EOS parameter \( B \) and the mole fraction of liquid, Li and Johns (LJ) used a total of six reduced parameters. Unlike the SD approach, the number of reduced parameters in their approach is always six, eliminating the need to determine how many eigenvalues to retain for phase behavior accuracy.

For all reduced methods, the reduced parameters of the reference phase are updated after each NR iteration. The reduced parameters for the second phase are calculated by a simple material balance equation. The fugacity coefficients are then calculated from the reduced parameters at each iteration to update the K-values. Because the mole fraction of liquid is known
(it is a reduced parameter), the liquid equilibrium phase compositions are then directly computed from the mass balance equations 

\[ x_i = z_i \left/ \left[ (1 - L) K_i + L \right] \right. \]

Since the equilibrium phase compositions are calculated from the reduced parameters, the phase compositions only exactly satisfy 

\[ \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = 1 \]

at convergence. Further, the values of the residual functions based on equality of fugacity coefficients could increase in the first NR iteration even though the residual parameters are converging.

Okuno et al. (2010a) corrected this mass balance error in the LJ method by adding a SS step after each NR iteration of the reduced parameters. That is, after the equilibrium phase compositions are first calculated from the reduced parameters following NR, the reduced parameters are recalculated based on these equilibrium phase compositions. These reduced parameters are then used to solve for new equilibrium phase compositions after calculation of fugacity coefficients and K-values. Although the SS step required additional computational time, Okuno et al. (2010a) showed that by calculating the fugacity coefficients at the same iteration as the reduced parameters they achieved faster convergence. In this research, we denote their approach as OJS. Mohebbinia et al. (2012) eliminated the additional SS step by calculating K-values using the derivatives that are used to construct the Jacobian matrix.

Nichita and Graciaa (2011) introduced new reduced parameters for the SD method. In their novel approach, they expressed the fugacity coefficient for a given phase as a linear function of the new reduced parameters:

\[ \ln \phi_i = \sum_{a=1}^{n^2} h_{ia} q_{ia} \quad i = 1, \ldots, N_C \]  

\[ \text{(2.160)} \]
where $h_o$ are the reduced parameters and $q_{io}$ are vectors of length $N_C$ with known elements. A significant advantage of this approach over the standard SD method is that the fugacity coefficients are easy to calculate and the expression is linear with the reduced parameters. Nichita and Graciaa showed that fewer iterations are required for convergence with their improved approach (ISD) over the SD method. Further this approach naturally uses the equality of fugacity coefficients as the convergence criterion. The Rachford-Rice equations are solved for the phase mole fractions after each iteration because the phase mole fractions are no longer reduced parameters.

2.9.4. Reduced Stability Analysis

Reduced stability analysis is very similar to flash calculations. Reduced methods express the fugacity coefficients by using the same reduced parameters as the flash calculations (see Eqs. (2.135), (2.148) and (2.158)). However, the residual functions used in reduced stability analysis are different than those in reduced flash calculations. The first reduced stability analysis was proposed by Michelsen (1986). He proposed the following residual functions:

\[ S_1 = \sum_{i=1}^{N_C} X_i \left( \Theta_i - \sqrt{A_i} \right) = 0 \]  

(2.161)

and

\[ S_2 = \sum_{i=1}^{N_C} X_i \left( \Theta_i - B_i \right) = 0. \]  

(2.162)
Stability analysis does not have phase mole fraction as independent parameters. Therefore, there is one less independent parameter than for flash calculation. The reduced parameters of Hendriks and Van Bergen (1992) are implemented for stability analysis by Firoozabadi and Pan (2002). Firoozabadi and Pan (2002) suggested that reduced methods have fewer minima in the tangent plane distance compared to the conventional method. They have further compared the reduced stability analysis of Hendriks and Van Bergen (1992) with the other conventional methods namely conventional minimization of TPD by using SS+Newton iterations and by using solely Quasi-Newton iterations. They found that reduced methods are significantly faster than both of the conventional methods while Quasi-Newton method is the second fastest. Pan and Tchelepi (2010) further implemented the reduced method of Hendriks and Van Bergen (1992) into a general purpose compositional simulator and found significant speed ups.

Okuno et al. (2010a) implemented the reduced parameters of Li and Johns (2006) to stability analysis by using the following error functions

\[ S_k = \sum_{i=1}^{n} \left( \Theta_i^j - q_{il} \right) \frac{z_i \phi_i^j (\tilde{z})}{\phi_i^j} = 0 \]

(2.163)

where the number of reduced parameters is five independent of the number of components. They implemented their reduced stability analysis into UTCOMP (an implicit pressure-explicit saturation compositional reservoir simulator) and concluded that their reduced method is significantly faster than the conventional method, which is based on minimization of Gibbs energy (Perschke, Chang, Pope, & Sepehrnoori, 1989).

Haugen and Beckner (2011), Michelsen et al. (2012), Yan et al. (2011) and Haugen and Beckner (2013) compared reduced methods based on spectral decomposition with the
conventional methods and found limited speed-up only for a large number of components. We analyze in more detail their findings in section 2.9.6.

2.9.5. Conventional and Reduced Multi-Phase Flash Calculations

When a solvent is injected into a reservoir multiple phases can occur. For example, low temperature CO$_2$ injection into Texas oil reservoirs can result in a hydrocarbon-rich liquid phase, CO$_2$-rich liquid phase, and a vapor phase. The tangent plane distance analysis for a multiphase system was carried out by Baker et al. (1982). Three-phase flash calculations may be initialized with several sets of K-values e.g.

$$K_1 = \frac{x_{i1}}{x_{i3}} \quad \text{and} \quad K_2 = \frac{x_{i2}}{x_{i3}}$$

(2.164)

where $x$ is phase composition, $i$ is component index and the second subscript index is the phase index. Generally, the first two phase compositions are taken from two-phase flash calculations and the third phase composition is taken from the two-phase stability analysis. Globally convergent multiphase constant-K flash calculations (Rachford-Rice) have been proposed. We use the Rachford-Rice algorithm of Okuno et al. (2010c). Constant-K flash calculations update the phase compositions once the K-values are given. Michelsen (1982b) solved three-phase flash calculations with successive substitution iterations followed by second order Newton’s minimization where phase mole numbers are independent parameters. Perschke (1988) implemented multiphase flash calculations into a compositional reservoir simulator (UTCOMP). Successive substitution iterations update the three fugacity coefficients and the K-values are updated from
\[
\ln f_{i1} = \ln f_{i2} = \ln f_{i3} .
\]

Newton iterations minimize

\[
g^* = \frac{\Delta G}{RT} = \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} n_{ij} \ln f_{ij}
\]

with respect to first and second phase mole numbers. Therefore, the size of the Hessian matrix is \(2N_C\) by \(2N_C\).

Okuno et al. (2010a) implemented the reduced parameters of Li and Johns (2006) to three-phase flash calculations. They have twelve reduced parameters, two of which are phase mole fractions. Their reduced parameters are

\[
\psi = \{\Theta_{11}, \ldots, \Theta_{51}, \beta_1, \Theta_{12}, \ldots, \Theta_{52}, \beta_2\}
\]

where \(\Theta_{jk}\) can be seen at (2.158), \(k\) is the phase index, and \(\beta\) is phase mole fraction where

\[
\sum_{k=1}^{N_c} \beta_k = 1 .
\]

The residual functions are (Okuno, 2009)
Furthermore, Okuno et al. (2010b) implemented their three-phase flash calculations into a compositional reservoir simulator (UTCOMP) and showed significant speed-up compared to the conventional method (Perschke, 1989).

Normally, cubic EOS’s do not account for the interactions between water and other components. However, cubic equations of state can be modified to take these interactions into account. Therefore, four-phase flash calculations are carried out to compute the equilibrium compositions of CO2-rich liquid, hydrocarbon-rich liquid, gaseous, and aqueous phases. Mohebbinia et al. (2012) implemented reduced parameters to four-phase flash calculations and showed even more speed-up compared to the conventional method based on solution of fugacity equations.

2.9.6. Critical Reviews of the Reduced Methods

Reduced methods have been implemented for stability analysis, two-, three-, and four–phase equilibrium calculations. Firoozabadi and Pan (2002) test reduced stability analysis and conventional stability analysis based on tangent plane distance. They conclude the TPD surface becomes smoother and has only one minimum with the reduced method. This finding is an indication that reduced methods may improve the robustness. Even though they do not find a
decrease in the number of iterations, computational speed-up is found compared to the conventional method in batch mode calculations.

Hoteit and Firoozabadi (2006) compare three stability analysis techniques based on minimization by Newton’s method, minimization by quasi-Newton method with BFGS update, and using the reduced method based on SD. They conclude that their reduced method is the fastest method while conventional methods based on Newton’s method are the slowest.

Pan and Firoozabadi (2003) analyze conventional and reduced methods. They apply SS, Newton’s minimization and the Newton-Raphson method. They conclude successive substitution followed by the reduced method based on solution of nonlinear equations is “extremely efficient”.

Similar speed ups are found by Li and Johns (2006) and Okuno et al. (2010a) where LJ reduced parameters are used. Okuno et al. (2010b) apply reduced methods to three-phase equilibrium calculations. They compare conventional methods with the reduced method in a reservoir simulation. They report significant speed up. Mohebbinia et al. (2012) apply reduced methods to four-phase equilibrium calculations where the water component is dissolved in hydrocarbon phases and vice versa. Reduced methods become even more beneficial as the number of phases increases because the Jacobian for the conventional method is \((N_P-1)(N_C+1)\) where \(N_P\) is the number of phases.

Pan and Tchelepi (2010) compare reduced methods with the conventional method for a general purpose reservoir simulator. They only used reduced methods based on spectral decomposition. Normally, eigenvalues which are larger than 0.001 are used with the SD approach. However, they decreased this value to 0.07 for their fluids. This larger value results in significant speed ups compared to the conventional method as the number of independent parameters is small. However, this could distort the phase behavior significantly especially if there are eigenvalues close to but lower than 0.07.
Recently, several authors (Haugen & Beckner, 2011; Michelsen et al., 2012; Yan et al., 2011) report that reduced methods can be faster than the conventional methods only if the fluid has over ten components. Haugen and Beckner (2011) critically compare conventional phase equilibria calculations with the reduced phase equilibria calculations using only spectral decomposition (SD). The calculations include both stability analysis and flash calculations. All of the algorithms are based on solution of nonlinear equations. The calculations start with successive substitution (SS) and then continue with Newton-Raphson (NR) iterations. The switch criterion from SS to NR is that the infinity norm of the residuals is smaller than $10^{-3}$. The NR convergence criterion used here is that the infinity norm of the residuals is smaller than $10^{-12}$. Their algorithms are written in C++ with inlining, pointer arithmetic and loop optimizations. Significant speed-up is achieved owing to code optimization (Haugen & Beckner, 2011).

The results from Haugen and Beckner (2011) show smaller speed up than previously reported for the SD reduced method. Two fluids are tested namely SPE3 and SPE5 from the comparative SPE project. SPE3 has nine components and six significant eigenvalues resulting in an $8 \times 8$ Jacobian matrix for the reduced method. SPE5 has six components and three significant eigenvalues. The methods are tested for 1,000,000 phase equilibrium calculations where T and P space is divided into $1000 \times 1000$ points. SPE3 and SPE5 exhibit equal computational speed for reduced and conventional techniques at nine and six components, respectively. Two fold speed ups in the reduced methods are reported at around 15-20 components. Also, as the number of retained eigenvalues increases, the reduced method eventually becomes slower than the conventional method. Another result is that as fewer eigenvalues are retained, accuracy decreases for the spectral decomposition method (SD). Further, as TPD becomes smoother near the critical region, the reduced method performs better than the conventional method. This performance applies to stability analysis. Finally, they show that retaining eigenvalues greater than 0.07 causes a small change in the phase behavior.
The reason for the smaller speed up than previously reported is explained in two ways. For SS steps, an additional $\frac{\partial A}{\partial n_i}$ has to be calculated by the chain rule. This doubles the computational time for that part of the SS steps for the same size of independent parameters. However, an SS algorithm that does not need any partial derivative expression could have been used. There is no need to calculate either the fugacity coefficients or the A term by using derivatives. Apart from the computation of $\frac{\partial A}{\partial n_i}$, it is reported that the SS step computational time is the same for reduced and conventional techniques.

The paper by Haugen and Beckner also reports additional calculations for the reduced NR steps. That is, construction of the Jacobian matrix requires an additional matrix multiplication. We present the derivations required for the conventional method and the reduced method (SD) below:

$$J_{\text{(conventional)}} = \frac{\partial x_i}{\partial n_k} \phi^L_i + \frac{\partial \phi^L_i}{\partial n_k} x_i^L - \frac{\partial y_i}{\partial n_k} \phi^V_i - \frac{\partial \phi^V_i}{\partial n_k} y_i$$

The above equation requires the calculations of $\frac{\partial A}{\partial n_k}, \frac{\partial B}{\partial n_k}, \frac{\partial Z}{\partial n_k}, \frac{\partial \sum A_{ij} x_j}{\partial n_k}, \frac{\partial x_i}{\partial n_k}, \frac{\partial \phi_i}{\partial n_k}$ for two phases, so that,

$$J_{\text{(reduced)}} = 1 - \sum q_{aa} \frac{\partial x_i}{\partial Q_k}$$
This requires the calculation of \( \frac{\partial A}{\partial Q_k}, \frac{\partial B}{\partial Q_k}, \frac{\partial Z}{\partial Q_k}, \frac{\partial \sum A_y x_j}{\partial Q_k}, \frac{\partial x}{\partial Q_k}, \frac{\partial \phi}{\partial Q_k} \) for two phases.

Also, \( \frac{\partial K}{\partial Q_k} \) has to be calculated. Haugen and Beckner (2011) state that the calculation time for the derivatives are almost the same until the construction of the Jacobian matrix. Construction of the Jacobian matrix requires an additional matrix multiplication for the reduced method. However, as shown above, construction of the Jacobian matrix requires four matrix-vector multiplications for the conventional method. Therefore, it can be concluded that there is not much difference in terms of computations for the reduced and the conventional method contrary to what is reported by Haugen and Beckner (2011). The reason they do not see speed up until 10 components is that their reduced Jacobian matrix has a rank of 8 in their example. Considering, the size of the reduced Jacobian is large, we cannot expect significant speed up.

Haugen and Beckner (2013) showed that the reduced methods of Jensen and Fredenslund (1987), Hendriks and Van Bergen (1992) and Li and Johns (2006) can be generalized as

\[
A = \sum_{\alpha=1}^{M} L_{\alpha} Q_{\alpha}^2 \quad \text{and} \quad Q_{\alpha} = \sum_{i=1}^{N_c} q_{\alpha i} x_i
\]  

(2.171)

where \( Q_{\alpha} \) is made up of the reduced parameters, \( L_{\alpha} \) are scalars, \( q_{\alpha i} \) is a constant matrix.

Therefore, Haugen and Beckner (2013) stated that the reduced algorithms can be written in a generalized fashion, and hence, there is no difference between these methods. However, generalized algorithms may slow down the execution time.

Haugen and Beckner (2013) take the infinity norm of their residual functions as convergence criterion. Therefore, the number of iterations is the same for all the algorithms considered. However, the number of iterations will vary when the convergence criterion is based
on the equality of fugacities criterion. For the conventional technique, their independent parameters are not phase composition but rather $n_i^L - n_i^V$ in order to avoid numerical problems near the phase boundaries. Moreover, their reduced independent parameters are $Q_{\alpha}^L - Q_{\alpha}^V$ for the same reason.

Haugen and Beckner (2013) explain why reduced methods may not be as fast as previously thought. They hypothesize that the matrix operations can be optimized by using code optimization and a significant amount of time is spent on intrinsic functions such as computing Z-factors where reduced methods show no speed-up. As the matrix operations can be optimized, the importance of the reduced methods decreases. They do not consider, however, additional matrix operations in reduced Jacobian matrix construction using the reduced method. In their figures they compare the computational times for a complete flash calculation including SS steps and their switch criterion is $10^{-4}$.

SS iterations can be very costly especially near the critical region but they are not significant in reservoir simulation owing to good initial guesses from a prior time step. Moreover, matrix operations are much costlier than intrinsic functions from our experience. Even though matrix operations can be optimized, the optimization would be applicable both for reduced and conventional NR steps. Unfortunately, Haugen and Beckner do not separately report their computational results for NR iterations. They do show that the bulk of the computational time goes to non-matrix operations. Reduced methods show significant speed-up when only the matrix operations are considered. It is very likely that the bulk of the non-matrix operations go to the SS iterations as they require more iteration. The best way to compare methods is by incorporating them in compositional simulation (Okuno et. al., 2010b) where prior initial guesses and other factors become important.
2.9.7. Reduced Methods Using Minimization of Gibbs Energy

There have been several attempts to couple reduced methods with the minimization techniques (Michelsen et al., 2012; Pan & Firoozabadi, 2003; Yan et al., 2011). Pan and Firoozabadi (2003) previously used Lagrange multipliers in the reduced minimization technique (Pan & Firoozabadi, 2003). This resulted in an asymmetric matrix. Moreover, the reference phase mole fraction was included in the reduced parameters. Pan and Firoozabadi (2003) concluded that reduced methods are more efficient using the solution of the nonlinear equations technique.

Nichita and Graciaa (2011) introduced new independent parameters, which are also unconstrained. Moreover, phase mole fraction does not need to be included as an independent parameter. Therefore, Michelsen et al. (2012) and Yan et al. (2011) implemented the reduced methods of Nichita and Graciaa (2011) to the Gibbs minimization technique. However, the resulting gradient is more complicated than that of the conventional minimization approach. This also should result in a more complicated Hessian matrix. Below, we explain why the reduced gradient vector and Hessian matrix expressions are much more complicated than the conventional ones. With minimization of Gibbs energy, the objective function for flash calculations is

\[ g^* = \frac{\Delta G}{RT} = \sum_{j=1}^{N} \sum_{i=1}^{N} n_{ij} \ln f_{ij} \]  

(2.172)

When reference phase mole number is taken as the independent parameter, the gradient vector becomes

\[ d_i = \frac{\partial g^*}{\partial n_{i1}} = \sum_{k=1}^{N} \left( \frac{\partial n_{k1} \ln f_{k1}}{\partial n_{k1}} + \frac{\partial \ln f_{i1}}{\partial n_{k1}} n_{k1} \right) . \]  

(2.173)
Gibbs-Duhem equation states

\[ \sum_{j=1}^{N_c} \frac{\partial \ln f_{ij}}{\partial n_{kj}} n_{kj} = 0 \quad . \tag{2.174} \]

We know \( \partial n_i / \partial n_{ki} = 0 \) if \( i \neq k \). Therefore, the gradient vector reduces to

\[ d_i = \ln f_{i2} - \ln f_{ii} \quad . \]

This last expression is the same as the residual function used to solve a flash calculation by solution of the nonlinear equations technique. With the reduced methods, we cannot therefore take advantage of the Gibbs-Duhem equation and simplify the gradient vector expression. As the Hessian matrix is computed by taking the derivative of the gradient vector with respect to phase mole numbers, a complicated expression of gradient vector makes reduced methods unsuitable for Gibbs energy minimization.

Yan et al. (2011) and Michelsen et al. (2012) applied Gibbs energy minimization to the reduced independent parameters of Nichita and Graciaa (2011). The reduced gradient vector is

\[ d_\alpha = \frac{\partial g^*}{\partial \Delta h_\alpha} = \sum_{i=1}^{N_c} \frac{\partial g^*}{\partial n_i} \frac{\partial n_i}{\partial \Delta h_\alpha} = \sum_{i=1}^{N_c} \frac{\partial g^*}{\partial n_i} W_{i\alpha} \tag{2.175} \]

where \( W \) is the transformation matrix. The Hessian matrix becomes

\[ H_{\alpha k} = \frac{\partial^2 g^*}{\partial \Delta h_\alpha \partial \Delta h_k} = \sum_{i=1}^{N_c} \left( \frac{\partial^2 g^*}{\partial \Delta h_\alpha \partial n_i} \frac{\partial n_i}{\partial \Delta h_k} + \frac{\partial^2 g^*}{\partial \Delta h_k \partial n_i} \frac{\partial n_i}{\partial \Delta h_\alpha} \right) \quad . \tag{2.176} \]

The second term in the summation bracket cancels because \( \partial g^* / \partial n_i = 0 \) at the solution.

The first term becomes
Finally, the reduced Hessian matrix and reduced gradient vector become

\[ H^C \approx WHW^T \quad \text{and} \quad \mathbf{d}^r = \mathbf{Wd} \]  \hspace{1cm} (2.178)

where \( H^C \) is the reduced Hessian matrix, \( W \) is the transformation matrix, \( H \) is the conventional Hessian matrix, \( \mathbf{d}^r \) is the reduced gradient and \( \mathbf{d} \) is the conventional gradient. This technique requires computation of the conventional gradient vector and Hessian matrix. In addition to these calculations, the reduced gradient vector and the reduced Hessian matrix need to be computed. This will result in more computational time for construction of the Hessian matrix even though its rank is smaller. The only advantage is that modified Cholesky factorization and LU decomposition would be less costly because of the smaller size of the Hessian matrix. Michelsen et al. (2012) also applied Minimization of Gibbs energy to the reduced stability analysis. Similar to the flash calculations, their reduced stability analysis techniques requires additional calculations to compute the reduced Hessian matrix.

Yan et al. (2011) report speed-up only after 20 components for the case they have tested. We reproduced their calculations for the SPE3 mixture with three non-zero BIP columns at 100 \(^\circ\)F and 2800 psia. Both conventional and reduced methods require the same number of iterations. We found that the reduced method becomes faster than the conventional method at around 25 components. They also reported almost a linear relationship in the computational time with the number of components. We found an almost linear relationship when SS steps are included.
However, there is no linear relationship between computational time and number of components when only Newton-Raphson computations are included. Several authors have reported no speed up for reduced methods using the SS steps (Haugen & Beckner, 2011; Okuno et al., 2010a). Therefore, it is important to note that NR computations are not linearly proportional for the conventional methods. We should also note that reduced Gibbs minimization (RGM) is much slower than the reduced methods for the solution of nonlinear equations.

