PHASE BEHAVIOUR OF SOLVENT(S)/WATER/HEAVY OIL SYSTEMS AT HIGH PRESSURES AND ELEVATED TEMPERATURES BASED ON ISENTHALPIC FLASH

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Desheng Huang, candidate for the degree of Doctor of Philosophy in Petroleum Systems Engineering, has presented a thesis titled, *Phase Behaviour of Solvent(s)/ Water/Heavy Oil Systems at High Pressures and Elevated Temperatures Based on Isenthalpic Flash*, in an oral examination held on August 27, 2020. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

The hybrid steam-solvent injection processes have been proved to be a promising technique for enhancing heavy oil recovery as they combine the advantages from both heat transfer of steam and mass transfer of solvent(s) to further reduce the viscosity of heavy oil. Multiphase isenthalpic flash calculation is required in compositional simulations of the aforementioned processes, which involve vapour, oleic, and aqueous three-phases since water is inevitably associated with steam injection processes. As such, it is of fundamental and pragmatic importance to accurately quantify the phase behaviour of solvent(s)/water/heavy oil systems at high pressures and elevated temperatures by use of isenthalpic flash algorithms.

A modified correlation and a new enthalpy determination algorithm have been developed to more accurately predict ideal gas heat capacities and enthalpies for normal alkanes/alkenes and hydrocarbon fractions, respectively. By assuming that only the presence of water and solvents with high solubilities in water is considered in the aqueous phase, a robust and pragmatic water-associated isenthalpic flash (WAIF) model has been developed to perform multiphase isenthalpic flash calculations for solvent(s)/water/heavy oil mixtures at high pressures and elevated temperatures. The new isenthalpic flash model developed in this work can handle multiphase equilibria flash calculations at high pressures and elevated temperatures.
Subsequently, phase boundaries of C$_3$H$_8$/CO$_2$/water/heavy oil mixtures in both the pressure-temperature ($P$-$T$) and enthalpy-temperature ($H$-$T$) phase diagrams have been determined, respectively. Experimentally, the phase boundary pressures are determined for three C$_3$H$_8$/CO$_2$/water/heavy oil mixtures by using a conventional pressure-volume-temperature (PVT) setup in the $P$-$T$ phase diagram. Theoretically, the previously developed WAIF model and the new isenthalpic determination algorithm together with the new alpha functions for water and non-water components are applied as the thermodynamic model to reproduce the multiphase boundaries of the aforementioned systems. The water-associated model is able to provide a good prediction of the experimental measurement in terms of phase boundaries and phase compositions. In addition, a new algorithm is developed to determine vapour/liquid/liquid (VL$_1$L$_2$) phase boundaries of alkane solvent(s)/CO$_2$/heavy oil mixtures.

A new thermodynamic model based on the modified Peng-Robinson equation of state (PR EOS) together with the Huron-Vidal mixing rule is developed to experimentally and theoretically quantify the phase behaviour of dimethyl ether (DME)/water/heavy oil mixtures which include polar components. The new model is capable of accurately reproducing the experimentally measured multiphase $P$-$T$ and $H$-$T$ boundaries, phase volumes, and swelling factors, while it can also be used to determine DME partition coefficients and DME solubility.
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DEDICATION

This dissertation is dedicated to my beloved wife, Mrs. Jingjing Tao and my dearest parents, Mrs. Cuie Zhang and Mr. Wanjin Huang
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NOMENCLATURE

Notations

\( a \)  attraction parameter defined in Equation [3-1]

\( a_c \)  constant defined in Equation [3-2a]

A  aqueous phase

\( A \)  constant defined in Equation [3-4a]

\( A_0, A_1, \ldots, A_8 \)  empirical constants

\( A^E \)  excess Helmholtz free energy

\( b \)  van der Waals volume, \( m^3/kmol \)

B  parameter defined in Equation [7-2c]

\( B \)  constant defined in Equation [3-4b]

\( B_0, B_1, B_2 \)  empirical constants

\( c_1, c_2, \ldots, c_4 \)  empirical constants

\( C_F \)  corrective factor defined in Equation [3-8]

\( C_i \)  volume-shift parameter of the \( i \)th component

\( C_p \)  ideal gas heat capacity, \( J/(mol\cdot K) \)

\( C_p^{\text{cal}} \)  calculated heat capacity, \( J/(mol\cdot K) \)

\( C_p^{\exp} \)  measured heat capacity, \( J/(mol\cdot K) \)

\( C_p^L \)  liquid specific heat capacity, \( J/(mol\cdot K) \)
\( C_{pi}^0 \) ideal gas heat capacity coefficient of the \( i \)th component

\( C_{p2i}^0 \) ideal gas heat capacity coefficient of the \( i \)th component

\( C_{p3i}^0 \) ideal gas heat capacity coefficient of the \( i \)th component

\( C_{p4i}^0 \) ideal gas heat capacity coefficient of the \( i \)th component

\( C_p^v \) specific heat capacity of vapour, J/(mol·K)

\( e_1, e_2, \ldots, e_4 \) coefficients defined in Equation [5-3]

\( f_i \) fugacity of the \( i \)th component

\( f_{ix} \) fugacity of the \( i \)th component in hydrocarbon-rich liquid phase

\( f_{iy} \) fugacity of the \( i \)th component in vapour phase

\( f_{iw} \) fugacity of the \( i \)th component in aqueous phase

\( g_{\mu} \) energy parameter defined in Equation [7-7], J/mol

\( g_s^L \) residual of the energy conservation equation at the lower boundary temperature

\( g_s^U \) residual of the energy conservation equation at the upper boundary temperature

\( g_{s\mu}^{lev} \) residual of the energy conservation equation

\( G_{\infty}^E \) excess Gibbs free energy at infinite pressure, J/mol

\( H_{dep}^c \) enthalpy departure, J/mol

\( H_{cal}^c \) calculated enthalpy, J/mol

\( H_{meas}^c \) measured molar enthalpy, J/mol
\( H^L \) liquid enthalpy, J/mol

\( H^{IG} \) ideal gas enthalpy, J/mol

\( H_k \) molar enthalpy of phase \( k \), J/mol

\( H^IGM_k \) molar ideal gas mixture enthalpy of phase \( k \), J/mol

\( H^\text{dep}_k \) molar enthalpy departure, J/mol

\( H_{\text{spec}} \) specified molar enthalpy, J/mol

\( H_t \) total enthalpy, J/mol

\( H^V \) vapour enthalpy, J/mol

\( H^{\text{vap}} \) enthalpy of vaporization at the boiling point temperature, J/mol

\( \text{iter} \) number of iterations

\( K_{iy} \) equilibrium ratio of the \( i \)th component in vapour phase

\( K_{iw} \) equilibrium ratio of the \( i \)th component in aqueous phase

\( K_W \) Watson factor

\( L \) hydrocarbon-rich liquid phase

\( n \) number of data points

\( N \) number of data points

\( N_c \) number of components

\( N_p \) number of phases

\( P \) pressure, kPa

\( P_c \) critical pressure, kPa

xxv
$P_{cw}$ critical pressure of water, kPa

$P_{i}^{cal}$ calculated phase boundary, kPa

$P_{i}^{exp}$ measured phase boundary, kPa

$P_{sat}^{w}$ saturation pressure of water, kPa

$R$ universal gas constant, J/(mol·K)

$SF$ swelling factor

$SG$ specific gravity

$S$ DME solubility in heavy oil

$S_{k}$ molar entropy of phase $k$

$S_{t}$ total entropy

$T$ temperature, K

$T_{0}$ reference temperature, 273.15 K

$T^{i}$ initial temperature, K

$T_{b}$ normal boiling point at 1 atm, K

$T_{br}$ reduced normal boiling point

$T_{bR}$ normal boiling point temperature, °R

$T_{c}$ critical temperature, K

$T_{cR}$ critical temperature, °R

$T_{cw}$ critical temperature of water, K

$T_{K}$ temperature, K
$T_L$  
the lower boundary temperature, K

$T_r$  
reduced temperature

$T_U$  
the upper boundary temperature, K

$T_{U1}$  
phase transition temperature, K

$T_{U2}$  
phase transition temperature, K

$T_{U3}$  
phase transition temperature, K

$T_{rw}$  
reduced temperature of water

$V$  
vapour phase

$V$  
molar volume, m$^3$/kmol

$V_1$  
molar volume of DME-heavy oil mixtures at saturation state, m$^3$/kmol

$V_2$  
molar volume of dead heavy oil at saturation temperature and atmospheric pressure, m$^3$/kmol

$V_c$  
corrected molar volume, m$^3$/kmol

$V_{eos}$  
original molar volume, m$^3$/kmol

$V_M$  
molar volume

$w_i$  
mole fraction of the $i$th component in aqueous phase

$x_i$  
mole fraction of the $i$th component in hydrocarbon-rich liquid phase

$x_{ik}$  
mole fraction of the $i$th component in phase $k$

$x_{iNp}$  
mole fraction of the $i$th component in the reference phase

$y_i$  
mole fraction of the $i$th component in vapour phase
\( z_i \)  
mole fraction of the \( i \)th component in the feed

\( Z \)  
compressibility factor

\( Z_L \)  
liquid compressibility factor

\( Z_{RA} \)  
Rackett compressibility factor

\( Z_V \)  
vapour compressibility factor

**Greek Letters**

\( \alpha \)  
alpha function in the PR EOS defined in Equation [3-2a]

\( \alpha_{H,O} \)  
alpha function for water in PR EOS

\( \alpha_{ji} \)  
non-randomness parameter

\( \beta \)  
parameter in Equation [7-2b]

\( \beta_x \)  
phase fractions in hydrocarbon-rich liquid phase

\( \beta_y \)  
phase fractions in vapour phase

\( \beta_k \)  
phase fractions in phase \( k \)

\( \beta_w \)  
phase fractions in aqueous phase

\( \varepsilon \)  
tolerance

\( \delta \)  
BIP

\( \delta_{H,O-water} \)  
BIP for heavy oil-water pair

\( \phi_i \)  
fugacity coefficient of the \( i \)th component

\( \phi_{ix} \)  
fugacity coefficient of the \( i \)th component in hydrocarbon-rich liquid phase
\( \phi_{iy} \)  
- fugacity coefficient of the \( i \)th component in vapour phase

\( \phi_{ix} \)  
- fugacity coefficient of the \( i \)th component in aqueous phase

\( \gamma_i \)  
- activity coefficient

\( \lambda \)  
- EOS-dependent parameter

\( \rho_o \)  
- density of the heavy oil, kg/m\(^3\)

\( \tau_{ji} \)  
- parameter defined in Equation [7-7]

\( \omega \)  
- acentric factor

**Abbreviations**

ARD  
- absolute relative deviation

AARD  
- absolute average relative deviation

API  
- American Petroleum Institute

BIP  
- binary interaction parameter

BWR EOS  
- Benedict-Webb-Rubin equation of state

CCE  
- constant composition expansion

CEOS  
- cubic equation of state

CHOPS  
- cold heavy oil production with sand

CTIF  
- conventional three-phase isenthalpic flash

CSS  
- cyclic steam stimulation

DME  
- dimethyl ether
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOR</td>
<td>enhanced oil recovery</td>
</tr>
<tr>
<td>ES-SAGD</td>
<td>expanding solvent steam-assisted gravity drainage</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>IFT</td>
<td>interfacial tension</td>
</tr>
<tr>
<td>MARD</td>
<td>maximum absolute relative deviation</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>OOIP</td>
<td>original oil in place</td>
</tr>
<tr>
<td>PR EOS</td>
<td>Peng-Robinson equation of state</td>
</tr>
<tr>
<td>RF</td>
<td>recovery factor</td>
</tr>
<tr>
<td>RMSRE</td>
<td>root-mean-squared relative error</td>
</tr>
<tr>
<td>RTD</td>
<td>resistance temperature device</td>
</tr>
<tr>
<td>SAGD</td>
<td>steam-assisted gravity drainage</td>
</tr>
<tr>
<td>SF</td>
<td>steam flooding</td>
</tr>
<tr>
<td>SOR</td>
<td>steam-oil ratio</td>
</tr>
<tr>
<td>SRK EOS</td>
<td>Soave-Redlich-Kwong equation of state</td>
</tr>
<tr>
<td>VAPEX</td>
<td>vapour extraction</td>
</tr>
<tr>
<td>VLE</td>
<td>vapour-liquid equilibrium</td>
</tr>
<tr>
<td>WAIF</td>
<td>water-associated isenthalpic flash</td>
</tr>
<tr>
<td>WFIF</td>
<td>water-free isenthalpic flash</td>
</tr>
</tbody>
</table>
CHAPTER 1 INTRODUCTION

1.1 Heavy Oil Recovery

It has been estimated that the amount of heavy oil and bitumen is about 6-8 trillion barrels which accounts for more than two thirds of the worldwide crude oil resources (Dong et al., 2019). It is difficult to effectively and efficiently recover heavy oil and bitumen as there are many technical challenges such as high viscosity and density as well as low API gravity and low mobility of these resources under the original reservoir conditions (Butler, 1991; Jiang et al., 2009; Lin et al., 2014).

The primary, secondary, and tertiary oil recovery or enhanced oil recovery (EOR) processes have been extensively employed for producing heavy oil in Canada and the other parts of the world. Cold heavy oil production with sand (CHOPS) is a common primary recovery technique used for heavy oil production in Canada because of its low capital and operating investments (Zhao and Gates, 2015). Economical recovery factors of CHOPS can reach up to 15% of original oil in place (OOIP) due to the solution gas drive energy from a reservoir and application without sand control operations (Sheng, 2013). However, this method has limitations because of quick depletion of the reservoir energy and restricted reservoir conditions and characteristics such as high permeability (i.e., wormholes) and relatively low oil viscosity (Tremblay et al., 1997; Istchenko and Gates, 2014; Fan et al., 2019; 2020; Yang et al., 2020). Waterflooding and polymer
flooding are the widely used secondary oil recovery techniques to improve heavy oil recovery (Zhao and Gates, 2015). Although they are technically simple with low operating costs, the oil recovery factors are pretty low owing to the displacement disability resulting from unfavourable mobility ratio and viscous fingering (Mai and Kantzas, 2009; Lin et al., 2014).

There are two major categories of EOR techniques for heavy oil reservoirs, i.e., steam- and solvent-based EOR methods, together with other auxiliary methods such as chemical flooding and in-situ combustion. The steam-based oil recovery methods such as cyclic steam stimulation (CSS) and steam-assisted gravity drainage (SAGD) have wide applications in the oil industry for several decades because of their capability of significantly reducing heavy oil viscosity (Farouq Ali, 1994; Albahlani and Babadagli, 2008; Jimenez, 2008; Jiang et al., 2010). As for solvent-based heavy oil recovery techniques, a solvent or a mixture of several solvents is injected into a reservoir to dilute the heavy oil and reduce its viscosity. Although they have many significant advantages in comparison to the steam-based methods in terms of cost effectiveness, energy efficiency, and environmental footprints (James et al., 2008; Lin et al., 2014), these processes have not achieved a high commercial level in the oilfields due to the slow solvent diffusion into heavy oil and low oil production rate (Das and Butler, 1998; Jang et al., 2008).
Although CSS and SAGD have been commercially applied in the oilfields to successfully enhance heavy oil recovery (Jiang et al., 2009), there are several technical and environmental issues associated with the steam-based thermal methods, such as extensive heat losses and large energy and water consumptions as well as expensive water treatment and significant greenhouse gas emissions (Lin et al., 2014). Recently, hybrid steam-solvent processes are proposed to combine the advantages from both the steam- and solvent-based heavy oil recovery methods. Expanding solvent steam-assisted gravity drainage (ES-SAGD) and liquid addition to steam for enhancing recovery (LASER) are typical hybrid steam-solvent processes with promising applications with respect to heavy oil production rates, ultimate recovery factors (RFs), and steam-oil ratios (SORs) (Sheng et al., 2018).

The phase behaviour of solvent(s)/water/heavy oil mixtures is of significance to help reservoir engineers monitor and evaluate the change of reservoir fluid properties as a function of reservoir pressure, temperature, and compositions during the aforementioned hybrid steam-solvent processes (Jia et al., 2011; Venkatramani and Okuno, 2017). Conventionally, effects of aqueous phase on the phase behaviour of solvent(s)/water/heavy oil mixtures are not considered in most of the compositional models and experimental measurements because of the inherent difficulties and physical constraints (Coats, 1980; Young and Stephenson, 1983; Jia et al., 2011). It is well-known that water plays a significant role in accurately quantifying phase behaviour of such
systems (Lapene et al., 2010); however, few attempts have been made to quantify the phase behaviour of solvent(s)/water/heavy oil systems for thermal heavy oil recovery processes in which temperature variations occur. Phase behaviour and physical properties of reservoir fluids at each grid and each time step can be well captured by using EOS-based thermal simulators, while input variables selected for performing flash calculations in each grid are feed composition, pressure, and enthalpy. In particular, isenthalpic flash is more general than isothermal flash because the former can be applied to the cases of one degree of freedom (Brantferger et al., 1991; Zhu and Okuno, 2014; 2015; 2016). In addition, thermal recovery processes involve large temperature changes, which invalidates the isothermal assumptions. The governing equations require an energy balance, though the temperature in each grid-block is unknown, leading to an isenthalpic flash problem (Paterson et al., 2016). Furthermore, convergence difficulties are encountered during steam injection simulations (Brantferger, 1991; Heidari et al., 2014), while these difficulties may be better handled in flow simulation with isenthalpic flash than isothermal flash because the former can handle narrow-boiling behaviour in local flash calculations that are decoupled from the global mass and energy flow equations (Zhu, 2017). As such, it is of fundamental and practical importance to accurately quantify the phase behaviour of solvent(s)/water/heavy oil mixtures at high pressures and elevated temperatures by use of isenthalpic flash.
1.2 Objectives of This Study

The main objective of this thesis study is to develop pragmatic algorithms together with theoretical models/correlations to accurately determine the phase behaviour of solvent(s)/water/heavy oil systems at high pressures and elevated temperatures for the hybrid thermal-solvent EOR methods in heavy oil reservoirs. The detailed objectives are listed as follows:

1) To develop correlations and algorithms to improve enthalpy prediction of heavy hydrocarbons;

2) To develop an isenthalpic flash algorithm for solvent(s)/water/heavy oil mixtures to accurately and efficiently obtain system temperature, phase fractions, and phase compositions;

3) To develop a reliable and robust thermodynamic model to accurately describe the interaction of polar components for solvent(s)/water/heavy oil mixtures; and

4) To conduct PVT tests to measure phase behaviour and physical properties of CO$_2$/C$_3$H$_8$/water/heavy oil and DME/water/heavy oil systems at high pressures and elevated temperatures to validate the proposed theoretical models as well as to improve modeling the phase behaviour of solvent(s)/water/heavy oil systems.
1.3 Outline of the Dissertation

There are eight chapters in this dissertation. Chapter 1 introduces the research topic together with the main objectives. Chapter 2 provides a comprehensive literature review on heavy oil recovery processes, isothermal flash, and isenthalpic flash algorithms, together with phase behaviour of solvent(s)/water/heavy oil systems. Chapter 3 proposes a modified correlation and new enthalpy determination method to more accurately predict ideal gas heat capacities and enthalpies for normal alkanes/alkenes and hydrocarbon fractions, respectively. Chapter 4 presents a modified water-associated isenthalpic flash model for solvent(s)/water/heavy oil systems with the consideration of solvents with high solubilities in the aqueous phase. Chapter 5 provides the experimentally measured and theoretically calculated phase boundaries of C₃H₈/CO₂/water/heavy oil mixtures in both the $P$-$T$ and $H$-$T$ phase diagrams, respectively. Chapter 6 states the determination of multiphase boundaries of solvent(s)/heavy oil mixtures in $P$-$T$, $H$-$T$, and pressure-enthalpy ($P$-$H$) phase diagrams, respectively. Chapter 7 presents the experimentally measured and theoretically calculated phase behaviours of DME/water/heavy oil systems. Finally, major scientific conclusions of the current research and recommendations for future work are addressed in Chapter 8.
CHAPTER 2 LITERATURE REVIEW

2.1 Steam-Based EOR

The major challenge and difficulty in heavy oil and bitumen recovery is their inherent high viscosity and low mobility under reservoir conditions (Ardali et al., 2012). Steam-based thermal recovery techniques such as CSS, steam flooding (SF), and SAGD have been proven to be effective for recovering heavy oil and bitumen to a certain extent due to the fact that the injected thermal energy is able to significantly reduce the viscosity of heavy oil and bitumen (Gates and Larter, 2014; Rui et al., 2018). It is well-known that steam is an effective agent to deliver heat to mobilize heavy oil that is essential for the success of any steam-based EOR processes. As can be seen from Figure 2-1, oil viscosity is decreased rapidly with an increase in temperature, especially at relatively low temperatures. This means that injecting thermal energy (e.g., steam) into a cold heavy oil reservoir can considerably reduce oil viscosity, and thus, enhance heavy oil recovery.

The most popular steam-based EOR methods applied currently will be discussed in the following sections, which include CSS, SF, and SAGD. These techniques have been successfully demonstrated to be able to achieve high oil production rates and ultimate oil recovery factors in Canada, Venezuela, and other parts of the world (Al-Bahlani and Babadagli, 2009).
Figure 2-1 A typical viscosity-temperature profile of Athabasca bitumen (modified from Nasr and Ayodele, 2005)
(I) CSS

CSS involves injecting steam into a reservoir periodically, during which the same well is used for both steam injection and heavy oil production (see Figure 2-2). In general, each cycle consists of three stages: steam injection, steam soaking, and oil production. Specifically, a predetermined amount of steam is injected into a well at a high pressure for a period of time from a couple of weeks to a few months (i.e., injection stage). Subsequently, the well is shut down for several days to weeks to allow the heat to propagate into the reservoir (i.e., soaking stage). In the last stage, the injection well is converted to a production mode and hot oil and water is pumped out of the well for several weeks or months (i.e., production stage). Afterwards, new cycles are repeated until its uneconomical limits are reached. CSS is most commonly applied to reservoirs with high porosity and oil saturation as well as a pay thickness greater than 30 ft (9 m) and depth less than 3000 ft (915 m) (Taber et al., 1997). Typical recovery factors for CSS are in a range of 10-30% of original oil in place (OOIP) (Alvarez and Han, 2013).

There are two major recovery mechanisms involved with a CSS process: (1) The most important one is viscosity reduction because of an increase of reservoir temperature (see Figure 2-1); and (2) Wettability change is the second one to facilitate mobilizing the heated heavy oil. The reservoir becomes more water-wet because the injected steam forms a thin water layer and adheres to rock surface, preventing oil from contacting the rock surface (Escrochi et al., 2008).
Figure 2-2 Schematic of a CSS process (Source: Imperial Oil)
(2) SF

Similar to the conventional waterflooding operation, SF is a heavy oil recovery method that high quality steam is continuously injected into injection wells and the heated oil is driven to production wells (see Figure 2-3). The SF has seen successful applications to reservoirs with depth less than 5000 ft (1520 m) and permeability higher than 200 mD (Butler, 1991).

Compared to CSS, two principal EOR mechanisms are involved in a SF process: (1) The drastic oil viscosity reduction due to the increasing of reservoir temperature; and (2) Physical displacement of oil by steam and hot water. Other mechanisms may include thermal swelling, relative permeability modification, and wettability alteration (Doscher, 1967). Although SF is more expensive than CSS since more steam is required during its field operations, the typical recovery factors of SF can be up to 50% of OOIP, which are higher than those from CSS (Harrigal and Clayton, 1992).

In addition to providing a higher oil recovery factor, SF is also able to produce oil at a faster rate than that of CSS. The main drawbacks of SF are high SOR and difficult to start production flow. The former is ascribed to the fact that it is necessary to heat a larger portion of a given reservoir, unlike a CSS process where the heating is confined to a smaller region near the wellbore. The latter is due mainly to the lack of flow communication between injection wells and production wells (Butler, 1991).
Figure 2-3 Schematic of a SF process (Sabatino et al., 2013)
(3) SAGD

SAGD is originally invented by Dr. Roger Butler and his colleagues in Imperial Oil in the late 1970s, which is a dominant commercial technology employed for in-situ recovery of heavy oil and bitumen in Canada (Ardali et al., 2012; Esmaeili et al., 2020). In a SAGD process, a pair of parallel horizontal wells are placed near the bottom of the formation with one a few meters (4-6 m) above another on the same vertical plane. The upper well is used as a steam injector, whereas the lower one is used as a producer (see Figure 2-4). The injected steam rises under buoyancy forces and forms a steam chamber above the injection well (Nasr and Ayodele, 2005). Then, the steam grows both vertically and horizontally and condenses near the boundary of the chamber to heat the heavy oil, resulting in significant oil viscosity reduction. The mobilized oil and steam condensate together with formation water are produced from the lower production well. The dominant EOR mechanisms of a SAGD process are viscosity reduction and gravity drainage compared to others such as solution gas drive, steam drive, thermal expansion, and steam distillation (Edmunds and Chhina, 2001).

A recovery factor of 60% can be achieved in a SAGD process compared to CSS and SF due to the gravitational force (Jiang et al., 2010). Based on the commonly accepted economic cutoff values, the minimum requirements for SAGD are reservoirs with a pay thickness greater than 40 ft (12 m) and permeability higher than 3 D without bottom water and/or gas cap (McCormack, 2001).
Figure 2-4 Schematic of a SAGD process and a steam chamber (Kumar, 2013)
2.2 Solvent-Based EOR

Due to the high energy intensity and the associated environmental impacts of steam-based heavy oil recovery processes, solvent-based EOR methods have been proposed as an alternative and novel approach for heavy oil and bitumen production, especially for thin heavy oil reservoirs where steam-based EOR methods are not suitable due to excessive heat losses and extensive steam consumption (Lin et al., 2014). In general, solvent-based EOR methods mainly include cyclic solvent injection (CSI), vapour extraction (VAPEX), and its variations. CSI, a cyclic solvent injection process, which is analogous to CSS, is suggested to apply for thin reservoirs after primary production (Bayestehparvin et al., 2016; Jia et al., 2020). As for a thicker reservoir, however, VAPEX is recommended to dilute heavy oil by injecting solvent(s) into it, similar to that of a SAGD process.

Recently, hot solvent techniques (e.g., warm VAPEX and N-Solv) are proposed as promising methods for thin heavy oil reservoirs by taking advantage of the synergistic contribution of viscosity reduction due to thermal energy and mass transfer due to solvent dissolution (Pathak, 2011; Lin et al., 2014; Nasr and Ayodele, 2015). The injected hot solvent is able to establish communication between the injector and the producer as well as to mobilize the heated oil by solvent dispersion due to front instability (Bayestehparvin et al., 2016). As for both N-Solv and warm VAPEX, their fundamental infrastructure and operational procedures are essentially the same (Nasr and Ayodele, 2005; Sabatino et al., 2013; Lin et al., 2014). For the former, where a pure gaseous
solvent with a high temperature, typically propane, is injected at a pressure lower than its vapour pressure, which means that the solvent is always in vapour phase under reservoir conditions (Nenninger and Nenninger, 2005; Bayestehparvin et al., 2016). As for the latter, however, a solvent mixture is often used to improve the dew point of the solvent. The solvent mixture is injected into the upper horizontal well, heating the heavy oil and reducing its viscosity. The schematic diagram of a warm VAPEX process is shown in Figure 2-5.

2.3 Hybrid Steam-Solvent Processes

All of the aforementioned steam-based thermal recovery methods have the following disadvantages: a large amount of greenhouse gas emissions and fresh water consumption, high operational and postproduction costs, and extensive produced water treatment (Hascakir, 2016). As for the solvent-based recovery methods, however, the low mass transfer of a solvent into heavy oil leads to low oil production rates and ultimate oil recovery factors, limiting their field applications (Hascakir, 2016). Recently, co-injecting steam and solvent has been proven to be a promising technique in terms of oil production rate and ultimate oil recovery as it combines the advantages from both heat transfer of steam and mass transfer of solvent(s) to further reduce the viscosity of heavy oil (Jha et al., 2013; Zhao et al., 2013; Ji et al., 2015; Liu et al., 2020).
Figure 2-5 Schematic of a warm VAPEX process (modified from Frauenfeld et al., 2007)
Alkane solvents (e.g., C₃H₈, n-C₅H₁₂, and n-C₆H₁₄) adding to the steam stream such as the expanding solvent SAGD (ES-SAGD) (Liu et al., 2018a; b) and LASER (Leaut and Carey, 2007) are found to be efficient because of their high solubilities in heavy oil. The co-injected solvents dissolving in heavy oil result in an enhanced swelling effect and a viscosity reduction of heavy oil as well as a reduced interfacial tension (IFT) between the solvents and heavy oil (Or et al., 2016). The commonly co-injected alkanes for hybrid steam-solvent processes are insoluble in water, which can reduce the steam chamber edge temperature when co-injected with steam; however, the chamber edge temperature can increase substantially if a solvent can partition into the aqueous phase at chamber edge conditions (Sheng et al., 2018). A promising a water-soluble solvent (i.e., DME) has recently been found to be an efficient additive to thermal-based recovery methods (Sheng et al., 2018; Baek et al., 2019) because of its first contact miscibility with hydrocarbons and preferentially partitioning from aqueous phase to oleic phase once being contacted with reservoir fluids, leading to rapid and strong oil swelling effect and viscosity reduction (Ratnakar et al., 2016; 2017a; b). On the other hand, utilization of carbon dioxide (CO₂) as a non-hydrocarbon solvent has been found to effectively recover heavy oil and bitumen resources (Shokri and Babadagli, 2017), which plays a significant role in carbon capture and storage (CCS) (Yan, 2015) as well as reduction of energy consumption (Nimana et al., 2015), and mitigation of the greenhouse gas emissions (Jiang and Guan, 2016; Du and Nojabaei, 2019).
In practice, co-injecting a solvent with steam into a heavy oil reservoir is able to achieve benefits in terms of technology, economics, and environment in comparison to the pure-steam or pure-solvent injection processes (Jha et al., 2013; Perez-Perez et al., 2016). As can be seen in Figure 2-6, the injected solvent propagates into the reservoir in conjunction with steam, diluting the heavy oil by the condensed solvent and heat from the steam. Plus, the injected solvent can be partially recovered and can be used in another co-injection cycle. Steam-solvent co-injection processes have seen successful applications at laboratory- and field-scale in terms of oil production rates as well as ultimate recovery factors (Ivory et al., 2010; Hascakir, 2016). Moreover, it is able to significantly reduce SOR in comparison with those of steam-only injection processes (Nasr et al., 2003; Gupta and Gittins, 2006; Ardali et al., 2012; Sheng et al., 2018).