2.10. Implementation

In this section, we show the implementation of the phase equilibrium calculations that we have used.

2.10.1. Reduced Stability Analysis

We now develop the residual functions for Li and Johns reduced stability analysis (Okuno et al., 2010a).

\[ S_i = \ln X_i + \ln \phi_i (\bar{X}) - \ln \left( z_i \phi_i \left( \bar{z} \right) \right) = 0. \]  

(2.179)

This can be written as

\[ X_i = \frac{z_i \phi_i \left( \bar{z} \right)}{\phi_i (x)}. \]  

(2.180)

We also know
Further manipulations are

\[ x_i \sum_{j=1}^{n} X_j - x \sum_{j=1}^{n} X_j = 0. \] (2.182)

Also, reduced parameters can be expressed as

\[ \Theta^j_k = \sum_{i=1}^{n} q_{ik} x_i. \] (2.183)

Combining Eq. (2.182) and Eq. (2.183) give

\[ \Theta^j_k \sum_{i=1}^{n} x_i \sum_{j=1}^{n} X_j - \sum_{i=1}^{n} q_{ik} x_i \sum_{j=1}^{n} X_j = 0. \] (2.184)

Substitution of Eq. (2.181) into Eq. (2.184),

\[ \Theta^j_k \sum_{i=1}^{n} X_j - \sum_{i=1}^{n} q_{ik} X_j = 0 \] (2.185)

\[ \sum_{i=1}^{n} (\Theta^j_k - q_{ik})X_i = 0 \] (2.186)
\[ S_k = \sum_{i=1}^{n} \left( \Theta_k' - q_{ik} \right) \frac{z_i \phi_i(z)}{\phi_i'} = 0. \] (2.187)

where \( q_{ik} = \left\{ \sqrt{A_1}, 2\sqrt{A_1} h_g, -\sqrt{A_2} g, -\sqrt{A_2} h_g^2 g, B_i \right\} \). Eq. (2.187) are the residual functions for the stability analysis. There are five independent parameters defined as in Eq. (2.183). The Jacobian matrix has the following elements:

\[ \frac{\partial S_i}{\partial \Theta_k} = \sum_{j=1}^{n} \frac{D_j}{\phi_j} \left( \delta_{ik} - \frac{\partial \ln \phi_j}{\partial \Theta_k} \left( \Theta_k - q_{ik} \right) \right) = 0. \] (2.188)

The \( \frac{\partial \ln \phi_j}{\partial \Theta_k} \) derivatives can be found in Li and Johns (2006). The residual and the Jacobian matrix are used to update the reduced parameters with Newton-Raphson iteration:

\[ \Delta \Theta_k = \left( \frac{\partial S_i}{\partial \Theta_k} \right)^{-1} S_i. \] (2.189)

### 2.10.2. Conventional Stability Analysis Based on Minimization of Tangent Plane Distance

In this section, we provide the equations to carry out stability analysis by using minimization of the tangent plane distance. Michelsen and Mollerup (2007) derive the Hessian matrix, gradient vector and objective function expressions. The objective function is

\[ tm(X) = 1 + \sum X_i (\ln X_i + \ln \phi_i(X) - d_i - 1) \] (2.190)
where \( X_i \) is a stationary point and \( d_i = \ln z_i + \ln \phi_i(x) \). The gradient vector is

\[
g_i = \frac{\partial \ln \phi_i}{\partial \alpha_i} = \sqrt{X_i} \left( \ln X_i + \ln \phi_i(X) - d_i \right)
\]

(2.191)

where \( \alpha_i = 2\sqrt{X_i} \) and the Hessian matrix is

\[
H_{ij} = \delta_{ij} + \frac{\partial \ln \phi_i}{\partial X_j} + \frac{1}{2} \frac{g_i}{\alpha_i} \delta_{ij}.
\]

(2.192)

The last term cancels because \( g_i = 0 \) at the solution. The fugacity derivative is shown in Appendix B.1.

2.10.3. Conventional Two-Phase Flash Calculations Based on Minimization of Gibbs Energy

We now develop the gradient and the Hessian matrix required for conventional flash calculations based on Minimization of Gibbs energy (Perschke, 1988). Eq. (2.28) gives the minimum Gibbs free energy. We write the residual Gibbs free energy as

\[
G_R = \sum_{j=1}^{N_x} \sum_{i=1}^{N_c} n_{ij} \ln f_{ij}
\]

(2.193)

Considering two phases, the gradient of the objection function is,
\[ \frac{\partial G_K}{\partial n_{i_1}} = \ln f_{i_1} \frac{\partial}{\partial n_{i_1}} \sum_{i=1}^{N_c} n_i + \ln f_{i_2} \frac{\partial}{\partial n_{i_1}} \sum_{i=1}^{N_c} n_i + \ln f_{i_2} \frac{\partial}{\partial n_{i_1}} \sum_{i=1}^{N_c} n_i \] (2.194)

\[ \frac{\partial G_K}{\partial n_{i_1}} = \ln f_{i_1} + \sum_{i=1}^{N_c} n_i \frac{\partial \ln f_{i_1}}{\partial n_{i_1}} - \ln f_{i_2} + \sum_{i=1}^{N_c} n_i \frac{\partial \ln f_{i_2}}{\partial n_{i_1}} \] (2.195)

because

\[ \frac{\partial}{\partial n_{i_1}} \sum_{i=1}^{N_c} n_i = - \frac{\partial}{\partial n_{i_1}} n_i = 1. \] (2.196)

From Gibbs-Duhem equation:

\[ \sum_{i=1}^{N_c} n_i \frac{\partial \ln f_{i_2}}{\partial n_{i_2}} = 0. \] (2.197)

Therefore,

\[ \frac{\partial G_K}{\partial n_{i_1}} = \ln f_{i_1} - \ln f_{i_2}. \] (2.198)

The final expression of the gradient is very simple. Unfortunately, this approach cannot be applied to the reduced methods as the reduced methods cannot benefit from use of the Gibbs-Duhem equation. Moreover, the gradient for the minimization technique is the same as the residual functions for the solution of fugacity equations.
The Hessian matrix is built by taking the second order partial derivative of the objective function with respect to mole numbers. That is,

\[ \mathbf{H} = \frac{\partial}{\partial n_{k_1}} \left( \frac{\partial G}{\partial n_{i_1}} \right) = \frac{\partial \ln f_{i_1}}{\partial n_{i_1}} + \frac{\partial \ln f_{i_2}}{\partial n_{i_2}} \]  

(2.199)

The derivative \( \partial \ln f_{ij} \big/ \partial n_{ij} \) is derived as follows,

\[ \frac{\partial \ln f_{i}^L}{\partial n_{k}^L} = \frac{\partial \ln \phi_{k}^L}{\partial n_{k}^L} + \frac{1}{L \left( \frac{\delta_k}{x_i} - 1 \right)} \]  

(2.200)

The fugacity derivatives are shown in Appendix B.2. The independent parameters are phase mole numbers.

### 2.10.3.1. Line Search Technique

A line search can be used for some iterations to improve the rate of convergence. A line search makes sure Gibbs energy at the new step is lower than that of the previous step. This happens by searching for an optimum step size for a given direction vector that gives the lowest Gibbs energy. Line searches can be applied both to the solution of nonlinear equations technique (Pan & Firoozabadi, 2003) and to the minimization of Gibbs energy technique (Perschke et al., 1989; Trangenstein, 1985).

A line search finds a scalar \( \alpha \), which is multiplied by the step direction in order to reduce or increase the magnitude of the step direction. The parameter \( \alpha=1 \) gives full Newton Raphson iteration, when \( \alpha>1 \) the scheme uses overrelaxation, and when \( \alpha<1 \) the scheme uses underrelaxation.
For the minimization technique, line search is basically a 1D minimization of the function \( f(n_i + \alpha d_i) \) with respect to \( \alpha \). A line search can be solved through several methods such as bisection, Newton’s method, cubic polynomial approximation etc. Perschke (1988) does cubic polynomial approximation (Bertsekas, 1999). Cubic interpolation is initialized by two points a and b where \( a < b \) and \( f(a) < f(b) \). The value of \( \alpha \) is initially very small and is doubled each time until \( f(a) < f(b) \) holds. Then cubic polynomial approximation finds a minimum point.

Gibbs energy calculation requires the multiplication of the fugacity coefficient with composition. Near the solution, Gibbs energy shows a horizontal surface with respect to \( \alpha \). If double precision is used, round off errors will create problems in the code as changes in the Gibbs energy may not be captured by the computer. Therefore, we recommend that quadruple precision be used instead of double precision if the line search method will be used.

We have plotted Gibbs energy with respect to \( \alpha \) for each iteration for oil A shown in Appendix C (Li & Johns, 2006) near critical point (484°F, 1044.41 psia) and Gibbs energy decreases for \( \alpha \in [0, 1] \). Moreover, a full Newton-Raphson step always gives a lower Gibbs energy for the 45 different cases that we have tested. The line search technique requires the comparison of Gibbs energy at different steps, which must be applied for all the tested cases. If the Gibbs energy is lower, the line search is skipped. Therefore, we decided to skip the line search algorithm as we already applied modified Cholesky decomposition.

**2.10.5. Conventional Two-Phase Flash Calculations Based on Solution of Fugacity Equations**

Below, we develop the Jacobian matrix required for the conventional method that is based on solution of nonlinear equations. The residual functions are
\[ R_i = \phi^L_i x_i - \phi^V_{ji} y_j = 0. \] (2.201)

The Jacobian matrix is

\[
J = \frac{\partial R_i}{\partial K_k} = \phi^L_i \left( x_i \frac{\partial \ln \phi^L_i}{\partial K_k} + \frac{\partial x_i}{\partial K_k} \right) - \phi^V_{ji} \left( y_j \frac{\partial \ln \phi^V_{ji}}{\partial K_k} + \frac{\partial y_j}{\partial K_k} \right). \tag{2.202}
\]

where

\[
\frac{\partial \ln \phi_{ji}}{\partial K_k} = \sum_{l=1}^{N 组} \frac{\partial \ln \phi_{jl}}{\partial x_l} \frac{\partial x_l}{\partial K_k}. \tag{2.203}
\]

Moreover, the fugacity derivatives are shown in Appendix B.3

### 2.10.6 Reduced Methods

We have implemented all of the various reduced methods in the literature. They can be found at the following references. Spectral decomposition equations can be found in Pan and Firoozabadi (2003). LJ and OJS equations can be found in Okuno (2009). The equations for the new reduced parameters based on linearization of fugacity expression by using spectral decomposition (improved spectral decomposition) can be found in Nichita and Graciaa (2011), and reduced minimization equations can be found in Yan et al. (2011) and Michelsen et al. (2012). We also introduce new reduced parameters based on Li and Johns (2006) and develop the equations in the next chapter.
Chapter 3

INTRODUCTION OF NEW REDUCED PARAMETERS

In this section, we (Gorucu & Johns, 2011; Gorucu & Johns, 2013b) combine the flash calculations of Nichita and Graciaa (2011) (ISD) with the flash calculations of Li and Johns (2006) and develop new reduced parameters that improve convergence. The improved LJ method developed in this research is denoted as ILJ.

Nichita and Graciaa (2011) showed that fugacity coefficients can be written as a linear combination of six reduced parameters. That is,

\[
\ln \phi_i = \sum_{a=1}^{6} h_a q_{ia}
\]  

(3.1)

For our reduced parameters, the parameters in Eq. (3.1) would be

\[
h_a = \frac{-2\Theta_a}{\Delta B} \ln \left( \frac{Z + \delta_a B}{Z + \delta_a B} \right) \quad \alpha = 1, \ldots, 4
\]  

(3.2)

\[
h_5 = \frac{(Z-1)}{B} \frac{A}{\Delta B^2} \ln \left( \frac{Z + \delta_5 B}{Z + \delta_5 B} \right)
\]  

(3.3)

\[
h_6 = -\ln(Z - B)
\]  

(3.4)

\[
q_{ia} = \left\{ \sqrt{A_{1} \alpha} h_1 g_1, -\sqrt{A_{1} g_1} \right\}, \ldots, \left\{ -\sqrt{A_{1} h_2^2 g_2}, B, 1 \right\}
\]  

(3.5)

Eq. (3.5) is very similar to Eq. (2.159), but the reduced parameters given by Eqs. (3.2)-(3.4) are completely different. In our approach, we embed the LJ reduced parameters defined in Eqs. (2.158) into the new reduced parameters through Eq. (3.2) although they are not used as
reduced parameters. Further, there is no direct relationship to relate \( h_\alpha \) from one phase to another phase. Thus, we solve for the difference in the reduced parameters defined by,

\[
h_{\lambda \alpha} = h_{\lambda \alpha} - h_{\nu \alpha}.
\]

(3.6)

With this approach, K-values are updated easily once the independent parameters are solved (see Eq. (3.10)). The residual functions to be solved are then

\[
e_{\alpha} = h_{\lambda \alpha} - h_{\nu \alpha} - h_{\lambda \alpha}, \quad \alpha = 1, \ldots, 6,
\]

(3.7)

and the Jacobian matrix is given by

\[
J_{\alpha \beta} = \frac{\partial e_{\alpha}}{\partial h_{\lambda \beta}} = \frac{\partial h_{\lambda \alpha}}{\partial h_{\lambda \beta}} - \frac{\partial h_{\nu \alpha}}{\partial h_{\lambda \beta}} - \delta_{\alpha \beta}, \quad \alpha = 1, \ldots, 6 \quad \beta = 1, \ldots, 6
\]

(3.8)

where \( \delta_{\alpha \beta} = 1 \) when \( \alpha = \beta \) or zero otherwise.

We refer to our new algorithm in this dissertation as improved Li and Johns (ILJ). As for all conventional and reduced methods, the procedure for the new reduced method (ILJ) begins by making SS iterations using the conventional approach to get a good initial guess for the Newton-Raphson iterations. Unless otherwise noted, we use a criterion of \( \| L_i - f_i^{\nu} \|_\infty < 10^{-3} \) to switch from SS iterations to NR iterations.

The procedure for the subsequent two-phase Newton-Raphson (NR) iterations is:
1. Calculate the LJ reduced parameters for the liquid phase using Eqs. (2.158), and
   \[ B = \sum_{i=1}^{N_i} B_i x_i. \]

2. Calculate the LJ reduced parameters for the vapor phase using the linear relation,
   \[ \Theta_{V\alpha} = \frac{\Theta_{\alpha\alpha} - L\Theta_{L\alpha}}{1 - L} \]
   \[ B_V = \frac{B_z - L B_L}{1 - L} \]  (3.9)
   where \( z \) indicates that the overall composition \( z_i \) is used in the calculation of that parameter.

3. Calculate \( A_L \) and \( A_V \) from Eq. (2.156).

4. Calculate compressibility factors \( Z_L \) and \( Z_V \) by solving the cubic EOS equation. We used Peng and Robinson EOS (Peng & Robinson, 1978).

5. Calculate \( h_{L\alpha} \) and \( h_{V\alpha} \) from Eqs. (3.2)-(3.4). Also, calculate \( h_{\alpha\alpha} \) from Eq. (3.6).

6. Update the logarithm of the component fugacity coefficients for each phase by Eq. (3.1).

7. Calculate the Jacobian matrix.

8. Solve for \( h_{\alpha\alpha} \) using Newton-Raphson iteration.

9. Calculate K-values using,
   \[ \ln K_i = \ln \frac{\phi_L}{\phi_V} = \sum_{\alpha=1}^{\gamma} h_{\alpha\alpha} q_{i\alpha} \]  (3.10)

10. Solve the Rachford-Rice equations to update the equilibrium phase compositions and liquid mole fraction.
11. Check for NR convergence when \( \| \lnf_L - \lnf_Y \|_\infty < 10^{-10} \). Other criteria and tolerances can be used as needed. If not converged, go to step 1).

The above procedure is extended to perform a stability analysis and also to three phase-flash calculations in Chapter 5. The Rachford-Rice procedure for multiphase flash calculations from Okuno et al. (2010c) is used for robustness and speed for all conventional and reduced methods.

The elements of the Jacobian matrix are given by

\[
\frac{\partial h_{i,j}}{\partial h_{\alpha,\beta}} = \sum_{\gamma=1}^{5} \frac{\partial h_{i,j}}{\partial Q_{\gamma,j}} \frac{\partial Q_{\gamma,j}}{\partial h_{\alpha,\beta}}, \quad \alpha, \beta = 1,\ldots, 6; \quad \gamma = 1,\ldots, 5; \quad \text{and } j = L, V
\] (3.11)

The derivatives on the right side of Eq. (3.11) are determined as,

\[
\frac{\partial h_{i,j}}{\partial Q_{\gamma,j}} = \left( \frac{\partial h_{i,j}}{\partial Q_{\gamma,j}} \right)_{Z_i} + \left( \frac{\partial h_{i,j}}{\partial Z_j} \right) \frac{\partial Z_j}{\partial Q_{\gamma,j}}
\] (3.12)

For liquid,

\[
\frac{\partial Q_{\gamma,j}}{\partial h_{\alpha,\beta}} = \sum_{\tau=1}^{j} \theta_{\gamma,\tau} \frac{\partial x_{i}}{\partial h_{\alpha,\beta}}
\] (3.13)

and for vapor,
\[
\frac{\partial Q_{\gamma}}{\partial h_{\chi\beta}} = \sum_{i=1}^{N} \theta_{i\gamma} \frac{\partial y_i}{\partial h_{\chi\beta}}
\]

where \( \theta_{i\gamma} = \left\{ \sqrt{A_i}, \sqrt{A_i h_i}, \sqrt{A_i h_i^2}, \sqrt{A_i g_i}, B_i \right\} \).

The analytical expression for Eq. (3.12) is:

\[
\left( \frac{\partial h_{a_j}}{\partial Q_{\gamma\gamma}} \right)_{Z_j} = \begin{cases} 
\frac{h_{a_j}}{Q_{\gamma\gamma}} \delta_{a\gamma} & \text{for } \alpha = 1, \ldots, 4; \gamma = 1, \ldots, 4 \\
\frac{\partial A}{\partial Q_{\gamma\gamma}} \ln \left( \frac{Z_j + \delta_1 B_j}{Z_j + \delta_2 B_j} \right) \left( \Delta B_j^2 \right) & \text{for } \alpha = 5; \gamma = 1, \ldots, 4 \\
-\frac{1}{B_j} \left( h_{a_j} + 2Q_{a_j} \frac{Z_j}{\pi_j} \right) & \text{for } \alpha = 1, \ldots, 4; \gamma = 5 \\
\frac{1}{B_j^2} \left( -2h_{a_j} B_j - 1 + Z_j \left( 1 + \frac{A_j}{\pi_j} \right) \right) & \text{for } \alpha = 5; \gamma = 5 \\
\frac{1}{Z_j - B_j} & \text{for } \alpha = 6; \gamma = 5 \\
0 & \text{otherwise}
\end{cases}
\]  

(3.15)

\[
\left( \frac{\partial h_{a_j}}{\partial Z_j} \right)_{Q_j} = \begin{cases} 
\frac{2Q_{a_j}}{\pi_j} & \text{for } \alpha = 1, \ldots, 4 \\
\frac{1}{B_j} \left( 1 - \frac{A_j}{\pi_j} \right) & \text{for } \alpha = 5 \\
-\frac{1}{Z_j - B_j} & \text{for } \alpha = 6
\end{cases}
\]  

(3.16)

where \( \pi_j = (Z_j + \delta_1 B_j)(Z_j + \delta_2 B_j) \).
\[
\frac{\partial Z_j}{\partial Q_{r_j}} = \begin{cases} 
\frac{\partial Z_j}{\partial A_j} \frac{\partial A_j}{\partial Q_{r_j}} & \text{for } y = 1, \ldots, 4 \\
\frac{\partial Z_j}{\partial B_j} = \frac{1}{\left(\frac{\partial F_j}{\partial Z_j}\right)_{Q_i}} \left[-(\delta_1 + \delta_2 - 1)Z_j^2 - 
\left[2B_j\delta_1\delta_2 - (\delta_1 + \delta_2)(2B_j + 1)Z_j + A_j\delta_1\delta_2(3B_j + 2)B_j\right]\right] & \text{for } y = 5
\end{cases}
\]

(3.17)

where

\[
\frac{\partial Z_j}{\partial A_j} = \frac{Z_j - B_j}{\left(\frac{\partial F_j}{\partial Z_j}\right)_{Q_i}}, \quad \frac{\partial A_j}{\partial Q_{r_j}} = \left[2Q_{i1}, 4Q_{i2}, -2Q_{i3}, -2Q_{i4}\right]
\]

(3.18)

and

\[
\left(\frac{\partial F_j}{\partial Z_j}\right)_{Q_i} = 3Z_j^2 + 2\left[(\delta_1 + \delta_2 - 1)B_j - 1\right]Z_j + \left[A_j + \delta_1\delta_2B_j^2 - (\delta_1 + \delta_2)B_j(B_j + 1)\right].
\]

(3.19)

The expressions for Eqs. (3.13) and (3.14) are

\[
\frac{\partial x_i}{\partial h_\beta} = -d_i \left[\frac{\partial K_i}{\partial h_\beta} V + \frac{\partial V}{\partial h_\beta}(K_i - 1)\right]
\]

(3.20)

and

\[
\frac{\partial y_i}{\partial h_\beta} = d_i \left[\frac{\partial K_i}{\partial h_\beta}(1 - V) - \frac{\partial V}{\partial h_\beta} K_i(K_i - 1)\right]
\]

(3.21)
where

\[
\frac{\partial V}{\partial h_\beta} = \sum_{i=1}^{N_i} d_i \frac{\partial K_i}{\partial h_\beta} \sum_{i=1}^{N_i} d_i (K_i - 1)^2
\]

(3.22)

\[
\frac{\partial K_i}{\partial h_\beta} = K_i q_i \beta
\]

(3.23)

\[
d_i = \frac{z_i}{(1 + V(K_i - 1))^2}
\]

(3.24)

3.1. Results

In this section, we compare our reduced method (ILJ) to two different reduced methods (LJ and OJS) and the conventional method using minimization of Gibbs energy (MG). MG is used for the conventional method since it is faster than solving a system of nonlinear algebraic (fugacity) equations.