### 2.4 Isothermal Flash

As a common approach for reservoir simulation, performing isothermal flash corresponds to computing phase fractions and phase compositions at a specified pressure, temperature, and given feed composition (Michelsen, 1982a; b). Some reservoir simulators use values of equilibrium constant ($K$-values) to study phase behaviour of gas-liquid systems, which are difficult to obtain for thermal-based heavy oil recovery processes due to the condition of high pressures and elevated temperatures. In addition, for the most cases of multiphase
Figure 2-6 Schematic diagram of a steam-solvent co-injection process (Frauenfeld et al., 2009)
isothermal flash, the number of the existing phases is not known at a specified pressure and temperature. As a result, it is challenging and difficult to acquire good initial $K$-values.

A more general method is to use the cubic equation of state (CEOS) such as the PR EOS or Soave-Redlich-Kwong equation of state (SRK EOS) to quantify the phase behaviour for a complicated gas-liquid mixture. The widely used approach is to conduct stability analysis prior to flash calculation. The mixture is tested using the tangent plane criterion to check whether the Gibbs energy of a given mixture can be further reduced by increasing the number of phases of the mixture (Michelsen, 1982a; b). The drawback of this method is the high computational costs for multiphase flash calculations (Li and Firoozabadi, 2012).

Since water is inevitably closely associated with the aforementioned thermal recovery processes (Shu and Hartman, 1988), three-phase ALV equilibria of solvent/water/heavy oil mixtures are frequently encountered at the edge of a steam chamber (Shu and Hartman, 1988; Brantferger et al., 1991). In a typical three-phase ALV equilibrium for solvent/water/heavy oil systems, the A phase refers to the aqueous phase, which is mainly composed of water and dissolved solvents and heavy oil. The L phase represents the hydrocarbon-rich liquid phase, which mainly contains heavy oil and solvents, while the V phase denotes the vapour phase, which mainly includes gaseous solvents. It is still a challenging task to quantify such phase equilibria in the presence of water because of the initialization and convergence problems associated with stability analysis and flash
calculations (Pang and Li, 2017). As such, it is of fundamental and practical importance to accurately quantify the phase behaviour of solvent(s)/water/heavy oil mixtures near the steam chamber boundary for clearly identifying the heavy oil recovery mechanisms and designing the viable steam-solvent co-injection processes (Jia et al., 2011).

Recently, robust and accurate three-phase isothermal flash algorithms based on the free-water and augmented free-water assumption have been proposed and developed to improve the calculation speed without compromising accuracy (Lapene et al., 2010; Pang and Li, 2017; Li and Li, 2018a; Pang and Li, 2018). Their algorithms can handle single phase, two-phase, and ALV three-phase equilibria calculations. It should be noted that the free-water assumption treats the aqueous phase as pure water, whereas only the solvents with relatively high solubilities in the aqueous phase are considered in the augmented free-water assumption.

2.4.1 Free-water algorithms

Based on the free-water assumption that only water component is considered in the aqueous phase, Lapene et al., (2010) developed a modified Rachford-Rice equation to perform three-phase equilibrium calculations for hydrocarbon/water systems. As for their algorithm, the conventional three-phase flash is replaced by a pseudo-two-phase flash, leading to enhanced computational efficiency. The Newton’s methods can be applied to
solve the newly modified Rachford-Rice equation due to the fact that it is guaranteed to be monotonically decreased. The constraints developed by Leibovici and Neoschil (1992) as well as the negative flash concept (Whitson and Michelsen, 1989) are used in their algorithm.

Li and Li (2018a) further improved the three-phase free-water algorithm to obtain phase fractions and compositions by minimizing the objective function together with the constraints proposed by Okuno et al. (2010) for multiphase flash calculations. In their algorithm, only the vapour phase fraction is not known in the objective function. Also, the negative flash concept and the approach to initialize the equilibrium ratios proposed by Lapene et al. (2010) are adopted. Case studies are conducted to demonstrate that the three-phase free-water algorithm is accurate, efficient, and robust. The number of stability test is reduced and the computational efficiency is significantly improved. There is a good agreement between the results obtained from their algorithm and those from the conventional three-phase algorithm.

2.4.2 Augmented free-water algorithms

With regard to CO₂/water/heavy oil systems, however, the free-water assumption is not appropriate as the solubility of CO₂ in water cannot be neglected. Consequently, Pang and Li (2017) proposed the augmented free-water three-phase algorithm that only water and CO₂ are assumed to be present in the aqueous phase. In the outer loop of their
algorithm, a pragmatic technique is proposed to initialize the equilibrium ratios of both CO₂ and water in the aqueous phase with respect to the hydrocarbon-rich liquid phase, whereas, in the inner loop, a newly modified Rachford-Rice equation is solved to obtain phase fractions and compositions. Compared to the free-water three-phase flash algorithm, more accurate results can be obtained by the augmented free-water three-phase flash method because the solubility of CO₂ in the aqueous phase is considered.

2.5 Isenthalpic Flash

2.5.1 Enthalpy determination

As for thermal-based recovery methods, such as CSS and SAGD processes (Mohammadzadeh et al., 2012; Naderi et al., 2013; Guo et al., 2016), phase behaviour quantification with isenthalpic flash has been commonly used as the temperature varies considerably in a heated heavy oil reservoir where isothermal conditions are not possible. In addition, simulation of thermal recovery processes requires an energy balance in the governing equations. It is often advantageous to specify enthalpy along with pressure and composition of a grid block and solve the isenthalpic flash algorithm (Zhu and Okuno, 2014; Paterson et al., 2016; Li and Li, 2018b). Thus, accurate determination of enthalpy for heavy oil components is crucial to quantify the inherent phase behaviour.
associated with thermal recovery processes during which enthalpy represents the total energy with a finite and fixed value (Huang and Daubert, 1974).

Enthalpy is a property of a thermodynamic system, which is defined as the sum of the system’s internal energy and the mathematical product of pressure and volume (Elliot and Lira, 2012). It is a state function that depends only on the current equilibrium state of a system. Various charts and empirical correlations have been developed to predict enthalpy of hydrocarbon fractions as experimental data are not available (Johnson and Grayson, 1961; Huang and Daubert, 1974).

Unlike pure chemical compounds, heavy hydrocarbon fractions, which consist of a limited number of individual chemicals with a specified boiling temperature range, average molecular weight, specific gravity, and boiling point temperature, can be obtained through a distillation process according to the lightest and heaviest compounds in heavy oil (Moharam et al., 1988; Riazi, 2005; Diaz et al., 2011). Traditionally, the pseudocomponent concept has been adopted by the petroleum and chemistry sectors to characterize hydrocarbon fractions (Nji et al., 2007; Li et al., 2013b), based on the assumption that these mixtures have similar physical properties as pure compounds under the same reduced conditions (Johnson and Grayson, 1961). So far, no attempts have been made to develop an enthalpy algorithm accounting for all the compositions of the complex mixtures.

In general, ideal gas heat capacity is a thermodynamic property of particular
importance as it is used as a reference state in many thermodynamic calculations. Conventionally, ideal gas enthalpy is computed by integrating the ideal gas heat capacity equation with respect to temperature (Himmelblau and Riggs, 2012). For a defined compound, it is convenient to determine its enthalpy with its corresponding ideal gas heat capacity coefficients (Poling et al., 2001). For an undefined component, however, methods pertaining to experimental determination of heat capacity for hydrocarbon fractions are scarce due to the unavailability of representation of the complex mixtures together with experimental limitations to generate stable vapour phase of heavy hydrocarbon fractions at constant compositions (Fang et al., 1988). For heavy oils, furthermore, it is impossible to measure the ideal gas heat capacity coefficients of each pseudocomponent separately. Therefore, it is of practical and important significance to develop a reliable method to accurately determine enthalpy of each hydrocarbon fraction in heavy oil and subsequently design technically viable thermal-based recovery processes for a heavy oil reservoir.

Numerous efforts have been made to correlate ideal gas enthalpy with the Watson characterization factor (Watson and Nelson, 1933) (which is a function of the boiling point temperature and specific gravity), molecular weight, and acentric factor. Bauer and Middleton (1953) developed charts that the enthalpies of vapour and liquid are correlated as a function of temperature and density. Although their charts provide reliable enthalpies for most cases, they failed to predict enthalpies in the critical region, which is not
indicated on their charts. Johnson and Grayson (1961) subsequently improved the enthalpy chart based on Bauer and Middleton’s work through the following contributions: (1) Introduction of saturated vapour-liquid domes to more conveniently estimate enthalpy of vaporization; (2) Development of four separate charts for different Watson characterization factors; (3) Improved representation of the effect of pressure on enthalpies; and (4) Change of reference temperature from 255.37 K to 144.26 K for a saturated liquid.

The accuracy of the Johnson and Grayson approach (1961) has been questioned at high pressures and near the critical region (Lenoir and Hipkin, 1971; 1973). Kesler and Lee (1976) improved the accuracy of enthalpy prediction particularly for high pressures and those near the critical regions while retaining the graphical form familiar to the petroleum and chemistry industry. Their main improvements include: (1) Improved correlations of specific heat capacities of vapour at zero pressure; (2) Improved representation of the enthalpy saturation envelopes; and (3) Introduction of new charts to more accurately represent the pressure effects on enthalpies of vapour and liquid. Although pressure effect on enthalpy is separately presented on the basis of the Lee-Kesler correlation (Lee and Kesler, 1975) on their charts, it is time-consuming and not convenient to be applied to computer applications.

All of the aforementioned enthalpy determination methods can only be applied to light to medium hydrocarbon fractions whose physical properties are known with a great
accuracy. For heavy oils which are ill-defined with heavier hydrocarbon fractions, however, large errors occur due to the fact that the ideal gas heat capacity equation developed by Kesler and Lee (1975) is obtained by fitting heat capacities of hydrocarbons from carbon number C₆ to C₂₂ (Lastovka and Shaw, 2013). In addition, enthalpies obtained from such charts are in doubt as they are often too small to be read accurately, which makes not only enthalpy prediction unreliable, but also inconvenient for computer applications (Fleckenstein, 1976).

### 2.5.2 Isenthalpic flash algorithms

Conventionally, isenthalpic flash is primarily employed to obtain phase distributions at equilibrium in simulating an adiabatic expansion process (Paterson et al., 2019). The renewed focus on multiphase isenthalpic flash is primarily motivated by the requirement for accurate numerical simulation of heavy oil production by using thermal methods such as steam or hot solvent or hybrid steam-solvent injection processes (Paterson et al., 2019). Numerical solution of non-isothermal fluid flow in a reservoir often requires robust and efficient isenthalpic flash (Zhu and Okuno, 2014). The mathematical calculation of phase behaviour for a given feed composition at a specified enthalpy and pressure is defined as the isenthalpic flash (Michelsen, 1987). The primary objective of isenthalpic flash is to obtain the system temperature as well as phase mole fractions and
compositions.

In general, isothermal flash is commonly used to determine phase behaviour pertaining to conventional crudes as their isothermal conditions can be assumed (Michelsen, 1982a; b); however, thermal-based recovery processes cannot be treated to be isothermal due to the fact that high-temperature steam is injected into a low-temperature heavy oil reservoir (Paterson et al., 2016). In this case, such a temperature variation voids the traditional assumption of constant temperature for conventional oil reservoirs during steam injection, resulting in large errors associated with the isothermal flash (Zhu and Okuno, 2016). As such, isenthalpic flash has been proposed to quantify the phase behaviour for the aforementioned steam injections where enthalpy can be assumed to be constant, though temperatures are varied within the matrix formation (Michelsen, 1987). Physically, it is difficult to perform robust isenthalpic flash calculations due to the following two challenges: (1) Number of the existing phases under flash conditions is unknown; and (2) The total enthalpy is significantly sensitive to temperature within the narrow-boiling region (Heidari et al., 2014; Zhu and Okuno, 2016). The former increases the computational expenses, whereas the latter causes convergence problems for the energy conservation equation.

(1) Conventional algorithms

As for the conventional full three-phase isenthalpic flash calculations, all the
compositions are taken into account in the three-phases, especially the compositions in the aqueous phase. Numerous efforts have been directed to tackle the aforementioned two challenges to a certain extent. Michelsen (1987) proposed a direct substitution multiphase isenthalpic flash method. The outer temperature iteration loop is used to satisfy the enthalpy constraint, while the inner loop is the traditional isothermal flash to determine the number of phases through stability analysis. By using a quasi-Newton iteration step to update $K$-values for the material balance equation and energy balance equation, Agarwal et al. (1991) subsequently modified this method and proposed three schemes to perform isenthalpic flash calculations for multiphases and multicomponents. Both of these two methods found their convergence difficulties in the narrow-boiling region. By simultaneously solving the matrix consisting of the Rachford-Rice equation, energy conservation equation, and stability equation, Gupta et al. (1990) found that robustness of the isenthalpic flash calculation method has been improved for some cases; however, its application is still limited due to its inherent complexity.

To overcome such a convergence problem, Zhu and Okuno (2014) employed the condition number of the Jacobian matrix for the Rachford-Rice equation and the energy conservation equation to detect the presence of the narrow-boiling behaviour, while the Newton’s method and bisection method are alternatively switched during the isenthalpic flash calculations, depending on the condition number of the Jacobian matrix. Paterson et al. (2016) generalized an isenthalpic flash method for multicomponent and multiphase
systems by employing the Newton’s approach and a $Q$-function maximization to improve computational efficiency as well as deal with the non-convergent problems. Later on, they further improved isenthalpic flash calculations by using full thermodynamics and correlations-based thermodynamics, respectively (Paterson et al., 2019). In addition, the modified Wilson equation for $K$-factor approximation is adopted, which can provide excellent initial $K$-factors for water/heavy oil mixtures.

(2) Free-water algorithms

Recently, efforts have been made to improve the computational efficiency of isenthalpic flash calculations. By using the water-free isothermal flash proposed by Lapene et al. (2010), Heidari et al. (2014) modified the hybrid scheme proposed by Agarwal et al. (1991) to drastically improve the computational speed by conducting pseudo-two-phase flash instead of the conventional three-phase flash calculations. Their algorithm is capable of dealing with difficult situations such as narrow-boiling regions and phase appearance and disappearance phenomenon. The success of their method, nevertheless, is highly dependent on selection of appropriate initial $K$-values for water-containing mixtures.

By using the new Rachford-Rice algorithm based on water-free assumption (Li and Li, 2018a) that the aqueous phase is pure water, Li and Li (2018b) have improved the method proposed by Zhu and Okuno (2014) to solve the inner loop isothermal flash calculation and the outer loop energy conservation equation. In their algorithm,
temperature is first calculated by solving the energy conservation equation in the outer loop based on the assumption that the given feed is at one-phase state. Then, stability analysis is performed to test whether the given feed is stable. If the system is found to be unstable, multiphase (two-phase or ALV three-phase) isothermal flash is conducted in the inner loop to determine phase fractions and compositions. Only one stability test is needed in their algorithm, which significantly improves the computational efficiency. However, all the aforementioned methods cannot be efficiently and accurately applied to cases where a solvent is highly soluble in the aqueous phase at high pressures and elevated temperatures.

2.6 Phase Boundary Determination

The presence of three-phase ALV equilibria for solvent/water/heavy oil mixtures during a hybrid steam-solvent process imposes a significant impact on the heavy oil recovery because the dissolved solvents and water in heavy oil result in viscosity reduction and oil swelling of hydrocarbon-rich liquid phase (Glandt and Chapman, 1995; Shu and Hartman, 1988; Luo and Barrufet, 2005), which is beneficial for enhancing heavy oil recovery.

Numerous efforts have been made available to determine the multiphase boundaries for the solvent(s)/water/heavy oil systems under reservoir conditions in the pressure-temperature space (i.e., $P-T$ phase diagram) (Amani et al., 2013; 2014; Li et al., 2013b; 2017a; b; Gao et al., 2017; Chen and Yang 2018). Li et al. (2012) determined
three-phase liquid-liquid-vapour (L\textsubscript{1}L\textsubscript{2}V) boundaries for C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2}-heavy oil mixture and \textit{n}-C\textsubscript{4}H\textsubscript{10}-CO\textsubscript{2}-heavy oil mixture from both experimental and theoretical aspects, respectively. Li et al. (2013b; 2017a) proposed a generalized methodology to determine multiphase boundaries and swelling factors of solvent(s)-CO\textsubscript{2}-heavy oil systems at high pressures and elevated temperatures by treating heavy oil as multiple pseudocomponents. They determined phase behaviour including phase boundaries, volumes, and compositions of C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2}-heavy oil systems in the presence of an aqueous phase by applying two different alpha functions for water and non-water components, respectively. Gao et al. (2017) experimentally measured multiphase boundaries of \textit{n}-C\textsubscript{4}H\textsubscript{10}/water/bitumen mixtures at temperatures up to 160°C and pressures up to 10 MPa. Chen and Yang (2018) developed a new and pragmatic methodology to predict phase boundaries and their types as well as solvent solubilities of solvents-heavy oil/bitumen-water systems in a temperature range of 298-573 K for different kinds of heavy oils by using new binary interaction parameters (BIPs) in the PR EOS. Chen et al. (2020) developed new experimental measurements together with a dynamic volume analysis (DVA) method to predict the phase behaviour of C\textsubscript{3}H\textsubscript{8}/water/heavy oil and CO\textsubscript{2}/water/heavy oil systems at pressures up to 20 MPa and temperatures up to 432.3 K, during which effective density is used in the ideal mixing rule (Chen and Yang, 2020a; b).

All of the aforementioned phase behaviour studies are related to isothermal conditions, assuming that temperature is constant during a heavy oil recovery process. In
other words, previous studies on determination of multiphase boundaries for solvents/CO₂/water/heavy oil systems are obtained in the \( P-T \) space. However, the temperature varies within the matrix formation during a steam injection process (Michelsen, 1987) since steam with a high temperature is injected into a relatively low-temperature reservoir, making the isothermal conditions unavailable. As water is inevitably used in a steam injection process, three-phase ALV equilibrium of solvent/water/heavy oil mixtures is frequently encountered at the edge of a steam chamber (Li and Li, 2018b). Nevertheless, few attempts have been made to quantify the phase behaviour of solvents-CO₂-heavy oil systems in the presence of water/steam under reservoir conditions. This is due to the following reasons: (1) It is technically difficult to perform three-phase ALV experiments at high pressures and elevated temperatures; (2) Emulsion phenomenon makes it challenging to clearly observe the interface between water and heavy oil; and (3) Temperature limitation of the current PVT equipment makes it impossible to conduct experiments at high temperatures (Jia et al., 2011; Li, 2015). Plus, no studies have been found on the investigation of multiphase boundaries for solvent/CO₂/water/heavy oil systems in the \( H-T \) phase diagrams, which is crucial for the field design of steam-solvent co-injection processes for heavy oil reservoirs.

2.7 Summary

A comprehensive literature review on thermal EOR processes, solvent EOR processes,
three-phase isothermal flash, three-phase isenthalpic flash, and phase boundary
determination has been performed. The following summary can be made:

1) The hybrid steam-solvent injection process is a promising technique to recovery
heavy oil and bitumen as it combines the merits from both heat transfer of steam
and mass transfer of solvent(s) to reduce viscosity of heavy oil;

2) Three-phase ALV equilibria of solvent(s)/water/heavy oil mixtures are frequently
encountered during a hybrid steam-solvent injection process. Isothermal flash
shall be replaced with isenthalpic flash in thermal EOR processes since the
enthalpy can be assumed as constant energy injected into a heavy oil reservoir
and temperature is unknown within the matrix formation;

3) Robust and efficient isenthalpic flash algorithm is required as narrow-boiling
regions occur and the number of the existing phases under flash calculations is
unknown;

4) Mutual solubility between water and solvents with high solubilities in the aqueous
phase cannot be neglected;

5) DME has been proposed as a potential agent for hybrid steam-solvent recovery
processes, while the phase behaviour of DME with reservoir fluids needs to be
experimentally and theoretically studied;

6) Enthalpy can be determined from charts, whereas it is time-consuming and not
convenient for computer applications. Furthermore, they can be only applied to
light to medium hydrocarbon fractions; and

7) Previous studies on determination of multiphase boundaries for solvents/CO$_2$/water/heavy oil systems are obtained in the $P$-$T$ phase diagrams, whereas no attempts have been made to determine multiphase boundaries in the $H$-$T$ phase diagrams.
CHAPTER 3 IMPROVED ENTHALPY PREDICTION OF HYDROCARBON FRACTIONS WITH A MODIFIED ALPHA FUNCTION FOR THE PENG-ROBINSON EQUATION OF STATE

3.1 Introduction

In this chapter, a pragmatic technique has been developed and validated to predict ideal gas heat capacities and enthalpies for normal alkanes/alkenes as well as hydrocarbon fractions over a wide range of temperatures and pressures (Huang and Yang, 2019a). More specifically, an existing correlation has been modified based on the ideal gas heat capacity data retrieved from API research project 44 (1972) to more accurately determine the ideal gas heat capacities for normal alkanes/alkenes, especially for heavy hydrocarbons. The modified correlation is obtained by minimizing the deviations between the experimentally measured and theoretically calculated ideal gas heat capacities of normal alkanes, including heavy alkanes up to \(n\)-tetracontane (\(n\)-C\(_{40}\)H\(_{82}\)).

Then, a reliable and convenient enthalpy algorithm for hydrocarbon fractions has been proposed by incorporating a recently modified alpha function into the PR EOS together with the newly modified ideal gas heat capacity correlation. Finally, it is demonstrated that the new algorithm proposed in this study can be applied to accurately predict enthalpy of two hydrocarbon fractions, i.e., the light naphtha and Alaska naphtha.
3.2 Mathematical Formulations

3.2.1 PR EOS

Because of its wide application as well as simplicity and computational accuracy (Li and Yang, 2011; Li et al., 2017a; b; Shi et al., 2017; Dong et al., 2018) in the petroleum and chemistry industry, the PR EOS (Peng and Robinson, 1976a) is chosen as the thermodynamic model in this study. The PR EOS is formulated as follows,

\[
P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}
\]  

\[
a = a_r \alpha(T_r, \omega)
\]

\[
a_r = \frac{0.457235R^2T_c^2}{P_c}
\]

\[
b = \frac{0.0777969RT_c}{P_c}
\]

where \(P\) is the pressure, \(T\) is the temperature, \(V\) is the molar volume, \(a\) and \(b\) are the constants at a given temperature, \(R\) is the universal gas constant, \(\alpha(T_r, \omega)\) is the alpha function which is a function of the reduced temperature \(T_r\) and acentric factor \(\omega\), \(T_c\) is the critical temperature, and \(P_c\) is the critical pressure.

The original alpha function used in the PR EOS given by Peng and Robinson (1976a) is expressed as,

\[
\alpha(T_r, \omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})\right]^2
\]

Numerous efforts have been made to modify Equation [3-3a] to more accurately quantify phase behaviour for different pure components and mixtures (Neau et al., 2009;
Privat et al., 2015). In general, three essential criteria should be satisfied for the alpha function: (1) It must be finite and positive at all temperatures; (2) It equals to unity at the critical temperature; and (3) It is finite when the temperature approaches infinity (Twu et al., 1991). Basically, alpha functions can be divided into two types, i.e., the Soave-type (Soave, 1972) and the logarithm-type (Heyen, 1981). Though the former has been widely used for the equation of state (EOS), it fails to accurately quantify the phase behaviour of heavy hydrocarbons because only light hydrocarbons (lighter than C\textsubscript{10}) are used to develop the Soave-type alpha function. The latter meets all the aforementioned three criteria; however, it can only be applied to accurately predict phase behaviour of \( n \)-paraffins up to \( n \)-octacosane (\( n \)-C\textsubscript{28}H\textsubscript{58}) (Gasem et al., 2001).

Based on the available vapour pressures for 59 non-hydrocarbon and hydrocarbon compounds including heavy alkanes up to \( n \)-tritetracontane (\( n \)-C\textsubscript{43}H\textsubscript{88}), the recently modified alpha function proposed by Li and Yang (2011), which combines the advantages of both the Soave-type alpha function and the logarithm-type function, provides more accurate prediction of vapour pressures with an absolute average relative deviation (AARD) of 1.90\% and a maximum absolute relative deviation (MARD) of 21.22\% for the 1165 data points (Li and Yang, 2011). In addition, the newly developed alpha function results in the best prediction of the vaporization enthalpy data with an AARD of 3.92\% in comparison with the other existing alpha functions evaluated (Li and Yang, 2011). Subsequently, this modified alpha function (i.e., Equation [3-3b]) has been
found to more accurately predict phase behaviour not only for light hydrocarbons and non-hydrocarbon substances, but also for heavy hydrocarbons by treating heavy oil as a single pseudocomponent (Li et al., 2013a; 2017c; Li and Yang, 2013; 2016; Jang and Yang, 2020; 2021) and multiple pseudocomponents (Shi et al., 2016; Li et al., 2017a; b; Zheng et al., 2016a; b; Zheng and Yang, 2017a; b). Other details regarding the modified alpha function can be found elsewhere (Li and Yang, 2011).

The newly modified alpha function is formulated as follows (Li and Yang, 2011),

\[
\alpha(T_r, \omega) = \exp \left\{ \left[ (0.13280-0.05052 \omega+0.25948 \omega^2) \left( 1-T_r \right) \\
+0.81769 \ln \left[ 1+ \left( 0.31355+1.86745 \omega-0.52604 \omega^2 \right) \left( 1-\sqrt{T_r} \right) \right]^2 \right] \right\}
\]

[3-3b]

The parameter \( a \) and \( b \) in the PR EOS expressed in a dimensionless form are listed as,

\[
A = \frac{aP}{RT^2}
\]

[3-4a]

\[
B = \frac{bP}{RT}
\]

[3-4b]

The compressibility factor \( Z \) is calculated from the PR EOS,

\[
Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z + (B^3+B^2-AB) = 0
\]

[3-5]

The derivative of parameter \( a \) associated with the PR EOS with respect to \( T \) is expressed as,

\[
\frac{da}{dT} = -0.457235 R^2 T_r^{1.5} \left( 0.37464+1.54226 \omega-0.26992 \omega^2 \right) \left[ 1+ \left( 0.37464+1.54226 \omega-0.26992 \omega^2 \right) \left( 1-T_{r,0.5} \right) \right] \left( P_e T_{0.5} \right)
\]

[3-6a]
\[
\frac{da}{dT} = \frac{0.457235 R^2 T_c^2}{P_c} \exp \left\{ \left( 0.13280 - 0.05052 \omega + 0.25948 \omega^2 \right) \left( 1 - \frac{T_a}{T_c} \right) \right\} \times \\
\left\{ \frac{0.13280 - 0.05052 \omega + 0.25948 \omega^2}{T_c} \cdot \frac{0.81769 \left( 0.31355 + 1.86745 \omega - 0.52604 \omega^2 \right)}{T_c \sqrt{T_c} \left[ 1 + \left( 0.31355 + 1.86745 \omega - 0.52604 \omega^2 \right) \left( 1 - \sqrt{T_c} \right) \right]} \right\}
\]

[3-6b]

It is worthwhile to mention that Equations [3-6a] and [3-6b] are obtained by deriving Equation [3-2a] incorporated with Equations [3-3a] and [3-3b], respectively. Plus, Equations [3-3a] and [3-6a] as well as Equations [3-3b] and [3-6b] are employed by the Kesler and Lee (1976) method and the algorithm proposed in this study to calculate the total enthalpies, respectively.

### 3.2.2 Ideal gas heat capacity

In this study, the experimental data for ideal gas heat capacity of normal alkanes ranging from C\textsubscript{7}H\textsubscript{16} to C\textsubscript{40}H\textsubscript{82} collected from the API research project 44 (1972) are used to develop a new ideal gas heat capacity correlation that can be applied to heavy hydrocarbon fractions. Based on the Kesler and Lee’s work (1976), the form of the new equation proposed in this study is formulated as,

\[ C_p' = MW \left[ A_0 + A_1 T_K + A_2 T_K^2 + C_p \left( B_0 + B_1 T_K + B_2 T_K^2 \right) \right] \]

[3-7]

where $C_p$ is the ideal gas heat capacity, J/(mol·K), $MW$ is the molecular weight, g/mol, $A_0$, $A_1$, $A_2$, $B_0$, $B_1$, and $B_2$ are the derived coefficients, $T_K$ is the temperature, K, and $C_p'$ is the corrective factor and given by,
\[ C_p = \left[ \frac{(12.8/K_w - 1) \times (10/K_w - 1) \times 100}{100} \right]^2 \]  

[3-8]

where \( K_w \) is the Watson characterization factor that indicates chemical character of a compound (Lastovka and Shaw, 2013) and defined as,

\[ K_w = \left( \frac{1.8T_k}{SG} \right)^{1/3} \]  

[3-9]

where \( SG \) is the specific gravity defined at 288.71 K.