Five different fluids are used for the comparison that provide a good range in the number of components, namely oil A (seven components), B (12 components) and C (15 components) from Li and Johns (2006); and mixture 1 (ten components) and mixture 2 (11 components) from Firoozabadi and Pan (2002). These fluid properties are shown in Appendix C. Moreover, we split the heaviest pseudo-component of oil C into 20 identical pseudo-components to obtain a 34 component mixture (C34). This new fluid (C34) gives the same flash calculation results as for oil C, but allows for an estimate of the speed up for a larger number of components.

These five fluids together with oil C34 are flashed at a variety of different temperatures and pressures as shown in Table 3.1. These conditions were chosen to sample the composition
space near and far from the critical region as is evidenced by the calculation of the tie-line length (TLL), where \( TLL = \sqrt{\sum_{i=1}^{N_C} (y_i - x_i)^2} \). Table 3.1 also gives the variation in the overall CO\(_2\) mole percentage for mixture 2.

### 3.2. Convergence Behavior

Figure 3.1 shows the residuals for each NR iteration for oil A near the critical region (484°F, 1044.41 psia). The residuals for the LJ reduced method increase for the first NR iteration owing to the material balance error discussed in the previous section. That is, the equilibrium phase compositions are not consistent with the fugacity coefficients and overall material balances. This material balance error eventually decays to zero as iterations converge.

The other three methods (OJS, ILJ, and MG) do not have this problem and converge in fewer iterations as shown in Figure 3.1. Less iterations are required with these methods compared to LJ for all 45 flash calculations in Table 3.1.

Figure 3.2 shows the number of iterations required to achieve convergence for the 45 flash calculations as a function of the length of the tie-line. The tie-line length approaches zero at the critical point and therefore gives a good indication of how far the tie-line is from the critical locus. As shown, the number of iterations increases substantially as the flash approaches a critical point. In general, the number of iterations is fairly independent of the number of components and hence the type of oil. Figure 3.2 also shows that LJ converges in one more iteration away from the critical region and in two more iterations near the critical region with respect to the other methods. The other methods that we have tested (MG, ILJ, OJS) converge in nearly the same number of iterations. The fact that ILJ and OJS converge in the same number of iterations shows
that the new reduced parameters in this research (ILJ) successfully eliminate the need for additional SS steps implemented in OJS.

### 3.3. Robustness

The primary advantage of the ILJ method compared to the other methods is that it is more robust, at least for the 45 flash calculations studied in this section. Both LJ and OJS fail more often for flash calculations near the phase envelope and critical region. For example, we repeated our flash calculations using less stringent convergence criterion of 0.1 and 0.01 for switching from the SS iterations to NR iterations (instead of the typical value of 0.001 used in simulation). All 45 flash calculations converged when the SS to NR switch criterion is 0.001 and 0.01. When the criterion is 0.1, MG and ILJ failed for only two and one cases, respectively, near the phase envelope, while LJ and OJS failed for five and four cases near the critical region and phase envelope, respectively as shown in Table 3.2. Table 3.2 also shows the number of iterations executed if convergence is achieved. The next chapter will examine in more detail and with many more flash calculations the robustness of these new reduced parameters, and all other conventional and reduced methods.

### 3.4. Computational Time

An important factor that affects overall computational time is the computational time per iteration. Figure 3.3 compares the computational time required per iteration for the reduced algorithms for all 53 flash calculations in Table 3.1, where oil C34 is now used to provide additional flash calculations for 34 components at the same conditions as oil C. The compositions from Figs. 3.3 to 3.8 are arranged from left to right in order of increasing number of components (oil A is a seven-component model, while oil C34 is thirty-four components). The
flash calculation times are computed with an Intel Xeon CPU with 3.06 GHz and 12 GB RAM using an optimized Intel Fortran compiler. Every flash calculation is repeated 100,000 times to reduce the uncertainty in computational time per iteration.

Figure 3.3 shows that LJ is the fastest method per NR iteration, just slightly faster than OJS. This occurs because of the additional SS step included in OJS to reconcile the material balance error. ILJ is slightly slower than both OJS and LJ, but is faster than the conventional MG method even for seven components. These results are similar to the findings of Okuno et al. (2010b). One should note that the Jacobian matrix for ILJ, LJ, and OJS is always of rank six, while the Hessian matrix for MG is of a rank equal to the number of components. Therefore, the construction of the Hessian matrix and the solution of the system of equations for MG becomes more time consuming as the number of components increases. As shown in Figure 3.3, the computational times for the reduced methods are significantly less sensitive to the number of components.

The total average NR computational time for all flash calculations to convergence is shown in Figure 3.4. The convergence criterion for all methods is identical as discussed previously. The results show that the OJS reduced method per flash is slightly faster than the LJ method, largely because LJ requires more iterations for convergence. Although ILJ eliminates the SS step required in OJS, it is still somewhat slower than OJS because more time is spent in the construction of the Jacobian matrix. Moreover, it should be noted that even though the Jacobian matrix for ILJ is six, the reference phase mole fraction is another independent parameter that is solved using the Rachford-Rice equations. All of these reduced methods are substantially faster than the conventional MG method especially as the number of components increases.

Figure 3.4 also shows that the computational time for NR calculations per flash is smaller for oil B (12 components) than for mixture 1 (10 components). The reason is that oil B is not often tested near the critical region and hence converges in fewer iterations.
Figure 3.5 shows the total computational time per flash calculation including the SS steps. SS steps dominate the computational time especially for the reduced methods. One of the reasons for the expensive SS time in these cases is that most flash calculations are performed near the critical region, and the initial guesses for the K-values in these stand-alone calculations are far from the converged values. For these calculations, four to five SS iterations were needed away from the critical region, while up to 100 SS iterations were required near the critical region (33 SS iterations on average for all flash calculations). In general, NR iterations will dominate more when these flash calculations are embedded into a compositional simulator.

As the reduced methods speed up only the NR iterations, the ratio of the total flash execution time to the SS execution time is a good indicator of how fast the reduced methods are. Figure 3.6 gives the ratio of the total flash execution time to the SS execution time. As this ratio increases the importance of the NR iterations increase. The figure shows that all reduced methods become much less sensitive to the NR iterations as the number of components increases, while the conventional MG method becomes more dependent on the NR iterations.

SS computations take less time compared to NR iterations for oil B. The reason is that most flash calculations for oil B are further from the critical region. For example, the average number of SS iterations per flash for oil B is 14 whereas this number is about 35 for the other fluids.

Figure 3.7 shows the speed-up of the NR iterations using reduced methods compared to the conventional (MG) NR computations. OJS, LJ, and ILJ are 16, 13, and 9 times faster using oil C34, respectively. The speed ups for OJS, LJ, and ILJ are 4.9, 4.2, and 3.5 for oil C (15 components), respectively. The results are consistent with those of Okuno et al. (2010a) where OJS has a speed-up of 10 to 11 compared to MG for 35 components in their simulations.

The speed up for the total flash calculation time for NR and SS iterations using reduced methods is given in Figure 3.8. We use the conventional SS steps for all methods. The three
reduced methods are about 26-28% faster than MG for oil C (15 components), and about 49-51% faster for oil C34. Reduced methods give greater speed-ups for oil B (12 components) than for oil C because oil B is less dominated by the SS iterations. Reduced methods are 36-45% faster than MG for oil B.

3.5. Conclusions

We extended the approach by Nichita and Graciaa to develop new reduced parameters based on the Li and Johns two-parameter BIP formulation. The main conclusions are:

1. The improved LJ method (ILJ) requires fewer iterations than the standard LJ method.
2. Rachford-Rice iteration is performed with our new reduced parameters so that it is easy to implement in existing compositional codes.
3. OJS is the fastest method tested, but ILJ is nearly as fast.
4. The new reduced parameters (ILJ) are more robust than the flash calculations using MG or OJS for the 45 flash calculations tested (based on five different fluids).

The next chapter examines robustness in a more systematic way for all published reduced and conventional flash methods.
Table 3.1. Temperature and pressure values used in flash calculations.

<table>
<thead>
<tr>
<th>Case #</th>
<th>Mixture 1</th>
<th>Mixture 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(F)</td>
<td>P(psi)</td>
<td>TLL</td>
</tr>
<tr>
<td>1</td>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>1000</td>
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<td>4</td>
<td>450</td>
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<td>9</td>
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<tr>
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<td>1187</td>
</tr>
<tr>
<td>13</td>
<td>568</td>
<td>1163</td>
</tr>
</tbody>
</table>

Table 3.2. Flash calculations that fail from the 45 tested. The number of iterations are shown if converged.

<table>
<thead>
<tr>
<th>Case #</th>
<th>Fluid</th>
<th>MG</th>
<th>OJS</th>
<th>LJ</th>
<th>ILJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Mixture 2: 520 F, 1670 psi, 25% CO₂</td>
<td>Diverges</td>
<td>Diverges</td>
<td>Diverges</td>
<td>8</td>
</tr>
<tr>
<td>30</td>
<td>Oil A: 484 F, 1044 psi</td>
<td>Diverges</td>
<td>Diverges</td>
<td>Diverges</td>
<td>10</td>
</tr>
<tr>
<td>31</td>
<td>Oil A: 484 F 1044.41 psi</td>
<td>Diverges</td>
<td>Diverges</td>
<td>Diverges</td>
<td>13</td>
</tr>
<tr>
<td>36</td>
<td>Oil B: 200 F 5000 psi</td>
<td>Diverges</td>
<td>Diverges</td>
<td>Diverges</td>
<td>5</td>
</tr>
<tr>
<td>37</td>
<td>Oil B: 180 F 5500 psi</td>
<td>Diverges</td>
<td>Diverges</td>
<td>Diverges</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.1. Convergence of flash calculations for oil A near the critical point for four different methods. LJ (Li & Johns, 2006), OJS (Okuno et al., 2010a), MG (Perschke et al., 1989).

Figure 3.2. Number of iterations needed for convergence for three different methods.
Figure 3.3. Comparison of computational time per iteration for all fluids for four different methods. The x-axis is in the order of increasing number of components from oil A (7 components) to oil C34 (34 components). Computational speed is averaged per flash for each fluid based on 100,000 repeated flash calculations.

Figure 3.4. Comparison of NR computational time per flash for four different methods, and for all fluids. Computational speed is averaged for every fluid based on 100,000 repeated flash calculations.
Figure 3.5. Comparison of total computational time per flash for four different methods, and for all fluids. Computation of the SS steps dominates for the reduced methods. This shows NR computations are not costly for the reduced methods.

Figure 3.6. Ratio of total flash execution time to SS execution time for different reduced methods, and for all fluids. The figure shows reduced methods are dominated by the SS calculations.
Figure 3.7. NR speed-up of three reduced methods (LJ, ILJ, and OJS) with respect to MG for six different fluids.

Figure 3.8. Total flash calculation speed-up of three reduced methods (LJ, ILJ, and OJS) with respect to MG for six different fluids.
Chapter 4

COMPARISON OF FLASH CALCULATIONS

In this chapter, we, (Gorucu & Johns, 2013a), compare five different reduced methods and two conventional methods using six different fluids, namely oil A, B and C from (Li & Johns, 2006); and mixtures 1 and 2 from Firoozabadi and Pan (2002). Moreover, we divided the last component of Oil C into 20 components of the same composition. We call this oil, C34, as it has 34 components as described in Chapter 3. Table 3.1 shows the temperature and pressure conditions for 45 different flash calculations. More explanations on the fluids and flash calculations can be found in Chapter 3.

4.1. Convergence Behavior

Figure 4.1 shows the residuals for each NR iteration, for example, oil A near the critical region (484°F, 1044.41 psia). The residuals for the standard SD and LJ reduced methods increase for the first NR iteration owing to the material balance error discussed in the previous section. That is, the equilibrium phase compositions are not consistent with the fugacity coefficients and overall material balances. This material balance error eventually decays to zero as iterations converge.

The other three reduced methods (OJS, ILJ, and ISD) do not have this problem and converge in fewer iterations as shown in Figure 4.1. This is also true for all 45 flash calculations in Table 3.1.

Figure 4.2 shows the number of iterations required to achieve convergence for the 45 flash calculations as a function of the length of the tie line, i.e. \( \sqrt{\sum_{i=1}^{N_c}(y_i-x_i)^2} \). The tie-line length approaches zero at the critical point and therefore gives a good indication of how far the tie-line is from the critical locus. As shown, the number of iterations increases substantially as the
flash approaches a critical point. In general, the number of iterations is fairly independent of the number of eigenvalues used in the SD method, except for one flash that did not converge. The phase behavior changes only slightly in the SD approach when eigenvalues greater than 0.001 are used (denoted SD>0.001) compared to when all eigenvalues are used (denoted SD (All)). The phase behavior change is more significant when only eigenvalues greater than 0.07 are retained, as was suggested by Pan and Tchelepi (2010). Table 4.1 shows the number of eigenvalues used for each fluid based on these criteria. The LJ method always has six reduced parameters and does not have the problem of selecting the number of eigenvalues to retain.

Near the critical region, the ILJ, OJS, and ISD converge in two fewer iterations. Slight differences in convergence between ILJ and ISD may result from slightly different fluid characterizations owing to the eigenvalue approximations.

4.2. Computational Time

Another factor that affects overall computational time is the computational time per iteration. Figure 4.3 compares the computational time required per iteration for the reduced algorithms for all 45 flash calculations in Table 3.1, and for 8 flash calculations for Oil C34. The compositions in the figure are arranged from left to right in order of increasing number of components (oil A is a seven-component model, while oil C34 is 34 components). The flash calculation times are computed with an Intel Xeon CPU with 3.06 GHz and 12 GB RAM.

Figure 4.3 shows that LJ is the fastest method per iteration. ILJ is slower than OJS. Even though ILJ does not require an additional SS step, it is slower than OJS because it requires more time to construct the Jacobian matrix. MG, FG, ISD(All), and SD(All) take significantly more computational time as the number of components increases.
Figure 4.4 shows that OJS is the fastest method out of all of the reduced and conventional methods for an average flash calculation. The flash calculation computation times are averaged for each fluid, but OJS is the fastest method for all the fluids. Although LJ is the fastest method per iteration, OJS is slightly faster for a flash calculation.

Newton Raphson computational time for OJS is so fast that the greatest majority of the time per flash is consumed by SS iterations. All of the flash calculations start with conventional SS($10^3$) and switch to NR unless otherwise stated. Figure 4.5 shows that almost all of the time is spent on the SS iterations for reduced methods. However, NR iterations consume more time with the conventional methods.

We also compared the methods in terms of the ratio of total flash calculation time to its SS iterations cost. Figure 4.6 shows that NR iterations of OJS consume much less time than its SS iterations per flash. However, this ratio increases for the other methods. The ratio for OJS decreases as the number of components increases.

We minimized the number of operations required in our codes and used the optimized Intel Fortran compiler embedded in Microsoft Visual Studio. Because the number of reduced parameters depends on the number of eigenvalues retained, the SD approach also requires computer code to allow for an arbitrary number of eigenvalues. Thus, the code for SD requires several inner and outer loops, which slows its efficiency. Moreover, SD uses more variable operations than LJ. Therefore, even though SD and LJ require a similar number of operations, SD and its variant (ISD) becomes slower. Since LJ, ILJ and OJS have fixed number of independent variables, optimized compilers can take advantage of these algorithms.

Although modern compilers include complex program analysis and optimization techniques, they must still be conservative and generate code that is correct for all possible values of program inputs. ILJ, LJ and OJS methods replace some variables (whose values are unknown at compile time) with static constants (i.e., values fixed at compile time), which enables better optimization
of the target code. The efficiency of various compiler optimizations such as loop unrolling and vectorization depend on this factor, i.e. having static constants.

In order to demonstrate that the computational time difference between LJ and SD is due to compiler optimization, we wrote a generalized algorithm that accepts both LJ and SD parameters. We denote the results from the generalized code as GLJ or GSD depending on which parameters are used. Both LJ and SD parameters go through the exactly same code, except for some parts of the code, we used “if else” clauses to handle LJ and SD separately to minimize the number of calculations. Table 4.2 shows the computational time for LJ, GSD and GLJ. The row named as ‘Same’ denotes the section of the code that is exactly the same between the generalized code and LJ e.g. compressibility factor calculations or fugacity calculations. Computational time for this section is identical for all codes. However, the ‘generalized’ section that is written to accept any number of independent parameters slows down both for GLJ and GSD. Therefore, we conclude that the computational time difference between LJ and SD is due to the fact that SD is written to accept an undetermined number of parameters. Moreover, we converted the generalized code so that it accepts only four SD reduced parameters, which is denoted as GFSD in Table 4.3. As the number of parameters for the generalized code is fixed, GFSD shows similar computational time as LJ.

Haugen and Beckner (2013) stated that FG and SD have the same speed when six eigenvalues are retained for a fluid with nine components. We repeat Haugen and Beckner’s calculations using the FG and SD method for the SPE3 (Kenyon & Alda Behie, 1987) fluid at 100°F and 2800 psi. In their case, the reduced Jacobian size is of rank 8. Therefore, it is expected that SD becomes faster than FG only when the reduced Jacobian matrix size is smaller than that of FG. The flash calculations begin with Wilson’s correlation to estimate K-values. SPE3 is a nine component fluid but we divided the last component into pseudo-components to obtain more components for comparison of computational times. We retain six eigenvalues. Figure 4.8 shows the
computational speed for a flash that includes the SS iterations. Our results are very similar to Haugen and Beckner (2011). FG and SD show the same speed at 9 components and SD becomes faster than FG only after about 10 components.

Yan et al. (2011) and Michelsen et al. (2012, 2013) implemented the Nichita and Garcia’s reduced method within a Gibbs energy minimization framework, which we label RMG here. They concluded that all reduced methods are not worthwhile based on their reported computational times. Yan et al. (2011), for example, compared RMG to the MG conventional method and reported no speed up until more than 20 components are used.

We reproduced the flash calculations of Yan et al. (2011) and also those of Michelsen et al. (2012) for the SPE3 mixture with three non-zero BIP columns for a flash calculation near the critical region (see Figure 4.9). For comparison we added the ILJ method. As shown, the total NR computational time per flash for RMG is only faster than MG when more than 23 components are used, which is very similar to the results of Yan et al. and Michelsen et al. The ILJ method however is always much faster than either MG or RMG independent of the number of components. The comparison in Figure 4.9 demonstrates that the RMG method using spectral decomposition is much slower than the method of Li and Johns, and its offshoot methods.

Michelsen et al. also find little speed-up at a large number of components. Flash calculations show significantly less speed-up when SS iterations are included. Especially near the critical region, thousands of SS iterations may be needed before switching to NR. Therefore, the speed-up decreases when SS iterations are included. However, LJ-type reduced methods are significantly faster than the conventional methods in NR iterations. SS iterations are generally less important during IMPEC reservoir simulation since typically the solution in the prior time step for a given grid block can be used.

The explanation for the slow computational times of the RMG method is that its implementation first requires the calculation of the conventional Hessian matrix and gradient
vector as would be done for the MG approach alone. Additional operations are required in the RMG method to compute the elements in the reduced Hessian matrix and gradient vector. Speed-up with RMG compared to MG only occurs therefore when the number of components is large enough that the increased computational time for the construction of the elements of the reduced Hessian matrix is outweighed by the decrease in computational time that results from a smaller rank reduced Hessian matrix. Our results show this takes a substantial number of components to achieve, which limits using reduced methods in a MG framework.

4.3. Phase Behavior Accuracy

As shown in Figure 4.7, phase mole fraction error is generally less than 1% for the reduced methods. LJ and ILJ are exactly the same since they use the same BIPs ($h_i$ and $g_i$ parameters are the same).

The mole fraction of liquid shows a much larger error as the number of eigenvalues used are reduced compared to the case when all eigenvalues are retained. There is no generally accepted method for determining how many eigenvalues to keep with the SD or ISD approach. With the LJ and ILJ methods, the $h_i$ and $g_i$ parameters should be tuned to the PVT data for best accuracy. We examine the accuracy of fluid characterization using the LJ method in Chapter 6.

4.4. Robustness

The primary advantage of the ILJ method compared to the other conventional and reduced methods is that it is more robust. We decided to do a systematic study of robustness of the reduced methods for oil A. We performed 416, 268, 692, 475, and 425 flash calculations near the phase envelope of oil A, B, C, mixture 1 and 2 (see Figure 4.11), where the overall compositions
were determined using an unbiased approach. We began at 100°F and 100 psia, and increased pressure by 0.01 psi increments. Every flash calculation starts with Wilson’s correlation of the K-values. We stored the largest pressure that converged to a non-trivial two-phase solution using only SS iterations with a convergence criterion of $10^{-10}$. We then selected the overall composition corresponding to the pressure within the two-phase region as the test composition for robustness. We then increased the temperature by 1 °F and decreased pressure by 10 psia and repeated the procedure to find additional test compositions. These steps were repeated until a high temperature was reached and a total of 2276 overall test compositions were identified, several of which were very close to the critical point. None of the flash results with SS give a trivial solution.

We used these SS flash calculations to test if the conventional and reduced methods (LJ, ILJ, MG, FG and OJS) that use NR iterations would also converge to the same phase compositions. The flash calculations for these methods also used SS iterations initially, but to test the radius of convergence we switched from SS to NR iterations at various switch criteria of $10^{-4}$, $10^{-3}$, $10^{-2}$, and $10^{-1}$. The initial $K_i$ values for every test were based on Wilson’s correlation.