Since the coefficients in Equation [3-7] are linear, the root-mean-squared relative error (RMSRE) is used as the objective function to obtain the coefficients by minimizing the deviations between the experimentally measured and theoretically calculated heat capacities (Schaffer et al., 2014). The objective function is defined as,

\[ \text{RMSRE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{C_p^{\text{exp}} - C_p^{\text{cal}}}{C_p^{\text{exp}}} \right)^2} \times 100\% \]  

[3-10]

where \( C_p^{\text{exp}} \) is the measured heat capacity, \( C_p^{\text{cal}} \) is the calculated heat capacity, and \( n \) is the number of data points.

Table 3-1 presents the ideal gas heat capacity data of normal alkanes used in this study to develop the new correlation (API Research Project, 1972), while their respective physical properties are tabulated in Table 3-2 (API, 1983; Poling et al., 2001; Kim et al., 2019).

After performing regression analysis, the modified ideal gas heat capacity equation is obtained as follows,
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>(T), K</th>
<th>(C_p), J/(mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-heptane</td>
<td>C(<em>7)H(</em>{16})</td>
<td>127.65</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-octane</td>
<td>C(<em>8)H(</em>{18})</td>
<td>144.77</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-nonane</td>
<td>C(<em>9)H(</em>{20})</td>
<td>161.92</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-decane</td>
<td>C(<em>{10})H(</em>{22})</td>
<td>179.08</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-undecane</td>
<td>C(<em>{11})H(</em>{24})</td>
<td>196.23</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-dodecane</td>
<td>C(<em>{12})H(</em>{26})</td>
<td>213.38</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tridecane</td>
<td>C(<em>{13})H(</em>{28})</td>
<td>230.54</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tetradecane</td>
<td>C(<em>{14})H(</em>{30})</td>
<td>247.69</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-pentadecane</td>
<td>C(<em>{15})H(</em>{32})</td>
<td>264.85</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-hexadecane</td>
<td>C(<em>{16})H(</em>{34})</td>
<td>282.00</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-heptadecane</td>
<td>C(<em>{17})H(</em>{36})</td>
<td>299.16</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-octadecane</td>
<td>C(<em>{18})H(</em>{38})</td>
<td>316.31</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-nonadecane</td>
<td>C(<em>{19})H(</em>{40})</td>
<td>333.46</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-eicosane</td>
<td>C(<em>{20})H(</em>{42})</td>
<td>350.62</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-heneicosane</td>
<td>C(<em>{21})H(</em>{44})</td>
<td>367.77</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-docosane</td>
<td>C(<em>{22})H(</em>{46})</td>
<td>384.93</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tricosane</td>
<td>C(<em>{23})H(</em>{48})</td>
<td>402.08</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tetracontane</td>
<td>C(<em>{24})H(</em>{50})</td>
<td>419.24</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-pentacosane</td>
<td>C(<em>{25})H(</em>{52})</td>
<td>436.39</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-hexacosane</td>
<td>C(<em>{26})H(</em>{54})</td>
<td>453.55</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-heptacosane</td>
<td>C(<em>{27})H(</em>{56})</td>
<td>470.70</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-octacosane</td>
<td>C(<em>{28})H(</em>{58})</td>
<td>487.85</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-nonacosane</td>
<td>C(<em>{29})H(</em>{60})</td>
<td>505.01</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-triacontane</td>
<td>C(<em>{30})H(</em>{62})</td>
<td>522.16</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-hetriacontane</td>
<td>C(<em>{31})H(</em>{64})</td>
<td>539.32</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-dotriacontane</td>
<td>C(<em>{32})H(</em>{66})</td>
<td>556.47</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tritriacontane</td>
<td>C(<em>{33})H(</em>{68})</td>
<td>573.63</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tetracontane</td>
<td>C(<em>{34})H(</em>{70})</td>
<td>590.78</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-pentatriacontane</td>
<td>C(<em>{35})H(</em>{72})</td>
<td>607.94</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-hexatriacontane</td>
<td>C(<em>{36})H(</em>{74})</td>
<td>624.24</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-heptatriacontane</td>
<td>C(<em>{37})H(</em>{76})</td>
<td>642.44</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-octatriacontane</td>
<td>C(<em>{38})H(</em>{78})</td>
<td>659.40</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-nonatriacontane</td>
<td>C(<em>{39})H(</em>{80})</td>
<td>676.55</td>
<td>298.15</td>
</tr>
<tr>
<td>(n)-tetracontane</td>
<td>C(<em>{40})H(</em>{82})</td>
<td>693.71</td>
<td>298.15</td>
</tr>
</tbody>
</table>

Ideal gas heat capacity database used in this study (API Research Project, 1972)
Table 3-2 Physical properties of the \( n \)-alkanes used in this study (API, 1983; Poling et al., 2001; Kim et al., 2019)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>( MW ), g/mol</th>
<th>( T_b ), K</th>
<th>( SG )</th>
<th>( K_W )</th>
<th>( C_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-heptane</td>
<td>C(<em>7)H(</em>{16})</td>
<td>100.205</td>
<td>371.55</td>
<td>0.6795</td>
<td>12.86990</td>
<td>0.01465</td>
</tr>
<tr>
<td>( n )-octane</td>
<td>C(<em>8)H(</em>{18})</td>
<td>114.232</td>
<td>398.75</td>
<td>0.6986</td>
<td>12.81630</td>
<td>0.00078</td>
</tr>
<tr>
<td>( n )-nonane</td>
<td>C(<em>9)H(</em>{20})</td>
<td>128.258</td>
<td>423.95</td>
<td>0.7176</td>
<td>12.73440</td>
<td>0.01222</td>
</tr>
<tr>
<td>( n )-decane</td>
<td>C(<em>{10})H(</em>{22})</td>
<td>142.286</td>
<td>447.27</td>
<td>0.7255</td>
<td>12.82262</td>
<td>0.00151</td>
</tr>
<tr>
<td>( n )-undecane</td>
<td>C(<em>{11})H(</em>{24})</td>
<td>156.313</td>
<td>469.05</td>
<td>0.7402</td>
<td>12.76874</td>
<td>0.00282</td>
</tr>
<tr>
<td>( n )-dodecane</td>
<td>C(<em>{12})H(</em>{26})</td>
<td>170.340</td>
<td>489.30</td>
<td>0.7495</td>
<td>12.78923</td>
<td>0.00034</td>
</tr>
<tr>
<td>( n )-tridecane</td>
<td>C(<em>{13})H(</em>{28})</td>
<td>184.367</td>
<td>507.15</td>
<td>0.7560</td>
<td>12.83161</td>
<td>0.00296</td>
</tr>
<tr>
<td>( n )-tetradecane</td>
<td>C(<em>{14})H(</em>{30})</td>
<td>198.394</td>
<td>526.65</td>
<td>0.7628</td>
<td>12.87817</td>
<td>0.01840</td>
</tr>
<tr>
<td>( n )-pentadecane</td>
<td>C(<em>{15})H(</em>{32})</td>
<td>212.421</td>
<td>543.75</td>
<td>0.7685</td>
<td>12.91953</td>
<td>0.04371</td>
</tr>
<tr>
<td>( n )-hexadecane</td>
<td>C(<em>{16})H(</em>{34})</td>
<td>226.448</td>
<td>559.95</td>
<td>0.7701</td>
<td>13.01948</td>
<td>0.15285</td>
</tr>
<tr>
<td>( n )-heptadecane</td>
<td>C(<em>{17})H(</em>{36})</td>
<td>240.475</td>
<td>575.15</td>
<td>0.7780</td>
<td>13.00284</td>
<td>0.12979</td>
</tr>
<tr>
<td>( n )-octadecane</td>
<td>C(<em>{18})H(</em>{38})</td>
<td>254.502</td>
<td>589.15</td>
<td>0.7768</td>
<td>13.12775</td>
<td>0.35382</td>
</tr>
<tr>
<td>( n )-nonadecane</td>
<td>C(<em>{19})H(</em>{40})</td>
<td>268.529</td>
<td>603.15</td>
<td>0.7855</td>
<td>13.08438</td>
<td>0.26249</td>
</tr>
<tr>
<td>( n )-eicosane</td>
<td>C(<em>{20})H(</em>{42})</td>
<td>282.556</td>
<td>616.25</td>
<td>0.7886</td>
<td>13.12662</td>
<td>0.35127</td>
</tr>
<tr>
<td>( n )-heneicosane</td>
<td>C(<em>{21})H(</em>{44})</td>
<td>296.583</td>
<td>629.65</td>
<td>0.7919</td>
<td>13.16599</td>
<td>0.44683</td>
</tr>
<tr>
<td>( n )-docosane</td>
<td>C(<em>{22})H(</em>{46})</td>
<td>310.610</td>
<td>641.75</td>
<td>0.7944</td>
<td>13.20810</td>
<td>0.56320</td>
</tr>
<tr>
<td>( n )-tricosane</td>
<td>C(<em>{23})H(</em>{48})</td>
<td>324.637</td>
<td>653.15</td>
<td>0.7969</td>
<td>13.24417</td>
<td>0.67484</td>
</tr>
<tr>
<td>( n )-tetracosane</td>
<td>C(<em>{24})H(</em>{50})</td>
<td>338.664</td>
<td>664.45</td>
<td>0.7991</td>
<td>13.28344</td>
<td>0.80927</td>
</tr>
<tr>
<td>( n )-pentacosane</td>
<td>C(<em>{25})H(</em>{52})</td>
<td>352.691</td>
<td>675.05</td>
<td>0.8012</td>
<td>13.31870</td>
<td>0.94172</td>
</tr>
<tr>
<td>( n )-hexacosane</td>
<td>C(<em>{26})H(</em>{54})</td>
<td>366.718</td>
<td>685.35</td>
<td>0.8032</td>
<td>13.35277</td>
<td>1.08045</td>
</tr>
<tr>
<td>( n )-heptacosane</td>
<td>C(<em>{27})H(</em>{56})</td>
<td>380.745</td>
<td>715.15</td>
<td>0.8051</td>
<td>13.51160</td>
<td>1.87349</td>
</tr>
<tr>
<td>( n )-octacosane</td>
<td>C(<em>{28})H(</em>{58})</td>
<td>394.772</td>
<td>704.75</td>
<td>0.8067</td>
<td>13.41911</td>
<td>1.38188</td>
</tr>
<tr>
<td>( n )-nonacosane</td>
<td>C(<em>{29})H(</em>{60})</td>
<td>408.799</td>
<td>716.15</td>
<td>0.8083</td>
<td>13.46438</td>
<td>1.61188</td>
</tr>
<tr>
<td>( n )-triacontane</td>
<td>C(<em>{30})H(</em>{62})</td>
<td>422.826</td>
<td>722.85</td>
<td>0.8133</td>
<td>13.42320</td>
<td>1.40184</td>
</tr>
<tr>
<td>( n )-hentriacontane</td>
<td>C(<em>{31})H(</em>{64})</td>
<td>436.853</td>
<td>731.15</td>
<td>0.8147</td>
<td>13.45123</td>
<td>1.54300</td>
</tr>
<tr>
<td>( n )-dotriacontane</td>
<td>C(<em>{32})H(</em>{66})</td>
<td>450.880</td>
<td>740.15</td>
<td>0.8160</td>
<td>13.48468</td>
<td>1.72162</td>
</tr>
<tr>
<td>( n )-tritriacontane</td>
<td>C(<em>{33})H(</em>{68})</td>
<td>464.907</td>
<td>747.15</td>
<td>0.8172</td>
<td>13.50719</td>
<td>1.84813</td>
</tr>
<tr>
<td>( n )-tetracontane</td>
<td>C(<em>{34})H(</em>{70})</td>
<td>478.934</td>
<td>756.15</td>
<td>0.8184</td>
<td>13.54133</td>
<td>2.04977</td>
</tr>
<tr>
<td>( n )-pentatriacontane</td>
<td>C(<em>{35})H(</em>{72})</td>
<td>492.961</td>
<td>763.15</td>
<td>0.8194</td>
<td>13.56641</td>
<td>2.20557</td>
</tr>
<tr>
<td>( n )-hexatriacontane</td>
<td>C(<em>{36})H(</em>{74})</td>
<td>506.988</td>
<td>770.37</td>
<td>0.8205</td>
<td>13.59082</td>
<td>2.36355</td>
</tr>
<tr>
<td>( n )-heptatriacontane</td>
<td>C(<em>{37})H(</em>{76})</td>
<td>521.015</td>
<td>778.15</td>
<td>0.8215</td>
<td>13.61981</td>
<td>2.55925</td>
</tr>
<tr>
<td>( n )-octatriacontane</td>
<td>C(<em>{38})H(</em>{78})</td>
<td>535.042</td>
<td>785.15</td>
<td>0.8224</td>
<td>13.64558</td>
<td>2.74077</td>
</tr>
<tr>
<td>( n )-nonatriacontane</td>
<td>C(<em>{39})H(</em>{80})</td>
<td>549.069</td>
<td>790.66</td>
<td>0.8233</td>
<td>13.66247</td>
<td>2.86367</td>
</tr>
<tr>
<td>( n )-tetracontane</td>
<td>C(<em>{40})H(</em>{82})</td>
<td>563.096</td>
<td>797.03</td>
<td>0.8241</td>
<td>13.68577</td>
<td>3.03821</td>
</tr>
</tbody>
</table>
3.2.3 Total enthalpy

(1) Liquid enthalpy

Liquid enthalpies are determined by integrating the specific heat capacity equation developed by Watson and Nelson (1933), which has shown a satisfactory agreement with a wide range of hydrocarbon fractions and pure hydrocarbons, from the reference temperature 144.26 K to the boiling point temperature $T_b$, namely,

$$H^L = \int_{144.26}^{T_b} C'_P dT$$  \[3-12\]

$$C'_P = 2.326MW \left( 0.35 + 0.055K_w \right) \left[ 0.6811 - 0.308SG + \left( 0.000815 + 0.000306SG \right) \right] \times \left( T_k - 273.15 \right) \times 1.8 + 32$$  \[3-13\]

where $H^L$ is the liquid enthalpy, J/mol, $T_b$ is the boiling point temperature, K, and $C'_P$ is the liquid specific heat capacity, J/(mol·K).

(2) Enthalpy of vaporization

The enthalpy of vaporization, which represents the difference between the enthalpy of a vapour and that of a liquid at the saturation temperature, can be readily expressed as the following,

$$C'_P = MW \left[ 0.0240296 + 0.0062421T_k - 2.60151 \times 10^{-6}T_k^2 + C'_P \left( 0.0022514 - 1.15054 \times 10^{-5}T_k + 2.39542 \times 10^{-8}T_k^2 \right) \right]$$  \[3-11\]
\[ H^{\text{vap}} = RT(Z_V - Z_L) + \frac{T}{2\sqrt{2}b} \left( \frac{da}{dT} - a \right) \left\{ \ln \left[ \frac{Z_V + (1 + \sqrt{2})B}{Z_V + (1 - \sqrt{2})B} \right] - \ln \left[ \frac{Z_L + (1 + \sqrt{2})B}{Z_L + (1 - \sqrt{2})B} \right] \right\} \]  

[3-14]

where \( H^{\text{vap}} \) is the enthalpy of vaporization at the boiling point temperature, J/mol, \( Z_V \) and \( Z_L \) are the vapour and liquid compressibility factors, respectively.

In this chapter, the newly developed alpha function proposed by Li and Yang (2011), which has been proved to be successfully incorporated into the PR EOS that greatly enhances its ability to accurately predict enthalpy of vaporization for pure hydrocarbons, is applied to predict hydrocarbon fraction enthalpies. Table 3-3 lists the predicted vaporization enthalpy of pure hydrocarbons by using two different alpha functions (i.e., Equations [3-3a] and [3-3b]) associated with the PR EOS (Li and Yang, 2011). As can be seen, the newly proposed alpha function provides more accurate prediction of enthalpy of vaporization than those of the original alpha function proposed by Peng and Robinson (1976a) in terms of AARDs.

### (3) Vapour enthalpy

Enthalpy of vapour at zero pressure is calculated by integrating the ideal gas heat capacity equation from the boiling point temperature \( T_b \) to the specified temperature, \( T \), which is expressed as,

\[ H^v = \int_{T_b}^{T} C^v_p dT \]  

[3-15]

Kesler and Lee (1976) proposed a correlation for the prediction of ideal gas heat
Table 3-3 Predicted vaporization enthalpy of pure hydrocarbons using the PR EOS with different alpha functions (Li and Yang, 2011)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>AARD, %</th>
<th>Model #1</th>
<th>Model #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>3.83</td>
<td>3.76</td>
<td></td>
</tr>
<tr>
<td>ethane</td>
<td>C₂H₆</td>
<td>2.36</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td>propane</td>
<td>C₃H₈</td>
<td>2.46</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>n-pentane</td>
<td>C₅H₁₂</td>
<td>0.14</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>C₆H₁₄</td>
<td>0.94</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>n-heptane</td>
<td>C₇H₁₆</td>
<td>1.81</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>n-octane</td>
<td>C₈H₁₈</td>
<td>2.47</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>n-nonane</td>
<td>C₉H₂₀</td>
<td>3.11</td>
<td>3.14</td>
<td></td>
</tr>
<tr>
<td>n-decane</td>
<td>C₁₀H₂₂</td>
<td>0.94</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>n-undecane</td>
<td>C₁₁H₂₄</td>
<td>4.25</td>
<td>4.13</td>
<td></td>
</tr>
<tr>
<td>n-dodecane</td>
<td>C₁₂H₂₆</td>
<td>4.95</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>n-tridecane</td>
<td>C₁₃H₂₈</td>
<td>5.34</td>
<td>5.10</td>
<td></td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>C₁₄H₃₀</td>
<td>7.33</td>
<td>6.15</td>
<td></td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>C₁₅H₃₂</td>
<td>6.40</td>
<td>6.07</td>
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</tr>
<tr>
<td>n-hexadecane</td>
<td>C₁₆H₃₄</td>
<td>8.40</td>
<td>6.43</td>
<td></td>
</tr>
<tr>
<td>n-heptadecane</td>
<td>C₁₇H₃₆</td>
<td>8.38</td>
<td>6.34</td>
<td></td>
</tr>
<tr>
<td>n-eicosane</td>
<td>C₂₀H₄₂</td>
<td>5.54</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>n-tetracontane</td>
<td>C₂₄H₅₀</td>
<td>4.82</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>n-octacosane</td>
<td>C₂₈H₅₈</td>
<td>1.33</td>
<td>6.15</td>
<td></td>
</tr>
<tr>
<td>n-triacontane</td>
<td>C₃₀H₆₂</td>
<td>4.81</td>
<td>5.02</td>
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</tr>
<tr>
<td>n-hentriacontane</td>
<td>C₃₁H₆₄</td>
<td>7.56</td>
<td>3.03</td>
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</tr>
<tr>
<td>n-tetriacontane</td>
<td>C₃₄H₇₀</td>
<td>6.65</td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td>n-pentriacontane</td>
<td>C₃₅H₇₂</td>
<td>7.19</td>
<td>2.29</td>
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</tr>
<tr>
<td>n-hexatriacontane</td>
<td>C₃₆H₇₄</td>
<td>9.37</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>n-tritriacontane</td>
<td>C₄₃H₈₈</td>
<td>17.26</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>5.11</td>
<td>3.34</td>
<td></td>
</tr>
</tbody>
</table>

Note:
Models #1 and #2 are the PR EOS incorporated with alpha function Equations [3-3a] and [3-3b], respectively.
capacities and vapour enthalpies, which is a function of the boiling point temperature and specific gravity and expressed as,

\[
C_v^V = 2.326MW \left[ -0.32646 + 0.02678K_w - \left( 2.5006 - 2.1820K_w + 0.06845K_w^2 \right) \times 10^{-4}T_k^2 \right] \\
- 4.9873 \times 10^{-7}T_k^2 - C_f \left( 0.084773 - 0.60809SG - \left( 3.9191 - 3.7487SG \right) \times 10^{-4}T_k \right) \\
+ (2.54822 - 2.28171SG) \times 10^{-7}T_k^2
\]

[3-16]

where \( H^V \) is the vapour enthalpy, J/mol, and \( C_v^V \) is the specific heat capacity of vapour, J/(mol·K).

It is worthwhile mentioning that the coefficients in Equation [3-16] are obtained by regressing heat capacities of pure compounds and mixtures which include equal proportions of paraffins, naphthenes, and aromatics. As for the new correlation proposed in this work, the expression of \( C_v^V \) is expressed in Equation [3-11].

(4) Enthalpy departure

The variation of enthalpy between an ideal gas and a real gas can be represented by enthalpy departure at a given temperature and pressure (Riazi, 2005). At a low pressure, the ideal gas heat capacities are accurate approximations of the heat capacities of real gases, and thus the pressure effect on enthalpies can be neglected. At a high pressure, however, the enthalpy departure function associated with the EOS should be used to account for pressure effect on enthalpies. Kesler and Lee (1975; 1976) improved the three-parameter corresponding states correlation proposed by Pitzer and co-workers (1955; 1957) for the prediction of volumetric and thermodynamic properties of vapour
and liquid as a function of reduced temperature, reduced pressure, andacentric factor by using a modified Benedict-Webb-Rubin equation of state (BWR-EOS). Accordingly, their generalized thermodynamic correlation that represents pressure effect on enthalpies is represented as follows,

\[
\frac{(H - H_{IG})}{RT_e} = \left[ \frac{H - H_{IG}^{(0)}}{RT_e} \right] + \omega \left[ \frac{H - H_{IG}^{(1)}}{RT_e} \right]
\]

[3-17]

The values for the first and second order terms in Equation [3-17] are established by Lee and Kesler (1975) in both tabular and graphical form.

In this study, the specific thermodynamic expression for the isothermal effect of pressure on enthalpy can be formulated as (Raizi, 2005; Sandler, 2006),

\[
H^{dep} = H_t - H_{IG}^{dep} = PV - RT + \int \left[ T \frac{\partial P}{\partial T} \right] - P \right] dV
\]

[3-18]

The pressure derivative can be obtained directly from the PR EOS, i.e.,

\[
\left( \frac{\partial P}{\partial T} \right) = \frac{R}{V - b} - \frac{da/dT}{V^2}
\]

[3-19]

After substitution and rearrangement, the specific expression for the enthalpy departure can be given by,

\[
H^{dep} = RT(Z - 1) + \frac{T \frac{da}{dT} - a}{2\sqrt{2b}} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]
\]

[3-20]

where \( H^{dep} \), \( H_t \), and \( H_{IG}^{dep} \) are the enthalpy departure, total enthalpy, and ideal gas enthalpy, respectively.
In this work, Equation [3-17] can be replaced by Equation [3-20], which is not only more convenient for programming purposes, but also higher accuracy has been achieved.

It should be noted that the ideal gas enthalpy is computed to the selected reference (i.e., 144.26 K for a saturated liquid) by adding the enthalpy of vaporization from Equation [3-14], the liquid enthalpy obtained from Equation [3-12] at the average boiling point temperature and vapour enthalpy determined from Equation [3-15]. Finally, summarizing the aforementioned mathematical formulations, the total enthalpy can be obtained as (Fleckenstein, 1976),

$$H_i = H^L + H^V + H^{\text{vap}} + H^{\text{dep}}$$  \[3-21\]

In this study, the performance of the newly proposed enthalpy determination algorithm is evaluated through two criteria, i.e., AARD and MARD, which are respectively expressed as follows,

$$AARD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{H^\text{cal}_i - H^\text{exp}_i}{H^\text{exp}_i} \right| \times 100\%$$  \[3-22a\]

$$MARD = \max \left\{ \left| \frac{H^\text{cal}_i - H^\text{exp}_i}{H^\text{exp}_i} \right| \times 100\%, \quad i = 1, 2, 3, ..., N \right\}$$  \[3-22b\]

where $N$ is the number of data points, $H^\text{cal}_i$ is the calculated enthalpy, and $H^\text{exp}_i$ is the measured enthalpy.
3.3 Results and Discussion

3.3.1 Ideal gas heat capacity

*(I) Normal alkanes*

As aforementioned, 340 experimental ideal gas heat capacity data points at temperatures from 200.00 K to 1000.00 K are included in the database to develop the correlation in this work. The corresponding AARDs and MARDs for the predicted ideal gas heat capacities for normal alkanes ranging from C7H16 to C40H82 by using Equation [3-11] and Equation [3-16] are listed in Table 3-4, respectively. It is worthwhile noting that the AARD for each normal alkane is obtained by averaging 10 data points from 200.00 K to 1000.00 K, while the overall AARDs are calculated by averaging all of the 340 data points for the 34 normal alkanes. It can be seen that the new correlation is able to accurately reproduce ideal gas heat capacities of normal hydrocarbons with AARDs smaller than 2.18%. Furthermore, it is found that the overall AARD and MARD of ideal gas heat capacity between the experimental measurements and theoretical calculations by using the Kesler and Lee correlation are 6.96% and 10.69% compared with those of 1.24% and 6.21% obtained from the newly proposed correlation. There exist larger deviations for predicting ideal gas heat capacities of heavy hydrocarbons when using the Kesler and Lee correlation. This is because the ideal gas heat capacity equation developed by Kesler and Lee (1976) is based on the experimental data of light to medium paraffin/aromatic/naphthenic...
Table 3-4 AARDs and MARDs for the predicted ideal gas heat capacities for normal alkanes with Equation [3-11] and Equation [3-16] in a temperature range of 200.00-1000.00 K, respectively

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>NPTS &amp;</th>
<th>Equation [3-11]</th>
<th>Equation [3-16]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>AARD, %</td>
<td>MARD, %</td>
</tr>
<tr>
<td>n-heptane</td>
<td>C₇H₁₆</td>
<td>10</td>
<td>2.18</td>
<td>8.47</td>
</tr>
<tr>
<td>n-octane</td>
<td>C₈H₁₈</td>
<td>10</td>
<td>1.91</td>
<td>7.99</td>
</tr>
<tr>
<td>n-nonane</td>
<td>C₉H₂₀</td>
<td>10</td>
<td>1.71</td>
<td>7.64</td>
</tr>
<tr>
<td>n-decane</td>
<td>C₁₀H₂₂</td>
<td>10</td>
<td>1.57</td>
<td>7.35</td>
</tr>
<tr>
<td>n-undecane</td>
<td>C₁₁H₂₄</td>
<td>10</td>
<td>1.45</td>
<td>7.11</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>C₁₂H₂₆</td>
<td>10</td>
<td>1.36</td>
<td>6.92</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>C₁₃H₂₈</td>
<td>10</td>
<td>1.29</td>
<td>6.75</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>C₁₄H₃₀</td>
<td>10</td>
<td>1.17</td>
<td>6.60</td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>C₁₅H₃₂</td>
<td>10</td>
<td>1.16</td>
<td>6.48</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>C₁₆H₃₄</td>
<td>10</td>
<td>1.14</td>
<td>6.37</td>
</tr>
<tr>
<td>n-heptadecane</td>
<td>C₁₇H₃₆</td>
<td>10</td>
<td>1.13</td>
<td>6.27</td>
</tr>
<tr>
<td>n-octadecane</td>
<td>C₁₈H₃₈</td>
<td>10</td>
<td>1.12</td>
<td>6.20</td>
</tr>
<tr>
<td>n-nonadecane</td>
<td>C₁₉H₄₀</td>
<td>10</td>
<td>1.12</td>
<td>6.12</td>
</tr>
<tr>
<td>n-eicosane</td>
<td>C₂₀H₄₂</td>
<td>10</td>
<td>1.13</td>
<td>6.05</td>
</tr>
<tr>
<td>n-heneicosane</td>
<td>C₂₁H₄₄</td>
<td>10</td>
<td>1.14</td>
<td>6.00</td>
</tr>
<tr>
<td>n-docosane</td>
<td>C₂₂H₄₆</td>
<td>10</td>
<td>1.14</td>
<td>5.95</td>
</tr>
<tr>
<td>n-tricosane</td>
<td>C₂₃H₄₈</td>
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<td>1.14</td>
<td>5.90</td>
</tr>
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<td>n-tetracosane</td>
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</tr>
<tr>
<td>n-pentacosane</td>
<td>C₂₅H₅₂</td>
<td>10</td>
<td>1.15</td>
<td>5.84</td>
</tr>
<tr>
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<td>C₂₆H₅₄</td>
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<td>1.15</td>
<td>5.79</td>
</tr>
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<td>10</td>
<td>1.13</td>
<td>5.81</td>
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<td>1.15</td>
<td>5.74</td>
</tr>
<tr>
<td>n-nonacosane</td>
<td>C₂₉H₆₀</td>
<td>10</td>
<td>1.15</td>
<td>5.72</td>
</tr>
<tr>
<td>n-triacontane</td>
<td>C₃₀H₆₂</td>
<td>10</td>
<td>1.15</td>
<td>5.70</td>
</tr>
<tr>
<td>n-hentriacontane</td>
<td>C₃₁H₆₄</td>
<td>10</td>
<td>1.18</td>
<td>5.66</td>
</tr>
<tr>
<td>n-dotriacontane</td>
<td>C₃₂H₆₆</td>
<td>10</td>
<td>1.17</td>
<td>5.64</td>
</tr>
<tr>
<td>n-tritriacontane</td>
<td>C₃₃H₆₈</td>
<td>10</td>
<td>1.14</td>
<td>5.67</td>
</tr>
<tr>
<td>n-tetratriacontane</td>
<td>C₃₄H₇₀</td>
<td>10</td>
<td>1.13</td>
<td>5.67</td>
</tr>
<tr>
<td>n-pentatriacontane</td>
<td>C₃₅H₇₂</td>
<td>10</td>
<td>1.13</td>
<td>5.66</td>
</tr>
<tr>
<td>n-hexatriacontane</td>
<td>C₃₆H₇₄</td>
<td>10</td>
<td>1.15</td>
<td>5.59</td>
</tr>
<tr>
<td>n-heptatriacontane</td>
<td>C₃₇H₇₆</td>
<td>10</td>
<td>1.14</td>
<td>5.65</td>
</tr>
</tbody>
</table>

52
Table 3-4 AARDs and MARDs for the predicted ideal gas heat capacities for normal alkanes with Equation [3-11] and Equation [3-16] in a temperature range of 200.00-1000.00 K, respectively (Cont’d)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>NPTS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>AARD, %</th>
<th>MARD, %</th>
<th>AARD, %</th>
<th>MARD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octatriacontane</td>
<td>C₃₈H₇₈</td>
<td>10</td>
<td>1.14</td>
<td>5.64</td>
<td>12.02</td>
<td>14.58</td>
</tr>
<tr>
<td>n-nonatriacontane</td>
<td>C₃₉H₈₀</td>
<td>10</td>
<td>1.14</td>
<td>5.63</td>
<td>12.18</td>
<td>14.66</td>
</tr>
<tr>
<td>n-tetracontane</td>
<td>C₄₀H₈₂</td>
<td>10</td>
<td>1.14</td>
<td>5.64</td>
<td>12.61</td>
<td>14.88</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>340</td>
<td>1.24</td>
<td>6.21</td>
<td>6.96</td>
<td>10.69</td>
</tr>
</tbody>
</table>

<sup>a</sup> NPTS represents the number of experimental data points.
compounds. In general, the ideal gas heat capacities calculated by the newly proposed correlation for normal alkanes have a good agreement with the experimentally measured data with a satisfying overall AARD of 1.24% and MARD of 6.21% for 340 experimental points included in the database.

(2) Normal alkenes

Such a new correlation, i.e., Equation [3-11], has been further validated with normal alkenes ranging from \( C_{10}H_{20} \) to \( C_{40}H_{80} \). As tabulated in Table 3-5, their respective ideal gas heat capacities are calculated with the correlation developed in this work and the Kesler and Lee correlation (Lee and Kesler, 1975; Kesler and Lee, 1976; Zhu and Okuno, 2015) and then compared with the corresponding experimental measurements. As can be seen from Table 3-5, the overall AARD and MARD of ideal gas heat capacity between the experimental measurements and theoretical calculations by using the Kesler and Lee correlation are 8.44% and 10.57% compared with those of 2.04% and 2.58% resulting from the newly developed correlation. The Kesler and Lee correlation leads to larger deviations for predicting ideal gas heat capacities, especially for heavy hydrocarbons. As mentioned earlier, this is ascribed to the fact that the ideal gas heat capacity equation developed by Kesler and Lee (1976) is based on the experimental data of light to medium paraffin/aromatic/naphthenic compounds. Also, the MARD for each normal alkene in a
Table 3-5 Comparison of the ideal gas heat capacities for normal alkenes calculated from the empirical correlations against the experimental measurements in a temperature range of 298.15-1000.00 K

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>NPTS</th>
<th>Equation [3-11]</th>
<th>Equation [3-16]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>AARD, %</td>
<td>MARD, %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AARD, %</td>
<td>MARD, %</td>
</tr>
<tr>
<td>1-decene</td>
<td>C_{10}H_{20}</td>
<td>9</td>
<td>3.53</td>
<td>5.51</td>
</tr>
<tr>
<td>1-undecene</td>
<td>C_{11}H_{22}</td>
<td>9</td>
<td>3.12</td>
<td>3.65</td>
</tr>
<tr>
<td>1-dodecene</td>
<td>C_{12}H_{24}</td>
<td>9</td>
<td>2.95</td>
<td>3.47</td>
</tr>
<tr>
<td>1-tridecene</td>
<td>C_{13}H_{26}</td>
<td>9</td>
<td>2.82</td>
<td>3.33</td>
</tr>
<tr>
<td>1-tetradecene</td>
<td>C_{14}H_{28}</td>
<td>9</td>
<td>2.69</td>
<td>3.21</td>
</tr>
<tr>
<td>1-pentadecene</td>
<td>C_{15}H_{30}</td>
<td>9</td>
<td>2.59</td>
<td>3.11</td>
</tr>
<tr>
<td>1-hexadecene</td>
<td>C_{16}H_{32}</td>
<td>9</td>
<td>2.49</td>
<td>3.00</td>
</tr>
<tr>
<td>1-heptadecene</td>
<td>C_{17}H_{34}</td>
<td>9</td>
<td>2.40</td>
<td>2.87</td>
</tr>
<tr>
<td>1-octadecene</td>
<td>C_{18}H_{36}</td>
<td>9</td>
<td>2.38</td>
<td>3.00</td>
</tr>
<tr>
<td>1-nonadecene</td>
<td>C_{19}H_{38}</td>
<td>9</td>
<td>2.31</td>
<td>2.95</td>
</tr>
<tr>
<td>1-eicosene</td>
<td>C_{20}H_{40}</td>
<td>9</td>
<td>2.18</td>
<td>2.68</td>
</tr>
<tr>
<td>1-heneicosene</td>
<td>C_{21}H_{42}</td>
<td>9</td>
<td>2.11</td>
<td>2.62</td>
</tr>
<tr>
<td>1-docosene</td>
<td>C_{22}H_{44}</td>
<td>9</td>
<td>2.05</td>
<td>2.55</td>
</tr>
<tr>
<td>1-tricosene</td>
<td>C_{23}H_{46}</td>
<td>9</td>
<td>1.99</td>
<td>2.48</td>
</tr>
<tr>
<td>1-tetracosene</td>
<td>C_{24}H_{48}</td>
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<td>1.93</td>
<td>2.42</td>
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<td>1.87</td>
<td>2.37</td>
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<td>1-hexacosene</td>
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<td>1.76</td>
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<td>1-nonacosene</td>
<td>C_{29}H_{58}</td>
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<td>1.72</td>
<td>2.20</td>
</tr>
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<td>1-triacontene</td>
<td>C_{30}H_{60}</td>
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<td>1.69</td>
<td>2.16</td>
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<td>1-hentriacontene</td>
<td>C_{31}H_{62}</td>
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<td>1.66</td>
<td>2.12</td>
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<td>1.62</td>
<td>2.09</td>
</tr>
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<td>C_{33}H_{66}</td>
<td>9</td>
<td>1.59</td>
<td>2.05</td>
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<td>C_{34}H_{68}</td>
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<td>C_{35}H_{70}</td>
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<td>1.53</td>
<td>1.99</td>
</tr>
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<td>C_{36}H_{72}</td>
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<td>1.50</td>
<td>1.96</td>
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<td>C_{40}H_{80}</td>
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<td>1.38</td>
<td>1.84</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>279</td>
<td>2.04</td>
<td>2.58</td>
</tr>
</tbody>
</table>

AARD: Average Absolute Relative Deviation, MARD: Mean Absolute Relative Deviation.
The temperature range of 298.15 K to 1000.00 K obtained from the newly proposed formulation is found to be at relative low temperatures from 300.00 K to 700.00 K, while those obtained from the Kesler and Lee correlation mostly occur at high temperatures (e.g., 900.00 K or 1000.00 K). This is attributed to the fact that the maximum deviations occur near the critical region as stated by Kesler and Lee (1976).

Figure 3-1 shows the measured and predicted ideal gas heat capacities for normal alkenes with different correlations. In general, the Kesler and Lee equation (1976) is found to be accurate in predicting the ideal gas heat capacities of normal alkenes when the experimentally measured ideal gas heat capacities are lower than $2 \times 10^6$ J/(mol·K); however, there exist larger errors for normal alkenes when the experimentally measured enthalpies are higher than $2 \times 10^6$ J/(mol·K). It is also interesting to note that the theoretically calculated ideal gas heat capacities deviated considerably from the experimental measurements for heavy alkenes by applying the Kesler and Lee method.

In other words, the Kesler and Lee method yields relatively large deviations for ideal gas heat capacity prediction of heavy hydrocarbons. This is attributed to the fact that the Kesler and Lee correlation is developed based on the 24 hydrocarbons ranging from carbon number C$_6$ to C$_{22}$. In contrast, the new correlation developed in this study demonstrates much better prediction accuracy of the ideal gas heat capacities not only for light hydrocarbons, but also for heavy hydrocarbons. This is due to the fact that the ideal gas heat capacities of heavy hydrocarbons are included in the database to develop
Figure 3-1 Measured and predicted ideal gas heat capacities of normal alkenes with different correlations
the new ideal gas heat capacity correlation (see Table 3-1). It is worthwhile noting that
the data used for correlation development in this study are excluded from further
validating the newly developed correlation.

Figures 3-2a and 3-2b illustrate the variation of AARDs as a function of the Watson
colorization factor, $K_w$, and molecular weight, $MW$ of the normal alkenes,
respectively. The modified correlation developed in this study is found to provide
reliable and consistent performance over a wide range of $K_w$ and $MW$ values, even for
heavy hydrocarbons, whereas the Kesler and Lee correlation can be used to have
relatively accurate prediction for $K_w$ less than 12.8 and $MW$ smaller than 220 g/mol with
an AARD lower than 5.00%, respectively. For heavier hydrocarbons, however, the
Kesler and Lee correlation leads to large deviations. Moreover, the heavier the
hydrocarbon is, the larger the deviation of the Kesler and Lee correlation will generate.
Plus, the AARDs obtained from the Kesler and Lee correlation increase quickly with an
increase in either $K_w$ or $MW$. For the AARDs calculated from the newly developed
correlation in this work, however, their values reduce more and more slowly with
temperature and they are much smaller with a satisfactory range than those from the
Kesler and Lee correlation. This indicates that the newly proposed correlation has better
performance to predict ideal gas heat capacities of hydrocarbons over a wide range of
either $K_w$ or $MW$ than that of the Kesler and Lee method.
Figure 3-2 Variation of AARDs as a function of (a) Watson characterization factor, $K_w$, and (b) molecular weight, $MW$ by using two ideal gas heat capacity correlations.
3.3.2 Total enthalpy

Lenoir and Hipkin (1971; 1973) performed extensive experiments to measure both liquid and vapour enthalpies for a number of hydrocarbon fractions. In their first publication (Lenoir and Hipkin, 1971), enthalpies of the light naphtha are reported, while, in their subsequent publication (Lenoir and Hipkin, 1973), enthalpies of eight hydrocarbon fractions, which include five naphthas and three gas oils, are provided. All the measurements were made possible using a flow calorimeter that the enthalpy differences between the fluid entering the calorimeter with a higher temperature and departing with a selected reference temperature of 297.04 K are recorded. To the best knowledge of the authors, they are believed to be the only hydrocarbon fractions enthalpy data available in the literature.

Ideal gas heat capacity equations are frequently integrated to calculate the ideal gas enthalpy. To evaluate the prediction accuracy of the newly proposed enthalpy algorithm, two representative hydrocarbon fractions (i.e., the light naphtha and Alaska naphtha) with different values of specific gravity are selected, while their physical and critical properties are tabulated in Table 3-6 (Lenoir and Hipkin, 1971; 1973).

(1) Light naphtha

Light naphtha, which is a straight-run product from a California crude (Lenoir and Hipkin, 1971) is used to evaluate the performance of the newly proposed enthalpy
Table 3-6 Physical and critical properties of hydrocarbon fractions (Lenoir and Hipkin, 1971; 1973)

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<th>Name</th>
<th>MW, g/mol</th>
<th>( T_b ), K</th>
<th>( T_c ), K</th>
<th>( P_c ), psi</th>
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<th>SG</th>
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algorithm. Table 3-7 compares the experimental enthalpies against with those obtained from the Kesler and Lee (1976) method and the newly developed algorithm in this work for the light naphtha over a wide range of temperatures and pressures. It should be noted that all the data listed in Table 3-7 are on the basis of enthalpy equal to zero for a saturated liquid at 144.26 K. As can be seen from Table 3-7, the predicted enthalpies by applying the new algorithm are very close to the measured ones, with an AARD of 1.25% for all the tested data points compared with 7.19% by using the Kesler and Lee method, respectively.

The comparison between the experimentally measured and theoretically calculated enthalpies by employing the new algorithm as well as the Kesler and Lee method is plotted in Figure 3-3. As can be seen, the calculated enthalpies by applying the new algorithm developed in this work agree well with the experimental measurements, indicating that it is reliable and accurate to predict the enthalpies for light naphtha under a wide variety of experimental conditions. Furthermore, it is found that the predicted enthalpies are slightly higher than the measured ones for the light naphtha; however, large deviations are observed for the Kesler and Lee method, especially at relatively low temperatures. This is because the values of the first and second terms in Equation [3-17] obtained from the tables (Lee and Kesler, 1975) or charts (Kesler and Lee, 1976) are uncertain, yielding inaccurate pressure effects on enthalpy.
Table 3-7 Comparison for enthalpies of the light naphtha between the experimental measurements and those obtained from the new algorithm developed in this study and the Kesler and Lee method (Kesler and Lee, 1976)

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Figure 3-3 Comparison of the experimental light naphtha enthalpies against with the corresponding predictions from the newly proposed algorithm and the Kesler and Lee (1976) method
Figures 3-4a and 3-4b illustrate the AARDs between the experimentally measured and theoretically predicted enthalpies at different temperatures and five pressures (i.e., 100, 200, 300, 400, and 500 psi). As for the results obtained from the new algorithm (see Figure 3-4a) at pressures from 100 to 400 psi, the higher the pressure is, the larger the AARDs will be, though the AARDs fluctuate at some temperatures. As can also be observed, the overall AARDs are less than 2.03%, implying that the prediction accuracy of the newly enthalpy correlation is satisfactory. At the highest pressure among all the examined pressures, i.e., 500 psi, the AARDs are less than 0.92%, indicating that not only the enthalpy algorithm proposed in this work is accurate even at high pressures, but also the enthalpy departure function, which accounts for the pressure effects on enthalpies, is accurate. As can be seen from Figure 3-4b, however, the results obtained from the Kesler and Lee method (1976) yield large errors, indicating that it cannot be applied to accurately predict enthalpies of the light naphtha at the testing pressures and temperatures.

(2) Alaska naphtha

The predictive capability of the new enthalpy algorithm is compared with the traditional Kesler and Lee (1976) method for the Alaska naphtha as well. Their corresponding AARDs are summarized in Table 3-8 for a total of 25 data points tested. Compared the results from Table 3-8 with those from Table 3-7, it is found that the overall accuracy of
Figure 3-4 AARDs for the light naphtha enthalpies obtained by applying (a) the new enthalpy determination algorithm, and (b) the Kesler and Lee (1976) method.
Table 3-8 Comparison on the enthalpies of the Alaska naphtha between the experimental measurements and those obtained from the new algorithm developed in this study and the Kesler and Lee method (Kesler and Lee, 1976)

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<td>Overall</td>
<td></td>
<td></td>
<td>19.18</td>
<td></td>
<td>2.78</td>
</tr>
</tbody>
</table>
the predicted enthalpies by applying the new algorithm for the Alaska naphtha is slightly lower than that for the light naphtha. The AARD and MARD for predicting the Alaska naphtha enthalpies are calculated to be 2.78% and 3.51%, respectively, implying that the new algorithm can also be applied to predict enthalpies for the Alaska naphtha. As for the Kesler and Lee method, however, the AARD and MARD can be as large as 19.18% and 81.40%, respectively, this is because the ideal gas heat capacity correlation that is applied to calculate the ideal gas enthalpy is not accurate and the enthalpy departure data reading from the tables or charts (Lee and Kesler, 1975; Kesler and Lee, 1976) is uncertain.

Figure 3-5 shows the predicted enthalpies of Alaska naphtha by using different enthalpy algorithms against with the experimental measurements. Again, there exists a good agreement between the calculated and measured enthalpies by using the new algorithm in this work. Through further observation, it is found that the predicted enthalpies are gradually higher with an increase in temperature, whereas the Kesler and Lee method provides less accurate enthalpy predictions. Figures 3-6a and 3-6b plot the AARDs for enthalpy calculation obtained from the newly proposed method together with the Kesler and Lee method. Obviously, there exists an excellent agreement between the measured and calculated enthalpies with the new algorithm. It is important to note that the AARDs obtained at 100 psi is slightly higher than those achieved at a lower pressure of 30 psi. In addition, the AARDs calculated at 30 psi and 100 psi are only 2.42% and 3.23%, respectively. Also, it can be found that the AARDs obtained by using the new algorithm
Figure 3-5 Comparison on the enthalpies of the Alaska naphtha between the experimental measurements and those obtained from the theoretical calculations
Figure 3-6 AARDs for the Alaska naphtha enthalpy prediction with temperature for (a) the new enthalpy algorithm, and (b) the Kesler and Lee (1976) method
are all below 4.00% within the entire temperature range, and their values increase slightly with an increase in temperature for pressures at both 30 psi and 100 psi. As for the Kesler and Lee method, however, large discrepancies are found between the theoretically predicted and experimentally measured enthalpies, indicating the newly proposed enthalpy algorithm outperforms the Kesler and Lee method.

Comparisons for the light naphtha and Alaska naphtha obtained from the Kesler and Lee method and the algorithm proposed in this work are summarized in Table 3-9. As can be seen, the improvement in prediction accuracy is found to be rather obvious. Overall, the AARDs and MARDs for the corresponding parameters of the light naphtha and Alaska naphtha are very small, implying that the prediction method proposed in this study can be used to calculate enthalpies for hydrocarbon fractions both accurately and conveniently. On the contrary, large AARDs are found between the measured enthalpies and those obtained by the Kesler and Lee (1976) model, especially at low temperatures and pressures (see Tables 3-7 and 3-8). This is mainly due to the follow reasons: (1) Values of enthalpy departure reading from charts are questionable; and (2) The ideal gas heat capacity correlation (i.e., Equation [3-16]) used for enthalpy calculation is not applicable for heavy hydrocarbon fractions.
<table>
<thead>
<tr>
<th>Hydrocarbon fraction</th>
<th>Kesler and Lee model</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NPTS</td>
<td>AARD, %</td>
</tr>
<tr>
<td>Light naphtha</td>
<td>43</td>
<td>7.19</td>
</tr>
<tr>
<td>Alaska naphtha</td>
<td>25</td>
<td>19.18</td>
</tr>
</tbody>
</table>
3.4 Summary

A modified correlation and a new enthalpy determination algorithm have been developed to more accurately predict ideal gas heat capacities and enthalpies for normal alkanes/alkenes and hydrocarbon fractions, respectively. The newly proposed correlation is able to predict ideal gas heat capacities of hydrocarbons more accurately at high pressures and elevated temperatures with a good accuracy. A good agreement is observed between the experimental measurements and theoretical calculations by applying the new enthalpy algorithm; however, large discrepancies are found for the Kesler and Lee method. Furthermore, the enthalpy departure function used in the new algorithm is more accurate and convenient in representation of the pressure effects on enthalpy, resulting in more accurate prediction of enthalpy for hydrocarbon fractions. The new algorithm proposed in this study can be applied to predict enthalpy of ill-defined hydrocarbons such as heavy oil pseudocomponents both accurately and efficiently.
CHAPTER 4 A ROBUST MULTIPHASE ISENTHALPIC FLASH MODEL FOR SOLVENT/WATER/HEAVY OIL SYSTEMS AT HIGH PRESSURES AND ELEVATED TEMPERATURES

4.1 Introduction

Based on the assumption that only the presence of solvent with a high solubility in water is considered in the aqueous phase, a robust and pragmatic technique has been developed to perform isenthalpic flash calculation for solvent/water/heavy oil systems at high pressures and elevated temperatures (Huang and Yang, 2019b). More specifically, the phase boundary diagram in $H$-$T$ space is constructed first for a given solvent/water/heavy oil system at a specified pressure. Then, the phase transition enthalpies and temperatures are determined from the $H$-$T$ diagram, and thus one-, two-, or three-phase isenthalpic flash calculations can be conducted directly without resorting to the so-called stability test for a given system at a specified enthalpy and pressure. In addition, a recursive method has been proposed to initialize the temperature so that the energy conservation equation and material balance equation can be solved simultaneously to overcome the convergence difficulties. The newly proposed isenthalpic flash model has been compared with the water-free isenthalpic flash (WFIF) model and conventional three-phase isenthalpic flash (CTIF) model through three case studies.
4.2 Mathematical Formulations

4.2.1 PR EOS

The PR EOS with the van der Waals’ mixing rule is a thermodynamic model used in this work because of its simplicity and computational accuracy. The detailed formulations of the PR EOS can be found in CHAPTER 3.

For a mixture system, \( a \) and \( b \) in the PR EOS can be calculated with the van der Waals’ mixing rule, i.e.,

\[
a = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} y_i y_j (a_i a_j)^{0.5} (1 - \delta_{ij}) \quad [4-1]
\]

\[
b = \sum_{i=1}^{N_c} y_i b_i \quad [4-2]
\]

where the subscript \( i \) and \( j \) are the component index, \( N_c \) is the number of the components, \( y_i \) and \( y_j \) are the mole fractions of the \( i \)-th and \( j \)-th component, respectively, and \( \delta_{ij} \) is the BIP between the \( i \)-th and \( j \)-th component.

The derivatives of various parameters associated with the PR EOS with respect to \( T \) are expressed as,

\[
\frac{\partial a_i}{\partial T} = -0.457235 R^2 T_i^{1.5} \left( 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \right) \left[ 1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2)(1 - T_i^{0.5}) \right] (P_c T_i)^{0.5} \quad [4-3]
\]

\[
\frac{\partial a_{\alpha \beta}}{\partial T} = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} 0.5 \chi_{\alpha \beta} \chi_{ij} (a_i a_j)^{-0.5} \left( a_i \frac{\partial a_i}{\partial T} + a_j \frac{\partial a_j}{\partial T} \right) (1 - \delta_{ij}) \quad [4-4a]
\]
where the subscript \( k \) is the phase index, and \( m \) is the mixture index.

It is worthwhile to mention that Equation [4-3] is obtained by deriving Equation [3-2a] with respect to \( T \), and alpha function is expressed as Equation [3-3a].

Then, the fugacity coefficient of the \( i \)th component can be formulated as,

\[
\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln (Z - B) + \frac{A}{2\sqrt{2B}} \left( \frac{b_i}{b} - \frac{2\sum_{j=1}^{N_c} y_j a_{ij}}{a} \right) \ln \left( \frac{Z + (1 + \sqrt{2}) B}{Z + (1 - \sqrt{2}) B} \right) \tag{4-5}
\]

where \( \phi_i \) is the fugacity coefficient of the \( i \)th component, and \( Z \) is the compressibility factor.

### 4.2.2 Three-phase isothermal flash

For three-phase equilibrium of solvent/water/heavy oil mixtures, equal chemical potential of each component in each phase are to be satisfied (Yokozeki, 2005a; b),

\[
f_{ix} = f_{iy} = f_{iw}, \quad i = 1, 2, \ldots, N_c \tag{4-6}
\]

where \( f_{ix}, f_{iy}, \) and \( f_{iw} \) represent the fugacity of the \( i \)th component in hydrocarbon-rich liquid phase, vapour phase, and aqueous phase, respectively, and \( N_c \) is number of components.

The component and phase material balance constraints can be expressed as,
\[ \beta_x + \beta_y + \beta_w = 1 \]  \[4-7\]

\[ \beta_x x_i + \beta_y y_i + \beta_w w_i = z_i \]  \[4-8\]

where \( \beta_x \), \( \beta_y \), and \( \beta_w \) are phase fractions in the hydrocarbon-rich liquid phase, vapour phase, and aqueous phase, respectively, \( x_i \), \( y_i \), and \( w_i \) are mole fractions of the \( i \)th component in the hydrocarbon-rich liquid phase, vapour phase, and aqueous phase, respectively.

Additionally, the mole fraction of each equilibrium phase must sum to unity,

\[ \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = \sum_{i=1}^{N} w_i = 1 \]  \[4-9\]

Introducing the equilibrium ratios (hydrocarbon-rich liquid phase is chosen as the reference phase),

\[
\begin{align*}
K_{iy} &= \frac{y_i}{x_i} = \frac{\phi_{iy}}{\phi_y} \\
K_{iw} &= \frac{w_i}{x_i} = \frac{\phi_{iw}}{\phi_w}
\end{align*}
\]  \[4-10\]

where \( K_{iy} \) and \( K_{iw} \) are equilibrium ratios of the \( i \)th component in the vapour phase and aqueous phase with respect to the hydrocarbon-rich liquid phase, respectively, \( \phi_x \), \( \phi_y \), and \( \phi_w \) are fugacity coefficients of the \( i \)th component in the hydrocarbon-rich liquid phase, vapour phase, and aqueous phase, respectively.

Combining Equations \[4-7\]–\[4-10\] yields the following two Rachford-Rice equations for conventional full three-phase isothermal flash, which are commonly used to solve for phase fractions and compositions (Rachford and Rice, 1952; Li and
By solving Equations [4-10] and [4-11], phase compositions can be determined from the material balance equations,

\[
RR_y = \sum_{i=1}^{N} (y_i - x_i) = \sum_{i=1}^{N} \frac{z_i(K_{iy} - 1)}{1 + \beta_y(K_{iy} - 1) + \beta_w(K_{iw} - 1)} = 0
\]

\[
RR_w = \sum_{i=1}^{N} (w_i - x_i) = \sum_{i=1}^{N} \frac{z_i(K_{iw} - 1)}{1 + \beta_y(K_{iy} - 1) + \beta_w(K_{iw} - 1)} = 0
\]

Based on the water-free assumption that the aqueous phase consists of only pure water, Li and Li (2018a) simplified the work of Lapene et al. (2010) and Okuno et al. (2010) and then proposed an optimization method for the three-phase isothermal flash with water-free assumption. The objective function and constraints are expressed as follows (Li and Li, 2018a),

\[
\begin{align*}
\min & : f(\beta_y) = \sum_{i=2}^{N} z_i \ln \left[ (K_{iy} - K_{iy}^*) + K_{iy}^* \right] \\
\text{subject to} & : (K_{wy}^* - K_{ij}) \beta_y \leq \min \{K_{wz}^* - z_i, K_{wz}^* - K_{ij} z_i \}, i \neq 1
\end{align*}
\]

where

\[
\begin{align*}
K_{wy}^* &= \frac{1 - y_w}{1 - x_w} \\
K_w^* &= \frac{1 - z_w}{1 - x_w}
\end{align*}
\]

Equation [4-14] is the “effective” equilibrium constants defined by Tang and Saha (2003). By combining Equations [4-13] and [4-14], phase compositions can then be
obtained,

\[
\begin{aligned}
x_i &= \frac{z_i}{(K_{ij} - K_{ij}^*) + K_{ij}^*}, i \neq H_2O \\
x_i &= \frac{1}{K_{iw}}, i = H_2O \\
y_i &= K_{ij} x_i \\
w_i &= 1
\end{aligned}
\]  

[4-15]

where

\[
\begin{aligned}
K_{ww} &= \frac{K_{wy}}{y_w} \\
K_{wy} &= \frac{T}{T_{cw}} \frac{P_{cw}}{P} \\
y_w &= \frac{P_{sat}^w}{P}
\end{aligned}
\]  

[4-16]

where \( P_{cw} \) and \( T_{cw} \) are the critical pressure and temperature of water, \( P_{sat}^w \) denotes the saturation pressure of pure water that can be obtained by using the empirical correlation developed by Bridgeman and Aldrich (1964).