Figure 4.12 to Figure 4.16 show the percentage of failed flash calculations for oil A, B, C, and mixture 1 and 2. For mixture 1, we also tested ISD(All) as the BIPs are the same. Expectedly, as the switch criterion is relaxed, more flash calculations fail for every algorithm. However, ILJ stands out as the most robust technique for these fluids as it fails for many fewer cases. Table 4.3 shows the number of flash calculations that failed for every fluid for oil A. We wanted to see where the flash calculations start to fail. Figure 4.17 to Figure 4.20 show the failed flash calculations for oil A at different switch criterion when ILJ is used. Figure 4.21 to Figure 4.24 show the failed flash calculations for oil A at different switch criterion when MG is used. Both methods start to fail near the critical region and the failure zone grows as the switch criterion is relaxed. However, ILJ fails in a smaller region than MG.
4.5. Conclusions

We compared all reduced and conventional two-phase flash calculation methods published to date – MG, FG, RMG, SD, ISD, LJ, ILJ. The main conclusions are:

- The improved LJ method (ILJ) requires fewer iterations than the standard LJ method based on the fluids tested.
- Flash calculations with the improved LJ reduced parameters are significantly more robust than any other algorithm tested based on thousands of flash calculations and the fluids tested.
- The improved spectral decomposition method (ISD) of Nichita & Graciaa (2011) gave similar computational speed improvements compared to the standard SD method.
- Neglecting eigenvalues less than 0.07 in the SD and ISD approach can result in significantly less phase behavior accuracy than if all eigenvalues greater than 0.001 are retained.
- OJS has the fastest computational time per iteration, it is the fastest method based on the example fluids tested.
- The results by Haugen and Beckner (2011, 2013), which show that the SD approach is slower than previously thought using the algebraic fugacity method are confirmed. The reduced method of Li and Johns is much faster.
- The results by Michelsen et al. (2012) and Yan et al. (2011) confirm that the use of reduced methods using Gibbs minimization is not efficient.
Table 4.1. Number of eigenvalues used for various fluids based on the eigenvalue magnitude.

<table>
<thead>
<tr>
<th></th>
<th>Mixture 1</th>
<th>Mixture 2</th>
<th>Oil A</th>
<th>Oil B</th>
<th>Oil C</th>
<th>Oil C34</th>
</tr>
</thead>
<tbody>
<tr>
<td>All ( \lambda )'s</td>
<td>10</td>
<td>11</td>
<td>7</td>
<td>12</td>
<td>15</td>
<td>34</td>
</tr>
<tr>
<td>(</td>
<td>\lambda</td>
<td>&gt; 0.001 )</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>(</td>
<td>\lambda</td>
<td>&gt; 0.07 )</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.2. Computational time in seconds for a NR iteration for oil C (15 components) at 780 °F and 1725 psia. GSD and GLJ are produced from the same generalized code. Only the four most significant eigenvalues are retained for GSD. GFSD is a generalized SD code, which accepts four eigenvalues only. ‘Same’ shows the computational time where LJ and generalized codes are identical.

<table>
<thead>
<tr>
<th></th>
<th>LJ</th>
<th>GSD</th>
<th>GLJ</th>
<th>GFSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generalized</td>
<td>3.21E-06</td>
<td>9.08E-06</td>
<td>6.91E-06</td>
<td>3.90E-06</td>
</tr>
<tr>
<td>Same</td>
<td>3.25E-06</td>
<td>3.57E-06</td>
<td>4.01E-06</td>
<td>3.12E-06</td>
</tr>
<tr>
<td>NR iteration</td>
<td>6.46E-06</td>
<td>1.26E-05</td>
<td>1.09E-05</td>
<td>7.02E-06</td>
</tr>
</tbody>
</table>

Table 4.3. Number of flash calculations from a total of 416 that diverge near the phase envelope of oil A.

<table>
<thead>
<tr>
<th>Switch Criterion</th>
<th>SS ((10^3))</th>
<th>FG</th>
<th>MG</th>
<th>LJ</th>
<th>ILJ</th>
<th>OJS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS ((10^3))</td>
<td>0</td>
<td>16</td>
<td>51</td>
<td>50</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>SS ((10^2))</td>
<td>0</td>
<td>48</td>
<td>97</td>
<td>139</td>
<td>11</td>
<td>125</td>
</tr>
<tr>
<td>SS ((10^1))</td>
<td>0</td>
<td>212</td>
<td>159</td>
<td>225</td>
<td>17</td>
<td>150</td>
</tr>
</tbody>
</table>
Figure 4.1. Convergence of flash calculations for oil A near the critical point for four different methods. LJ: (Li & Johns, 2006), OJS (Okuno et al., 2010a)

Figure 4.2. Number of iterations needed for convergence for the two standard reduced methods. SD>0.001 denotes only eigenvalues greater than 0.001 were retained.
Figure 4.3. Comparison of computational time per iteration for all six fluids.

Figure 4.4. Comparison of NR computational time per flash for all six fluids.
Figure 4.5. Comparison of total computational time per flash for all six fluids including the SS iterations. Computation of the SS steps dominates when the rank of the Jacobian/Hessian matrix is smaller.

Figure 4.6. Ratio of total flash execution time / SS execution time for different reduced methods. The figure shows OJS has the lowest ratio (close to one).
Figure 4.7. Speed-up compared to SS>0.001

Figure 4.8. Computational time for a flash calculation for SPE3 fluid at 100°F and 2800°psia for FG, SD(6), and ILJ. SD(6) retains six eigenvalues.
Figure 4.9. Computational time for a flash calculation for SPE3 for RMG, MG, and ILJ near the critical region.

Figure 4.10. Average error in liquid phase mole fractions with the reduced methods compared to the original fluid characterization with all eigenvalues retained. The improved methods yield identical accuracy to the standard methods.
Figure 4.11. The last flash calculations that converged to nontrivial solution below the phase envelope.

Figure 4.12. Percentage of failed flash calculations for several algorithms for oil A.
Figure 4.13. Percentage of failed flash calculations for several algorithms for oil B.

Figure 4.14. Percentage of failed flash calculations for several algorithms for oil C.
Figure 4.15. Percentage of failed flash calculations for several algorithms for Pan 1.

Figure 4.16. Percentage of failed flash calculations for several algorithms for Pan 2.
Figure 4.17. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for ILJ with $10^{-4}$ convergence criterion.

Figure 4.18. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for ILJ with $10^{-3}$ convergence criterion.
Figure 4.19. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for ILJ with $10^{-2}$ convergence criterion.

Figure 4.20. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for ILJ with $10^{-1}$ convergence criterion.
Figure 4.21. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for MG with $10^{-4}$ convergence criterion.

Figure 4.22. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for MG with $10^{-3}$ convergence criterion.
Figure 4.23. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for MG with $10^{-2}$ convergence criterion.

Figure 4.24. Phase envelope for Oil A. Red circle shows the critical point. Green triangles show the failed flash calculations for MG with $10^{-3}$ convergence criterion.
Chapter 5

IMPLEMENTATION OF NEW REDUCED PARAMETERS TO STABILITY ANALYSIS AND THREE-PHASE FLASH CALCULATIONS

In the previous chapters, we introduced new reduced parameters, applied the new reduced parameters to two-phase flash calculations and compared the new reduced flash calculations with several conventional and reduced methods. In this chapter, we apply our new reduced parameters to stability analyses and three-phase flash calculations. We also compare our multi-phase equilibrium calculations with those of Okuno et al. (2010a). Our results suggest that our two-phase flash calculations show remarkable robustness in the three-phase region. Moreover, our three-phase flash calculations are significantly more robust than those of Okuno et al. (2010a).

5.1. Introduction

Compositional reservoir simulations are important to model gas injection, or condensate gas/volatile oil production. Phase equilibrium calculations, which are repeated in compositional reservoir simulations, can be excessively time consuming as the number of components and phases increases.

A typical oil reservoir consists of thousands of components, most of which are hydrocarbon components. As mentioned earlier in Chapter 2, however, it is not practical to identify all of these components during laboratory conditions. Further, retaining a large number of components increases the computational time of phase equilibrium calculations dramatically. Therefore, similar reservoir components are lumped into pseudo-components. This lumping
procedure consists of linearized averaging of several reservoir properties, which decreases the accuracy of simulations.

Phase equilibrium calculations become slower due to not only an increased number of components but also an increased number of phases. Especially during low temperature gas injection, e.g. N$_2$ or CO$_2$ injection, the occurrence of a third phase is very common. These three phases are gaseous phase, oil-rich liquid phase and injected gas-rich liquid phase.

Phase equilibrium calculations consist of two basic steps: stability analyses and flash calculations. Stability analysis determines the number of stable phases and flash calculations compute phase compositions and phase mole fractions. Typically, phase equilibrium calculations start assuming a single phase exists. If an additional phase is found, two-phase flash calculations are carried out. We can also search for a third phase by carrying out two-phase stability analysis, where an additional phase is searched for. If the stability analysis concludes that there are three phases, then three-phase flash calculations are carried out. This procedure can be extended to search for more phases.

Reduced methods are one way to avoid excessive computational times when multiple phases and components are present. Previous research studies (Hendriks, 1988; Hendriks & Van Bergen, 1992; Jensen & Fredenslund, 1993; Li & Johns, 2006; Michelsen, 1986; Nichita & Graciaa, 2011; Okuno et al., 2010a) have proposed and analyzed new reduced methods. All of these aforementioned authors have focused on the computational speed, or number of iterations of the reduced methods.

While many reduced methods have been proposed and their computational improvements have been investigated, there has been very little research on the robustness improvements of the reduced methods (Gorucu & Johns, 2013a; Okuno, 2009; Pan & Firoozabadi, 2002). For example, Pan and Firoozabadi (2002) analyzed the tangent plane distance (TPD) for a fluid and stated that reduced methods have only one minimum while the conventional technique has two
minima for the fluid tested. Okuno (2009) reported the number of flash calculations that fail as the number of components increases. He found that as the number of components increases, the conventional technique starts to fail for more cases. However, the reduced method of Okuno et al. (2010a), which we refer to as OJS, fails for fewer cases. The difference between the reduced and conventional technique becomes more significant as the number of components increases. As the reduced methods decrease the number of independent parameters, it can be expected that they will show less complicated behavior compared to the conventional technique. Gorucu and Johns (2013a) implemented several two-phase reduced and conventional flash calculations and compared these techniques in terms of speed and robustness. Their results suggest that the reduced parameters of Nichita and Gracia (2011) are significantly more robust compared to all of the other reduced and conventional techniques likely because of the linearization of the fugacity expression. Their results are based on thousands of two-phase flash calculations. Therefore, there has not been significant research to date on the potential robustness improvements of reduced methods.

Further, the robustness of reduced methods compared to conventional methods for three-phase equilibrium calculations have not yet been studied. In this research, we implement the reduced parameters of Gorucu and Johns (2011, 2013b) to stability analysis and three-phase flash calculations. We further compare our new reduced one-phase stability analysis, two-phase flash calculations, two-phase stability analysis and three-phase flash calculations with the reduced method of Okuno et al. (2010a).

The structure of this chapter is as follows. We present the stability analysis approach based on our new reduced parameters. Then, we present three-phase flash calculations based on reduced parameters. Then, we give our methodology to test different algorithms. Finally, we compare ILJ and OJS in terms of robustness and give conclusions.
5.2. New Reduced Stability Analysis

One of the important parts of a three-phase equilibrium calculation is first to do a stability analysis. In this section, we show how to perform stability analysis with our new reduced method. Our stability analysis algorithm is very similar to that of Nichita and Petitfrere (2013). Okuno et al. (2010a) proposed a reduced stability analysis algorithm based on the reduced method of Li and Johns (2006). We refer to their reduced technique as OJS.

OJS stability analysis is based on

\[ \Theta_k - \sum_{i=1}^{N_c} q_{ik} x_i = 0 \]  \hspace{1cm} (5.1)

where \( \Theta_k \) are the reduced parameters of Li and Johns (2006), \( \Theta_k = \sum_{i=1}^{N_c} q_{ik} x_i \), \( x \) is phase composition, and \( N_c \) is the number of components. We also know that

\[ x_i = \frac{X_i}{\sum_j X_j} \]  \hspace{1cm} (5.2)

where \( X_i \) is stationary point. Multiply Eq. (5.1) with \( \sum_j X_j \).

\[ \Theta_k \sum_j X_j - \sum_{i=1}^{N_c} q_{ik} x_i \sum_j X_j = 0 \ . \]  \hspace{1cm} (5.3)

Insert Eq. (5.2) into Eq. (5.3) to obtain,
Conventional residual functions for stability analysis are

\[ S_i = \ln X_i + \ln \phi(\bar{X}) - \ln \left( z_i \phi \left( \bar{z} \right) \right) = 0. \quad (5.5) \]

Therefore,

\[ X_i = \frac{z_i \phi(\bar{X})}{\phi(\bar{X})}. \quad (5.6) \]

Finally, substitution of Eq. (5.7) into Eq. (5.8) gives the OJS stability analysis residual functions as,

\[ S_c = \sum_{i=1}^{n} \left( \Theta'_i - q_\Delta \right) \frac{z_i \phi(\bar{z})}{\phi'_i} = 0. \quad (5.9) \]

OJS residual functions benefit from the fact that \( \bar{\Theta} = \bar{q} \bar{X}^T \). Our reduced improved Li-Johns (ILJ) parameters – Gorucu and Johns (2011, 2013b) – express \( \ln K_i \) as

\[ \ln \bar{K} = \bar{q} \Delta \bar{h}^T \quad (5.10) \]
where $\Delta \vec{h}$ is the vector of independent parameters of size six, $\vec{q}$ is a constant matrix and $\Delta \vec{h} = \vec{h}_L - \vec{h}_V$ where $L$ is liquid mole fraction and $V$ is vapor mole fraction. Unfortunately, neither $\Delta \vec{h}$ nor $h_j$ ($j =$ phase index) can be expressed as $\vec{h} = \vec{q} \vec{x}^T$. Therefore, we cannot express our residuals as shown in Eq. (5.9). Instead, we use the following residual functions for ILJ where $h_\alpha$ are reduced parameters:

$$R_\alpha = h_\alpha^{n+1} - h_\alpha^n = 0 \quad \text{for } \alpha = 1, \ldots, 6. \quad (5.11)$$

Reduced parameters are updated with

$$\bar{\mathbf{J}} \Delta \vec{h} = -\bar{R} \quad (5.12)$$

Hence, the Jacobian matrix is

$$\mathbf{J} = \frac{\partial R_\alpha}{\partial h_k} = \frac{\partial h_\alpha^{n+1}}{\partial h_k^n} - \delta_{\alpha k} \quad (5.13)$$

Once we solve for the independent parameter $h_\alpha^{n+1}$, we can easily calculate the fugacity coefficient by

$$\ln \phi_i = \sum_{\alpha = 1}^{6} h_\alpha q_{i\alpha} \quad (5.14)$$
Subsequently, we update $X_i$ and $x_i$ with Eqs. (5.6) and (5.2), respectively. When $|S|_\infty < 0.001$ in Eq. (5.5), we switch to Newton-Raphson (NR) iterations.

The procedure for stability analysis is as follows. We start with successive substitution (SS) iterations and then continue with NR iterations. SS iterations are as follows.

1. Calculate A and B.
2. Calculate the compressibility factor by using a cubic EOS. The correct compressibility factor is a real, positive value that gives the minimum Gibbs free energy. While calculating the Gibbs free energy, store the fugacity coefficient.
3. Check for convergence. If convergence is achieved, switch to NR iterations. Otherwise continue with step 4).
4. Once the fugacity coefficient is updated, Eqs. (5.6) and (5.2) are repeated to update the composition. Go back to step 1).

Note that the $h$ value that is used in Eq. (5.11) needs to be stored at the last iteration of the SS. The parameter $h$ is used in the NR iterations. The NR iterations start after repeating step 4) of SS steps one last time. NR iterations are as follows:

1. Calculate A and B.
2. Calculate the compressibility factor by using a cubic EOS. The correct compressibility factor is a real, positive value that gives the minimum Gibbs free energy. While calculating the Gibbs free energy, store the $h$ value.
3. Update the residuals by using Eq. (5.11).
4. Construct the Jacobian matrix with Eq. (5.13)
5. Update the $h$ value with Eq. (5.12).
6. Update the fugacity coefficient.
7. Check for convergence. If convergence is achieved, stop after step 6). Otherwise continue.

8. Once the fugacity coefficient is updated, Eqs. (5.6) and (5.2) are repeated to update the composition. Go back to step 1).

This procedure avoids the extra SS steps required by OJS. The derivatives for the Jacobian matrix construction are

\[
\frac{\partial h_{a}^{n+1}}{\partial h_{b}^{n}} = \sum_{\gamma=1}^{5} \frac{\partial h_{a}^{n+1}}{\partial \Theta_{\gamma}} \frac{\partial \Theta_{\gamma}}{\partial h_{b}^{n}}. \quad (5.15)
\]

The expressions for \( \frac{\partial h_{a}^{n+1}}{\partial \Theta_{\gamma}} \) are the same as in the two-phase flash calculations. The analytical derivatives for \( \frac{\partial \Theta_{\gamma}}{\partial h_{b}^{n}} \) are different than those of the flash calculations. The derivations for the derivatives are found below.

\[
\frac{\partial Q_{ij}}{\partial h_{\beta}} = \sum_{i=1}^{N} \theta_{ij} \frac{\partial \chi_{i}}{dh_{\beta}} \quad (5.16)
\]

where \( \theta_{ij} = \left\{ \sqrt{A_i}, \sqrt{A_i h_i g_i}, \sqrt{A_i h_i^2 g_i}, \sqrt{A_i g_i}, B_i \right\} \). The required analytical derivatives in eq. (5.16) are
\[
\frac{\partial X_i}{\partial h_{\alpha}} = \frac{\frac{\partial X_i}{\partial h_{\alpha}} \sum_j X_j - X_i \sum_j \frac{\partial X_j}{\partial h_{\alpha}}}{\left( \sum_j X_j \right)^2}.
\]

(5.17)

\[
\frac{\partial X_i}{\partial h_{\alpha}} = -z_i \phi_i^j \frac{\partial \ln \phi_i^j}{\partial h_{\alpha}} = -z_i \phi_i^j q_{\alpha i}.
\]

(5.18)

### 5.3. Three-Phase Flash Calculations Using New Reduced Parameters

We have implemented our reduced parameters to three-phase flash calculations. The equations are solved with SS iterations followed by NR iterations. There are 12 independent parameters. The residual functions are given below:

\[
e_{\alpha} = h_{\alpha}^3 - h_{\alpha}^1 - \Delta h_{\alpha}^{13} \quad \alpha = 1, \ldots, 6
\]

\[
e_{\alpha} = h_{\alpha}^3 - h_{\alpha}^2 - \Delta h_{\alpha}^{23} \quad \alpha = 7, \ldots, 12
\]

(5.19)

Independent parameters are,

\[
\psi = \left\{ \Delta h_{13}^{13}, \Delta h_{23}^{13}, \Delta h_{13}^{13}, \Delta h_{63}^{13}, \Delta h_{53}^{13}, \Delta h_{63}^{23}, \Delta h_{53}^{23}, \Delta h_{53}^{23}, \Delta h_{63}^{23}, \Delta h_{63}^{23}, \Delta h_{53}^{23} \right\}
\]

(5.20)

where \( \Delta h_{\alpha}^{13} = h_{\alpha}^3 - h_{\alpha}^1 \) and \( \Delta h_{\alpha}^{23} = h_{\alpha}^3 - h_{\alpha}^2 \). We express K-values as

\[
\ln K_{12} = \sum_{\alpha=1}^{6} \Delta h_{\alpha}^{23} q_{\alpha i} \quad \text{and} \quad \ln K_{11} = \sum_{\alpha=1}^{6} \Delta h_{\alpha}^{13} q_{\alpha i}
\]

(5.21)
The procedure is as follows: start with successive substitution (SS) iterations; initialize K-values with stability analysis and flash calculations; apply constant-K flash calculations from Okuno et al. (2010c); and calculate fugacity coefficients.

1. Update K values.
2. If convergence is achieved, exit. Otherwise continue to step 4).
3. Apply constant-K flash calculations. Go back to step 1).

Additional constant-K flash calculations are repeated between SS and NR iterations. NR iterations are as follows:

4. Calculate fugacity coefficients.
5. If convergence is achieved, stop.
6. Update the residuals with Eq. (5.22).
7. Construct the Jacobian matrix with Eq. (5.23).
8. Solve the system of equations.
9. Update independent parameters.
10. Update K values with Eq. (5.24).
11. Do constant-K flash calculations (Okuno et al., 2010c).
12. Go back to step 5.