Considering that the solubility of some solvents in the aqueous phase cannot be negligible under reservoir conditions, Pang and Li (2017; 2018) improved the water-free three-phase isothermal flash and proposed a new isothermal flash algorithm on the basis of the augmented water-free assumption. Based on the assumption that only a solvent (e.g., CO₂) or DME and water are present in the aqueous phase at high pressures and elevated temperatures (Sheng et al., 2018), the objective function and constraints are modified as follows,
By solving the above formula, the phase compositions can be expressed as,

\[
\begin{align*}
x_i &= \frac{z_i}{1 + \beta_y(K_y - 1) - \beta_w}, \quad i \neq \text{H}_2\text{O}, \text{DME or CO}_2 \\
x_i &= \frac{z_i}{1 + \beta_y(K_y - 1) + \beta_w(K_w - 1)}, \quad i = \text{H}_2\text{O}, \text{DME or CO}_2 \\
y_i &= K_y x_i \\
w_i &= K_w x_i, \quad i = \text{H}_2\text{O}, \text{DME or CO}_2
\end{align*}
\]

4.2.3 Isenthalpic flash

Isenthalpic flash calculations correspond to obtaining the temperature \( T \), phase mole fraction \( \beta_k \), and phase composition \( x_{ik} \) which maximize the total entropy \( S_t \) of a system at a specified pressure \( P \), enthalpy \( H_{\text{spec}} \), and feed composition \( z_i \) (Michelsen, 1987; 1999).

\[
S_t = \sum_{k=1}^{N_p} \beta_k S_{k}, \quad k = 1, 2, \ldots, N_p
\]

The following \( N_p - 1 \) material balance equation and energy conservation equation are to be satisfied,
where $S_t$ is the total molar entropy of the system, $\beta_k$ is the phase mole fraction of phase $k$, $S_k$ is the molar entropy of phase $k$, $z_i$ is the overall mole fraction of the $i$th component, $x_{ik}$ is the mole fraction of the $i$th component in phase $k$, $x_{iNp}$ is the mole fraction of the $i$th component in the reference phase, $H_t$ is the total molar enthalpy of the system, $H_k$ is the molar enthalpy of phase $k$, J/mol, and $H_{spec}$ is the specified molar enthalpy, J/mol.

The total molar enthalpy of $N_p$ phases is expressed as (Kesler, Lee, 1976; Michelsen, 1987),

$$H_t = \sum_{k=1}^{N_p} \beta_k \left( H_k^{IGM} + H_k^{dep} \right)$$

[4-21]

More specifically, the molar ideal gas mixture enthalpy of phase $k$ as well as the molar ideal gas enthalpy of the $i$th component can be calculated by using the following formula (Passut and Danner, 1972; Poling et al., 2001),

$$H_k^{IGM} = \sum_{i=1}^{N_p} x_{ik} H_i^{IG}$$

[4-22]

$$H_i^{IG} = C_{p_{1i}}^0 (T - T_0) + C_{p_{2i}}^0 \left( T^2 - T_0^2 \right)/2 + C_{p_{3i}}^0 \left( T^3 - T_0^3 \right)/3 + C_{p_{4i}}^0 \left( T^4 - T_0^4 \right)/4$$

[4-23]

where $H_t$ is the total molar enthalpy, J/mol, $H_k^{IGM}$ is the molar ideal gas mixture enthalpy of phase $k$, J/mol, $H_i^{IG}$ is the molar ideal gas enthalpy of the $i$th component, J/mol, $H_k^{dep}$ is the...
is the molar enthalpy departure, J/mol, $C_{p,i}^0$, $C_{p_{2i}}^0$, $C_{p_{3i}}^0$, and $C_{p_{4i}}^0$ are ideal gas heat capacity coefficients of the $i$th component, and $T_0$ is the reference temperature, which is 273.15 K in this work.

Then, the molar enthalpy departure for phase $k$ is given by,

$$H_k^{dep} = \left[ (RT^2 \frac{\partial A_{mk}}{\partial T} + RTA_{mk}) \right] \ln \left( \frac{Z_k + (1 + 2^{0.5})B_{mk}}{Z_k + (1 - 2^{0.5})B_{mk}} \right) + RT(Z_k - 1) \quad [4-24]$$

### 4.3 Modified Algorithms

This section presents a modified isenthalpic flash algorithm based on the augmented water-free assumption, which is referred as water-associated isenthalpic flash (WAIF) model in this work. Two methods have been made available to perform the isenthalpic flash calculations in the literature, i.e., (1) The water-free isenthalpic flash (WFIF) model which is based on the water-free assumption that the solvent solubility in the aqueous phase is zero; and (2) The conventional three-phase isenthalpic flash (CTIF) model which considers all the solvent solubility in the aqueous phase. The former enhances the computational efficiency by solving the modified Rachford-Rice monotonic objective function (Li and Li, 2018a), but it is not suitable for the system with a high solvent solubility in the aqueous phase. The latter can predict all the solvent solubility in the aqueous phase; however, it is time-consuming because it needs numerous stability analyses to determine the number of phases of the system involved. The main objective
of developing a WAIF model in this study is to improve the computational efficiency for solvent/water/heavy oil systems by avoiding stability analysis as those for the CTIF model while maintaining prediction accuracy for solvent solubility in the aqueous phase compared with the WFIF model.

The new isenthalpic flash algorithm adopts a modified Rachford-Rice monotonic function i.e., Equation [4-17] and the negative flash concept (Whitson and Michelsen, 1989) for calculating phase fractions and compositions. Therefore, there is no need to perform stability analysis to determine the number of phases for a given mixture. As for the WAIF model, it is the first task to determine the upper phase transition temperatures (\(T^U\)) for a given feed composition consisting of solvent/water/heavy oil mixtures at a specified pressure. More specifically, \(T^U_1\) is the temperature at which the vapor phase just appears in the system, \(T^U_2\) denotes the temperature at which the aqueous phase disappears, and \(T^U_3\) represents the temperature at which the hydrocarbon-rich liquid phase leaves the system. Accordingly, phase fractions and compositions at the phase boundary can also be determined. Then, the enthalpies at upper phase transition temperatures can be calculated, which is referred to as phase transition enthalpies. Finally, the relation (i.e., \(H-T\) diagram) between phase transition enthalpies and temperatures can be constructed. Therefore, one-, two-, or three-phase isenthalpic flash calculations can be conducted directly without performing stability analysis by comparing a specified enthalpy of a mixture to the phase transition enthalpy.
The energy conservation equation or material balance equation may not converge if a poor initial temperature $T^i$ is assumed for a given three-phase isenthalpic flash. Li and Li (2018a) proposed a scheme to switch from three-phase to two-phase isenthalpic flash without the prior knowledge of the existing phases. In this chapter, a recursive method is proposed to constrain the selection of initial temperature and overcome the problems associated with phase appearance and disappearance that are frequently encountered in a thermal recovery process.

The procedures for the new multiphase isenthalpic flash for solvent/water/hydrocarbon systems are briefly described below. The flowchart of the new algorithm is shown in Figure 4-1.

1). Specify $P$, $H_{spec}$, $z_i$, together with thermodynamic properties such as critical temperature $T_c$, critical pressure, $P_c$, acentric factor, $\omega$, and BIPs.

2). Construct the $H$-$T$ diagram at the specified $P$. In this step, detailed procedures are given to determine phase transition temperatures (i.e., appearance of a vapour phase at $T^{U1}$, disappearance of liquid water at $T^{U2}$, and disappearance of hydrocarbon liquid at $T^{U3}$) and the corresponding phase transition enthalpies.

(a). Appearance of a vapour phase at $T^{U1}$. Perform three-phase isothermal flash by estimating a series of temperatures at the prespecified pressure until the vapour
Figure 4-1 Flowchart of the WAIF algorithm
phase fraction just approaches zero. Then estimated temperature is $T_{U1}$, and the phase transition enthalpy at $T_{U1}$ is calculated as,

$$H_{r_{U1}} = H_{HC} \beta_{HC} + H_A \beta_A$$  \[4-25a\]

(b). Disappearance of liquid water at $T_{U2}$. Perform three-phase isothermal flash by estimating a series of temperatures at the prespecified pressure until the aqueous phase fraction just approaches zero. The estimated temperature is $T_{U2}$, and the phase transition enthalpy at $T_{U2}$ is calculated as,

$$H_{r_{U2}} = H_{HC} \beta_{HC} + H_V \beta_V$$  \[4-25b\]

(c). Disappearance of liquid hydrocarbon at $T_{U3}$. Perform two-phase isothermal flash by estimating a series of temperatures at the specified pressure until the hydrogen liquid phase fraction just approaches zero. The estimated temperature is $T_{U3}$, and the phase transition enthalpy at $T_{U3}$ is calculated as,

$$H_{r_{U3}} = H_V \beta_V$$  \[4-25c\]

3). Determine the multiphase isenthalpic flash region from the $H$-$T$ diagram by comparison with $H_{spec}$ and obtain the lower temperature $T_L$ as well as the upper temperature $T_U$ according to the determined isenthalpic flash region.

4). Set the initial temperature $T_{iter} = (T_L + T_U)/2$, the iteration number $iter = 1$, and tolerance $\varepsilon = 10^{-6}$.

5). Perform isothermal flash at $P$ and $T_{iter}$ at the specific phase region obtained
from Step #3 and calculate phase fractions, $\beta_i$, and compositions, $x_{ik}$. The method for initializing equilibrium ratios for the WAIF model is the same as that proposed by Pang and Li (2017), while the modified Rachford-Rice equation (i.e., Equation [4-17]) is solved by Newton with the line search method (Pang and Li, 2017).

6). If unphysical results, i.e., $\beta_i \notin (0,1)$ occur, let $T_{\text{iter}}^+=T_{\text{iter}}+\Delta T$ if $T_{\text{iter}}>(T^L+T^U)/2$ or $T_{\text{iter}}^-=T_{\text{iter}}-\Delta T$ if $T_{\text{iter}}<(T^L+T^U)/2$ and go to Step #5.

7). Calculate the residual of the energy conservation equation, $g_{N_p}^{\text{iter}}$,

$$g_{N_p}^{\text{iter}} = H_i - H_{\text{spec}}$$  \[4-26\]

8). If $|g_{N_p}^{\text{iter}}| < \varepsilon$, terminate the calculation; otherwise, continue to Step #9.

9). Update $T_{\text{iter}}$. The secant method is used to update the temperature,

$$T_{\text{iter}}^{+1} = T_{\text{iter}} - \frac{g_{N_p}^{\text{iter}} (T_{\text{iter}} - T_{\text{iter}}^{-1})}{g_{N_p}^{\text{iter}} - g_{N_p}^{\text{iter}^{-1}}}$$  \[4-27a\]

10). Check to see if $T^L < T_{\text{iter}}^{+1} < T^U$. If so, let $\text{iter} = \text{iter} + 1$ and go to Step #11; otherwise, update $T_{\text{iter}}$ by using the Regula Falsi method (Agarwal et al., 1991),

$$T_{\text{iter}}^{+1} = T_{\text{iter}} - \frac{g_{N_p}^{\text{iter}} (T^L - T^U)}{g_{N_p}^L - g_{N_p}^U}$$  \[4-27b\]

where $g_{N_p}^L$ and $g_{N_p}^U$ are the residual of the energy conservation equation at $T^L$ and $T^U$, respectively.
11). If \( |g^{\text{iter}-1}_{N_p}| < \epsilon \), terminate the calculation and output \( T^{\text{iter}-1}, x_{ik}, \text{ and } \beta_k \); otherwise, go back to Step #5.

4.4 Results and Discussion

Three representative solvent/water/heavy oil mixtures with different solvent solubilities in the aqueous phase are selected as case studies to not only test the robustness, efficiency, and accuracy of the WAIF model, but also handle the narrow-boiling constraints, especially in the three-phase region. These three mixtures associated with the same solvent/water/heavy oil ratio are selected to simulate a typical scenario which is frequently encountered in a solvent-steam co-injection process. More specifically, water represents the condensed steam, solvent represents the co-injected volatile components, and \( \text{C}_{16}\text{H}_{34} \) represents the oil phase. The results calculated from the WAIF model are compared against with those obtained from the WFIF model and the CTIF model. The WFIF model developed by Li and Li (2018b) has been demonstrated as accurate, efficient, and robust for water/heavy oil mixtures with water-insoluble solvents. Physical properties and BIPs for the mixtures are listed in Tables 4-1–4-6 (API, 1983; Lapene et al., 2010; Sheng, 2016; Li and Li, 2018b). Hereinafter, \( V \) represents the vapour phase, \( HC \) represents the hydrocarbon-rich liquid phase, and \( A \) represents the aqueous phase.
4.4.1 Case #1: C₃H₈/water/C₁₆H₃₄ mixture

The C₃H₈/water/C₁₆H₃₄ mixture is tested at 80 bar and different specified enthalpies. Li and Li (2018b) also used this mixture to compare the results obtained by the WFIF model with those of Zhu and Okuno (2015). Figure 4-2 shows the comparison between phase transition enthalpies and temperatures, i.e., phase boundaries in $H$-$T$ space, obtained by the WAIF model and the WFIF model at 80 bar. As can be seen, the phase transition enthalpies and temperatures obtained by the two isenthalpic flash models are in excellent agreement. The narrow-boiling behaviour occurs in the three-phase region, which is indicated by a significant change in enthalpy with a small change in temperature. The phase transition temperatures at 80 bar are determined to be $T_{U1}^L = 491.04$ K, $T_{U2}^L = 549.47$ K, and $T_{U3}^L = 598.85$ K. A number of different specified enthalpies are selected from the three-phase narrow-boiling region to evaluate the performance of the new isenthalpic flash model to handle the narrow-boiling constraints, as shown in Figures 4-3–4-6. Therefore, phase transition enthalpies for the three-phase region are determined to be -14073 and 17599 J/mol from Figure 4-2. Accordingly, $T_L = 491.04$ K, $T_U = 549.47$ K, and $T_I = (T_L + T_U)/2 = 520.255$ K, respectively.

Figure 4-3 compares the temperatures and phase fractions of each phase calculated by these two isenthalpic flash models at 80 bar in the narrow-boiling region, i.e., the three-phase region. A wide range of specified enthalpies is selected from
Table 4-1 Physical properties of component C$_3$H$_8$/H$_2$O/C$_{16}$H$_{34}$ (API, 1983)

<table>
<thead>
<tr>
<th>Component</th>
<th>$z_i$ (mol%)</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
<th>$\omega$</th>
<th>$C^0_{pi}$</th>
<th>$C^0_{p2i}$</th>
<th>$C^0_{p3i}$</th>
<th>$C^0_{p4i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$</td>
<td>15</td>
<td>369.8</td>
<td>42.46</td>
<td>0.152</td>
<td>-4.22</td>
<td>0.306300</td>
<td>-1.60×10$^{-4}$</td>
<td>3.215×10$^{-8}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>75</td>
<td>647.3</td>
<td>220.89</td>
<td>0.344</td>
<td>32.20</td>
<td>0.001907</td>
<td>1.06×10$^{-5}$</td>
<td>-3.596×10$^{-9}$</td>
</tr>
<tr>
<td>C$<em>{16}$H$</em>{34}$</td>
<td>10</td>
<td>717.0</td>
<td>14.19</td>
<td>0.742</td>
<td>-13.00</td>
<td>1.529000</td>
<td>-8.50×10$^{-4}$</td>
<td>1.850×10$^{-7}$</td>
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</tbody>
</table>
Table 4-2 BIPs between the components in the C₃H₈/H₂O/C₁₆H₃₄ mixture (Li and Li, 2018b)

<table>
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<tr>
<th>Component</th>
<th>C₃H₈</th>
<th>H₂O</th>
<th>C₁₆H₃₄</th>
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<td>0</td>
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<tr>
<td>H₂O</td>
<td>0.6841</td>
<td>0</td>
<td>0.3583</td>
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<td>C₁₆H₃₄</td>
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</table>
### Table 4-3 Physical properties of component CO$_2$/H$_2$O/C$_{16}$H$_{34}$ (API, 1983)

<table>
<thead>
<tr>
<th>Component</th>
<th>$z_i$ (mol%)</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
<th>$\omega$</th>
<th>$C^0_{P_{fi}}$</th>
<th>$C^0_{P_{f2}}$</th>
<th>$C^0_{P_{f3}}$</th>
<th>$C^0_{P_{f4}}$</th>
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<tr>
<td>CO$_2$</td>
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<td>304.2</td>
<td>73.76</td>
<td>0.225</td>
<td>19.795</td>
<td>0.073430</td>
<td>$-5.602 \times 10^{-5}$</td>
<td>$1.715 \times 10^{-8}$</td>
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<td>H$_2$O</td>
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<td>647.3</td>
<td>220.89</td>
<td>0.344</td>
<td>32.200</td>
<td>0.001907</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$-3.596 \times 10^{-9}$</td>
</tr>
<tr>
<td>C$<em>{16}$H$</em>{34}$</td>
<td>10</td>
<td>717.0</td>
<td>14.19</td>
<td>0.742</td>
<td>$-13.000$</td>
<td>1.529000</td>
<td>$-8.50 \times 10^{-4}$</td>
<td>$1.850 \times 10^{-7}$</td>
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Table 4-4 BIPs between the components in the CO$_2$/H$_2$O/C$_{16}$H$_{34}$ mixture (Lapene, 2010)

<table>
<thead>
<tr>
<th>Component</th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>C$<em>{16}$H$</em>{34}$</th>
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<td>CO$_2$</td>
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<tr>
<td>C$<em>{16}$H$</em>{34}$</td>
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<td>0.3583</td>
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Table 4-5 Physical properties of component DME/H2O/C16H34 (API, 1983)

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<th>Component</th>
<th>$z_i$ (mol%)</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
<th>$\omega$</th>
<th>$C_{Pi}^0$</th>
<th>$C_{P2i}^0$</th>
<th>$C_{P3i}^0$</th>
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<td>H2O</td>
<td>75</td>
<td>647.3</td>
<td>220.89</td>
<td>0.344</td>
<td>32.20</td>
<td>0.001907</td>
<td>1.060×10^{-5}</td>
<td>-3.596×10^{-9}</td>
</tr>
<tr>
<td>C16H34</td>
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<td>717.0</td>
<td>14.19</td>
<td>0.742</td>
<td>-13.00</td>
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<td>-8.500×10^{-4}</td>
<td>1.850×10^{-7}</td>
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Table 4-6 BIPs between the components in the DME/H₂O/C₁₆H₃₄ mixture (Sheng, 2016)

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<th>H₂O</th>
<th>C₁₆H₃₄</th>
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</thead>
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<td>0.0150</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.1700</td>
<td>0</td>
<td>0.3583</td>
</tr>
<tr>
<td>C₁₆H₃₄</td>
<td>0.0150</td>
<td>0.3583</td>
<td>0</td>
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Figure 4-2 Comparison between phase transition enthalpies and temperatures obtained from the WAIF model and the WFIF model (Li and Li, 2018b) at 80 bar for a mixture of 15 mol% C₃H₈, 75 mol% water, and 10 mol% C₁₆H₃₄
Figure 4-3 Comparison between the temperatures and phase fractions obtained from the WAIF model and the WFIF model in the three-phase region for the C₃H₈/water/C₁₆H₃₄ mixture at 80 bar and different enthalpies
Figure 4-4 Comparison of the temperatures and phase compositions that are obtained by using the WAIF model and the WFIF in three-phase region for the C₃H₈/water/C₁₆H₃₄ mixture at 80 bar and different enthalpies for (a) vapour phase, and (b) hydrocarbon-rich liquid phase
Figure 4-5 Mole fractions of C₃H₈ in the aqueous phase calculated by the WAIF model at 80 bar and different enthalpies in the three-phase region
Figure 4-6 The number of iterations required by the WAIF model and the WFIF model in the three-phase region for the C₃H₈/water/C₁₆H₃₄ mixture at 80 bar
this region to test the robustness and accuracy of the WAIF model. The calculated
temperatures and phase fractions by the two isenthalpic flash models agree well. An
AARD and a MARD calculated between the two models for predicting the temperature
are 0.001% and 0.003% as well as an AARD of 0.037% and a MARD of 0.057% for
predicting the phase fractions, which indicates that the WAIF model is capable of
dealing with narrow-boiling regions with high accuracy and robustness. Figure 4-4
illustrates the comparison of the temperatures and mole fractions of individual
components that are calculated by using the WFIF model and those calculated by using
the WAIF model at 80 bar and different enthalpies in the three-phase region for the
vapour phase and hydrocarbon-rich liquid phase, respectively. A good agreement is
observed between the calculated temperatures and mole fractions of individual
components by these two methods. It is interesting to note that mole fractions of water
in vapour phase and hydrocarbon-rich liquid phase both increase with an increment in
temperature. Dissolved water in $C_{16}H_{34}$ acts as a low viscosity solvent that results in
viscosity reduction of hydrocarbon-rich liquid phase, which is preferred in thermal
recovery processes (Glandt and Chapman, 1995).

Figure 4-5 shows the mole fractions of $C_3H_8$ in the aqueous phase calculated by
the WAIF model. As can be seen, the largest mole fraction of $C_3H_8$ in the aqueous
phase is less than $2.0 \times 10^{-5}$, which explains why the phase transition enthalpies,
temperatures, phase fractions and compositions obtained by the two isenthalpic flash
models are in an excellent agreement. Based on the results from Case #1, the two isenthalpic flash models can also be applied to other water/heavy oil mixtures in which the solvent has a similar solubility of C₃H₈ in the aqueous phase. Figure 4-6 shows the comparison of the number of iterations required by the two models in the narrow-boiling three-phase region. Compared with the WFIF model, the number of iterations required the WAIF model in the three-phase region, especially near the phase boundary between the three-phase and two-phase vapour-liquid regions, is reduced, indicating that the new isenthalpic flash model is efficient and robust in dealing with the narrow-boiling constraints. It is worthwhile noting that the initial temperature has a significant effect on the isenthalpic flash calculations. As such, a recursive method has been proposed in this study to accelerate the convergence speed within the narrow-boiling regions, resulting in a reduced number of iterations and thus less computational time.

4.4.2 Case #2: CO₂/water/C₁₆H₃₄ mixture

This mixture, which includes a slightly water-soluble solvent, CO₂, is used to evaluate the performance of the two isenthalpic flash models. Multiphase isenthalpic flash calculations are conducted at 80 bar and different specified enthalpies. Figure 4-7 shows the comparison between phase transition enthalpies and temperatures obtained by the WAIF model and those obtained by the WFIF model. The three-phase region
Figure 4-7 Comparison between phase transition enthalpies and temperatures obtained from the WAIF model and the WFIF model at 80 bar for a mixture of 15 mol% CO$_2$, 75 mol% water, and 10 mol% C$_{16}$H$_{34}$
temperatures are located at 316.99–547.82 K, while the corresponding enthalpy is located at -39091–14903 J/mol. Compared to Case #1, there exists a relatively small discrepancy between the phase boundaries in the $H-T$ space obtained from the two isenthalpic flash models.

Figure 4-8 illustrates the comparison between the temperatures and phase fractions of the three phases obtained from the two isenthalpic flash models at 80 bar in the three-phase region. As can be seen from Figure 4-8, there is a good agreement between the temperatures and phase fractions obtained by the two isenthalpic flash models. The AARDs for predicting the temperature and phase fractions are 0.037% and 0.734% and the MARDs for predicting the temperature and phase fractions are 0.057% and 2.673%, respectively, implying that the two isenthalpic flash models both work well for the CO$_2$/water/C$_{16}$H$_{34}$ mixture with a relatively small deviation. Figure 4-9 compares the temperatures and phase compositions in the vapour phase that are obtained by the WFIF model and those obtained from the WAIF model for the water/CO$_2$/C$_{16}$H$_{34}$ mixture at 80 bar within the three-phase region. Obviously, an excellent agreement between the temperatures and phase compositions in the vapour phase is achieved.

Figure 4-10 shows the dissolution of CO$_2$ in the aqueous phase obtained by the WAIF model at 80 bar in the three-phase region. Compared to Figure 4-5, the solubility of CO$_2$ in the aqueous phase is a slightly higher than that of C$_3$H$_8$ in the aqueous phase.
Figure 4-8 Comparison between the temperatures and phase fractions obtained from the WAIF model and the WFIF model in the three-phase region for the CO$_2$/water/$C_{16}H_{34}$ mixture at 80 bar and different enthalpies
**Figure 4-9** Comparison between the temperatures and phase compositions in the vapour phase that are obtained from the WAIF model and the WFIF model in the three-phase region for the CO$_2$/water/C$_{16}$H$_{34}$ mixture at 80 bar and different enthalpies for (a) vapour phase compositions, and (b) absolute deviations of vapour phase compositions
Figure 4-10 Mole fractions of CO₂ in the aqueous phase calculated by the WAIF model at 80 bar and different enthalpies within the three-phase region
which explains why there exists a relatively small discrepancy between the phase boundaries in the $H-T$ space obtained from the two isenthalpic flash models. It is obvious that the mole fraction of CO$_2$ in the aqueous phase increases first, and then decreases with an increase in temperature. In addition, the largest mole fraction of CO$_2$ in the aqueous phase is less than $5.0\times10^{-3}$. Figure 4-11 depicts the number of iterations and temperatures obtained by the WAIF model and the WFIF model in the three-phase region for CO$_2$/water/C$_{16}H_{34}$ mixture at 80 bar. Again, the number of iterations of the WAIF model in which a recursive method is used for initializing the temperature for the inner loop isothermal flash is reduced compared with the WFIF model, illustrating the computational efficiency of the new isenthalpic flash model.

4.4.3 Case #3: DME/water/C$_{16}H_{34}$ mixture

This mixture, which is comprised of water, heavy hydrocarbon C$_{16}H_{34}$ and DME, a partially water-soluble solvent due to its slight polarity (Ratnakar et al., 2016), is used to evaluate the performance of the two isenthalpic flash models. The main objective of Case #3 is to examine the superiority of the WAIF model of dealing with narrow-boiling regions, i.e., the three-phase region, in terms of accuracy, robustness, and efficiency. Another purpose is to investigate the deviation of the results obtained from the WAIF model against with those from the WFIF model which uses water-free assumption and the CTIF model which considers the mutual solubility of components.
Figure 4-11 The number of iterations required by the WAIF model and the WFIF model in the three-phase region for the CO$_2$/water/C$_{16}$H$_{34}$ mixture at 80 bar
in all phases. Figure 4-12 compares the phase transition enthalpies and temperatures obtained from the two isenthalpic flash models. The three-phase region temperature is located at 513.95-549.03 K, while the corresponding enthalpy is located at -9000 to 15500 J/mol. Compared to Cases #1 and #2, large discrepancies are observed between the phase boundaries in $H$-$T$ space obtained from the WAIF model and the WFIF model due to that the solubility of DME in the aqueous phase is much higher than those of C$_3$H$_8$ and CO$_2$ in the aqueous phase. More specifically, DME (i.e., CH$_3$-O-CH$_3$) is fairly soluble in water due to the presence of its oxygen atom which can interact with hydrogen atom in water to form hydrogen bonds (Hine and Mookerjee, 1975). As for C$_3$H$_8$ (i.e., CH$_3$-CH$_2$-CH$_3$), the -CH$_3$ group is hydrophobic and cannot form hydrogen bonds with water, thus its solubility in the aqueous phase is quite small (Chapoy et al., 2004; Floweers et al., 2016). With respect to CO$_2$ (i.e., O=C=O), it has a slight negative charge near the oxygen atom and a slight positive charge near the carbon atom, resulting in polarized bonds (Hine and Mookerjee, 1975). CO$_2$ is slightly soluble in water because water molecules are attracted to these polar areas and the bond between the carbon and oxygen atoms is not as polar as the bond between the hydrogen and oxygen atoms (Hine and Mookerjee, 1975).
Figure 4-12 Comparison between phase transition enthalpies and temperatures obtained from the WAIF model and the WFIF model at 80 bar for a mixture of 15 mol% DME, 75 mol% water, and 10 mol% C_{16}H_{34}
Figure 4-13 presents the comparison between the temperatures and phase fractions that are obtained from the WAIF model and those obtained by the WFIF model for the DME/water/C_{16}H_{34} mixture at 80 bar and different enthalpies in the three-phase region. It is obvious that there exist large discrepancies between the temperatures and phases fractions that are obtained from the two isenthalpic flash models. This is due to the fact that the water-free isenthalpic flash model does not consider the DME solubility in the aqueous phase, i.e., the DME solubility in the aqueous phase is assumed as zero. In reality, however, the solubility of DME in the aqueous phase cannot be neglected. Figure 4-14 plots the absolute deviations of phase fractions obtained by applying the WFIF model compared with the WAIF model in the three-phase region for the DME/water/C_{16}H_{34} mixture at 80 bar. As can be seen, large absolute deviations are observed for the prediction of phase fractions by applying the WFIF model, especially for vapor phase fractions. The AARD and MARD for predicting phase fractions are 17.022% and 236.756%, respectively, implying that the WFIF model can cause significant deviations if applied to Case #3.

Figure 4-15 demonstrates the temperatures and phase compositions obtained from the WAIF model and the WFIF model for the DME/water/C_{16}H_{34} mixture at 80 bar in the three-phase region over a wide range of specified enthalpies for the vapour phase. As can be seen, large deviations are found between the calculated phase compositions by applying the two isenthalpic flash models. More specifically, the WFIF model
Figure 4-13 Comparison between the temperatures and phase fractions obtained from the WAIF model and the WFIF model for the DME/water/C_{16}H_{34} mixture at 80 bar and different enthalpies in the three-phase region.
Figure 4-14 Absolute deviations of phase fractions obtained by applying the WAIF model and the WFIF model in the three-phase region for the DME/water/C_{16}H_{34} mixture at 80 bar
Figure 4-15 Comparison between the temperatures and phase compositions in the vapour phase that are obtained from the WAIF model and the WFIF in three-phase region for the DME/water/C_{16}H_{34} mixture at 80 bar for (a) vapour phase compositions, and (b) absolute deviations of vapour phase compositions
yields an AARD of 2.128% and MARD of 4.597% for predicting phase compositions, indicating that the water-free assumption is not applied for Case #3. Figure 4-16 compares the temperatures and phase compositions obtained from the WAIF model and the CTIF model in which the solubility of all components including the heavy hydrocarbon in the aqueous phase is taken into account. It should be noted that numerous stability analysis is required in the CTIF model to determine the number of phases for a given system at different enthalpies, which leads to more computational time compared with the WAIF model, though the CTIF model is able to predict the solubility of all the solvent in the aqueous phase. As can be seen from Figure 4-16, an excellent agreement is achieved between the calculated phase compositions by these two isenthalpic flash methods. More specifically, the WAIF model is calculated to yield an AARD of 0.003% and MARD of 0.005% for predicting phase compositions, implying that the WAIF model is also capable of predicting the phase behaviour of Case #3 without compromising prediction accuracy while improving computational efficiency.