The Jacobian matrix is given by the equations,

\[
\begin{align*}
\frac{\partial e_\alpha}{\partial \psi_k} &= \frac{\partial h^3_\alpha}{\partial \psi_k} - \frac{\partial h^1_\alpha}{\partial \psi_k} - \delta_{ak} & \alpha = 1, \ldots, 6 \\
\frac{\partial e_\alpha}{\partial \psi_k} &= \frac{\partial h^3_\alpha}{\partial \psi_k} - \frac{\partial h^2_\alpha}{\partial \psi_k} - \delta_{ak} & \alpha = 7, \ldots, 12
\end{align*}
\]

Thus, the Jacobian matrix can be illustrated as follows.
The derived equations are similar to those of Nichita & Gracia (2011) and Okuno (2009). The analytical derivations are

\[ \frac{\partial h_{\alpha j}}{\partial \Delta h_\beta} = \sum_{\gamma=1}^5 \frac{\partial h_{\alpha j}}{\partial Q_{\gamma j}} \frac{\partial Q_{\gamma j}}{\partial \Delta h_\beta} \quad \alpha, \beta = 1, \ldots, 6; \quad \gamma = 1, \ldots, 5 \quad \text{and} \quad j = 1, \ldots, 3 \quad (5.27) \]

where \( \frac{\partial h_{\alpha j}}{\partial Q_{\gamma j}} \) is the same as the two-phase flash calculations. Analytical expressions for \( \frac{\partial Q_{\gamma j}}{\partial \Delta h_\beta} \) are different and are shown below.

\[ \frac{\partial Q_{\gamma j}}{\partial \Delta h_\beta} = \sum_{i=1}^{N_i} \theta_{i\gamma} \frac{\partial x_i^j}{\partial \Delta h_\beta} \quad \text{where} \quad h_\beta = \Delta h_{k1} \quad \text{or} \quad \Delta h_{k2}. \quad (5.28) \]

Material balance gives,

\[ x_i^1 = \frac{K_{i1} z_i}{t_i}, \quad x_i^2 = \frac{K_{i2} z_i}{t_i}, \quad x_i^3 = \frac{z_i}{t_i} \quad (5.29) \]
where \( t_i = K_{i} \beta_i + K_{i2} \beta_2 + \beta_3 \), \( K_{i1} = \phi_{i1} / \phi_i \), \( K_{i2} = \phi_{i2} / \phi_i \). \( x^1_i \), \( x^2_i \) and \( x^3_i \) are phase compositions, respectively. The parameter \( \beta \) is phase mole fraction, \( i \) is component index, and \( j \) is phase index. Therefore, the following can be derived:

\[
\frac{\partial x^1_i}{\partial \Delta h^1_k} = \frac{z_i}{(t_i)^2} \left( \frac{\partial K_{i1}}{\partial \Delta h^1_k} [K_{i2} \beta_2 + \beta_3] - K_{i1} \left( \frac{\partial \beta_1}{\partial \Delta h^1_k} (K_{i1} - 1) + \frac{\partial \beta_2}{\partial \Delta h^1_k} (K_{i2} - 1) \right) \right)
\]

\[
\frac{\partial x^1_i}{\partial \Delta h^i_k} = -\frac{K_{i1} z_i}{(t_i)^2} \left( \frac{\partial \beta_1}{\partial \Delta h^i_k} (K_{i1} - 1) + \frac{\partial \beta_2}{\partial \Delta h^i_k} (K_{i2} - 1) \right)
\]

\[
\frac{\partial x^2_i}{\partial \Delta h^2_k} = \frac{K_{i2} z_i}{(t_i)^2} \left( \frac{\partial \beta_1}{\partial \Delta h^2_k} (K_{i1} - 1) + \frac{\partial \beta_2}{\partial \Delta h^2_k} (K_{i2} - 1) \right)
\]

\[
\frac{\partial x^3_i}{\partial \Delta h^3_k} = \frac{z_i}{(t_i)^2} \left( \frac{\partial K_{i1}}{\partial \Delta h^3_k} [K_{i2} \beta_2 + \beta_3] - K_{i2} \left( \frac{\partial \beta_1}{\partial \Delta h^3_k} (K_{i1} - 1) + \frac{\partial \beta_2}{\partial \Delta h^3_k} (K_{i2} - 1) \right) \right)
\]

\[
\frac{\partial x^3_i}{\partial \Delta h^i_k} = -\frac{z_i}{(t_i)^2} \left( \frac{\partial \beta_1}{\partial \Delta h^i_k} (K_{i1} - 1) + \frac{\partial \beta_2}{\partial \Delta h^i_k} (K_{i2} - 1) \right)
\]

Material balance has to be satisfied. Hence,

\[
\sum_{i=1}^{N_k} z_i (K_{i1} - 1) = 0
\]

Introduce \( \beta_1 + \beta_2 + \beta_3 = 1 \), \( \frac{\partial K_{i2}}{\partial \Delta h^1_k} = 0 \) and \( \frac{\partial \beta_3}{\partial \Delta h^i_k} = -\frac{\partial \beta_1}{\partial \Delta h^i_k} - \frac{\partial \beta_2}{\partial \Delta h^i_k} \). Then,
\[
\frac{\partial \beta_i}{\partial \Delta h_3} = \frac{c \sum_{i=1}^{N_c} d_i (K_{i2} - 1) \frac{\partial K_{ii}}{\partial \Delta h_3} \beta_i + b \sum_{i=1}^{N_c} d_i \frac{\partial K_{ii}}{\partial \Delta h_3} (K_{i2} \beta_i - \beta_i + 1)}{ab - c^2} \quad (5.37)
\]

\[
\frac{\partial \beta_i}{\partial \Delta h_{23}} = \frac{-c \sum_{i=1}^{N_c} d_i (K_{i2} - \beta_i + 1) \frac{\partial K_{i23}}{\partial \Delta h_{23}} \beta_i - b \sum_{i=1}^{N_c} d_i \frac{\partial K_{i23}}{\partial \Delta h_{23}} (K_{ii} - 1) \beta_i)}{ab - c^2} \quad (5.38)
\]

where \( a = \sum_{i=1}^{N_c} d_i (K_{ii} - 1)^2 \), \( b = \sum_{i=1}^{N_c} d_i (K_{i2} - 1)^2 \), and \( c = \sum_{i=1}^{N_c} d_i (K_{i2} - 1) (K_{ii} - 1) \). The derivatives \( \frac{\partial \beta_2}{\partial \Delta h_3}, \frac{\partial \beta_3}{\partial \Delta h_3}, \frac{\partial \beta_3}{\partial \Delta h_{23}}, \frac{\partial \beta_3}{\partial \Delta h_{23}} \) are easily solved after calculating \( \frac{\partial \beta_i}{\partial \Delta h_3} \) and \( \frac{\partial \beta_i}{\partial \Delta h_{23}} \).

5.4. Methodology

This section describes the methodology for three-phase equilibrium calculations. Phase equilibrium calculations consist of starting with a single-phase stability analysis, then proceeding to make two-phase flash calculations if that result is unstable. Once two-phase flash calculations are complete, one of the two phases (preferably the one with the smallest Gibbs energy) is tested for stability. We call this a two-phase stability analysis in this research. Three-phase flash calculations follow the two-phase stability analysis if one of those phases is found to be unstable. Our methodology is similar to that of Li and Firoozabadi (2012).

5.4.1. Stability analysis

Single-phase stability analysis is initialized with the following K-values (Li & Firoozabadi, 2010; Li & Firoozabadi, 2012).
where

$$K_i^{\text{CO}_2} = \begin{cases} 
0.9 / z_i^{\text{test}} & \text{if } i = n_{\text{CO}_2} \\
0.1 / (N_c - 1) / z_i^{\text{test}} & \text{if } i \neq n_{\text{CO}_2}
\end{cases}$$ (5.40)

and $i$ is the component index, and $n_{\text{CO}_2}$ is the CO$_2$ tag. Two-phase stability analysis is initialized with the following K-values (Li & Firoozabadi, 2010; Li & Firoozabadi, 2012).

$$K_i^{2\phi-\text{stab}} = \left\{ K_i^{\text{Wilson}}, 1 / K_i^{\text{Wilson}}, \sqrt{K_i^{\text{Wilson}}}, 1 / \sqrt{K_i^{\text{Wilson}}}, K_i^{\text{CO}_2}, K_i^{1\phi-\text{stab}}, 1 / K_i^{1\phi-\text{stab}}, K_i^{2\phi-\text{flash}}, 1 / K_i^{2\phi-\text{flash}} \right\}$$ (5.41)

Once the initial K-value estimates are computed, stationary points can be found by iterating with the variable

$$X_i = K_i^{\text{stab}, \text{test}} z_i^{\text{test}}$$ (5.42)

where $z_i^{\text{test}}$ is the initial composition tested for stability. For single-phase stability analysis $z_i^{\text{test}} = z_i$. For two-phase stability analysis, $z_i^{\text{test}}$ is the phase composition from the equilibrium compositions of the two-phase flash calculations that has the lowest molar Gibbs energy. Molar Gibbs energy for a phase is calculated as
where $i$ is component index, $j$ is phase index, $x$ is phase composition, and $\phi$ is fugacity coefficient.

The convergence criterion used is

$$
\left\| \Delta G \right\|_\infty = \left\| \ln \left( \Phi \left( \bar{X} \right) \right) + \ln X_j - \ln \Phi \left( \bar{z} \right) - \ln z_j \right\|_\infty < 10^{-10}.
$$

At the end of every stability analysis, we first check whether convergence is achieved within a maximum number of iterations. We then also check whether a trivial solution is reached, and whether a positive TPD is achieved, or whether the stationary point is undefined (NaN). If none of these cases are achieved, the single phase being tested is unstable so that another phase must appear. The trivial solution for single-phase stability analysis is recognized when

$$
\left\| X_i / z_i \right\|_\infty < 10^{-8}.
$$

Trivial solutions for two-phase stability analysis are identified when

$$
\left\| X_i / x_i \right\|_\infty < 10^{-8} \text{ or } \left\| X_i / y_i \right\|_\infty < 10^{-8}.
$$

If an additional phase is found, stability analysis is stopped and then flash calculations begin. If an additional phase is not found, we discontinue the phase equilibrium calculations for that composition and the single phase is assumed stable.

### 5.4.2. Flash Calculations

The initial $K_i$ values for two-phase flash calculations are

$$
K_i^{\phi, \text{flash}} = \left\{ K_i^{\phi, \text{stab}}, K_i^{\text{Wilson}} \right\}
$$
from Li & Firoozabadi (2010) and Li & Firoozabadi (2012). Baker (1980) shows for binary mixtures that flash calculations do not guarantee convergence to the global minimum. Therefore, we carry out two-phase flash calculations several times even if the first estimate converges to a physical two-phase solution. We want to find the two-phase solution that gives the lowest Gibbs energy, where the residual Gibbs energy is calculated by

$$G_R = \sum_{j=1}^{N_c} \sum_{i=1}^{N_r} \beta^j x_i^j \left( \ln \phi^j x_i^j \right)$$  \hspace{1cm} (5.46)

where $\beta$ is phase mole fraction and $N_p$ is number of phases. This strategy not only improves the results for two-phase flash calculations but also it improves the initial estimates for two-phase stability analysis and three-phase flash calculations.

Three-phase flash calculations begin with the following two $K_i$ estimates namely $K_{i1}$ and $K_{i2}$. We carry out three-phase flash calculations with two different initial estimates. The first $K_i$ estimates are

$$K_{i1} = \frac{x_i}{X_i} \quad \text{and} \quad K_{i2} = \frac{y_i}{X_i}$$  \hspace{1cm} (5.47)

where $x_i$ and $y_i$ are phase compositions from the two-phase flash calculations and $X_i$ is the stationary point from two-phase stability analysis. A second set of $K_i$ estimates is

$$K_{i1} = K_i^{2\phi_{\text{stab}}} \quad \text{and} \quad K_{i2} = K_i^{2\phi_{\text{flash}}}.$$  \hspace{1cm} (5.48)
We use the constant-K flash calculations outlined in Okuno et al. (2010c). The convergence criterion for two-phase flash calculations is

$$\|R\|_{\infty} = \left\| \ln \phi_i (x) + \ln x_i - \ln \phi_j (y) - \ln y_j \right\|_{\infty} < 10^{-10} \quad (5.49)$$

We use two convergence criterion for three-phase flash calculations:

$$\|R\|_{\infty} = \left\| \ln \phi_i (x) + \ln x_i - \ln \phi_j (x) - \ln x_j \right\|_{\infty} < 10^{-10} \quad (5.50)$$

and

$$\|R\|_{\infty} = \left\| \ln \phi_i (x) + \ln x_i - \ln \phi_j (x) - \ln x_j \right\|_{\infty} < 10^{-10}. \quad (5.51)$$

If the first estimate successfully converges to a non-trivial physical solution, the second initial guess is not carried out. At the end of a flash calculation, we check for the following in the order given. We check whether the maximum number of iterations is reached, a non-physical solution is achieved, the solution is defined as NaN, or if a trivial solution is achieved. If none of these conditions are satisfied, the flash calculation is assumed to converge to a non-trivial physical solution. A trivial solution for two-phase flash calculations is assumed when

$$\sqrt{\sum_{i=1}^{N} (x_i - y_i)^2} < 10^{-5} \quad \text{and} \quad \sqrt{\sum_{i=1}^{N} (z_i - y_i)^2} < 10^{-5}.$$  

For three-phase flash calculations, the trivial solution is reached when either $$\|KK_{11} - 1\|_{\infty} < 10^{-5}$$ or $$\|KK_{12} - 1\|_{\infty} < 10^{-5}$$ conditions are satisfied.
5.4.3. Strategy

We carry out phase equilibrium calculations in the following ways.

- Make phase equilibrium calculations with SS with $10^{-10}$ convergence criterion. The maximum number of SS iterations is one million.
- Start with SS and switch to ILJ-NR at varying switch criterion. The switch criterion is varied here using $10^{-1}, 10^{-2}$, or $10^{-3}$. Maximum number of SS and NR iterations are 100 and 20, respectively.
- Start with SS and switch to OJS-NR at varying switch criterion. The switch criteria used are $10^{-1}, 10^{-2}$, or $10^{-3}$. Maximum number of SS and NR iterations are 100 and 20, respectively.
- Do one SS and switch to ILJ-NR. Maximum number of NR iterations are 20.
- Do one SS and switch to OJS-NR. Maximum number of NR iterations are 20.

Convergence criterion is $10^{-10}$ for all of the strategies. The first strategy, where only SS iterations are carried out, is the most robust strategy and is taken as the reference case for the conventional and reduced methods with NR iterations.

5.5. Results and Discussion

We compare ILJ and OJS three-phase equilibrium calculations by plotting pressure-temperature (PT), and pressure-composition (PX) diagrams of two fluids from the literature. We use North Ward Estes (NWE) fluid from Khan et al. (1992), and Maljamar separator oil from Orr et al. (1981) for the test fluids. The fluid properties can be found in Appendix C.
Phase equilibrium calculations are more robust when only SS iterations are carried out. However, SS iterations are very slow. Therefore, we switch to NR iterations after several SS iterations and compare the results to SS iterations only. The fewer the SS iterations, the less robust a method may be. We relax the switch criterion from SS to NR to determine which method (ILJ or OJS) fails the most, i.e. which one has the largest convergence region.

In Table 5.1, we report the results for NWE fluid. In Table 5.1, there are four main sections namely single-phase stability analysis, two-phase flash calculations, two-phase stability analysis and three-phase flash calculations. For stability analysis of a single-phase mixture, we report the average number of SS iterations, average number of NR iterations and how many K-value initializations on average are required to achieve negative TPD. The reported SS and NR iterations belong to the final stability analysis only. That is, SS and NR iterations only from the stability analysis that give two-phase solutions are reported. Almost all of the stability analysis calculations converge to negative TPD at the first initialization. Only a few require a second initial $K_i$ estimation. The number of SS iterations is identical and NR iterations vary slightly between ILJ and OJS. ILJ shows somewhat slower convergence behavior than OJS.

Table 5.1 also reports the results for the NWE fluid for two-phase flash calculations. For two-phase flash calculations, both initializations are carried out. However, only the solution with lower Gibbs energy is reported. Therefore, the reported SS and NR iterations belong to the corresponding flash calculation only. When SS ($10^{-10}$) convergence criterion is used, all of the flash calculations converge to a non-trivial two-phase solution. SS iterations are exactly the same for ILJ and OJS when the same flash calculation is used. The slight difference is caused by the fact that initializations are not the same for a few cases due to stability analysis. Moreover, ILJ shows a slightly faster convergence behavior than OJS. When SS switches to NR at $10^{-3}$ convergence criterion, both ILJ and OJS converge to a non-trivial two-phase solution for almost all of the cases. When the SS switch criterion is relaxed to 0.1, OJS starts to fail more often. At a
0.1 switch criterion, OJS converges to a two-phase solution only 94.7% of the cases whereas ILJ converges to a two-phase solution 98.3% of the cases. This indicates that ILJ is more robust than OJS for two-phase flash calculations. The improved robustness in the two-phase region improves the results of three-phase region as well.

The two-phase stability analysis section reports the average number of SS, NR iterations and initializations. Two-phase stability analysis gives a three-phase solution only with the first three initializations. That is, the other initializations were never needed. The reported SS and NR iterations in Table 5.1 belong to the last stability analysis only. The average number of initializations is similar for ILJ and OJS. However, ILJ requires slightly more initializations at relaxed switch criterion (0.1). Moreover, ILJ converges in more NR iterations using relaxed switch criterion. Note that OJS computed two-phase stability analysis for fewer cases as it failed for more two-phase flash calculations.

The section on three-phase flash calculations reports the average number of SS, NR iterations and initializations only for the non-trivial physical three phase region. ILJ requires more initializations at a relaxed switch criterion. This is due to the fact that ILJ was able to carry out three-phase flash calculations at the region where OJS had failed for two-phase flash calculations. Moreover, ILJ converges in somewhat fewer NR iterations.

Figure 5.1 shows the number of phases for NWE oil calculated by SS iterations only. There is no single-phase region. When ILJ and OJS are used with a $10^{-3}$ SS switch criterion, the results are still robust. However, when we relax the switch criterion to 0.1, ILJ and OJS start to fail. Figure 5.2 and Figure 5.3 show the results for two-phase flash calculations at 0.1 switch criterion for OJS and ILJ, respectively. ILJ fails for fewer cases. In fact, OJS and ILJ fail for 1635 and 524 flash calculations, respectively, out of 30,844. Figure 5.4 and Figure 5.5 show the results of two-phase stability analysis for OJS and ILJ, respectively. Even though both OJS and ILJ give similar results to SS ($10^{-10}$) when a two-phase stability analysis is carried out, the single-phase
region for OJS is larger due to the failures of the two-phase flash calculations. Figure 5.6 and Figure 5.7 show the results of three-phase flash calculations for OJS and ILJ, respectively. The dark region shows the false single-phase region resulting from two-phase flash calculations. Moreover, there are some three-phase flash calculations that converged to trivial solutions or undefined (NaN) both for OJS and ILJ. However, these situations are not significant in number.

Finally, ILJ and OJS successfully identify 86.6% and 80% of the three-phase region that was found solely by SS iterations, respectively. Moreover, ILJ and OJS successfully identify 97.19% and 93.34% of the two-phase region found by only SS iterations, respectively. Also, OJS gives a single-phase solution inside the three-phase region much more often than ILJ.

We now use only one SS iteration and make NR iterations until the convergence criterion of $10^{-10}$ is satisfied. The maximum number of NR iterations allowed is 20. Figure 5.8 and Figure 5.9 show the results for ILJ and OJS, respectively. Both methods give two phases after single-phase stability analysis. However, OJS fails for the majority of the cases in the two-phase flash calculations. For example, phase equilibrium calculations converge to the two-phase region 24,527 times when only SS iterations are used. Out of 24,527 cases, OJS and ILJ fail 51.67% and 11.2% of the time, respectively, and give a single-phase region. Therefore, ILJ two-phase flash calculations stand out compared to OJS in terms of robustness when only one SS iteration is used. The difference is even more pronounced in the three-phase region. When only SS iterations are used 6317 cases converge to the three-phase region. When only one SS iteration is used, OJS and ILJ fail for 59.14% and 7.95% of these 6137 cases. Therefore, OJS and ILJ give one or two phases when in fact they are in the three-phase region. Hence, the comparatively robust behavior of ILJ for two-phase flash calculations not only improves the results for the two-phase region, but also for the three-phase region.

As two-phase OJS flash calculations failed for 59.14% of the cases in the three-phase region, it is hard to compare OJS and ILJ two-phase stability analysis and three-phase flash
calculations. Therefore, we carry out a one-phase stability analysis and two-phase flash calculations with ILJ (one SS iteration only) and then compare ILJ and OJS by carrying out two-phase stability analysis using the same initial guess. Figure 5.10 and Figure 5.11 show the failed two-phase stability analysis for ILJ and OJS. These stability analyses may not converge, or may converge to a single-phase or to a trivial solution. ILJ and OJS fail to identify a third phase for 299 and 371 cases, respectively. If both of the stability techniques give a three-phase region, it takes 2.14 and 2.19 K-value initializations for OJS and ILJ, respectively. Therefore, we can conclude that both ILJ and OJS show similar robustness for two-phase stability analysis with ILJ being somehow more robust.

We also compare OJS and ILJ three-phase flash calculations both of which are initialized by ILJ two-phase flash calculations and stability analysis. Only one K-value initialization is used for three-phase flash calculations at this time. The number of three-phase flash calculations that fail are 92 and 235 for ILJ and OJS, respectively. The reason for robustness difference between ILJ and OJS is that OJS is more likely to converge to negative phase mole fraction and/or the trivial solution. For example, Figure 5.12 shows the reduced molar Gibbs free energy for 11 three-phase flash calculations. We looked for positive flash calculations where either ILJ or OJS converged to the trivial solution. There is no case where OJS converges to non-trivial solution and ILJ converges to trivial solution. However, there are 11 cases where ILJ converges to positive non-trivial physical solution and OJS converges to trivial physical solution. Figure 5.13 shows that OJS converges to a local minimum but ILJ converges to an even lower Gibbs free energy. These results indicate the improved robustness of ILJ compared to OJS. We further plot the residual Gibbs free energy of a three-phase flash calculation from NWE oil. We see that ILJ converges to a lower Gibbs free energy.

We plot the pressure-CO\textsubscript{2} composition (PX) diagram for the Maljamar separator oil (Orr et al. 1981) by dividing the PX dimension into 176×161=28336 grid blocks. Figure 5.14 shows
the number of phases computed by the SS only strategy with $10^{-10}$ convergence criterion. Figure 5.15 and 5.16 show the number of phases generated by OJS and ILJ where NR iterations are carried out after one SS iteration, respectively. Both OJS and ILJ converge to the same solution after the same number of initializations for one-phase stability analysis. OJS fails for significantly more two-phase flash calculations that are in the single-phase region. Three-phase flash calculations with OJS fail only at 0.998 CO$_2$ mole fraction and 74.4 psi, while ILJ does not fail at all. This flash is near the bi-critical point, where two of the three phases approach a critical point.

In order to analyze three-phase flash calculations more completely, we plot the PX diagram of Maljamar separator oil by carrying out stability analyses and two-phase flash calculations by SS iterations only. Then, we start three-phase flash calculations with Eq. (5.48). ILJ and OJS with the strategy that is explained in the previous paragraph converge to 333 and 323 three-phase results out of 1405, respectively.

### 5.6. Summary and Conclusions

In this research, we have proposed new reduced stability analysis and three-phase flash calculations based on the reduced parameters of Gorucu and Johns (2011, 2013). We have also compared our three-phase equilibrium calculations (ILJ) with those of Okuno et al. (2010a) (OJS) in terms of robustness. We have plotted a PT diagram of NWE oil from Khan et al. (1992) and a PX diagram of Maljamar separator oil from Orr et al. (1981). Our results suggest that

- ILJ and OJS stability analysis show similar robustness with ILJ being slightly more robust.
- ILJ two-phase flash calculations are remarkably more robust than OJS two-phase flash calculations.
- The robustness of ILJ two-phase flash calculations is more pronounced in the three-phase region. That is, OJS two-phase flash calculations fail more often, and hence three-phase flash calculations cannot be carried out.

- ILJ three-phase flash calculations are more robust than OJS. For example, ILJ and OJS fail for 92 and 235 three-phase flash calculations when started with the same K values for NWE oil.

- Generally, ILJ is more robust because OJS tends to converge to the trivial solution more often for the cases studied.

Robust phase equilibrium calculations are very important when the initial K-values are not close to the solution. When implicit reservoir simulators are used, large time steps may be taken. Therefore, the initial K-values may be far from the solution. A more robust algorithm for phase equilibrium calculations improves the results of compositional reservoir simulators, avoiding failure.

Table 5.1. Summary of phase equilibrium calculations for NWE oil. SS: Average number of SS iterations. NR: Average number of iterations. Trial: Number of K-value initializations.

<table>
<thead>
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<th>One-Phase Stability Analysis</th>
<th>Two-Phase Flash Calculations</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SS</td>
<td>NR</td>
</tr>
<tr>
<td>SS (1E-10)</td>
<td>21.63</td>
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</tr>
<tr>
<td>SS (1E-3)+OJS</td>
<td>8.55</td>
<td>1.3</td>
</tr>
<tr>
<td>SS (1E-3)+ILJ</td>
<td>8.55</td>
<td>1.39</td>
</tr>
<tr>
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<td>SS (1E-1)+ILJ</td>
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<table>
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<th>Two-Phase Stability Analysis</th>
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<td>NR</td>
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<tr>
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</tr>
<tr>
<td>SS (1E-3)+OJS</td>
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<tr>
<td>SS (1E-1)+OJS</td>
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<tr>
<td>SS (1E-1)+ILJ</td>
<td>5.6</td>
<td>3.38</td>
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</table>
Figure 5.1. Number of phases for NWE oil. Phase equilibrium calculations are carried out with SS iterations only. Maximum number of SS iterations are one million. There are at least two phases over the PT range shown due to high concentration of CO₂.

Figure 5.2. Number of phases for NWE oil assuming maximum of two phases exist. Two-phase flash calculations fail in the green region when SS switches to OJS-NR at 0.1 switch criterion. Therefore, some of the three-phase region is misidentified as one phase.
Figure 5.3. Number of phases for NWE oil assuming maximum of two phases exist. Two-phase flash calculations fail in the green region when SS switches to ILJ-NR at 0.1 switch criterion. Therefore, some of the three-phase region is misidentified as one phase.

Figure 5.4. Results of two-phase stability analysis when SS switches to OJS-NR at 0.1 switch criterion.
Figure 5.5. Results of two-phase stability analysis when SS switches to ILJ-NR at 0.1 switch criterion.

Figure 5.6. Number of phases for NWE oil. Results of three-phase flash calculations when SS switches to ILJ-NR at 0.1 switch criterion.
Figure 5.7. Number of phases for NWE oil. Results of three-phase flash calculations when SS switches to OJS-NR at 0.1 switch criterion. OJS converges to false one- and two-phase regions more often than ILJ.

Figure 5.8. Number of phases for NWE oil from three-phase flash calculations when SS switches to ILJ-NR after one iteration.
Figure 5.9. Number of phases for NWE oil from three-phase flash calculations when SS switches to OJS-NR after one iteration.

Figure 5.10. Results of two-phase stability analysis for ILJ for NWE oil. One-phase stability analysis and two-phase flash calculations are made with ILJ where only one SS iteration is carried out. Blue dots are where ILJ fails to identify a third phase.
Figure 5.11. Results of two-phase stability analysis for OJS for NWE oil. One-phase stability analysis and two-phase flash calculations are made with ILJ where only one SS iteration is carried out. Blue dots are where OJS fails to identify a third phase.

Figure 5.12. Residual Gibbs energies of three-phase flash calculations when trivial convergence is achieved. The results are from NWE fluid. Both flash calculations are initialized with the same K-values. OJS converges to a higher Gibbs energy. Red dots and blue dots are the residual Gibbs energies for OJS and ILJ, respectively.
Figure 5.13. Convergence behavior of a three-phase flash calculation from NWE oil (T=59 °F, P=891 psi). Constant K-flash forces ILJ to be in the physical region. Therefore, we see a non-monotonic behavior. The first iteration is SS. OJS converges to trivial solution.

Figure 5.14. Number of phases generated by using SS only strategy. Maximum number of SS iterations are one million. This is taken as the truth model.
Figure 5.15. Number of phases generated by using OJS. NR iterations start after only one SS iteration. Maximum number of NR iterations are 20.

Figure 5.16. Number of phases generated by using ILJ. NR iterations start after one SS iteration. Maximum number of NR iterations are 20. ILJ is able to identify two- and three-phase regions better than OJS.
FLUID CHARACTERIZATION FOR REDUCED METHODS

In the previous chapters, we focused on the robustness and computational speed aspects of reduced methods. Another important aspect that should be covered is accuracy of the fluid characterization. As reduced methods may modify the binary interaction parameter (BIP-$k_{ij}$) matrix, the accuracy of the phase equilibrium calculations might not be the same as conventional techniques (Hendriks & Van Bergen, 1992; Jensen & Fredenslund, 1987; Li & Johns, 2006; Nichita & Minescu, 2004). In fact, the first reduced method was only applicable for fluids with zero BIPs (Michelsen, 1986).

Commonly used reduced methods are those based on spectral decomposition (SD) (Hendriks & Van Bergen, 1992) and Li-Johns (LJ) (Li & Johns, 2006). BIPs are zero for most components, except for those between hydrocarbon-non-hydrocarbon pairs and light-heavy hydrocarbon pairs (Perschke, 1988). Many reservoir fluids have up to three non-zero BIP columns due to the presence of N$_2$, CO$_2$ and H$_2$S. There might also be nonzero BIPs between light and heavy hydrocarbons. As most BIP matrices are sparse, the significant eigenvalues of the 1-$k_{ij}$ matrix are few. Therefore, Hendriks and Van Bergen (1992) proposed spectral decomposition of the 1-$k_{ij}$ matrix to obtain,

$$1 - k = \mathbf{v} \mathbf{\lambda} \mathbf{v}^T.$$  \hspace{1cm} (6.1)

where the $\mathbf{v}$ matrix contains the eigenvectors, and $\mathbf{\lambda}$ is a diagonal matrix that contains the eigenvalues.

Michelsen, Yan and colleagues (Michelsen, Yan, & Stenby, 2012; Yan, Michelsen, Stenby, & Belkadi, 2011) show that the number of significant eigenvalues is $2m+1$ where $m$ is the
number of non-zero BIP columns. Furthermore, the number of reduced parameters is \( n+2 \) where \( n \) is the number of significant eigenvalues. Therefore, for a BIP with three non-zero columns, there are seven nonzero eigenvalues and nine reduced parameters in the SD reduced method approach.

Recently, Haugen and Beckner (2011; 2013) compared SD with conventional methods, both based on solution of nonlinear equations. Their results show SD is only slightly faster even for fifteen components representing the fluid. Similar results have been found by Yan et al. (2011) and Michelsen et al. (2012). As the number of retained eigenvalues increases, the speed of the SD reduced method decreases. As the number of retained eigenvalues decreases, however, accuracy in matching the phase behavior could worsen.

The BIP matrix only affects the attraction parameter \( A \).

\[
A = \sum_{i=1}^{N_C} x_i \sqrt{A_i} \sum_{j=1}^{N_C} \left( x_j \sqrt{A_j} \left( 1 - k_j \right) \right).
\]  

(6.2)

Changes to BIPs therefore will only affect the ‘A’ parameter in phase equilibrium calculations. Gaganis and Varotsis (2012) minimized the square of the errors in A estimation for various compositions and temperatures by taking the significant eigenvalues as independent parameters. This method reduces the error in phase behavior accuracy when some of the non-zero eigenvalues are discarded. Haugen and Beckner (2013) proposed a new flash algorithm that is suitable for all approximations of the BIP matrix while calculating the convergence criterion with the original BIP matrix. Therefore, as the difference between the original and approximated BIP increases, the number of iterations increases, which eliminates the speed advantage of the reduced methods.

The LJ reduced method (Li & Johns, 2006) expresses the BIP matrix as
\[ k_{ij} = (h_i - h_j)^2 g_i g_j . \] \hspace{2cm} (6.3)

Therefore, a symmetric zero-diagonal matrix is achieved. However, there is no explicit expression for \( h \) and \( g \) parameters. One way to compute \( h \) and \( g \) is to minimize

\[
\sqrt{\sum_{i=1}^{N_c} \left( \sum_{j=1}^{N_c} (k_{ij}^{\text{reduced}} - k_{ij}^{\text{conventional}})^2 \right)}
\]

by taking \( h \) and \( g \) as independent parameters. All of these previous techniques take the original BIP matrix as the reference. However, BIPs are not exact, as they should be composition dependent instead of constant parameters. Even though BIP has a physical meaning, it should be viewed rather as a parameter to be tuned to match the phase behavior of mixtures. In this section, we carry out fluid characterization by using the BIPs reproduced from \( h \) and \( g \) vectors using the Li and Johns expression in Eq. (6.3).

Fluid characterization optimizes phase behavior estimations by fitting several EOS parameters to laboratory data. These EOS parameters should be tuned. Several methods for fluid characterization have been proposed (Pedersen & Christensen, 2006; Whitson & Brule, 2000;). Pedersen and Christensen (2006) tune \( C_7^+ \) acentric factor (\( w \)), critical temperature (\( T_C \)), critical pressure (\( P_C \)), volume shift parameters and plus fraction molecular weight (\( M^+ \)) to fit the laboratory data. They only vary the most sensitive coefficients in Eqs. (6.4) to (6.5). \( M^+ \) and volume shift parameters are varied up to 10% and 50%, respectively. The optimization is carried out simultaneously. The parameters \( T_C, P_C \) and \( w \) are varied up to 20%. In this research, the SRK EOS is used.
6.1. Fluid Characterization

In this section, we carry out fluid characterization for conventional and reduced methods. We compare the results in terms of accuracy in phase behavior fitting and prediction.

6.1.1. Fluid #7 From Calsep

Table D.1-D3 show the compositional data, differential liberation (DL) data, and BIPs for fluid #7 from Calsep Inc (PVTSIM, a commercial PVT simulator). We carry out fluid characterization by tuning volume shift parameters up to 50%, M* up to 5%; and $T_C$ and $P_C$ up to 20%. We characterize the fluid with six and twenty-two components, separately. The $h$ and $g$ values shown in Table 6.1 are calculated by best fit to the BIPs determined conventionally. We compare the accuracy of results in absolute terms in Table 6.2. As the number of data to be fitted is limited to differential liberation, all of the three characterizations fit well. However, as Fig. 6.1. shows, only the phase envelopes for twenty-two component fluids match each other. As differential liberation data is at 98 °C, all of the fluid characterizations fit well. However, due to extensive lumping of several fluid properties, a six-component fluid system shows a significant alteration of the phase envelope.

6.1.2. Fluid F1

We also carry out fluid characterization for oils F1, F2 and F3 from Jaubert et al. (2002). For these oils, we use the same $h$ and $g$ vectors to reproduce the BIPs. The $h$ and $g$ vectors can be found in Table 6.3. These two vectors are produced by a best fit to real BIPs by minimizing
where $k_{ij}^{\text{reduced}}$ are produced from the reduced $h$ and $g$ vectors, and $k_{ij}^{\text{conventional}}$ are the conventional BIPs from PVTSim. Table 6.3 also shows the conventional BIPs for these oils.

Table D.4 shows the composition of oil F1, and Table D.5 shows CME data (constant mass expansion) and the MMP at 374.85 °K. The injected gas G1 is shown in Table D.10. PVTSim was not able to compute the MMP. Therefore, we tuned to constant mass expansion (CME) data only. $M^*$ and volume shift parameters are varied up to 5% and 50%, respectively. The optimization is carried out simultaneously. $c_1$, $c_2$, $d_1$, and $d_2$ are varied up to 10%. We lumped the data into 22 components by using conventional and reduced BIPs, separately. We also did tuning of an eight component model by using conventional BIPs. With the latter, we used three $C_7^+$ pseudo-components because $C_7^+$ mole fraction is 0.44 (Khan et al., 1992). Also, we lumped the defined components into five: 1) CO$_2$ 2) N$_2$ 3) C$_1$ 4) C$_2$-C$_3$ 5) C$_{4}$-C$_6$. The procedure is as follows:

1) Lump plus fraction into 12 pseudo-components by using conventional BIPs.

2) Lump plus fraction into 12 pseudo-components by using reduced BIP, which is the best fit of $h_i$ and $g_i$ to the BIPs.

3) Lump plus fraction into three pseudo-components and defined components into five pseudo-components, as described above.

Table 6.4 shows the results for fluid characterization. The twenty-two-component fluid characterization shows similar results for conventional and reduced BIPs. Eight-component fluid characterization shows better error values.
6.1.3. Fluid F2

In this section, we carry out fluid characterization for oil F2 from Jaubert et al. (2002). The BIPs, reduced $h$ and $g$ vectors, tuning parameters and procedure are the same as oil F1. The parameters $c_1$, $c_2$, $d_1$, and $d_2$ are varied up to 20%. The molecular weight ($\text{M}^*$) and volume shift parameters are varied up to 10% and 50%, respectively. Table 6.5 shows the errors for different characterizations. Figure 6.3 gives the calculated phase envelopes.

6.1.4. Fluid F3

Compositional data; CME, DL (differential liberation), swelling test, and slim tube test results for oil F3 are given in in Table D.10 and Table D.9, respectively. MMP is not used for regression because MMP calculations for PVTSim did not converge. For DL data, $V_{rel}$ needs to be converted to oil formation volume factor ($B_o$) for use in PVTSim. $V_{rel}$ is defined as

$$V_{rel} = \frac{V_{liq}(P)}{V_{liq}(P_b)}.$$  \hspace{1cm} (6.7)

where $P_b$ is the bubble-point pressure. Equation (6.7) is only applicable for differential liberation. $B_o$ is defined as

$$B_o = \frac{V_{liq}(P)}{V_{liq}(T,P)_{STP}}.$$  \hspace{1cm} (6.8)

Therefore,
\[
\frac{V_{rel}}{B_o} = \frac{V_{liq}(P)}{V_{liq}(P_b)} \frac{V_{liq}(T,P)|_{STP}}{V_{liq}(P)|_{STP}} = \frac{V_{liq}(T,P)|_{STP}}{V_{liq}(P_b)}. \tag{6.9}
\]

For oil F3,

\[
\frac{V_{liq}(T,P)|_{surface}}{V_{liq}(P_b)} = 0.5925. \tag{6.10}
\]

where 0.5925 comes from Table D.9. The surface conditions are 15 °C and 1 atm. From the equations above, \(B_o\) is computed by dividing \(V_{rel}\) by 0.5925.

Moreover, \(GOR_{LG}\) is defined as the gas-oil ratio of the liberated gas (m³ of gas at 15 °C, 1 atm per m³ of residual oil at 15 °C, 1 atm). This definition is not exactly the same as \(R_{so}\), which is quite the opposite of \(GOR_{LG}\). Therefore, \(R_{so}\) is read in the reverse order from how it is defined in Table D.9.

During the swelling test, CME is carried out at various amounts of gas injection. \(X_{gas}\) is defined as

\[
X_{gas} = \frac{n_g}{n_g + n_o} \tag{6.11}
\]

where \(n_g\) is the mole number of gas injected and \(n_o\) is the mole number of the reservoir oil. The value for \(n_g\) can be calculated as \(n_g = n_o \frac{X_{gas}}{(1 - X_{gas})}\).

We tune \(M^*\) up to ±10\%. The properties \(T_C, P_C\) and \(w\) are tuned up to ±20\%, and volume shift parameters up to ±100\%. We tuned all of the four coefficients in \(T_C, P_C\) and \(w\) expressions. Errors for fitted PVT data can be seen in Table 6.6. Figure 6.4 shows the phase envelopes for oil...
F3 with three different characterization procedures. There is a good fit for all of the three procedures.

### 6.1.5. Conclusions

We have carried out fluid characterization with the following three strategies.

1. Characterize the fluid into 22 components by using the conventional BIPs.
2. Do a best fit to the conventional BIPs by using reduced $h$ and $g$ parameters. Reproduce the BIP by using the reduced $h$ and $g$ parameters. Characterize the fluid into 22 components by using the reduced BIPs.
3. Characterize the fluid into eight components by using the conventional BIPs.

Our results suggest that the errors shown in Tables 6.2-6.6 are not significantly different for any of the aforementioned strategies. The reduced two-parameter BIPs formula (use of $hi$ and $gi$) are not an obstacle to estimate the PVT data for the cases studied. Figures 6.1-6.4 suggest that the phase envelopes for three different strategies do not significantly differ. However, the phase envelopes for the first and the third strategy are closer to each other than the phase envelope for the second strategy. These results suggest that characterizing the fluids into a larger number of components by using the reduced vectors might be the best strategy because the accuracy of the fluid behavior will not be lost, and the reduced methods are significantly faster than the conventional methods when the number of components is large.
Table 6.1. The $h$ and $g$ parameters for fluid number 7. These values are best fit to BIPs. Fluid number 7 is found in the PVTSim database from Calsep Inc.

<table>
<thead>
<tr>
<th></th>
<th>$h$</th>
<th>$g$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1.40516</td>
<td>0.621765</td>
</tr>
<tr>
<td>2</td>
<td>1.410979</td>
<td>0.907301</td>
</tr>
<tr>
<td>3</td>
<td>0.98641</td>
<td>0.733725</td>
</tr>
<tr>
<td>4</td>
<td>0.986261</td>
<td>0.73321</td>
</tr>
<tr>
<td>5</td>
<td>0.982858</td>
<td>0.7216</td>
</tr>
<tr>
<td>6</td>
<td>0.982395</td>
<td>0.720042</td>
</tr>
<tr>
<td>7</td>
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<td>0.733665</td>
</tr>
<tr>
<td>8</td>
<td>0.989763</td>
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</tr>
<tr>
<td>9</td>
<td>0.985028</td>
<td>0.728972</td>
</tr>
<tr>
<td>10</td>
<td>0.985676</td>
<td>0.731195</td>
</tr>
<tr>
<td>11</td>
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<td>0.606348</td>
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</tbody>
</table>

Table 6.2. Summary of fluid characterization results for fluid number 7 from Calsep Inc. Errors before and after regression in percentages are given.

<table>
<thead>
<tr>
<th></th>
<th>22 Components</th>
<th>22 Components</th>
<th>6 Components</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Conventional BIP</td>
<td>Reduced BIP</td>
<td>Conventional BIP</td>
</tr>
<tr>
<td></td>
<td>Before regression</td>
<td>After regression</td>
<td>Before regression</td>
</tr>
<tr>
<td>$P_{sat}$</td>
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<td>1.050</td>
<td>2.517</td>
</tr>
<tr>
<td>$B_o$</td>
<td>1.366</td>
<td>0.891</td>
<td>1.372</td>
</tr>
<tr>
<td>$R_x$</td>
<td>10.270</td>
<td>2.487</td>
<td>10.299</td>
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<tr>
<td>$\rho$</td>
<td>1.848</td>
<td>1.939</td>
<td>1.845</td>
</tr>
<tr>
<td>$Z_{-gas}$</td>
<td>1.823</td>
<td>1.825</td>
<td>1.836</td>
</tr>
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</table>
Table 6.3. First two columns show $h$ and $g$ parameters for oils F1-13. The third and fourth columns show the BIPs for N$_2$ and CO$_2$, respectively. The remaining BIPs are zero.

<table>
<thead>
<tr>
<th></th>
<th>$h$</th>
<th>$g$</th>
<th>$k_{ij}$ (N$_2$)</th>
<th>$k_{ij}$ (CO$_2$)</th>
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<tr>
<td>N$_2$</td>
<td>1.189722</td>
<td>0.886824</td>
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<td>1.261101</td>
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<tr>
<td>C$_4$</td>
<td>0.930118</td>
<td>0.980141</td>
<td>0.0407</td>
<td>0.12</td>
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<tr>
<td>C$_5$</td>
<td>0.923096</td>
<td>0.988669</td>
<td>0.0763</td>
<td>0.12</td>
</tr>
<tr>
<td>C$_6$</td>
<td>0.881024</td>
<td>0.885383</td>
<td>0.0944</td>
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</tr>
<tr>
<td>iC$_4$</td>
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<td>0.80029</td>
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<td>nC$_4$</td>
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<td>0.938146</td>
<td>0.0867</td>
<td>0.12</td>
</tr>
<tr>
<td>iC$_5$</td>
<td>0.861375</td>
<td>0.825927</td>
<td>0.0878</td>
<td>0.12</td>
</tr>
<tr>
<td>nC$_5$</td>
<td>0.859178</td>
<td>0.819883</td>
<td>0.08</td>
<td>0.12</td>
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<tr>
<td>C$_6$</td>
<td>0.875514</td>
<td>0.870752</td>
<td>0.08</td>
<td>0.12</td>
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<td>iC$_5$</td>
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<td>nC$_5$</td>
<td>0.859178</td>
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<td>0.12</td>
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<tr>
<td>C$_6$</td>
<td>0.875514</td>
<td>0.870752</td>
<td>0.08</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 6.4. Summary of fluid characterization results for oil F1. Errors before and after regression in percentages are shown.

<table>
<thead>
<tr>
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<th>15 Components</th>
<th>15 Components</th>
<th>8 Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional BIP</td>
<td>Reduced BIP</td>
<td>Conventional BIP</td>
</tr>
<tr>
<td></td>
<td>Before regression</td>
<td>After regression</td>
<td>Before regression</td>
</tr>
<tr>
<td>$\Delta p_{sat}$</td>
<td>10.1</td>
<td>0</td>
<td>11.3</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>2.86</td>
<td>0.4</td>
<td>2.86</td>
</tr>
<tr>
<td>$\Delta V/V_b$</td>
<td>0.98</td>
<td>0.52</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 6.5. Summary of fluid characterization results for oil F2. Errors before and after regression in percentage are shown.