Figure 4-17 plots the variation of DME solubility in the aqueous phase calculated by the WAIF model for the DME/water/C_{16}H_{34} mixture at 80 bar in the three-phase region. As can be observed, the smallest mole fraction of DME in the aqueous phase is larger than $2.0 \times 10^{-2}$, which cannot be neglected. This explains why there exist large discrepancies between the phase transition enthalpies, temperatures, phase fractions,
Figure 4-16 Comparison between the temperatures and phase compositions in the vapour phase that are obtained from the WAIF model and the CTIF model in three-phase region for the DME/water/C₁₆H₃₄ mixture at 80 bar for (a) vapour phase compositions, and (b) absolute deviations of vapour phase compositions.
Figure 4-17 Mole fractions of DME in the aqueous phase calculated by the WAIF model for the DME/water/C_{16}H_{34} mixture at 80 bar in the three-phase region
and compositions determined by the two isenthalpic flash models. In addition, the solubility of DME in the aqueous phase decreases with an increase in temperature, showing a different trend of solvent solubility in the aqueous phase compared to Cases #1 and #2. Figure 4-18 shows the number of iterations used by the WAIF model and the CTIF model in the three-phase narrow-boiling region for the DME/water/C_{16}H_{34} mixture at 80 bar. Clearly, the number of iterations is significantly reduced by using the WAIF model, indicating the superiority of the new isenthalpic flash model proposed in this study to handle the narrow-boiling constraints. The reason why the number of iterations of the CTIF model is higher than that of the WAIF model is that the phase appearance and disappearance issue could happen for the CTIF model. It should be noted that the number of iterations is increased slightly when the specified enthalpies are near the phase boundary between the three-phase and two-phase vapour-hydrocarbon regions, whereas it is still 10 or less required by the WAIF model.

Figure 4-19 compares the computational time obtained by the WAIF model and the CTIF model for DME/water/C_{16}H_{34} mixture at 80 bar in the three-phase region. The recursive method for the initial temperature estimation is applied in the WAIF model, which accelerates the energy conservation equation convergence speed. As can be seen from Figure 4-19, the computational time is significantly reduced by using the WAIF model because a modified Rachford-Rice equation (i.e., Equation [4-17]) is solved by the WAIF model instead of using two Rachford-Rice equations (i.e.,
Figure 4-18 The number of iterations required by the WAIF model and the CTIF model in the three-phase region for the DME/water/C$_{16}$H$_{34}$ mixture at 80 bar
Figure 4-19 Comparison between the computational time required by the WAIF model and the CTIF model in the three-phase region for the DME/water/C_{16}H_{34} mixture at 80 bar
Equation [4-10]) used by the CTIF model, implying that the WAIF model is superior than the CTIF model in terms of the computational efficiency.

4.5 Summary

In this chapter, practical computational techniques and formulations have been developed to determine phase boundaries in the enthalpy-temperature space (i.e., $H-T$ diagram) together with water-associated isenthalpic flash calculations. The new isenthalpic flash model in this work can handle multiphase equilibria flash calculations at high pressures and elevated temperatures. By constructing an $H-T$ phase boundary diagram, this new isenthalpic flash model can be conducted straightly at one-, two-, or three-phase region without performing stability test for a given feed at a specified enthalpy. The WAIF model is found to handle the narrow-boiling constraints effectively and accurately. In addition, both the WAIF model and the WFIF model work well for Cases #1 and #2 where the amount of solvent dissolved in the aqueous phase is quite small; however, large discrepancies are found for the WFIF model in Case #3 where the solubility of DME in the aqueous phase cannot be neglected. Therefore, the newly developed WAIF model can be applied to calculate phase behavior of solvent/water/heavy oil mixtures which are frequently encountered in
solvent-steam co-injection processes, especially for cases where the solvents are soluble in both the aqueous phase and the oil phase.
5.1 Introduction

In this chapter, techniques have been developed to determine the phase boundaries of C₃H₈/CO₂/water/heavy oil mixtures in both the P-T and H-T phase diagrams, respectively (Huang et al., 2020b). Experimentally, the phase boundary pressures between AL and ALV phases are determined for three C₃H₈/CO₂/water/heavy oil mixtures by using a traditional PVT setup in the P-T phase diagram at a temperature range of 298.95-421.55 K. Moreover, the fluid samples in both L and V phases are collected to conduct compositional analysis by using the gas chromatography (GC) method. Theoretically, the previously developed water-associated model, which considers only the solvent with a high solubility in water, together with the new alpha functions for water and non-water components is applied as the thermodynamic model to predict the multiphase boundaries of the aforementioned systems. A newly developed ideal gas heat capacity correlation and enthalpy determination algorithm especially for heavy hydrocarbon fractions are also employed in this work to improve the enthalpy prediction of the Lloydminster heavy oil.
5.2 Experimental

5.2.1 Materials

The heavy oil sample used in this study is collected from the Lloydminster area in Saskatchewan, Canada, with a measured molecular weight and specific gravity of 482 g/mol and 0.9997, respectively. The viscosity of the Lloydminster heavy oil is measured to be 8251.0 cP at room temperature (i.e., 25°C). The detailed description of density and viscosity measurements can be found elsewhere (Li, 2013). The compositional analysis result of the Lloydminster heavy oil measured by the Saskatchewan Research Council (SRC) is tabulated in Table 5-1. The gas solvents of C₃H₈ and CO₂ have purities of 99.99 wt% and 99.998 mol% (Praxair, Canada), respectively, while the distilled water has the dissolved mineral salts of 2 ppm.

5.2.2 Experimental setup

In this study, a traditional mercury-free DBR PVT system (PVT-0150-100-200-316-155, DBR, Canada) is used to conduct all the experiments of C₃H₈/CO₂/water/heavy oil mixtures. Figure 5-1 shows the schematic diagram of the PVT system.

In general, the PVT system is composed of four units, i.e., PVT cell, pressure and temperature control unit, fluid injection unit, and volume measurement unit. More specifically, the core component of this system is a visual PVT cell equipped in the air-bath. A glass tube inside the cell has an inner diameter of 3.177 cm and a total
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<th>mol%</th>
<th>Carbon No.</th>
<th>wt%</th>
<th>mol%</th>
</tr>
</thead>
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<td>C_{45}</td>
<td>0.929</td>
<td>0.650</td>
</tr>
<tr>
<td>C_{15}</td>
<td>2.300</td>
<td>4.830</td>
<td>C_{46}</td>
<td>0.700</td>
<td>0.480</td>
</tr>
<tr>
<td>C_{16}</td>
<td>2.143</td>
<td>4.220</td>
<td>C_{47}</td>
<td>0.833</td>
<td>0.560</td>
</tr>
<tr>
<td>C_{17}</td>
<td>2.286</td>
<td>4.240</td>
<td>C_{48}</td>
<td>0.792</td>
<td>0.530</td>
</tr>
<tr>
<td>C_{18}</td>
<td>2.238</td>
<td>3.920</td>
<td>C_{49}</td>
<td>0.792</td>
<td>0.510</td>
</tr>
<tr>
<td>C_{19}</td>
<td>2.048</td>
<td>3.400</td>
<td>C_{50}</td>
<td>0.733</td>
<td>0.460</td>
</tr>
<tr>
<td>C_{20}</td>
<td>1.857</td>
<td>2.930</td>
<td>C_{51}</td>
<td>0.750</td>
<td>0.470</td>
</tr>
<tr>
<td>C_{21}</td>
<td>2.071</td>
<td>3.110</td>
<td>C_{52}</td>
<td>0.717</td>
<td>0.440</td>
</tr>
<tr>
<td>C_{22}</td>
<td>1.329</td>
<td>1.910</td>
<td>C_{53}</td>
<td>0.717</td>
<td>0.430</td>
</tr>
<tr>
<td>C_{23}</td>
<td>1.743</td>
<td>2.390</td>
<td>C_{54}</td>
<td>0.683</td>
<td>0.400</td>
</tr>
<tr>
<td>C_{24}</td>
<td>1.571</td>
<td>2.070</td>
<td>C_{55}</td>
<td>0.650</td>
<td>0.370</td>
</tr>
<tr>
<td>C_{25}</td>
<td>1.714</td>
<td>2.170</td>
<td>C_{56}</td>
<td>0.650</td>
<td>0.370</td>
</tr>
<tr>
<td>C_{26}</td>
<td>1.600</td>
<td>1.950</td>
<td>C_{57}</td>
<td>0.667</td>
<td>0.370</td>
</tr>
<tr>
<td>C_{27}</td>
<td>1.583</td>
<td>1.850</td>
<td>C_{58}</td>
<td>0.667</td>
<td>0.360</td>
</tr>
<tr>
<td>C_{28}</td>
<td>1.650</td>
<td>1.860</td>
<td>C_{59}</td>
<td>0.667</td>
<td>0.360</td>
</tr>
<tr>
<td>C_{29}</td>
<td>1.452</td>
<td>1.580</td>
<td>C_{60}</td>
<td>0.767</td>
<td>0.410</td>
</tr>
<tr>
<td>C_{30}</td>
<td>1.281</td>
<td>1.350</td>
<td>C_{61+}</td>
<td>35.397</td>
<td>14.600</td>
</tr>
<tr>
<td>C_{31}</td>
<td>1.390</td>
<td>1.420</td>
<td>Total</td>
<td>100.000</td>
<td>100.000</td>
</tr>
</tbody>
</table>
Figure 5-1 Schematic diagram of the experimental setup for conducting PVT measurements for the C₃H₈/CO₂/water/heavy oil systems
length of 20.320 cm, while it can sustain pressure up to 69.00 MPa over a wide temperature range of 238.15-473.15 K. A floating piston in the glass tube separates the fluid sample from the hydraulic oil. Meanwhile, a magnetic mixer is equipped at the bottom of the PVT cell, which can be used to sufficiently stir the C3H8/CO2/water/heavy oil mixtures to quickly reach the phase equilibrium. The PVT cell temperature is maintained by the air-bath equipped with a microprocessor-based temperature controller in conjunction with a resistance temperature device (RTD) sensor, while the cell pressure can be controlled by using a high-pressure automatic positive-displacement pump (PMP-0500-1-10-MB-316-M4-C0, DBR, Canada) to drive the piston upward or downward. The fluid samples, including C3H8, CO2, water, and heavy oil which are respectively prepared in four transfer cylinders, are injected into the PVT cell in sequence by a syringe pump (500 DX, ISCO Inc., USA). A video-based digital cathetometer with a resolution of 0.002 cm connected to a monitor is employed to directly measure the volume of the fluid sample inside the PVT cell. The dead volume of this PVT system is calibrated to be 1.75 cm³.

5.2.3 Experimental procedures

In this study, three feeds of C3H8/CO2/water/heavy oil mixtures are prepared to measure the phase boundary pressures and phase compositions at various temperatures in the PVT equipment. The aforementioned mixtures contain solvent, water, and heavy
oil, which is proposed to emulate the solvent/water/heavy oil mixtures associated with a solvent-SAGD process. The detailed compositions of these mixtures in terms of both weight and mole percentages as well as the experimental temperatures and measured phase boundary pressures are respectively listed in Table 5-2.

(1) Phase boundary measurement

Phase boundary pressures are determined by using the constant composition expansion (CCE) method with the PVT equipment. Prior to each CCE measurement, the PVT cell and the inlet tubing are thoroughly cleaned with kerosene and ethanol, flushed with air for sufficient time to remove any traces of solvents. Then, a leakage test is conducted to ensure that the entire system can properly work at high pressures and elevated temperatures. Finally, a vacuum pump is employed to evacuate all the air in the PVT cell and tubing.

As for the phase boundary measurements, gaseous C$_3$H$_8$, CO$_2$, water, and heavy oil are charged into the cell in sequence by using a syringe pump; meanwhile, their respective volume and pressure as well as room temperature are recorded for further determination of their quantities. Then, the air-bath is set to the pre-specified temperature for at least 12 h to ensure that the viscosity of the mixture is low enough so that the magnetic mixer can be turned on and functioned properly. The fluid mixture is compressed to only liquid phases for the existing A and L phases in the cell by
Table 5-2 Compositions of C₃H₈/CO₂/water/heavy oil systems and measured phase boundaries at different temperatures

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>Composition, wt%</th>
<th>Composition, mol%</th>
<th>T, K</th>
<th>Phase boundary, kPa</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₃H₈</td>
<td>CO₂</td>
<td>water</td>
<td>heavy oil</td>
<td>C₃H₈</td>
</tr>
<tr>
<td>1</td>
<td>4.2</td>
<td>9.1</td>
<td>11.8</td>
<td>74.9</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.1</td>
<td>8.7</td>
<td>11.3</td>
<td>71.9</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.8</td>
<td>3.8</td>
<td>24.6</td>
<td>67.8</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>
slowly injecting hydraulic oil from the DBR pump to move the piston downward. Subsequently, the magnetic mixer is kept running for at least 24 h to sufficiently stir the mixture to establish the thermal equilibrium state before any further measurement.

At each temperature, phase boundary pressure measurements are started from a relatively high pressure at which only liquid phases including A and L phases exist in the PVT cell. Then, the system pressure is gradually decreased by withdrawing the hydraulic oil in the DBR pump at a flowrate of 3.0 cm³/h to move the piston upward. The relation of pressure and volume of the mixture is continuously monitored and recorded at each time step and plotted on a $P-V$ phase diagram. Therefore, the turning point on the $P-V$ phase diagram is the measured upper three-phase ALV boundary pressure.

(2) Phase composition measurement

In this study, phase compositions of Feed #3 are analyzed by using the GC method. Once the saturation pressure at the last test temperature (i.e., 421.55 K) is measured, the system pressure is reduced to a certain value (e.g., 2992 kPa for Feed #3) to ensure that enough vapour can be sampled for compositional analysis. It is worth noting that at least 24 h is required to ensure the mixture is completely separated into three phases, i.e., A, L, and V phases. Then, a stainless-steel gas sampler (Swagelok, Canada) with a volume of 70 ml is used to collect the gas sample for the GC analysis. Before sampling,
the sampler and tubing should be vacuumed to remove air. As for sampling the hydrocarbon-rich liquid phase, the remaining vapour should be completely displaced from the PVT cell by slowly opening the discharge valve. Meanwhile, the piston in the PVT cell is moving simultaneously to maintain the constant system pressure. Subsequently, a certain amount of oil is displaced into a sampler for GC analysis. It should be noted that the collected liquid sample is at high pressures and elevated temperatures. Therefore, it can be segregated into vapour and liquid phases at the room condition. A high-precision pressure gauge (2089, Ashcroft, USA) with an accuracy of 0.05% full scale of 6895 kPa is attached to the sampler to measure the pressure inside the sampler. Thus, the mass of the evolved gas and the dead oil remaining in the sampler can be determined, respectively. The evolved gas and dead oil can be separately injected into GC for compositional analysis. Finally, the hydrocarbon-rich liquid phase compositions can be determined by combining the compositions of both the flashed vapour and liquid phases. It is important to mention that water content is not measured for vapour and hydrocarbon-rich liquid phase as it cannot be identified by the GC equipment.
5.3 Mathematical Formulations

5.3.1 PR EOS

Because of its wide application as well as simplicity and high computational accuracy (Dall’Acqua et al., 2017; Li et al., 2017b; Shi et al., 2017; Thakre and Jana, 2017) in the petroleum and chemistry industry, the PR EOS (Peng and Robinson, 1976a) with the conventional van der Waals’ mixing rule is chosen as the thermodynamic model in this study. The detailed formulations of the PR EOS together with the conventional van der Waals’ mixing rule can be found in CHAPTER 3.

Recently, a newly modified alpha function tailored for the PR EOS has been demonstrated to be able to accurately determine the vapour pressure of water in a temperature range of 273.16-647.10 K with an overall AARD of 0.07% (Li and Yang, 2013). In this study, this modified alpha function is employed to quantify the phase behaviour of water-associated systems (Li and Yang, 2013),

\[
\alpha_{H_2O} = \left[ c_1 + c_2(1-T_{rw}) - c_3(1-T_{rw}^{-1}) + c_4(1-T_{rw}^{-2}) \right]^2
\]

[5-1]

where \( T_{rw} \) is the reduced temperature of water, \( c_1 = 1.00095, c_2 = 0.39222, c_3 = 0.07294, \) and \( c_4 = 0.00706 \), respectively.

The derivative of parameter \( a \) in Equation [3-2a] with respect to \( T \) is expressed as,

\[
\frac{da}{dT} = 2 \cdot \frac{0.457235 R^2 T_c^2}{P_c} \left[ \frac{c_1 + c_2(1-T_{rw})}{-c_3(1-T_{rw}^{-1}) + c_4(1-T_{rw}^{-2})} \right]^2 \times \left( -c_2 T_{rw}^{-1} - c_3 T_{cw} T_{rw}^{-2} + 2 c_4 T_{cw}^2 T_{rw}^{-3} \right)
\]

[5-2]
5.3.2 BIPs

(1) BIPs for water-associated pairs

In this study, constant values of 0.1896 (Soreide and Whitson, 1992) and 0.5525 (Whitson and Brulé, 2000) are used as BIPs for CO$_2$-water pair and C$_3$H$_8$-water pair, respectively. The BIP for heavy oil-water pair is calculated by using the correlation proposed by Venkatramani and Okuno (2017) based on the experimentally measured ALV three-phase diagrams of water/n-alkane binaries by Brunner (1990). The correlation is expressed as,

$$
\delta_{HO-water} = e_1 \left[1 + \exp(e_2 - e_3 MW)\right]^{\frac{1}{e_4}}
$$

[5-3]

where $\delta_{HO-water}$ is the BIP for heavy oil-water pair, $MW$ is the molecular weight of the Lloydminster heavy oil, g/mol, $e_1 = 0.24200$, $e_2 = 65.90912$, $e_3 = 0.18959$, and $e_4 = -56.84257$.

(2) BIPs for solvent-heavy oil pairs

The BIPs for CO$_2$-heavy oil pair and C$_3$H$_8$-heavy oil pair are tuned to match the measured saturation pressures or CO$_2$ and C$_3$H$_8$ solubilities in heavy oil for the solvent-heavy oil systems (Shi, 2017; Zirrahi et al., 2017a; b; Chen and Yang, 2018; Chen, 2019), respectively. It is worthwhile to mention that the BIPs for CO$_2$-heavy oil pair and C$_3$H$_8$-heavy oil pair are directly used for C$_3$H$_8$/CO$_2$/water/heavy oil systems in this work. A constant value of 0.1350 is used as the BIP for the CO$_2$-C$_3$H$_8$ pair, which
is retrieved from the CMG WinProp database (CMG, 2011). Overall, the BIP matrix for C₃H₈/CO₂/water/heavy oil mixtures used in this work are tabulated in Table 5-3 (Li and Yang, 2011; Chen and Yang, 2018; Chen et al., 2019).

5.3.3 Heavy oil characterization

In this study, the Lloydminster heavy oil sample is characterized as a single pseudocomponent, while its physical and critical properties are calculated by using the following correlations with known specific gravity and molecular weight. The correlations are functions of only normal boiling point temperature, which are expressed as follows (Lee and Kesler, 1975; Kesler and Lee, 1976; Soreide, 1989),

\[
T_{br} = 1928.3 - (1.695 \times 10^5) MW^{-0.03522} SG^{1.266} \times \exp \left[ \frac{-(4.922 \times 10^{-3}) MW - 4.7685 SG}{+(3.462 \times 10^{-3}) MW \times SG} \right] \quad [5-4]
\]

\[
T_{cr} = 341.7 + 811SG + (0.4244 + 0.1174SG)T_{br} + (0.4669 - 3.2623SG) \times 10^{5T_{br}^{-1}} \quad [5-5]
\]

\[
p_{\text{psi}} = \exp \left\{ \frac{8.3634 - 0.0566SG^{-1} - \left[ (0.24244 + 2.2898SG^{-1} + 0.11857SG^2) \times 10^{-3} \right] T_{br}}{\left[ (1.4685 + 3.648SG^{-1} + 0.47227SG^2) \times 10^{-7} \right] T_{br}^2 - \left[ (0.42019 + 1.6977SG^2) \times 10^{-10} \right] T_{br}^3} \right\} \quad [5-6]
\]

\[
\omega = \frac{-\ln(p_{\text{psi}}/14.7) + A_1 + A_2 T_{br}^{-1} + A_3 \ln T_{br} + A_4 \ln T_{br}^6}{A_5 + A_6 T_{br}^{-1} + A_7 \ln T_{br} + A_8 \ln T_{br}^6} \quad (\text{for } T_{br} = T_{br}/T_{cr} < 0.8) \quad [5-7a]
\]

\[
\omega = -7.904 + 0.1352 K_{w} - 0.007465 K_{w}^2 + 8.359 T_{br} \quad (\text{for } T_{br} = T_{br}/T_{cr} < 0.8) \quad [5-7b]
\]

where \( T_{br} \) is the normal boiling point temperature in °R, \( T_{cr} \) is the critical temperature.
Table 5-3 BIP matrix for the C$_3$H$_8$/CO$_2$/H$_2$O/heavy oil system (Li et al., 2012; Chen and Yang, 2018)

<table>
<thead>
<tr>
<th>Component</th>
<th>C$_3$H$_8$</th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>Heavy oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$</td>
<td>0</td>
<td>0.1350</td>
<td>0.5525</td>
<td>0.0284</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.1350</td>
<td>0</td>
<td>0.1896</td>
<td>0.0968</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.5525</td>
<td>0.1896</td>
<td>0</td>
<td>0.2420</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>0.0284</td>
<td>0.0968</td>
<td>0.2420</td>
<td>0</td>
</tr>
</tbody>
</table>
in °R, $p_{\text{psi}}$ is the critical pressure in psi, $A_1 = -5.92714$, $A_2 = 6.09648$, $A_3 = 1.28862$, $A_4 = -0.169347$, $A_5 = 15.2518$, $A_6 = 15.6875$, $A_7 = -13.4721$, and $A_8 = 0.43577$.

The detailed physical and critical properties of the Lloydminster heavy oil are provided in Table 5-4. It should be noted that all the physical and critical properties of C$_3$H$_8$ and CO$_2$, and water are also tabulated in Table 5-4 (API, 1983; Shi et al., 2017).

5.3.4 Ideal gas heat capacity

In this study, a new ideal gas heat capacity correlation proposed by Huang and Yang (2019a) is used to obtain the ideal gas heat capacity coefficients, especially for heavy hydrocarbon fractions. This correlation is developed based on the experimental data for ideal gas heat capacity of normal alkanes ranging from C$_7$H$_{16}$ to C$_{40}$H$_{82}$ collected from the API research project 44 (1972), which has shown superiority for the prediction of ideal gas heat capacity and enthalpy for normal alkanes/alkenes and hydrocarbon fractions, respectively. It is expressed as (Huang and Yang, 2019a),

$$C_p = MW \left[ 0.0240296 + 0.0062421 T_K - 2.60151 \times 10^{-6} T_K^2 + C_F \left( 0.0022514 - 1.15054 \times 10^{-5} T_K + 2.39542 \times 10^{-8} T_K^2 \right) \right]$$  \[5-8\]

where $C_p$ is the ideal gas heat capacity, J/(mol·K), $MW$ is the molecular weight of hydrocarbons, g/mol, $T_K$ is the temperature, K, and $C_F$ is the corrective factor and given by,
<table>
<thead>
<tr>
<th>Component</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
<th>$\omega$</th>
<th>MW (g/mol)</th>
<th>$C_{Pli}^0$</th>
<th>$C_{P2i}^0$</th>
<th>$C_{P3i}^0$</th>
<th>$C_{P4i}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$</td>
<td>369.80</td>
<td>42.46</td>
<td>0.1520</td>
<td>44</td>
<td>-4.220</td>
<td>0.306300</td>
<td>-1.600×10$^{-4}$</td>
<td>3.215×10$^{-8}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>304.20</td>
<td>73.76</td>
<td>0.2250</td>
<td>44</td>
<td>19.795</td>
<td>0.073430</td>
<td>-5.602×10$^{-5}$</td>
<td>1.715×10$^{-8}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>647.30</td>
<td>220.89</td>
<td>0.3440</td>
<td>18</td>
<td>32.200</td>
<td>0.001907</td>
<td>1.060×10$^{-5}$</td>
<td>-3.596×10$^{-9}$</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>933.66</td>
<td>12.65</td>
<td>1.0288</td>
<td>482</td>
<td>14.059</td>
<td>2.996100</td>
<td>-1.228×10$^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>
\[ C_F = \left[ \left( \frac{12.8}{K_W} - 1 \right) \times \left( \frac{10}{K_W} - 1 \right) \times 100 \right]^2 \]  

where \( K_W \) is the Watson characterization factor that indicates chemical character of a compound and defined as (Lastovka and Shaw, 2013),

\[ K_W = \left( \frac{1.8T_e^{1/3}}{SG} \right) \]  

where \( SG \) is the specific gravity defined at 288.71 K.

5.3.5 **Multiphase boundaries**

In this study, multiphase phase boundaries in the \( P-T \) phase diagram are experimentally measured and theoretically determined by the water-associated isothermal flash model (Pang and Li, 2017), respectively, while multiphase phase boundaries in the \( H-T \) space are theoretically determined by the water-associated isenthalpic flash model (Pang and Li, 2017; Huang and Yang, 2019b).

As for the water-associated model, only a solvent with a high solubility in the aqueous phase is considered since it has been proven to accurately and efficiently to quantify phase behaviour of solvent/water/heavy oil mixtures (Huang and Yang, 2019b). In particular, the three-phase isothermal flash algorithm adopts a modified Rachford-Rice monotonic function and the negative flash concept (Whitson and Michelsen, 1989) to calculate phase fractions and compositions. As such, stability analysis is avoided in order to determine the number of phases for a given mixture at a
specified pressure ($P_{\text{spec}}$) and temperature because a negative value of a phase fraction means that the phase does not exist in the system. Specifically, as for a given feed consisting of water/solvent/heavy oil mixtures, saturation pressure is experimentally measured at one specified constant temperature (e.g., $T^I$), which is referred as the upper three-phase boundary pressure. Also, at temperature of $T^I$, the corresponding saturation pressure is theoretically calculated by using the three-phase water-associated isothermal flash model through a trial and error method until the pressure approaches a threshold value at which the vapour phase just disappears from the system. Subsequently, temperature is changed to other measured data points and the same method is applied to theoretically calculate the corresponding three-phase boundary pressures. Finally, phase boundary pressures between AL and ALV phases as a function of temperature can be plotted, which is the phase boundary in the $P$-$T$ space determined in this study.

As for a specified pressure, e.g., the measured upper three-phase boundary pressure in this work, the three-phase water-associated isothermal flash is conducted to obtain phase fractions and compositions at the corresponding saturation temperature $T^{U1}$. It should be noted that at the upper three-phase saturation pressure and temperature of $T^{U1}$, the vapour phase fraction approaches zero. The three-phase water-associated isothermal flash calculation is continuously performed by increasing a certain temperature until it approaches the temperature ($T^{U2}$) at which the aqueous phase just vanishes from the system. $T^{U2}$ is referred to as the ALV/LV phase transition temperature. Two-phase LV
isothermal flash is initiated at the specified pressure by estimating a series of temperatures until the temperature approaches the LV/N phase transition temperature ($T_{U3}$), where the hydrocarbon-rich liquid phase disappears from the system. As aforementioned, phase fractions and compositions at the phase boundary temperatures ($T_{U1}$, $T_{U2}$, and $T_{U3}$) at the specified pressure ($P_{spec}$) can be determined by conducting water-associated isothermal flash calculation. Then, the enthalpies at the phase transition temperatures and specified pressure can be calculated, which is called the phase transition enthalpies. Finally, the phase boundaries in the $H$-$T$ space (i.e., $H$-$T$ phase diagram) can be constructed, which illustrates the relation between phase transition enthalpies and temperatures.

5.4 Results and Discussion

Three C$_3$H$_8$/CO$_2$/water/heavy oil mixtures with different feed compositions (see Table 5-2) are used as case studies by employing the water-associated model to determine their phase boundaries in the $P$-$T$ space and the $H$-$T$ space, respectively. Considering the computational efficiency, the aqueous phase is often neglected in phase behaviour determination of solvent/water/heavy oil systems (Coats, 1980; Young and Stephenson, 1983). As mentioned by Shinta and Firoozabadi (1997), however, the presence of water reduces the three-phase bubble point pressure of water/reservoir-crude systems. Moreover, only conducting two-phase vapour-liquid equilibrium (VLE) calculations
may lead to inaccurate description of the real phase behaviour where a three-phase ALV equilibrium exists (Li and Li, 2018a). Therefore, the water-associated model (Pang and Li, 2017; Huang and Yang, 2019b), which considers the solvent with a high solubility in the aqueous phase, is applied in this study to quantify three-phase ALV phase behaviour of $C_3H_8/CO_2$/water/heavy oil systems at high pressures and elevated temperatures without tuning any parameters for the PR EOS. It is worthwhile to note that the solubilities of $C_3H_8$ and heavy oil in the aqueous phase is neglected in the water-associated model as their values are very small in this study.