<table>
<thead>
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<th>22 Components</th>
<th>22 Components</th>
<th>8 Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conventional BIPs</td>
<td>Reduced BIPs</td>
<td>Conventional BIPs</td>
</tr>
<tr>
<td></td>
<td>Before regression</td>
<td>After regression</td>
<td>Before regression</td>
</tr>
<tr>
<td>$\Delta p_{sat}$</td>
<td>4.70</td>
<td>0.00</td>
<td>3.50</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>1.00</td>
<td>0.37</td>
<td>1.02</td>
</tr>
<tr>
<td>$\Delta V/V_b$</td>
<td>0.63</td>
<td>0.43</td>
<td>0.60</td>
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Table 6.6. Summary of fluid characterization results for oil F3. Errors before and after regression in percentage are given.

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<th>Components</th>
<th>22 Components</th>
<th>8 Components</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Conventional BIPs</td>
<td>Reduced BIPs</td>
</tr>
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<td>Before regression</td>
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<td>CME</td>
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<td>Δp&lt;sub&gt;sat&lt;/sub&gt;</td>
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<td>Δρ</td>
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<td>ΔV/V&lt;sub&gt;b&lt;/sub&gt;</td>
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<td>Differential liberation</td>
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<tr>
<td>ΔB&lt;sub&gt;o&lt;/sub&gt;</td>
<td>3.99</td>
<td>3.93</td>
</tr>
<tr>
<td>ΔR&lt;sub&gt;s&lt;/sub&gt;</td>
<td>16.75</td>
<td>17.54</td>
</tr>
<tr>
<td>Δρ</td>
<td>3.09</td>
<td>3.18</td>
</tr>
<tr>
<td>ΔZ</td>
<td>1.89</td>
<td>1.84</td>
</tr>
<tr>
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<td></td>
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<tr>
<td>Δp&lt;sub&gt;sat&lt;/sub&gt;</td>
<td>3.79</td>
<td>3.40</td>
</tr>
<tr>
<td>ΔV/swell</td>
<td>2.55</td>
<td>2.55</td>
</tr>
<tr>
<td>Δρ</td>
<td>2.50</td>
<td>2.56</td>
</tr>
<tr>
<td>CME at X&lt;sub&gt;gas&lt;/sub&gt;=0.112</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2.87</td>
<td>1.56</td>
</tr>
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<tr>
<td>Δρ</td>
<td>0.72</td>
<td>0.69</td>
</tr>
<tr>
<td>CME at X&lt;sub&gt;gas&lt;/sub&gt;=0.222</td>
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</tr>
<tr>
<td>Δp&lt;sub&gt;sat&lt;/sub&gt;</td>
<td>1.40</td>
<td>1.39</td>
</tr>
<tr>
<td>ΔV/V&lt;sub&gt;b&lt;/sub&gt;</td>
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<td>0.23</td>
</tr>
<tr>
<td>Δρ</td>
<td>1.51</td>
<td>1.43</td>
</tr>
<tr>
<td>CME at X&lt;sub&gt;gas&lt;/sub&gt;=0.322</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.83</td>
<td>1.48</td>
</tr>
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<td>0.25</td>
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</tr>
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<td>CME at X&lt;sub&gt;gas&lt;/sub&gt;=0.414</td>
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<td>Δp&lt;sub&gt;sat&lt;/sub&gt;</td>
<td>4.48</td>
<td>1.50</td>
</tr>
<tr>
<td>ΔV/V&lt;sub&gt;b&lt;/sub&gt;</td>
<td>0.97</td>
<td>0.23</td>
</tr>
<tr>
<td>Δρ</td>
<td>2.94</td>
<td>2.77</td>
</tr>
<tr>
<td>CME at X&lt;sub&gt;gas&lt;/sub&gt;=0.5</td>
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<td>1.08</td>
</tr>
<tr>
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<td>0.10</td>
</tr>
<tr>
<td>Δρ</td>
<td>2.72</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Figure 6.1. Phase envelope for fluid number 7 with three different characterization models. The envelope for 22 components reduced and conventional regression coincide.

Figure 6.2. Phase envelope for oil F1 with three different characterization models.
Figure 6.3. Phase envelope for oil F2 with three different characterization models.

Figure 6.4. Phase envelope for oil F3 with three different characterization models.
Chapter 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

We carried out an in-depth analysis of EOS techniques and reduced methods. We introduced new reduced parameters and implemented them for stability analyses, two-phase flash calculations, and three-phase flash calculations. Moreover, we implemented all published two-phase conventional and reduced flash algorithms and compared them in terms of computational speed and robustness. Finally, we further carried out fluid characterization for the LJ reduced method to determine if the two-parameter BIP formula is able to reproduce fluid behavior accurately. The conclusions of this research are as follows:

1. Our new phase equilibrium calculations converge to the correct solution in one or two fewer iterations compared to the standard reduced algorithms. Standard reduced methods update the reduced parameters right after solving the system of equations. However, standard reduced methods do not update the composition at the same iteration level as the reduced parameters. Thus, standard reduced methods converge to the solution in one or two more iterations than conventional methods. With our new reduced parameters, our phase equilibrium calculations update the composition after solving for the independent parameters only with the expense of Rachford-Rice iterations. Therefore, our reduced methods converge to the solution in the same number of iterations as the conventional methods.

2. As the number of nonzero columns in a BIP matrix increases, the number of significant eigenvalues increases. A larger number of retained eigenvalues results in greater number of independent parameters, and hence a larger Jacobian matrix. Therefore, the SD
reduced method does not show significant speed up when the number of nonzero columns in a BIP matrix is large.

3. The LJ method has a fixed number of independent parameters. Therefore, LJ does not need to evaluate an undetermined number of independent parameters. LJ is coded by using a lower level of loops and more variables are constants. These characteristics of LJ, depending on the optimization level of the compiler, can improve the speed further.

4. Reduced methods are not suitable for minimization algorithms because the required derivations cannot be simplified. Conventional minimization algorithms take advantage of the Gibbs-Duhem equations. Therefore, conventional minimization algorithms express the gradient vector in a very simplified way resulting in a simplified Hessian matrix. Several authors implemented reduced minimization algorithms. However, we showed that these algorithms are inefficient.

5. Our reduced two-phase flash calculations show significantly improved robustness compared to several conventional and reduced techniques for the fluids tested. The improved behavior becomes more significant near the phase envelope and the critical point. Therefore, we can use fewer SS iterations to switch to NR, which improves the computational speed.

6. The robustness of our two-phase flash calculations is even more pronounced in the three-phase region. As two-phase flash calculations need to be carried out before the three-phase flash calculations, the three-phase flash calculations cannot be started if the two-phase flash calculations fail. In that case, the fluid is misidentified as single phase. We have shown that our new reduced algorithm improves the results of three-phase flash calculations because it shows robust behavior in the two-phase flash calculations.
7. The new reduced three-phase flash calculations are able to converge to the correct solution more often than the reference reduced algorithm (OJS) when they are both initialized with the same K-values.

8. OJS tends to converge to the trivial solution more often than our new reduced parameters algorithm.

9. We carried out fluid characterizations suitable for the LJ reduced method and its derivatives. Reduced methods are not an obstacle to fit the PVT data for the cases tested. Reduced methods fit the PVT data as well as conventional methods.

The recommendations for future research are as follows.

1. Compositional simulators can be developed with implicit pressure-explicit saturation (IMPES) and fully implicit techniques. The computational times of flow equations and phase equilibrium calculations can be dependent on the number of components depending on the algorithm. Therefore, future research could involve analyzing whether reduced methods are suitable for implicit and/or explicit reservoir simulations. Furthermore, one could also incorporate reduced methods with the flow equations.

2. Conventionally, BIP parameters can be used as tuning parameters. Tuning h and g vectors to the PVT data can be done. However, the tuning parameters should be constrained with the same constraints of the BIPs. That is, a change in one of the h or g components changes the whole column which might not be realistic. Therefore, the tuning of h and g vectors should be constrained with the physical constraints of the BIP matrix.

3. As laboratory results do not provide reliable information about the heavier hydrocarbons, retaining those eigenvalues may not improve the accuracy for many fluids. Therefore,
fluids that need characterization into a larger number of components need to be identified. Reduced methods should be very advantageous for these methods.

4. As the number of independent parameters is six, we cannot visualize the Gibbs free energy surface. Therefore, it is difficult to prove the robustness of a technique compared to another. More analysis is required to determine why our new reduced method is more robust. Compositional reservoir simulators can be used to test the robustness of our algorithm with various switch criteria from SS to NR.

5. More research is needed in terms of accuracy comparisons of SD and LJ. One can investigate this by doing fluid characterization with both methods. Moreover, LJ method might be disadvantageous when there are negative BIPs in a mostly positive BIP column. This disadvantage should be more pronounced at high levels of CO₂, N₂ or H₂S.

6. Fluid characterization should be carried out for a larger number of fluids and by using different PVT tools. The fluids that require more components should be identified.
REFERENCES


Appendix A – Numerical Optimization

This section summarizes various optimization methods used for minimization of a function.

A.1. Minimization of Sum of Square of Errors

The objective function is,

\[
E(\hat{\alpha}) = \sum_i (y_i - f(\alpha_i))^2
\]  \hspace{1cm} (F.12)

where \( E \) is the sum of square of errors, \( y \) is the data to be fit and \( f \) is the model. \( E \) can be approximated at point \( E^o \) as,

\[
E^* \approx E^o + \sum_i \Delta\alpha_i \frac{\partial E}{\partial \alpha_i}_{|E^o} + \frac{1}{2} \sum_{j=1}^n \sum_{i=1}^m \Delta\alpha_i \Delta\alpha_j \frac{\partial^2 E}{\partial \alpha_i \partial \alpha_j}_{|E^o}.
\]  \hspace{1cm} (F.13)

By analogy to minimization of an objective function,

\[
\frac{\partial E^*}{\partial \Delta\alpha_k} = d^*_k + \sum_{i=1}^n \Delta\alpha_i H^*_{ik} = 0.
\]  \hspace{1cm} (F.14)

This results in

\[
\Delta\alpha = H^{-1}d.
\]  \hspace{1cm} (F.15)
Eq. (A.4) is the Newton’s method when the full Hessian is used with no changes. However, there are several other methods to minimize the error function e.g. steepest descent, Gauss-Newton, Levenberg-Marquardt as explained next.

### A.2. Gauss-Newton

The Hessian matrix is,

\[
H_{ij} = -2 \left\{ -\frac{\partial^2 f_i}{\partial \alpha_i \partial \alpha_j} + (y_i - f_i) \frac{\partial^2 f_i}{\partial \alpha_i \partial \alpha_j} \right\}
\]

From the above, \( y_i = f_i \) near the solution. The Gauss-Newton method uses this result to cancel the term at the right and expresses \( H \) as

\[
H_{ij} = 2 \frac{\partial f_i}{\partial \alpha_i} \frac{\partial f_j}{\partial \alpha_j}
\]

This expression has the advantage of being positive definite. Also, Gauss-Newton method is not as costly as Newton’s method per iteration because no second order derivatives are computed.

### A.3. Steepest Descent

Steepest descent replaces the Hessian matrix with an identity matrix, which makes the \( H \) positive definite. Steepest descent forces the Hessian matrix to be positive definite as all the eigenvalues
are equal to one. This method is often very slow because it does not keep the curvature elements of the Hessian matrix. However, steepest descent does not have convergence problems, and eliminates the cost of calculating the Hessian matrix.

A.4. Levenberg Marquardt

Levenberg Marquardt approximates the Hessian matrix with $H^*$, where

$$H^* = H + \lambda I.$$  \hspace{1cm} (F.18)

With this method, the Hessian matrix becomes positive definite as $\lambda$ is increased. The Marquardt parameter $\lambda$ can be optimized with line search so that objective function is minimized in fewer iterations. When the Marquardt parameter $\lambda = 0$ the method reverts to Newton’s method while $\lambda \rightarrow \infty$ is steepest descent.
Appendix B – Analytical Derivatives

This appendix provides the analytical derivatives required in phase equilibrium calculations.

B.1. Conventional Stability Analysis by Minimization of Tangent Plane Distance

The fugacity derivatives for the stability analysis based on minimization of TPD are given below:

\[
\frac{\partial \ln \phi_i}{\partial X_j} = \frac{\partial Z}{\partial X_j} - \frac{B}{B^2} \frac{\partial B}{\partial X_j} - \frac{1}{Z-B} \left( \frac{\partial Z}{\partial X_j} \right)
\]

\[+ \left( \frac{1}{\Delta B \frac{\partial X_j}{\partial X_j}} \right) - \left( \frac{A}{\Delta B^2 \frac{\partial X_j}{\partial X_j}} \right) \left( \frac{B}{B^2} \frac{\partial B}{\partial X_j} \right) \left( \frac{Z + \delta_i B}{Z + \delta_i B} \right) \]

\[
+ \left( \frac{2}{A} \frac{\partial \sum_{k=1}^N A_k x_k}{\partial X_j} \right) - \left( \frac{2}{A^2} \frac{\partial A}{\partial X_j} \right) + \frac{B}{B^2} \frac{\partial B}{\partial X_j} \left( \frac{Z + \delta_i B}{Z + \delta_i B} \right)
\]

\[
+ \frac{A}{\Delta B} \left( \frac{\partial \sum_{k=1}^N A_k x_k}{\partial X_j} \right) \left( \frac{\partial Z}{\partial X_j} \right)
\]

\[
\frac{\partial A}{\partial X_j} = \sum_{i=1}^N \left( \sum_{k=1}^N (A_k x_k) \frac{\partial x_k}{\partial X_j} \right)
\]

\[
\frac{\partial B}{\partial X_j} = \sum_{i=1}^N \left( B_i \frac{\partial x_i}{\partial X_j} \right)
\]
From \( x_i = X / \sum X_k \)

\[
\frac{\partial x_i}{\partial X_j} = \frac{\partial X_i}{\partial X_j} \frac{\sum X_k}{\sum X_k} \frac{\partial \left( \sum X_k \right)}{\partial X_j} = \frac{\delta_j \sum X_k - X_i}{\left( \sum X_k \right)^2}
\]

(B.5)

**B.2. Conventional Flash Calculation Based on Minimization of Gibbs Energy**

The fugacity derivatives for the flash calculations based on minimization of Gibbs free energy are below:

\[
\frac{\partial \ln \phi_j^L}{\partial n_k} = \frac{\partial Z_j}{\partial n_{ij}} B_j \frac{(Z_j - 1)}{B_j^2} \frac{\partial B_j}{\partial n_{ij}} - \frac{1}{Z_j - B_j} \left( \frac{\partial Z_j}{\partial n_{ij}} - \frac{\partial B_j}{\partial n_{ij}} \right)
+ \left( \frac{1}{\Delta B_j} \frac{\partial A_j}{\partial n_{ij}} - A_j \frac{\partial B_j}{\partial n_{ij}} \right) \left\{ \frac{2 \sum A_k x_k}{A_j} - \frac{B_j}{B_j^2} \right\} \ln \left( \frac{Z_j + \delta_j B_j}{Z_j + \delta B_j} \right)
\]

\[
+ \left[ \frac{2 \sum A_k x_k}{A_j} - \frac{2 \sum A_k x_k}{A_j} \frac{\partial A_j}{\partial n_{ij}} + \frac{B_j}{B_j^2} \frac{\partial B_j}{\partial n_{ij}} \right] \frac{A_j}{\Delta B_j} \ln \left( \frac{Z_j + \delta_j B_j}{Z_j + \delta B_j} \right)
\]

\[
+ \frac{A_j}{\Delta B_j} \left( \frac{2 \sum A_k x_k}{A_j} - \frac{B_j}{B_j} \right) \left( \frac{\partial Z_j}{\partial n_{ij}} + \frac{\partial B_j}{\partial n_{ij}} \right) \frac{Z_j + \delta_j B_j}{Z_j + \delta B_j}
\]

(B.6)

where \( j \) is phase index, \( i \) is component index, \( \delta_j \) and \( \delta B_j \) are cubic EOS parameters. We know that,
\( B_j = \sum_{i=1}^{N_c} x_{ij} B_i , \quad x_i = \frac{n_{ij}}{n_j} = \frac{n_{ij}}{\beta_j n^T} . \) \hfill (B.7)

Assume \( n^T = 1 \). Then,

\( x_i = \frac{n_{ij}}{\beta_j} \) and \( B_{ij} = \sum_{i=1}^{N_c} n_{ij} B_i \) \hfill (B.8)

Therefore,

\[
\frac{\partial B_j}{\partial n_{ij}} = \frac{\partial}{\partial n_{ij}} \sum_i x_{ij} B_i = \frac{\partial}{\partial n_{ij}} \left( \frac{B_i n_{ij}}{\beta_j} \right) = \frac{1}{\beta_j} \frac{\partial}{\partial n_{ij}} \sum_i B_i n_{ij} + \sum_i B_i n_{ij} \frac{\partial}{\partial n_{ij}} \frac{1}{\beta_j} = \frac{B_k}{\beta_j} \frac{\partial}{\partial n_{ij}} \sum_i B_i n_{ij} \frac{\partial}{\partial n_{ij}} \frac{1}{\beta_j} = \frac{B_k}{\beta_j} \frac{\partial}{\partial n_{ij}} + \frac{B_k}{\beta_j} - \frac{B_k}{\beta_j} \frac{\partial}{\partial n_{ij}} = \frac{B_k - B_k}{\beta_j} \hfill (B.9)\]

Similarly,

\[
\frac{\partial}{\partial n_{ij}} \sum_i A_i x_i = \frac{\partial}{\partial n_{ij}} \sum_i \frac{A_i n_i}{\beta_j} = \frac{-\sum_i A_i n_i}{\beta_j^2} \frac{\partial}{\partial n_{ij}} \frac{1}{\beta_j} + \frac{1}{\beta_j} \frac{\partial}{\partial n_{ij}} \sum_i A_i n_i = \frac{-\sum_i A_i n_i}{\beta_j^2} + \frac{A_k}{\beta_j} = \frac{A_k - \sum_i A_i x_i}{\beta_j} \hfill (B.10)\]
\[
\begin{align*}
\frac{\partial Z_j}{\partial n_{ij}} &= \frac{\left\{ A_j \frac{\partial B_j}{\partial n_{ij}} + B_j \frac{\partial A_j}{\partial n_{ij}} - 3B_j^2 \frac{\partial B_j}{\partial n_{ij}} - 2B_j \frac{\partial B_j}{\partial n_{ij}} \right\}}{3Z_j^2 + 2Z_j \left[ B_j - 1 \right] + \left[ A_j - 3B_j^2 - 2B_j \right]} \\
\frac{\partial A_j}{\partial n_{ij}} &= -2 \sum_k \frac{A_{ik}n_{ij}^2}{\beta_j^3} + \frac{1}{\beta_j^2} \frac{\partial}{\partial n_{ij}} \sum_k A_{ik}n_{ij} \\
&= -2 \frac{A_j}{\beta_j} + \frac{2 \sum_k A_{ik}x_{ij}}{\beta_j} - A_j 
\end{align*}
\]
The fugacity derivatives with respect to reference phase composition are provided below:

\[
\frac{\partial \ln \phi_j}{\partial x_j} = \frac{B_j \partial Z}{B \partial x_j} - \frac{(Z-1)B_j \partial B}{B^2 \partial x_j} - \frac{1}{Z-B} \left( \frac{\partial Z}{\partial x_j} - \frac{\partial B}{\partial x_j} \right)
\]

\[
- \left( \frac{1}{\Delta B} \frac{\partial A}{\partial x_j} - \frac{A}{\Delta B^2} \frac{\partial B}{\partial x_j} \right) \left( \frac{2 \sum_{k=1}^{N_c} A_k y_k}{A} - \frac{B_i}{B} \right) \ln \left( \frac{Z + \delta_i B}{Z + \delta_2 B} \right)
\]

\[
- \frac{A}{\Delta B} \ln \left( \frac{Z + \delta_i B}{Z + \delta_2 B} \right) \left( 2A_y - \frac{2 \sum_{k=1}^{N_c} A_k y_k}{A^2} \frac{\partial A}{\partial x_j} + \frac{B_i}{B^2} \frac{\partial B}{\partial y_j} \right)
\]

\[
- \frac{A}{\Delta B} \left( \frac{2 \sum_{k=1}^{N_c} A_k x_k}{A} - \frac{B_i}{B} \right) \left( \frac{\partial Z}{\partial x_j} + \delta_1 \frac{\partial B}{\partial x_j} - \frac{\partial Z}{\partial x_j} + \delta_2 \frac{\partial B}{\partial x_j} \right)
\]

\[
\frac{\partial Z}{\partial x_j} = \frac{\frac{\partial B}{\partial x_j} \left[ A - 3B^2 - 2B - Z^2 + 6ZB + 2B \right] + \frac{\partial A}{\partial x_j} \left[ B - Z \right]}{3Z^2 + 2Z \left[ B - 1 \right] + \left[ A - 3B^2 - 2B \right]}.
\]
### Appendix C – Fluid Properties for Phase Equilibrium Calculations

Table C.1. Fluid properties of oil A. (Li & Johns, 2006)

<table>
<thead>
<tr>
<th>$z_i$</th>
<th>$T_c$ (°F)</th>
<th>$P_c$ (psia)</th>
<th>$w$</th>
<th>$h_i$</th>
<th>$g_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.05</td>
<td>87.89</td>
<td>1069.87</td>
<td>0.225</td>
<td>1</td>
</tr>
<tr>
<td>C$_1$</td>
<td>0.1</td>
<td>-116.59</td>
<td>667.2</td>
<td>0.008</td>
<td>0.3</td>
</tr>
<tr>
<td>C$_2$</td>
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<td>90.05</td>
<td>708.35</td>
<td>0.098</td>
<td>0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0.12</td>
<td>205.97</td>
<td>615.76</td>
<td>0.152</td>
<td>0</td>
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<tr>
<td>nC$_4$</td>
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<td>305.69</td>
<td>551.1</td>
<td>0.193</td>
<td>0</td>
</tr>
<tr>
<td>nC$_5$</td>
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<td>489.38</td>
<td>0.251</td>
<td>0</td>
</tr>
<tr>
<td>nC$_{10}$</td>
<td>0.29</td>
<td>652.01</td>
<td>305.68</td>
<td>0.49</td>
<td>2</td>
</tr>
</tbody>
</table>

Table C.2. BIPs for oil A.