5.4.1 $P$-$T$ phase diagram

Figure 5-2 plots the measured and predicted phase boundary pressures for Feed #1 by using the water-associated model from 321.55 to 373.15 K. It should be noted that the measured ALV three-phase boundary pressure in this work is the upper three-phase boundary pressure because it is impossible to measure the lower ALV three-phase boundary pressure since there is no available PVT equipment that can sustain temperature up to 550 K at this moment. As can be observed, the boundary pressures between AL and ALV phases are found to increase with temperature. Also, the experimentally measured and theoretically calculated three-phase ALV boundary pressures match quite well with each other, illustrating that the proposed water-
Figure 5-2 Comparison of the measured and predicted phase boundary pressures for \( \text{C}_3\text{H}_8 / \text{CO}_2 / \text{water/heavy oil system} \) with Feed #1 (8.6 mol\% \( \text{C}_3\text{H}_8 \), 18.5 mol\% \( \text{CO}_2 \), 58.9 mol\% water, and 14.0 mol\% Lloydminster heavy oil), Feed #2 (15.8 mol\% \( \text{C}_3\text{H}_8 \), 17.1 mol\% \( \text{CO}_2 \), 54.3 mol\% water, and 12.9 mol\% Lloydminster heavy oil), and Feed #3 (5.1 mol\% \( \text{C}_3\text{H}_8 \), 5.1 mol\% \( \text{CO}_2 \), 81.4 mol\% water, and 8.4 mol\% Lloydminster heavy oil)
associated model is accurate in predicting phase boundary pressures for Feed #1. As for the five tested temperatures, the phase boundary pressures predicted by the water-associated model leads to a MARD of 5.83% and an AARD of 2.74%, respectively, showing that the water-associated model can be applied to predict phase boundary pressures for Feed #1.

As for Feed #2, the experimentally measured three-phase ALV boundary pressures together with the theoretically calculated ones at a temperature range of 298.98 to 329.85 K are also depicted in Figure 5-2. Again, it is found that the measured phase boundary pressures agree well with the predicted ones by the PR EOS associated with the newly proposed alpha function, although the predicted AL/ALV phase boundary is slightly lower than the measured one at relatively high temperatures. More specifically, an AARD of 3.87% is obtained by applying the water-associated model for all the four measured temperatures, while large deviations occur at relatively high temperatures among all the tested temperatures. This is due to the fact that the high temperatures (e.g., 318.25 and 329.85 K) are beyond the critical temperature of CO₂ (i.e., 304.2 K). A good agreement between the measured upper three-phase ALV boundary pressures and the calculated ones implies that the proposed water-associated model works well in predicting phase boundary pressures for Feed #2.

Figure 5-2 also shows the comparison of the measured and calculated phase boundary pressures between AL and ALV phases for Feed #3 from 352.05 to 421.55 K.
in the $P-T$ phase diagram. A good agreement between the experimentally measured and theoretically calculated three-phase boundary pressures can be achieved with an AARD of 2.62% and a MARD of 4.34%, indicating that the water-associated model is also able to accurately predict three-phase ALV boundary pressures for Feed #3. Although the water-associated model does not consider $\text{C}_3\text{H}_8$ and heavy oil solubility in the aqueous phase, it can predict the upper three-phase boundary pressures quite well. This is ascribed to the fact that the solubility of $\text{C}_3\text{H}_8$ and heavy oil in the aqueous phase is nearly zero at the tested conditions (Shinta and Firoozabadi, 1997; Oliveira, 2007). Also, the phase boundary pressures are found to be almost linearly increased with temperature for Feed #3.

Compared Feed #3 with Feeds #1 and #2, it is found that the phase boundary pressure is reduced with an increase of water mole fraction in the feed at the same temperature. For example, at a temperature of 364.65 and 357.95 K for Feeds #3 and #1, their corresponding phase boundary pressure are measured at 7271 and 12259 kPa, respectively, implying that the phase boundary pressure of Feed #3 is much lower than that of Feed #1 even though the temperature of the former is higher. This is reasonable because the three-phase bubble point pressure can be reduced with the addition of water in the system (Li, 2015).
5.4.2 $H$-$T$ phase diagram

Figures 5-3a–e present the multiphase boundaries in the $H$-$T$ phase diagram for Feed #1 by employing the water-associated isenthalpic flash model at 7708, 9363, 10583, 12259, and 13893 kPa, respectively. As can be seen, the total enthalpies are found to increase with temperature. In particular, the total enthalpy is significantly sensitive to the change in temperature within the narrow-boiling region, which is indicated especially in the three-phase ALV region in a $H$-$T$ phase diagram, where a small change of temperature results in a large change in enthalpy. This phenomenon is also observed and reported in the literature (Michelsen, 1987; Agarwal et al., 1991). Also, it is found that the three-phase ALV region moves toward the right-hand side with an increase in a specified pressure. In other words, the three-phase ALV region at 7708, 10583, and 13893 kPa are located at 321.55-528.14 K, 344.95-542.26 K, and 373.15-553.13 K, respectively, while their corresponding phase transition enthalpies of AL/ALV and ALV/LV phases are determined at $-4.04 \times 10^4$ and $2.59 \times 10^4$, $-3.50 \times 10^4$ and $2.78 \times 10^4$, as well as $-2.84 \times 10^4$ and $2.96 \times 10^4$ J/mol. This phenomenon is consistent with the findings reported in the literature that enthalpy of liquids increases with pressure (Riazi, 2005).
Figure 5-3 \( H-T \) phase diagram for a mixture of 8.6 mol\% C\textsubscript{3}H\textsubscript{8}, 18.5 mol\% CO\textsubscript{2}, 58.9 mol\% water, and 14.0 mol\% Lloydminster heavy oil at (a) 7708 kPa, (b) 9363 kPa, (c) 10583 kPa, (d) 12259 kPa, and (e) 13893 kPa
Figure 5-4 shows the predicted $H$-$T$ phase diagrams for Feed #2 by using the water-associated model at 4040, 4868, 6212, and 7653 kPa, respectively. It is found that the four non-linear curves follow the similar trend that the total enthalpy is increased with temperature at their respective pressures. As can be seen from Figure 5-4, the $\text{C}_3\text{H}_8$/CO$_2$/water/heavy oil mixture of Feed #2 experiences the AL, ALV, and LV phase equilibrium in a sequential order with a gradual increment of the system temperature. As for the pressure of 4040 kPa, the phase transition temperatures between AL and ALV phases as well as ALV and LV phases are determined at 298.95 K and 491.13 K, respectively, while the corresponding phase transition enthalpies are $-4.27 \times 10^4$ and $1.88 \times 10^4$ J/mol, respectively. In comparison, at the pressure of 6212 kPa, the phase transition temperatures together with the corresponding phase transition enthalpies between AL and ALV phases as well as ALV and LV phases are determined at 318.25 K and 511.24 K as well as $-3.89 \times 10^4$ and $2.22 \times 10^4$ J/mol, respectively. As also can be seen, the narrow-boiling behaviour appears in the three-phase ALV equilibria region, which makes the conventional isothermal flash challenging. In the three-phase ALV equilibrium region, especially near the phase boundary between ALV and LV equilibrium, the enthalpy is extremely sensitive to the temperature change. Plus, it is found that the three-phase ALV region slightly tends to shift to the higher temperature side with an increase in a specified pressure. Such an observation is consistent with the findings obtained in Feed #1. This is attributed to the fact that the
Figure 5-4 $H-T$ phase diagram for a mixture of 15.8 mol% C$_3$H$_8$, 17.1 mol% CO$_2$, 54.2 mol% water, and 12.9 mol% Lloydminster heavy oil at 4040 kPa, 4868 kPa, 6212 kPa, and 7653 kPa, respectively.
saturation temperature is always increased with saturation pressure.

Figure 5-5 illustrates the theoretically calculated $H$-$T$ phase diagrams for Feed #3 at pressures of 6401, 7271, 7913, 9484, and 10901 kPa, respectively. As can be seen, the $H$-$T$ phase diagram can be divided into three different regions, i.e., AL, ALV, and LV equilibrium regions. It can also be noticed that the total enthalpy is increased with an increment in temperature, especially in the three-phase ALV equilibrium region, the total enthalpy increases fastest with temperatures among the three regions. In addition, the narrow-boiling behaviour occurs in the three-phase ALV region, which is indicated by a small variation in temperature, resulting in a large change in enthalpy. It can be observed from Figure 5-5 that the ALV phase boundary of Feed #3 spans within a wide region in the $H$-$T$ phase diagram. Specifically, the three-phase region temperatures at 6401, 7271, 7913, 9484, and 10901 kPa are determined at 352.05-542.20 K, 364.05-550.15 K, 375.05-555.41 K, 399.55-567.02 K, and 421.55-576.33 K, respectively, while their corresponding three-phase region enthalpies are at $-3.89 \times 10^4 - 2.09 \times 10^4 \, , \, -3.65 \times 10^4 - 2.19 \times 10^4 \, , \, -3.46 \times 10^4 - 2.25 \times 10^4 \, , \, -3.02 \times 10^4 - 2.37 \times 10^4 \, , \, \text{and} \, -2.62 \times 10^4 - 2.50 \times 10^4 \, \text{J/mol.}$ Similar to the findings of Feeds #1 and #2, the three-phase ALV equilibrium region is inclined to move to the higher temperature region with an increase in the specified pressure. This is consistent with the three-phase boundary measurements made on a water/$n$-butane/Athabasca bitumen mixture in the literature (Gao et al., 2017).
Figure 5-5 $H-T$ phase diagram for a mixture of 5.1 mol% C₃H₈, 5.1 mol% CO₂, 81.4 mol% water, and 8.4 mol% Lloydminster heavy oil at 6401 kPa, 7271 kPa, 7913 kPa, 9484 kPa, and 10901 kPa, respectively.
Overall, it can be concluded from the above discussion that the AL/ALV, ALV/LV, and LV/N phase boundaries in the $H$-$T$ phase diagram can be determined by using the water-associated model. The enthalpy of a water/solvent/heavy oil mixture is found to increase with an increment in temperature. In addition, it is found that the ALV phase boundary of $C_3H_8/CO_2$/water/heavy oil mixtures spans a wide region in the $H$-$T$ phase diagram with the phase boundary enthalpies increasing with temperature. Furthermore, the isenthalpic flash calculations can be conducted directly without performing stability test for a given feed at a specified enthalpy and pressure with the $H$-$T$ phase diagram.

5.4.3 Phase compositions

For a given water/solvent/heavy oil mixtures (e.g., Feed #3), the emergence of ALV three-phase coexistence occurs at a specific pressure and temperature range. In order to accurately analyze the vapour phase compositions, a sufficient amount of vapour phase should exist in the system because it is easily compressed. In this study, such a condition can be met at a respective pressure and temperature of 2992 kPa and 421.55 K as the saturation pressure for Feed #3 is measured to be 10901 kPa at 421.55 K (see Table 5-2). Such a condition of pressure and temperature (i.e., 2992 kPa and 421.55 K) is close to that of a typical thermal-based heavy oil reservoir condition. As such, three-phase ALV equilibrium should be taken into account when co-injecting solvents
with steam for recovering heavy oil. Since water content is not available to be identified by using the GC method, only vapour and hydrocarbon-rich liquid phases are sampled in this study. Accordingly, the theoretically calculated phase compositions are converted to a water-free system.

Figure 5-6 shows the vapour and hydrocarbon-rich liquid phase compositions obtained by experimental measurements and theoretical calculations through the water-associated model at 2992 kPa and 421.55 K, which is located within the three-phase ALV equilibrium region. As can be clearly observed from Figure 5-6, the measured and calculated mole fractions of individual components are in an excellent agreement, which indicates that the water-associated model is capable of predicting vapour and hydrocarbon-rich liquid phase compositions with a high accuracy. Plus, it is found that no heavy oil is present in the vapour phase as the heavy oil is not easily volatile. It is important to note that a significant amount of $\text{C}_3\text{H}_8$ is dissolved in the hydrocarbon-rich liquid phase (i.e., L phase). This is preferable for a heavy oil recovery process because the dissolved $\text{C}_3\text{H}_8$ is able to enhance swelling effect as well as viscosity reduction of heavy oil and reduce IFT between $\text{C}_3\text{H}_8$ and heavy oil (Li et al., 2012). It is worthwhile to mention that the measured compositions of $\text{C}_3\text{H}_8$ and $\text{CO}_2$ in the hydrocarbon-rich liquid phase are smaller than the calculated ones. This may be owing to the fact that some gases are trapped in heavy oil since it is difficult to stir the heavy oil in the sampler.
Figure 5-6 Comparison of experimentally measured and theoretically predicted compositions of vapour phase and hydrocarbon-rich liquid phase for Feed #3 at 2992 kPa and 421.55 K
5.5 Summary

The multiphase boundaries of three C$_3$H$_8$/CO$_2$/water/heavy oil mixtures with different feed compositions in the $P$-$T$ and $H$-$T$ phase diagrams are experimentally and theoretically determined at high pressures and elevated temperatures. It is found that the upper three-phase ALV boundary pressures increase with temperature and reduce with the water mole fraction in the feed. The previously proposed enthalpy determination algorithm has been successfully applied in this study to construct the $H$-$T$ phase diagram for C$_3$H$_8$/CO$_2$/water/heavy oil mixtures. As for the $H$-$T$ phase diagram, it is found that the three-phase ALV equilibrium region is inclined to move to the higher temperature region with an increase of the specified pressure. Plus, the ALV phase boundary of C$_3$H$_8$/CO$_2$/water/heavy oil mixtures spans a wide region in the $H$-$T$ phase diagram, indicating that three-phase behaviour may occur over a wide range of pressures and temperatures when steam and solvents are co-injected into a heavy oil reservoir. The newly developed water-associated model is found to accurately predict the upper three-phase boundary pressures and phase compositions of the three C$_3$H$_8$/CO$_2$/water/heavy oil mixtures with a generally good accuracy.
CHAPTER 6 MULTIPHASE BOUNDARIES AND PHYSICAL PROPERTIES OF SOLVENT(S)/HEAVY OIL SYSTEMS UNDER RESERVOIR CONDITIONS BY USE OF ISENTHALPIC FLASH ALGORITHMS

6.1 Introduction

In this chapter, a generalized methodology has been developed to determine multiphase boundaries of solvent(s)/heavy oil mixtures at various pressures and temperatures in $P-T$, $H-T$, and $P-H$ phase diagrams, respectively (Huang and Yang, 2020). Theoretically, the PR EOS incorporated with a modified alpha function as well as the previously developed enthalpy calculation algorithm are used to predict the multiphase boundaries of the solvent(s)/heavy oil systems consisting of non-hydrocarbon solvent of CO$_2$ as well as hydrocarbon solvents of C$_3$H$_8$ and $n$-C$_4$H$_{10}$ during thermal-solvent injection processes. The theoretical results obtained from the mathematical algorithms developed in this study have been compared with the experimental database including three feeds of VL$_1$L$_2$ (V represents the vapour phase, L$_1$ denotes the high density hydrocarbon-rich liquid phase, and L$_2$ refers to the low density CO$_2$ liquid phase) three-phase equilibrium scenario as well as four feeds of VL$_1$ two-phase equilibrium scenario. The case studies demonstrated that the newly proposed algorithm is accurate in reproducing the experimentally measured VL$_1$L$_2$ three-phase boundaries and VL$_1$ two-phase boundaries of solvent(s)/heavy oil mixtures in the $P-T$ phase diagram.
6.2. Experimental Database

The experimentally measured VL$_1$L$_2$ three-phase boundary pressures for three sets of solvent(s)/heavy oil systems with an excessive amount of CO$_2$ in each system as well as VL$_1$ two-phase boundary pressures for four sets of solvent(s)/heavy oil mixtures are collected from the literature (Li et al., 2012; 2017b). Their corresponding weight and molar compositions together with the tested temperatures and experimentally determined phase boundary pressures are respectively shown in Table 6-1. The molecular weight and specific gravity of the heavy oil sample (i.e., the Lloydminster heavy oil) are equal to 482 g/mol and 0.9997, respectively. In addition, the physical properties of the solvents and the Lloydminster heavy oil are provided in Table 6-2 (API, 1983; Poling et al., 2001; Li et al., 2012).

6.3 Theoretical Formulations

6.3.1 PR EOS

PR EOS (Peng and Robinson, 1976a) together with the van der Waals’ mixing rules are applied as the thermodynamic model due to its efficiency and high computational accuracy to quantify phase behaviour of reservoir fluids (Li et al., 2013a; b; Li and Yang, 2013; Shi et al., 2016; Shi et al., 2017; Dong et al., 2018). The detailed
Table 6-1 Compositions of solvent(s)/heavy oil mixtures and experimentally measured phase boundaries at different experimental temperatures (Li et al., 2012; 2017b)

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>Composition, wt%</th>
<th>Composition, mol%</th>
<th>$T$, K</th>
<th>Phase boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_3H_8$</td>
<td>$n-C_4H_{10}$</td>
<td>CO$_2$</td>
<td>heavy oil</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>0.0</td>
<td>60.4</td>
<td>39.6</td>
</tr>
<tr>
<td>5</td>
<td>12.3</td>
<td>0.0</td>
<td>35.1</td>
<td>52.6</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>10.1</td>
<td>54.2</td>
<td>35.7</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>0</td>
<td>3.4</td>
<td>96.6</td>
</tr>
<tr>
<td>8</td>
<td>10.3</td>
<td>0.0</td>
<td>11.0</td>
<td>78.7</td>
</tr>
<tr>
<td>9</td>
<td>0.0</td>
<td>10.1</td>
<td>7.0</td>
<td>82.9</td>
</tr>
<tr>
<td>10</td>
<td>3.2</td>
<td>3.7</td>
<td>5.7</td>
<td>87.4</td>
</tr>
</tbody>
</table>

Note: N/A denotes not available
<table>
<thead>
<tr>
<th>Component</th>
<th>$T_C$ (K)</th>
<th>$P_C$ (bar)</th>
<th>$\omega$</th>
<th>MW (g/mol)</th>
<th>$C_{p_0}^0$</th>
<th>$C_{p_2}^0$</th>
<th>$C_{p_3}^0$</th>
<th>$C_{p_4}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$</td>
<td>369.80</td>
<td>42.46</td>
<td>0.1520</td>
<td>44.10</td>
<td>-4.220</td>
<td>0.306300</td>
<td>$-1.600 \times 10^{-4}$</td>
<td>$3.215 \times 10^{-9}$</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>425.20</td>
<td>37.86</td>
<td>0.1930</td>
<td>58.12</td>
<td>9.487</td>
<td>0.331300</td>
<td>$-1.108 \times 10^{-4}$</td>
<td>$-2.822 \times 10^{-9}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>304.20</td>
<td>73.76</td>
<td>0.2250</td>
<td>44.01</td>
<td>19.795</td>
<td>0.073430</td>
<td>$-5.602 \times 10^{-5}$</td>
<td>$1.715 \times 10^{-8}$</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>933.66</td>
<td>12.65</td>
<td>1.0288</td>
<td>482.00</td>
<td>14.059</td>
<td>2.996100</td>
<td>$-1.228 \times 10^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>
formulations of the PR EOS together with the conventional van der Waals’ mixing rule can be found in CHAPTERs 3 and 4.

6.3.2 BIPs

For the thermodynamic model, 0.1350 and 0.1300 are respectively adopted as the BIPs for the CO\textsubscript{2}-C\textsubscript{3}H\textsubscript{8} pair and CO\textsubscript{2}-\textit{n}-C\textsubscript{4}H\textsubscript{10} pair, which are obtained from the CMG WinProp database (Computer Modelling Group Ltd., 2011). As for the BIPs of the solvent-heavy oil pair, their correlations are respectively expressed by (Li and Yang, 2013; Li, 2013),

\begin{equation}
\delta_{i4} = -0.4560T_{co} / T_{co} + 0.1817
\end{equation}

\begin{equation}
\delta_{24} = -0.2331T_{co} / T_{co} + 0.1198
\end{equation}

\begin{equation}
\delta_{34} = -0.5462T_{co} / T_{co} - 0.4596SG_o - 0.0238\omega_o + 0.7523
\end{equation}

where $\delta_{i4}$, $\delta_{24}$, and $\delta_{34}$ are the BIPs between C\textsubscript{3}H\textsubscript{8} and heavy oil, \textit{n}-C\textsubscript{4}H\textsubscript{10} and heavy oil, CO\textsubscript{2} and heavy oil, respectively, $T_{co}$, $SG_o$, and $\omega_o$ are the critical temperature, specific gravity, and acentric factor of the Lloydminster heavy oil, respectively.

Finally, the BIP matrix for solvents/heavy oil system used in this study is provided in Table 6-3.
<table>
<thead>
<tr>
<th>Component</th>
<th>C\textsubscript{3}H\textsubscript{8}</th>
<th>\textit{n}-C\textsubscript{4}H\textsubscript{10}</th>
<th>CO\textsubscript{2}</th>
<th>Heavy oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>0</td>
<td>0.00087</td>
<td>0.13500</td>
<td>(\delta)\textsubscript{4}</td>
</tr>
<tr>
<td>\textit{n}-C\textsubscript{4}H\textsubscript{10}</td>
<td>0.00087</td>
<td>0</td>
<td>0.13000</td>
<td>(\delta)\textsubscript{24}</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0.13500</td>
<td>0.13000</td>
<td>0</td>
<td>(\delta)\textsubscript{34}</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>(\delta)\textsubscript{4}</td>
<td>(\delta)\textsubscript{24}</td>
<td>(\delta)\textsubscript{34}</td>
<td>0</td>
</tr>
</tbody>
</table>
6.3.3 Isenthalpic flash

As for unconventional reservoir production processes, large temperature changes are frequently involved, which avoids the isothermal conditions. As such, isenthalpic flash is applied in the aforementioned circumstances, which corresponds to maximize the global entropy subjecting to both the material balance and energy constraints. The detailed description of isenthalpic flash can refer to Section 4.2.3.

6.3.4 Determination of three-phase VL₁L₂ boundaries

Three-phase VL₁L₂ boundary pressures in the $P$-$T$ space are experimentally determined by performing PVT tests by using a traditional PVT setup. Conventionally, phase boundaries are theoretically determined through continuously conducting stability tests and two-phase flash calculations by continually changing pressures at a given temperature. The procedures are briefly described as follows:

(1) One-phase stability analysis

For a given mixture consisting of $N_c$ compositions, the tangent-plane stability test is used to evaluate if the Gibbs energy can be further reduced by introducing a new phase. The expression of tangent-plane distance (TPD) function is formulated as (Firoozabadi, 1999; Li and Firoozabadi, 2012),
\[ TPD = 1 + \sum_{i=1}^{N_c} Y_i \left[ \ln \phi_i(Y_i) + \ln Y_i - \ln \phi_i(z_i) - \ln z_i - 1 \right] \]  

\[ Y_i = y_i e^{-W} \]

where \( y_i \) and \( z_i \) denote the \( i \)th component in the trial and test phases, respectively, and \( W \) represents the TPD value at one stationary point.

(2) Two-phase flash

Once instability is detected by performing single-stability analysis, two-phase flash is initiated to solve the following Rachford-Rice equation (Rachford and Rice, 1952),

\[ RR_j = \sum_{i=1}^{N_c} (y_i - x_i) = \sum_{i=1}^{N_c} \frac{n_i(K_{p_i} - 1)}{1 + \beta_i(K_{p_i} - 1)} = 0 \]  

(3) Two-phase stability analysis

Two-phase stability analysis is applied to test whether the mixture is stable at two-phase equilibrium state (Li and Firoozabadi, 2012). As mentioned by Li and Firoozabadi (2012), only the phase with a higher molar weight is selected to conduct two-phase stability test. The TPD function used for two-phase stability analysis is the same as the one used for one-phase.

In this study, a new algorithm is proposed to theoretically determine three-phase VL1L2 boundaries in the \( P-T \) phase diagram by conducting three-phase isothermal flash calculations with negative flash being allowed (Whitson and Michelsen, 1989). The brief
procedures are provided as follows:

1). As for the boundary between $L_1L_2$ and $VL_1L_2$ phases at a given temperature, three-phase isothermal flash is conducted by a trial and error method until the pressure reaches a threshold value at which the vapour volume approaches zero; and

2). As for the boundary between $VL_1L_2$ and $VL_1$ phases at a specified temperature, three-phase isothermal flash is performed by a trial and error method until the pressure reaches a threshold value at which the liquid CO$_2$ phase just vanishes from the mixture.

6.4 Results and Discussion

A total of seven solvent(s)/heavy oil mixtures (see Table 6-1) are selected as case studies to experimentally and theoretically quantify their corresponding phase behaviour. More specifically, Feeds #4-6 are in terms of $VL_1L_2$ three-phase equilibrium scenario, while Feeds #7-10 are in terms of $VL_1$ two-phase equilibrium scenario. It is important to note that the liquid-solvent phase (i.e., the liquid-CO$_2$ phase) appears at certain pressure and temperature conditions with excessive CO$_2$ content in the mixture. It is also worthwhile noting that the algorithm fails to determine the three-phase boundary of Feed #4 in this work. This is because Feed #4 is a two-component three-phase equilibrium scenario (i.e., the number of degrees of
freedom is equal to 1), making it difficult to perform three-phase flash calculations (Agarwal et al., 1991). Therefore, the \( H-T \) and \( P-H \) phase diagrams are generated only for Feeds #5 and #6, while Feed #4 is used in comparison with Feeds #5 and #6 in the \( P-T \) phase diagrams.

6.4.1 \( P-T \) phase diagram

(I) \( VL_1L_2 \) three-phase boundary

The experimentally measured and theoretically calculated phase boundary pressures of Feed #5 from 288.95 to 298.55 K are shown in Figure 6-1a, while both the upper and lower three-phase \( VL_1L_2 \) boundary pressures are included. As can be seen, the measured and calculated three-phase \( VL_1L_2 \) boundary pressures are in an excellent agreement, indicating that the proposed algorithm works pretty well in reproducing the phase boundary pressures for Feed #5. With respect to all the experimental temperatures, an overall AARD of 2.07% and an MARD of 2.74% are respectively obtained to predict the three-phase \( VL_1L_2 \) boundary pressures of Feed #5.

Figure 6-1b compares the calculated phase boundary pressures of Feed #6 against with the measured ones in a temperature range of 288.65-308.55 K. As can be seen, the theoretical calculations match very closely with the experimental measurements, implying that the proposed method is also capable of reproducing the measured
Figure 6-1 Comparison of the experimentally measured and theoretically calculated phase boundaries for solvent(s)/heavy oil mixtures with (a) Feed #5 (23.6 mol% C₃H₈, 67.2 mol% CO₂, and 9.2 mol% heavy oil), and (b) Feed #6 (11.8 mol% n-C₄H₁₀, 83.2 mol% CO₂, and 5.0 mol% heavy oil)
three-phase VL$_1$L$_2$ boundaries of Feed #6. As can also be observed, there exists a linear relation between the predicted phase boundary pressures and temperatures within the tested temperature range, though the theoretically determined three-phase boundaries between L$_1$L$_2$ and VL$_1$L$_2$ are slightly higher than the experimental measurements. Specifically, for the upper three-phase VL$_1$L$_2$ boundaries, the relationship between the predicted boundary pressures and temperatures of Feed #6 can be expressed as,

\[ P_{sat} = 0.1111T - 27.526 \quad (288.65 \text{ K} < T < 308.55 \text{ K}, \text{ and } R^2=0.9997) \]  \[6-4\]

As for the lower three-phase VL$_1$L$_2$ boundaries, however, their relationship can be formulated as,

\[ P_{sat} = 0.1078T - 27.233 \quad (288.65 \text{ K} < T < 308.55 \text{ K}, \text{ and } R^2=0.9952) \]  \[6-5\]

Table 6-4 compares the VL$_1$L$_2$ three-phase boundaries obtained from this work and those from the traditional phase boundary determination method, i.e., stability analysis together with two-phase isothermal flash calculations (Li et al., 2012). It is clearly seen that the results calculated from this work is better than those from Li et al. (2012) in terms of AARD, indicating that the isenthalpic-based phase boundary method is capable of determining VL$_1$L$_2$ three-phase boundaries of solvents/heavy oil mixtures without compromising accuracy. Specifically, the AARD and MARD calculated from this work for calculating VL$_1$L$_2$ three-phase boundaries are
Table 6-4 Comparison of the three-phase boundaries between the experimental measurements and those calculated from this work and Li et al. (2012)

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>T, K</th>
<th>Li et al. (2012)</th>
<th></th>
<th></th>
<th>This work</th>
<th></th>
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<tbody>
<tr>
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<td>L₁L₂/V₁L₁L₂</td>
<td>ARD, %</td>
<td>V₁L₂/V₁</td>
<td>ARD, %</td>
<td>L₁L₂/V₁L₁L₂</td>
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<td>4513</td>
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<tr>
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</table>
respectively equal to 1.97% and 4.34%, compared to those of 2.26% and 4.41% obtained from Li et al. (2012) where heavy oil was treated as one pseudocomponent.