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>nC$_4$</th>
<th>nC$_5$</th>
<th>nC$_{10}$</th>
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<td>0.12</td>
<td>0.12</td>
<td>0.114</td>
</tr>
<tr>
<td>0.144</td>
<td>0</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.071</td>
</tr>
<tr>
<td>0.12</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
</tr>
<tr>
<td>0.12</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
</tr>
<tr>
<td>0.12</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
</tr>
<tr>
<td>0.114</td>
<td>0.071</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0</td>
</tr>
</tbody>
</table>
Table C.3. Fluid properties of oil B. (Li and Johns, 2006)

<table>
<thead>
<tr>
<th></th>
<th>( z_i )</th>
<th>( MW )</th>
<th>( T_c (°F) )</th>
<th>( P_c (psia) )</th>
<th>( w )</th>
<th>( hi )</th>
<th>( gi )</th>
</tr>
</thead>
<tbody>
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<td>( \text{N}_2 )</td>
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<td>28.01</td>
<td>-232.51</td>
<td>492.32</td>
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<td>0.761</td>
<td>1.544</td>
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<td>44.01</td>
<td>87.89</td>
<td>1069.87</td>
<td>0.225</td>
<td>0.665</td>
<td>1.322</td>
</tr>
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<td>( \text{C}_1 )</td>
<td>81.35</td>
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<td>-116.59</td>
<td>667.2</td>
<td>0.008</td>
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</tr>
<tr>
<td>( \text{C}_2 )</td>
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<td>30.07</td>
<td>90.05</td>
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<td>97.21</td>
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<td>0.2569</td>
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<td>129.02</td>
<td>675.33</td>
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Table C.4. BIPs for oil B.

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<th>( \text{C}_1 )</th>
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<td>0.112</td>
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Table C.5. Fluid properties for oil C. (Hearn and Whitson, 1995)

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<th>P_c (psia)</th>
<th>w</th>
<th>h_i</th>
<th>g_i</th>
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<td>1069.87</td>
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<td>0.002151</td>
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<td>667.2</td>
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<td>708.35</td>
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<td>615.76</td>
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<td>1.003087</td>
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<tr>
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<td>3.270181</td>
<td>0.953135</td>
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<td>305.69</td>
<td>551.1</td>
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<td>489.38</td>
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<td>1.044192</td>
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<tr>
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<td>274.3</td>
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Table C.6. BIPs for oil C.

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<td>0.048</td>
<td></td>
</tr>
<tr>
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<td>0</td>
<td>0.003</td>
<td></td>
</tr>
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<td>0.003</td>
<td>0</td>
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<td>0.004</td>
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Table C.7. Fluid properties for mixture 1. (Firoozabadi & Pan (2002))

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<th>( P_c ) (psia)</th>
<th>( w )</th>
<th>( h_i )</th>
<th>( g_i )</th>
<th>( BIP ) (C(_1))</th>
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<tr>
<td>C(_1)</td>
<td>0.35</td>
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<td>667.2</td>
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<td>0.03</td>
<td>90.05</td>
<td>708.35</td>
<td>0.098</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C(_3)</td>
<td>0.04</td>
<td>205.97</td>
<td>615.76</td>
<td>0.152</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>nC(_4)</td>
<td>0.06</td>
<td>305.69</td>
<td>551.1</td>
<td>0.193</td>
<td>0</td>
<td>0.600538</td>
</tr>
<tr>
<td>nC(_5)</td>
<td>0.04</td>
<td>385.61</td>
<td>489.38</td>
<td>0.251</td>
<td>0</td>
<td>0.600538</td>
</tr>
<tr>
<td>nC(_6)</td>
<td>0.03</td>
<td>453.65</td>
<td>430.59</td>
<td>0.296</td>
<td>0</td>
<td>0.750673</td>
</tr>
<tr>
<td>nC(_7)</td>
<td>0.05</td>
<td>512.69</td>
<td>396.79</td>
<td>0.351</td>
<td>0</td>
<td>0.750673</td>
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<tr>
<td>nC(_8)</td>
<td>0.05</td>
<td>564.17</td>
<td>360.05</td>
<td>0.394</td>
<td>0</td>
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<td>235.14</td>
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Table C.8. Fluid properties for mixture 2. (Firoozabadi & Pan (2002))

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<th>( P_c ) (psia)</th>
<th>( w )</th>
<th>( h_i )</th>
<th>( g_i )</th>
<th>( BIP ) (CO(_2))</th>
<th>( BIP ) (C(_1))</th>
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<td>x</td>
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<td>1069.87</td>
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<tr>
<td>C(_1)</td>
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<td>-116.59</td>
<td>667.2</td>
<td>0.008</td>
<td>0.269</td>
<td>1.177</td>
<td>0.093</td>
</tr>
<tr>
<td>C(_2)</td>
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<td>90.05</td>
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<td>0.668</td>
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Table C.9. Fluid properties for SPE3. (Kenyon and Behie, 1987)

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Table C.10. BIPs for SPE3.

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Table C.11. Fluid properties for NWE oil. (Khan et al., 1992)

<table>
<thead>
<tr>
<th>$z_i$</th>
<th>$T_c$ (°R)</th>
<th>$P_c$ (psia)</th>
<th>$w$</th>
<th>$hi$</th>
<th>$gi$</th>
<th>BIP (CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.77</td>
<td>87.89</td>
<td>1069.87</td>
<td>0.225</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>C$_1$</td>
<td>20.25</td>
<td>-116.59</td>
<td>667.2</td>
<td>0.008</td>
<td>0</td>
<td>0.12</td>
</tr>
<tr>
<td>C$_{2-3}$</td>
<td>11.8</td>
<td>158.88</td>
<td>653.37</td>
<td>0.13</td>
<td>0</td>
<td>0.12</td>
</tr>
<tr>
<td>C$_{14-6}$</td>
<td>14.84</td>
<td>379.87</td>
<td>485.94</td>
<td>0.244</td>
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<td>0.12</td>
</tr>
<tr>
<td>C$_{7-14}$</td>
<td>28.63</td>
<td>625.86</td>
<td>351.54</td>
<td>0.6</td>
<td>0</td>
<td>0.09</td>
</tr>
<tr>
<td>C$_{15-24}$</td>
<td>14.9</td>
<td>861.15</td>
<td>261.51</td>
<td>0.903</td>
<td>0</td>
<td>0.09</td>
</tr>
<tr>
<td>C$_{25}$</td>
<td>8.81</td>
<td>1202.09</td>
<td>250.31</td>
<td>1.229</td>
<td>0</td>
<td>0.09</td>
</tr>
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Table C.12. Fluid properties for Maljamar separator oil. (Orr et al. 1981)

<table>
<thead>
<tr>
<th>$z_i$</th>
<th>$T_c$ (°R)</th>
<th>$P_c$ (psia)</th>
<th>$w$</th>
<th>$hi$</th>
<th>$gi$</th>
<th>BIP (CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.65</td>
<td>304.211</td>
<td>73.819</td>
<td>0.225</td>
<td>87.9098</td>
<td>1070.654</td>
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<tr>
<td>C$_{5-7}$</td>
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<td>516.667</td>
<td>28.82</td>
<td>0.2651</td>
<td>470.3306</td>
<td>417.9988</td>
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<tr>
<td>C$_{8-10}$</td>
<td>0.3295</td>
<td>590</td>
<td>23.743</td>
<td>0.3644</td>
<td>602.33</td>
<td>344.3631</td>
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<tr>
<td>C$_{11-14}$</td>
<td>0.1713</td>
<td>668.611</td>
<td>18.589</td>
<td>0.4987</td>
<td>743.8298</td>
<td>269.6107</td>
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<tr>
<td>C$_{15-20}$</td>
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<td>745.778</td>
<td>14.8</td>
<td>0.6606</td>
<td>882.7304</td>
<td>214.6559</td>
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<tr>
<td>C$_{21-28}$</td>
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<td>812.667</td>
<td>11.954</td>
<td>0.8771</td>
<td>1003.131</td>
<td>173.3781</td>
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<tr>
<td>C$_{29}$</td>
<td>0.0965</td>
<td>914.889</td>
<td>8.523</td>
<td>1.2789</td>
<td>1187.13</td>
<td>123.6157</td>
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</tbody>
</table>
Appendix D – Fluid Data for Fluid Characterization

Appendix D contains the fluid data for fluid characterization.

### D.1. Fluid #7 from Calsep

Table D.1. Molar composition for fluid #7 from Calsep.

<table>
<thead>
<tr>
<th></th>
<th>z</th>
<th>M</th>
<th>ρ (gr/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.56</td>
<td>28.01</td>
<td></td>
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<tr>
<td>CO₂</td>
<td>3.55</td>
<td>44.01</td>
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<tr>
<td>C₁</td>
<td>45.34</td>
<td>16.04</td>
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</tr>
<tr>
<td>C₂</td>
<td>5.48</td>
<td>30.1</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>3.7</td>
<td>44.1</td>
<td></td>
</tr>
<tr>
<td>iC₄</td>
<td>0.7</td>
<td>58.12</td>
<td></td>
</tr>
<tr>
<td>nC₄</td>
<td>1.65</td>
<td>58.12</td>
<td></td>
</tr>
<tr>
<td>iC₅</td>
<td>0.73</td>
<td>72.15</td>
<td></td>
</tr>
<tr>
<td>nC₅</td>
<td>0.87</td>
<td>72.15</td>
<td></td>
</tr>
<tr>
<td>C₆</td>
<td>1.33</td>
<td>86.18</td>
<td>0.664</td>
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<td>C₇</td>
<td>2.73</td>
<td>89.9</td>
<td>0.757</td>
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<tr>
<td>C₈</td>
<td>3.26</td>
<td>103.2</td>
<td>0.777</td>
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<td>2.14</td>
<td>117.7</td>
<td>0.796</td>
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<tr>
<td>C₁₀</td>
<td>1.94</td>
<td>133</td>
<td>0.796</td>
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<tr>
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<td>0.8</td>
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<tr>
<td>C₁₂</td>
<td>1.47</td>
<td>160</td>
<td>0.815</td>
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<tr>
<td>C₁₃</td>
<td>1.69</td>
<td>172</td>
<td>0.833</td>
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<tr>
<td>C₁₄</td>
<td>1.62</td>
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<td>0.843</td>
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<td>C₁₅</td>
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<tr>
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<td>0.851</td>
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<tr>
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<td>0.856</td>
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<td>0.868</td>
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<td>13.32</td>
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<td>0.914</td>
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</table>
Table D.2. Differential Liberation Data for fluid #7 from Calsep.

<table>
<thead>
<tr>
<th>Stage</th>
<th>P (bar)</th>
<th>Oil FVF Bod</th>
<th>Rsd Sm³/Sm³</th>
<th>Oil density g/cm³</th>
<th>Z gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>267.9</td>
<td>1.396</td>
<td>132.9</td>
<td>0.718</td>
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<tr>
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<td>119.4</td>
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<td>0.889</td>
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<tr>
<td>3</td>
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<td>1.329</td>
<td>103.7</td>
<td>0.735</td>
<td>0.888</td>
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<tr>
<td>4</td>
<td>179.8</td>
<td>1.297</td>
<td>89.6</td>
<td>0.744</td>
<td>0.876</td>
</tr>
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<td>1.265</td>
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<td>0.753</td>
<td>0.88</td>
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<td>58.6</td>
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<tr>
<td>7</td>
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<td>40.4</td>
<td>0.778</td>
<td>0.904</td>
</tr>
<tr>
<td>8</td>
<td>33.1</td>
<td>1.144</td>
<td>21.9</td>
<td>0.791</td>
<td>0.949</td>
</tr>
<tr>
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<td>1</td>
<td>1.067</td>
<td>0</td>
<td>0.816</td>
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</tr>
</tbody>
</table>

Table D.3. BIPs for fluid #7 from Calsep.

| N₂    | -0.0315 |
| CO₂   | 0.0278  |
| C₁    | 0.0407  |
| C₂    | 0.0763  |
| C₃    | 0.0944  |
| iC₄   | 0.07    |
| nC₄   | 0.0867  |
| iC₅   | 0.0878  |
| nC₅   | 0.08    |
| C₆    | 0.08    |
| C₇⁺   | 0.08    |
### D.2. Oil F1

Table D.4. Molar composition for oil F1 from Jaubert et al. (2002).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol %</th>
<th>Mol wt</th>
<th>Liquid Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.18</td>
<td>28.014</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.82</td>
<td>44.01</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>22.92</td>
<td>16.04</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>7.21</td>
<td>30.07</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>7.37</td>
<td>44.1</td>
<td></td>
</tr>
<tr>
<td>iC₄</td>
<td>1.58</td>
<td>58.12</td>
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</tr>
<tr>
<td>nC₄</td>
<td>5.23</td>
<td>58.12</td>
<td></td>
</tr>
<tr>
<td>iC₅</td>
<td>2.25</td>
<td>72.15</td>
<td></td>
</tr>
<tr>
<td>nC₅</td>
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<td>72.15</td>
<td></td>
</tr>
<tr>
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<td>4.84</td>
<td>86</td>
<td>0.67</td>
</tr>
<tr>
<td>C₇</td>
<td>4.72</td>
<td>92</td>
<td>0.70</td>
</tr>
<tr>
<td>C₈</td>
<td>4.52</td>
<td>102</td>
<td>0.73</td>
</tr>
<tr>
<td>C₉</td>
<td>4.07</td>
<td>117</td>
<td>0.76</td>
</tr>
<tr>
<td>C₁₀</td>
<td>3.5</td>
<td>134</td>
<td>0.78</td>
</tr>
<tr>
<td>C₁₁</td>
<td>2.91</td>
<td>151</td>
<td>0.79</td>
</tr>
<tr>
<td>C₁₂</td>
<td>2.42</td>
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<td>0.79</td>
</tr>
<tr>
<td>C₁₃</td>
<td>1.99</td>
<td>178</td>
<td>0.80</td>
</tr>
<tr>
<td>C₁₄</td>
<td>1.74</td>
<td>194</td>
<td>0.82</td>
</tr>
<tr>
<td>C₁₅</td>
<td>2.02</td>
<td>208</td>
<td>0.83</td>
</tr>
<tr>
<td>C₁₆</td>
<td>1.39</td>
<td>225</td>
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</tr>
<tr>
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<td>1.21</td>
<td>239</td>
<td>0.84</td>
</tr>
<tr>
<td>C₁₈</td>
<td>0.9</td>
<td>249</td>
<td>0.85</td>
</tr>
<tr>
<td>C₁₉</td>
<td>1.17</td>
<td>270</td>
<td>0.86</td>
</tr>
<tr>
<td>C₂₀</td>
<td>11.44</td>
<td>560</td>
<td>0.95</td>
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</tbody>
</table>
Table D.5. PVT data for oil F1 from Jaubert et al. (2002).

CME data at 374.85 °K

<table>
<thead>
<tr>
<th>P (kPa)</th>
<th>V/Vb</th>
<th>ρ (kg/m³)</th>
</tr>
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<tbody>
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<td>36500</td>
<td>0.959</td>
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</tr>
<tr>
<td>25700</td>
<td>0.971</td>
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</tr>
<tr>
<td>16000</td>
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</tr>
<tr>
<td>9350</td>
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<tr>
<td>8830</td>
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</table>

Slim tube test

<table>
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<th>P (kPa)</th>
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D.3. Oil F2

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<th>Mol %</th>
<th>Mol wt</th>
<th>Liquid Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.18</td>
<td>28.01</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.82</td>
<td>44.01</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>22.92</td>
<td>16.04</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>7.21</td>
<td>30.07</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>7.37</td>
<td>44.1</td>
<td></td>
</tr>
<tr>
<td>iC₄</td>
<td>1.58</td>
<td>58.12</td>
<td></td>
</tr>
<tr>
<td>nC₄</td>
<td>5.23</td>
<td>58.12</td>
<td></td>
</tr>
<tr>
<td>iC₅</td>
<td>2.25</td>
<td>72.15</td>
<td></td>
</tr>
<tr>
<td>nC₅</td>
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<td>72.15</td>
<td></td>
</tr>
<tr>
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<tr>
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<td>4.72</td>
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<td>0.70</td>
</tr>
<tr>
<td>C₈</td>
<td>4.52</td>
<td>102</td>
<td>0.73</td>
</tr>
<tr>
<td>C₉</td>
<td>4.07</td>
<td>117</td>
<td>0.76</td>
</tr>
<tr>
<td>C₁₀</td>
<td>3.5</td>
<td>134</td>
<td>0.78</td>
</tr>
<tr>
<td>C₁₁</td>
<td>2.91</td>
<td>151</td>
<td>0.79</td>
</tr>
<tr>
<td>C₁₂</td>
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<td>0.79</td>
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<tr>
<td>C₁₃</td>
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<td>0.80</td>
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<tr>
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<tr>
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<td>225</td>
<td>0.84</td>
</tr>
<tr>
<td>C₁₇</td>
<td>1.21</td>
<td>239</td>
<td>0.84</td>
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<tr>
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Table D.7. PVT data for oil F2 from Jaubert et al. (2002).

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<tr>
<td>293.2</td>
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<tr>
<td>234.8</td>
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<td>177.4</td>
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<td>114.6</td>
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<table>
<thead>
<tr>
<th>Slim tube test</th>
</tr>
</thead>
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</tr>
<tr>
<td>---</td>
</tr>
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D.4. Oil F3

Table D.8. Molar composition for oil F3 from Jaubert et al. (2002).

<table>
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<tr>
<th>Component</th>
<th>Mol %</th>
<th>Mol wt</th>
<th>Liquid Density g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.450</td>
<td>28.014</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.640</td>
<td>44.010</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>45.850</td>
<td>16.043</td>
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</tr>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.7294</td>
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<tr>
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<td>106.000</td>
<td>0.7509</td>
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<td>120.000</td>
<td>0.7739</td>
</tr>
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<td>137.000</td>
<td>0.7835</td>
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<td>C₁₁</td>
<td>1.810</td>
<td>146.000</td>
<td>0.7968</td>
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<td>C₁₂</td>
<td>1.470</td>
<td>159.000</td>
<td>0.8057</td>
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<tr>
<td>C₁₃</td>
<td>1.450</td>
<td>172.000</td>
<td>0.8151</td>
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<tr>
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<td>183.000</td>
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<td>0.820</td>
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<td>249.000</td>
<td>0.8491</td>
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Table D.9. PVT Data for oil F3 from Jaubert et al. (2002).

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>V/Vₕ</th>
<th>ρ (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>391</td>
<td>0.965</td>
<td>640.21</td>
</tr>
<tr>
<td>351.8</td>
<td>0.973</td>
<td>634.52</td>
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<td>626.17</td>
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<td>0.998</td>
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<td>255.6</td>
<td>1.000</td>
<td>617.67</td>
</tr>
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<td>252.9</td>
<td>1.003</td>
<td>615.76</td>
</tr>
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<td>248.9</td>
<td>1.009</td>
<td>612.75</td>
</tr>
<tr>
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</table>
### DL data at 387.35 °K

<table>
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<tr>
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<th>$\rho$ (kg/m³)</th>
<th>GOR$_{LG}$</th>
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<td>-</td>
</tr>
<tr>
<td>351</td>
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### Swelling test at 387.35 °K

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<th>$100\times X^\text{gas}$</th>
<th>$P_{sat}$/bar</th>
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<th>$V_{swell}$</th>
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<td>575</td>
<td>1.149</td>
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<tr>
<td>32.2</td>
<td>364.8</td>
<td>551.7</td>
<td>1.25</td>
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<tr>
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<td>400</td>
<td>528.9</td>
<td>1.37</td>
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<td>50</td>
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<td>1.513</td>
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### CME at $X^\text{gas} = 0.112$

<table>
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### CME at $X^\text{gas} = 0.222$

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<tr>
<td>387.8</td>
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<td>347.8</td>
<td>0.9922</td>
<td>579.37</td>
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<tr>
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<td>0.9983</td>
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<td>322.6</td>
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### CME at $X_{\text{gas}} = 0.322$

<table>
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</thead>
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<tr>
<td>438.6</td>
<td>0.9723</td>
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<td>418.2</td>
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### CME at $X_{\text{gas}} = 0.414$

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### CME at $X_{\text{gas}} = 0.5$

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</thead>
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<tr>
<td>549.3</td>
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<tr>
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<td>0.9668</td>
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</tr>
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### Slim tube test

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### D.5. Injected gas compositions

Table D.10. Molar compositions of the injected gases from Jaubert et al. (2002).

<table>
<thead>
<tr>
<th>Compound</th>
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<th>G₂</th>
<th>G₃</th>
<th>G₄</th>
<th>G₅a</th>
<th>G₅b</th>
<th>G₆a</th>
<th>G₆b</th>
<th>G₇</th>
<th>G₈</th>
<th>G₉</th>
<th>G₁₀</th>
<th>G₁₁</th>
<th>G₁₂</th>
<th>G₁₃</th>
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<td>1</td>
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<tr>
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<td>0.48</td>
<td>0.49</td>
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<td>0</td>
<td>1.15</td>
<td>0.97</td>
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<td>0.42</td>
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<td>0.91</td>
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<td>0.26</td>
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<td>0.41</td>
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</tbody>
</table>
VITA

Seyhan Emre Gorucu

Seyhan Emre Gorucu received a BSc degree in Mining Engineering from the Middle East Technical University, Ankara, Turkey in 2008, an MSc degree and a PhD degree in Petroleum Engineering from the Penn State, PA in 2010 and 2013, respectively. During his Master’s degree, he developed an Artificial Neural Network toolbox to estimate the gas production from Tight Gas Reservoirs. During his PhD research, he worked on phase equilibrium calculation algorithms. He is currently working as a reservoir simulation engineer at Computer Modelling Group in Dubai.