The extended $P$-$T$ phase diagrams including L$_1$L$_2$, VL$_1$L$_2$, and VL$_1$ phases obtained by employing the newly proposed phase boundary determination method in this study for Feeds #5 and #6 are plotted in Figures 6-2a and 2b, respectively. It is clearly seen from Figure 6-2a that the $K$-point (where the V phase and L$_2$ phase become critically identical (Miller and Luks, 1989; Li et al., 2012)) of Feed #5 is calculated to be at 308.3 K and 6529 kPa, compared to 300.9 K and 6842 kPa of Feed #4. As aforementioned, the method proposed in this work to determine three-phase boundaries fails to locate VL$_1$L$_2$ boundaries for Feed #4 as the number of components is smaller than the number of the existing phases. Further study is needed to tackle this technical challenge. Figure 6-2a also plots the theoretically predicted three-phase VL$_1$L$_2$ region of Feed #4 that is collected from the literature (Li et al., 2012). Compared to Feed #4, it is found that the VL$_1$L$_2$ three-phase boundary of Feed #5 moves toward to the higher temperature and lower pressure region in the $P$-$T$ phase diagram.

It can be observed from Figure 6-2b that the $K$-point of Feed #6 is determined to be at 313.9 K and 7181 kPa, which is higher than that of Feed #4 in terms of both temperature and pressure. It can also be found from Figure 6-2b that the three-phase region expands first, and then shrinks at the critical end point (i.e., $K$-point) with a gradual increment of temperature from 250 to 313.9 K. In addition, the three-phase
Figure 6-2 $P-T$ phase diagram for (a) Feed #5 of 23.6 mol% C$_3$H$_8$, 67.2 mol% CO$_2$, and 9.2 mol% heavy oil, and (b) Feed #6 of 11.8 mol% $n$-C$_4$H$_{10}$, 83.2 mol% CO$_2$, and 5.0 mol% heavy oil.
envelope of Feed #6 spans within a wider region than that of Feed #4. Furthermore, the proposed phase boundary determination algorithm is found to be capable of detecting the phase boundary of Feed #6 even at the K-point where boundaries between L_1L_2 and VL_1L_2 as well as VL_1L_2 and VL_1 vanish. In addition, the saturation pressure of Feed #4 is higher than that of Feed #6, which is similar to the finding of Feed #5.

(2) VL_1 two-phase boundary
In order to examine the effect of CO_2 concentration on phase variations, four feeds of solvent(s)/heavy oil mixtures are selected with a small amount of CO_2, where the CO_2-liquid phase does not exist in the system. Figure 6-3 presents the experimentally measured and theoretically calculated VL_1 two-phase boundaries for solvent(s)/heavy oil mixtures including binary (CO_2/heavy oil), ternary (C_3H_8/CO_2/heavy oil and n-C_4H_10/CO_2/heavy oil), as well as quaternary (C_3H_8/n-C_4H_10/CO_2/heavy oil) systems with less amount of CO_2 than those in Feeds #4-6. As can be seen, only one liquid phase (i.e., the high density hydrocarbon-rich liquid phase) is present in the solvent(s)/heavy oil mixtures when the system pressure is higher than the VL_1 phase boundary, which is similar to the observation of Feeds #4-6. As for the four test mixtures (i.e., Feeds #7-10), it is found that the measured and calculated saturation pressure increase with an increase in temperature, implying that the solubility of solvents in heavy oil is lower at higher temperatures, leading to more solvents present in the vapour phase. Compared Feed #8
Figure 6-3 Comparison of the experimentally measured and theoretically calculated phase boundaries for solvent(s)/heavy oil mixtures of Feeds #7-10
with Feed #9, it is found that C$_3$H$_8$ leads to a larger saturation pressure of solvents/heavy oil mixtures than $n$-C$_4$H$_{10}$ for a mixture with a similar amount of CO$_2$ and heavy oil. For example, the saturation pressures of C$_3$H$_8$/CO$_2$/heavy oil at 298.15 and 318.15 K are respectively measured to be 4.65 and 6.60 MPa, whereas those of $n$-C$_4$H$_{10}$/CO$_2$/heavy oil are 3.13 and 4.06 MPa, respectively. As for the modeling results, it is observed that the new phase boundary determination method is able to reproduce the measured saturation pressures with a good accuracy, yielding an overall AARD of 4.52% for the 12 measured data points.

Table 6-5 shows the comparison of the results obtained from this work and those from the traditional phase boundary determination method based on the isothermal flash algorithm (Li et al., 2013b; 2017b). It is found that the VL$_1$ two-phase boundaries obtained from the two methods are close to each other, implying that the isenthalpic-based new phase boundary determination method proposed in this study is also accurate in predicting VL$_1$ two-phase boundaries for solvents/heavy oil systems.

By treating the same heavy oil as six pseudocomponents, Li et al. (2017b) compared their work with those obtained from the WinProp module (Computer Modelling Group Ltd., version 2017) in terms of prediction accuracy of saturation pressures for four quaternary C$_3$H$_8$/n-C$_4$H$_{10}$/CO$_2$/heavy oil mixtures which include Feed #10 in this study. It is found that the results obtained from Li et al. (2017b) are more accurate than those from WinProp module, showing an AARD of 6.7% resulted
Table 6-5 Comparison of the two-phase boundaries between the experimental measurements and those obtained from Li et al. (2013b; 2017b)

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>$T$, K</th>
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<td>AARD, %</td>
<td>4.41</td>
<td>AARD, %</td>
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</table>
from the former methodology compared to 35.6% resulted from the commercial simulator. Considering the fact that the results obtained from this work are very close to those from Li et al. (2017b), the new method proposed in this work is able to reproduce phase boundaries with a good accuracy, yielding a better prediction accuracy than the WinProp module.

6.4.2 \textit{H-T} phase diagram

Figure 6-4 illustrates the three-phase VL\textsubscript{1}L\textsubscript{2} boundaries in the \textit{H-T} phase diagram for Feeds #5 and #6 at a constant pressure of 4000 kPa, respectively. The detailed procedures to determine multiphase boundaries in the \textit{H-T} phase diagram can be found elsewhere (Huang and Yang, 2019a). As can be seen, \textit{n}-C\textsubscript{4}H\textsubscript{10} leads to a wider three-phase region of solvents/heavy oil mixtures in the \textit{H-T} phase diagram than that of C\textsubscript{3}H\textsubscript{8}. As for Feed #5, the three-phase transition enthalpies and temperatures between L\textsubscript{1}L\textsubscript{2} and VL\textsubscript{1}L\textsubscript{2} together with VL\textsubscript{1}L\textsubscript{2} and VL\textsubscript{1} phases at a constant pressure of 4000 kPa are determined at -22254 and -18120 J/mol as well as 283.51 and 286.05 K, respectively. With respect to Feed #6, however, the three-phase VL\textsubscript{1}L\textsubscript{2} region is located from 282.92 to 289.60 K, while the corresponding three-phase enthalpies are determined to be from -16471 to -10513 J/mol at 4000 kPa.

As shown in Figure 6-4, the total enthalpies are increased with temperature in the three-phase region. In particular, the narrow-boiling behaviour is observed in the three-
Figure 6-4 $H$-$T$ phase diagram at 4000 kPa for Feed #5 (23.6 mol% C$_3$H$_8$, 67.2 mol% CO$_2$, and 9.2 mol% heavy oil), and Feed #6 (11.8 mol% $n$-C$_4$H$_{10}$, 83.2 mol% CO$_2$, and 5.0 mol% heavy oil)
phase region, i.e., the enthalpy changes rapidly with a small change in temperature within the three-phase zone. Also, it is found that the enthalpy increases at a faster rate at relatively lower temperatures of the three-phase region, and then a slower rate is observed at relatively higher temperatures of the three-phase zone with an increase in temperature. Compared to Feed #5, it can be found that the three-phase region of Feed #6 in the $H$-$T$ phase diagram spans within a wider space in terms of both temperature and enthalpy. This may be attributed to the fact that the critical temperature of butane (i.e., 425.20 K) is much higher than that of propane (i.e., 369.80 K).

Since thousands of separate isenthalpic flash calculations are required for large scale reservoir simulation (Huang et al., 2020b), it is advantageous to perform numerous isenthalpic flash calculations with the constructed $H$-$T$ phase diagrams illustrating number of phases in relation with enthalpy and temperature. Take Feed #5 for an example, the temperature, phase fractions, and compositions can be obtained by directly performing isenthalpic flash at 4000 kPa with the knowledge of phase transition enthalpies. The predicted temperature, phase fractions, and the amount of each component in each phase in the three-phase region are respectively shown in Figure 6-5 and Figures 6-6a to 6c.

6.4.3 $P$-$H$ phase diagram

Figure 6-7a presents the $P$-$H$ phase diagram for Feed #5 in a wide pressure range of 0
Figure 6-5 The predicted temperatures and phase fractions of Feed #5 in the three-phase region at 4000 kPa
Figure 6-6 The predicted temperatures and phase compositions of Feed #5 in the three-phase region at 4000 kPa for (a) vapour phase, (b) hydrocarbon-rich liquid phase, and (c) liquid-CO$_2$ phase
Figure 6-7 $P$-$H$ phase diagram for (a) Feed #5 (23.6 mol% C₃H₈, 67.2 mol% CO₂, and 9.2 mol% heavy oil), and (b) Feed #6 (11.8 mol% $n$-C₄H₁₀, 83.2 mol% CO₂, and 5.0 mol% heavy oil)
to 8.0 MPa, and enthalpy range of $-2.5 \times 10^4$ to $-1.5 \times 10^4$ J/mol, especially including the three-phase VL$_1$L$_2$ region. As can be seen, the new algorithm is capable of predicting the three-phase boundaries of solvents/heavy oil systems in the $P-H$ space.

It is worthwhile noting that the blue solid line is obtained by performing enthalpy determination calculation between L$_1$L$_2$ and VL$_1$L$_2$ phase boundaries, while the pink dash line is obtained between VL$_1$L$_2$ and VL$_1$ phase boundaries. For most cases, the enthalpy is gradually increased with pressure. Close to the K-point, however, the enthalpy decreases with an increase in pressure. This is because the amount of liquid CO$_2$, which has the largest heat capacity among the three components, decreases in the mixture, leading to the decrease of enthalpy. Compared Figure 6-7a with Figure 6-2a, it is clearly shown that enthalpy varies drastically with a small variation of temperature in the three-phase region. Similarly, the same pattern can be seen for Feed #6 in Figure 6-7b. It is interesting to note that the three-phase region of Feed #5 spans a wider range of pressure and enthalpy. This is attributed to the fact that the vapour pressure of C$_3$H$_8$ locates at a wider space than that of $n$-C$_4$H$_{10}$ in the temperature range of interest (i.e., 250-310 K).

### 6.5 Summary

Multiphase boundaries of solvent(s)/heavy oil systems in terms of $P-T$, $H-T$, and $P-H$ phase diagrams are respectively determined at various conditions of pressures and
temperatures. The thermodynamic model, i.e., the PR EOS incorporated with the modified alpha function, is found to be accurate in reproducing the experimentally measured VL\textsubscript{1}L\textsubscript{2} three-phase boundaries and VL\textsubscript{1} two-phase boundaries of solvent(s)/heavy oil mixtures in the $P$-$T$ space over a wide range of pressure and temperature conditions. For the extended $P$-$T$ phase diagrams of Feeds #4-6 in this study, it is found that the three-phase VL\textsubscript{1}L\textsubscript{2} region of solvents/heavy oil mixtures experiences a wider area with the addition of either C\textsubscript{3}H\textsubscript{8} or $n$-C\textsubscript{4}H\textsubscript{10} compared to CO\textsubscript{2}/heavy oil mixtures. As for the $H$-$T$ phase diagram in the three-phase region, it is found that the enthalpy changes rapidly with a small change in temperature. Isenthalpic flash is especially applicable for simulating phase behaviour for non-isothermal processes, during which isothermal flash is not suitable as the narrow-boiling behaviour occurs and the temperature under flash calculation is unknown. Moreover, isenthalpic flash can be conducted directly with the constructed $H$-$T$ phase diagram for a given mixture. With respect to the $P$-$H$ phase diagram, it is observed that the three-phase area of Feed #6 is wider than that of Feed #5.
7.1 Introduction

Phase behaviour and physical properties including saturation pressures, swelling factors, phase volumes, DME partition coefficients, and DME solubilities for heavy oil mixtures containing polar substances have been experimentally and theoretically determined (Huang et al., 2020a). Experimentally, novel phase behaviour experiments of DME/water/heavy oil mixtures spanning a wide range of pressures and temperatures have been conducted. More specifically, a total of five PVT experiments consisting of two tests of DME/heavy oil mixtures and three tests of DME/water/heavy oil mixtures have been performed to measure saturation pressures, phase volumes, and swelling factors. Theoretically, the modified PR EOS together with the Huron-Vidal mixing rule as well as the Péneloux volume-translation strategy is adopted to perform phase equilibrium calculations. The BIP between DME/heavy oil pair, which is obtained by matching the measured saturation pressures of DME/heavy oil mixtures, is applied for modeling the phase behaviour of DME/heavy oil mixtures in the presence and absence of water.
7.2 Experimental

7.2.1 Materials

The heavy oil sample used in this research is collected from the Lloydminster area, Saskatchewan, Canada, with its physical properties of density and viscosity being respectively measured to be 0.9997 g/cm$^3$ and 8251 cP at atmospheric pressure and room temperature of 25°C. The molecular weight of heavy oil sample is equal to 482.0 g/mol with a freezing point depression method, while the saturates/asphaltenes/resins/aromatics (SARA) analysis by using an extraction method with alumina shows 26.2 wt% saturates, 28.2 wt% aromatics, 24.2 wt% resins, and 21.4 wt% asphaltenes, respectively. It should be noted that the solvent used for the measurement of asphaltene content is \(n\)-pentane insoluble. Compositional analysis of the oil sample used in this research is obtained by using the simulated distillation method and tabulated in Table 5-1, while the calculated density of C\(_{60+}\) is 1.15 g/cm$^3$ by using the heavy oil characterization method (Li et al., 2013b). The solvent DME used for the PVT experiments is supplied by Praxair in Canada with purity of 99.5 wt%, while the distilled water has total dissolved solids of 2 ppm.

7.2.2 Experimental setup

A commonly used PVT setup (Model: PVT-0150-100-200-316-155) manufactured by DBR, Canada, is utilized to conduct the phase behaviour measurements of DME/water/
heavy oil mixtures. A schematic diagram of the setup can be found in Figure 7-1. The detailed description of the DBR PVT system can be found in CHAPTER 5.

7.2.3 Experimental procedures

A total of five feeds including two DME/heavy oil mixtures (i.e., Feeds #11-12) and three DME/water/heavy oil mixtures (i.e., Feeds #13-15) are generated to conduct phase behaviour measurements under various temperature and pressure conditions in the aforementioned PVT setup, while their compositions with respect to molar fractions and the corresponding test temperatures are respectively presented in Table 7-1. The purpose of designing DME/heavy oil mixtures without water is to tune the BIP between DME and heavy oil. As for a solvent-SAGD process, the overall mole fraction of water near the edge of the solvent-SAGD chamber under reservoir conditions is found to be the highest (Keshavarz et al., 2014). This serves as the criteria for the experimental feed compositions, and thus, water is the most dominant component in a solvent-SAGD process for heavy oil and bitumen recovery. In general, there are three phases near a solvent-SAGD chamber edge, i.e., vapour, aqueous, and oleic phases. As for DME/water/heavy oil mixtures, a small amount of DME is selected because the costly solvent used for a solvent-SAGD process is usually in a small quantity (Nasr et al., 2003; Sheng et al., 2018), and DME represents the major component in the vapour phase. Physically, a large amount of water with some
Table 7-1  Feed compositions of DME/water/heavy oil mixtures at different experimental temperatures

<table>
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</tr>
<tr>
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</tr>
</tbody>
</table>
Figure 7-1 Schematic diagram of the PVT system used in this study for phase behaviour measurements
mobilized oil is involved near the steam chamber edge (Sheng et al., 2018), while water represents the major component in the aqueous phase and heavy oil represents the major component in the oleic phase. As such, the water mole fraction in the feed compositions is the largest. In addition, three different water mole fractions are selected to examine the effect of water on the phase behaviour of DME/water/heavy oil mixtures.

(1) Saturation pressures

Traditionally, there are two methods to measure saturation pressures of a solvent(s)/heavy oil mixture, i.e., the continuous depressurization method (Badamchi-Zadeh et al., 2009a; b; Memon et al., 2010) and the discrete depressurization method (Badamchi-Zadeh et al., 2009a; b). Although it is time-consuming for the aforementioned mixtures to reach the corresponding equilibrium state, the latter is found to be more accurate because it can mitigate the supersaturation phenomenon that would occur in the former (Badamchi-Zadeh et al., 2009a; b). Such two aforementioned methods yield very similar saturation pressures for CO₂/C₃H₈/Athabasca bitumen with a small withdrawal rate of 3.0 cm³/h for the continuous depressurization method while the mixer keeps stirring (Badamchi-Zadeh et al., 2009a; b).

Also, in the previous studies made by our research group, Li et al. (2013a) used
these two methods to measure and compare the pressure-volume relations for solvent(s)-heavy oil systems and found that both the measured saturation pressures are almost identical. Since the same heavy oil is used in this work as that in our previous studies (Li et al., 2013a), the continuous depressurization method is employed to determine saturation pressures and swelling factors in this study for the immiscible DME/water/heavy oil systems as it is found to be more efficient than the discrete depressurization method without compromising the measurement accuracy. It is important to mention that both the expansion work and the work done by the mixer influence the energy balance of the system while the data points are measured.

To significantly accelerate the time for the mixture to reach its equilibrium state, a low-enough withdrawal rate (i.e., 3.0 cm$^3$/h) is applied and the magnetic mixer is always kept on to rigorously stir a solvent(s)/heavy oil mixture. The fact that the accuracy and reliability depending on the time scale (i.e., withdrawal rate) clearly indicates that the data obtained by the continuous depressurization method are at best only close to thermodynamic equilibrium. Also, such measured bubblepoint pressures are different from the pseudo-bubblepoint pressures under nonequilibrium conditions, during which the mixer is turned off when measuring the system pressure (i.e., pseudo-bubblepoint pressure) together with the height of the liquid phase (Chen et al., 2015; Shi et al., 2016; Shi and Yang, 2017a; b; Sun et al., 2017; Modaresghazani et al., 2019; Zhao et al., 2019; Dong et al., 2020). In this study, the thermodynamic
bubblepoint pressure obtained from PVT experiments is used for the subsequent mathematical calculations.

In this study, two tests of DME and heavy oil mixtures are conducted to measure their saturation pressures so that the BIP between DME and heavy oil components can be obtained for further phase behaviour modeling of DME/water/heavy oil systems. Before each PVT test, the whole system is completely cleaned with kerosene and ethanol, dried by air flush for 24 hours, and finally evacuated with a vacuum pump. The testing fluids including DME and heavy oil are introduced into the PVT cell, while their volumes, experimental temperatures and pressures are respectively recorded for mass calculation. Subsequently, set the system to the predetermined temperature for sufficient time (i.e., 12 hours) before turning on the mixer. The fluids in the cell are pressurized into only liquid phase using the DBR pump while keeping the mixer working for 24 hours to ensure that the mixture reaches its equilibrium prior to the corresponding measurements.

For each temperature, the continuous depressurization method (Badamchi-Zadeh et al., 2009; Memon et al., 2010) is used by slowly moving the piston upward to measure saturation pressures and swelling factors. Specifically, the mixture in an incipient state of only liquid phase is depressurized at a rate of 3.0 cm$^3$/h. Meanwhile, the system pressures together with volumes are continuously monitored and recorded,
respectively. Thus, the saturation pressure can be obtained from the constructed $P-V$ phase diagram where a sudden change point of the slope occurs.

(2) Oil swelling factors

The DME-saturated heavy oil volume (denoted as $V_{sat}$) at the saturation point can also be determined based on the measured height of the fluid. The heavy oil volume (denoted as $V_{dead}$) at the saturation temperature and atmospheric pressure is determined to be the ratio of the mass of injected heavy oil in the PVT cell to its density under the aforementioned temperature and pressure conditions. The Lloydminster heavy oil density is calculated by the following equation as it has high accuracy in reproducing the previously measured density data (Li et al., 2012),

$$\rho_o = \frac{\rho_o(T, P_0)}{1 - \beta \ln \left( \frac{B + 0.001P}{B + 0.1} \right)}$$ \hspace{1cm} [7-1]

$$\rho_o(T, P_0) = 784.0044 + 1.7217T - 3.3752 \times 10^{-3}T^2$$ \hspace{1cm} [7-2a]

$$\beta = -6.1774 + 0.0213T$$ \hspace{1cm} [7-2b]

$$B = 3.7614 \times 10^4 - 1.8009 \times 10^7T^{-1} + 2.0605 \times 10^9T^{-2}$$ \hspace{1cm} [7-2c]

where $\rho_o$ represents the heavy oil density, $P$ and $T$ denote the operating pressure and temperature, respectively.

Finally, the measured swelling factor can be determined using the following equation,
It is important to note that the swelling factor measured in this study is the so-called dynamic swelling factor, which is introduced to describe the dynamic volume increase of the solvent-diluted oleic phase during the continuous depressurization process.

It is worthwhile noting that the same operating procedure for DME/heavy oil mixtures is applied for DME/water/heavy oil mixtures. As for Feed #12, once the saturation pressures and swelling factors are completed, a desired amount of water is added into the PVT cell to constitute Feed #13, allowing us to examine the effect of water on phase behaviour. As for Feeds #14-15, DME, water, and heavy oil are charged into the PVT cell in sequence. First, a certain amount of DME is injected into the PVT cell during which the cell pressure is increased, while the piston is moved upward until the cell pressure is equal to the summation of DBR pump pressure and pressure drop in the tubing between the DBR pump and the PVT cell. Then, a certain amount of water is charged into the cell at a constant injection rate, while the interface between vapour and water phase can be clearly observed and measured. Finally, heavy oil is discharged into the cell at a constant injection rate. At beginning, when a small amount of heavy oil is injected into the cell, the heavy oil is at the bottom of the PVT cell because the injection port is located at the bottom. After heavy oil is injected into the PVT cell for a while, it begins to move to the top of water because of the density.
difference between water and heavy oil. Thus, the water phase is not completely pure because a small amount of heavy oil may have moved from the bottom of the PVT cell to the top of water phase.

(3) Phase volumes

After measuring the saturation pressures and swelling factors, the system is reduced to a lower pressure where both vapour and liquid phases can coexist. By using the mixer equipped in the PVT system, it takes about 24 hours for the DME/water/heavy oil mixtures to reach the equilibrium state during which the pressure of the DBR pump is set to a prespecified value (i.e., the pump is set in the constant pressure mode). The equilibrium state is considered to achieve for the aforementioned mixtures when the volume change of the pump fluid is smaller than 0.01 cm³ in an hour that is within the pump accuracy. It is worthwhile to mention that the interface between vapour and liquid phase is able to be clearly observed and measured, whereas it is difficult to identify the phase volumes of aqueous and oleic phases for DME/water/heavy oil mixtures as the occurrence of in-situ oil-water emulsion. In this study, the emulsion volume is not measured because it is difficult to visually observe the interface. Instead, the total volumes of the aqueous phase and oleic phase are measured as the liquid phase volume instead of measuring the volume of aqueous phase and oleic phase separately because the total volume of the liquid phase including both aqueous and oleic phases is
used for the theoretical calculations.

It is worthwhile noting that safety is important during the high pressure and temperature experiments, while the safe operating procedure (SOP) for PVT experiments involving DME is attached in the Appendix B.

7.3 Theoretical Formulations

7.3.1 PR EOS

The cubic three-parameter PR EOS has a wide application in the petroleum and chemistry industry because of its accuracy and simplicity in describing the phase behaviour of reservoir fluids. In particular, it is compatible with both the classical and non-classical mixing rules to evaluate mixture parameters (Ratnakar et al., 2017a). In this study, the PR EOS is utilized to perform two- and three-phase equilibria calculations to obtain saturation pressures, phase volumes and compositions as well as DME partition coefficients. The detailed formulation of the PR EOS can be found in CHAPTER 3.

7.3.2 van der Waals’ mixing rule

The detailed formulations of the van der Waals’ mixing rule are introduced in CHAPTER 4. The BIP matrix for DME/water/heavy oil mixtures employed in the PR
EOS and the classical mixing rule are provided in Table 7-2 (Venkatramani and Okuno, 2017; Huang and Yang, 2019b).

Although the van der Waals’ mixing rule has shown great performance in characterizing hydrocarbon systems, it is not appropriate for mixtures containing polar components (e.g., water and alcohol) (Zaghoul, 2006). Peng and Robinson (1976b) have shown that the prediction of hydrocarbon dissolution in water with the classical mixing rule is in poor accuracy by deviating from the experimental measurements with several orders of magnitude. As such, the more advanced mixing rules are required in order to better characterize the interaction of polar components.

### 7.3.3 Huron-Vidal mixing rule

As for polar components, non-classical mixing rules are used to predict the mixture properties because the classical mixing rule is inappropriate to represent the hydrogen bonds and polar interactions (Yushchenko and Brusilovsky, 2016). The Huron-Vidal mixing rule is widely used due to the fact that it leads to more accurate description of the phase behaviour and mutual solubility between water and solvents compared with the classical mixing rule (Huron and Vidal, 1979; Ratnakar et al., 2017a). In addition, it does not require many unknown parameters but can be reduced to the classical mixing rule for non-polar components. This is considered as the one of the great Huron-Vidal mixing rule is expressed as (Huron and Vidal, 1979; Lindeloff and
<table>
<thead>
<tr>
<th>Component</th>
<th>DME</th>
<th>H₂O</th>
<th>Heavy oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>0</td>
<td>-0.1700</td>
<td>0.0130</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.1700</td>
<td>0</td>
<td>0.2420</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>0.0130</td>
<td>0.2420</td>
<td>0</td>
</tr>
</tbody>
</table>
Michelsen, 2003; Pedersen et al., 2014; Yushchenko and Brusilovsky, 2016),

\[
a = b \left[ \sum_{i=1}^{N_c} y_i \left( \frac{a_i}{b_i} \right) + \frac{G^E_{\infty}}{\lambda} \right]
\]  

[7-4]

where the parameter \( b \) is represented in the same form as in Equation [4-1], \( \lambda \) is an EOS-dependent parameter, and \( G^E_{\infty} \) is the excess Gibbs free energy at infinite pressure. They are respectively expressed as follows (Huron and Vidal, 1979; Yushchenko and Brusilovsky, 2016),

\[
\lambda = \frac{1}{2\sqrt{2}} \ln \left( \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right)
\]  

[7-5]

\[
\frac{G^E_{\infty}}{RT} = \sum_{i=1}^{N_c} y_i \sum_{j=1}^{N_c} y_j b_{ji} \exp \left( -\alpha_{ji} \tau_{ji} \right)
\]  

[7-6]

where \( \alpha_{ji} \) is the interaction parameter, \( \alpha_{ii} = 0 \), \( \alpha_{ij} = \alpha_{ji} \), and the parameter \( \tau_{ji} \) for the Huron-Vidal mixing rule is defined by,

\[
\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}
\]  

[7-7]

where \( g_{ji} \) represents the so-called energy parameter. The linear dependency of \( g_{ji} \) and \( g_{ij} \) as a function of temperature used in this study are listed as follows (Yushchenko and Brusilovsky, 2016),

\[
g_{ij} - g_{ji} = \left( g_{ij}^{'} - g_{ji}^{'} \right) + T \left( g_{ij}^{''} - g_{ji}^{''} \right)
\]  

[7-8a]

\[
g_{ji} - g_{ij} = \left( g_{ji}^{'} - g_{ij}^{'} \right) + T \left( g_{ji}^{''} - g_{ij}^{''} \right)
\]  

[7-8b]

The expression of the fugacity coefficient of the \( i \)th component by the Huron-Vidal
mixing rule is written as,

$$\ln \phi_i = \frac{b_i}{b} (Z-1) - \ln(Z-B) - \frac{1}{2 \sqrt{2}} \left( \frac{a_i}{b_iRT} - \frac{\ln \gamma_i}{\lambda} \right) \ln \left[ \frac{Z + \left(1 + \sqrt{2} \right) B}{Z + \left(1 - \sqrt{2} \right) B} \right]$$ [7-9]

where $\gamma_i$ is the activity coefficient for the $i$th component and formulated as,

$$\ln \gamma_i = \frac{\sum_{j=1}^{Nc} y_j b_j \tau_{ji} \exp\left(-\alpha_{ji} \tau_{ji}\right)}{\sum_{k=1}^{Nc} y_k b_k \exp\left(-\alpha_{ki} \tau_{ki}\right)} + \sum_{j=1}^{Nc} \left\{ \frac{\sum_{k=1}^{Nc} y_k b_k \exp\left(-\alpha_{kj} \tau_{kj}\right)}{\sum_{k=1}^{Nc} \sum_{j=1}^{Nc} y_j b_j \exp\left(-\alpha_{ji} \tau_{ji}\right)} \right\} \tau_{ij} - \frac{\sum_{j=1}^{Nc} y_j b_j \tau_{ij} \exp\left(-\alpha_{ij} \tau_{ij}\right)}{\sum_{k=1}^{Nc} y_k b_k \exp\left(-\alpha_{kj} \tau_{kj}\right)}$$

[7-10]

As mentioned earlier, the Huron-Vidal mixing rule is able to represent polar and non-polar components, while it can be reduced to the classical mixing rule at the absence of polar components in a mixture. More specifically, the Huron-Vidal mixing rule can be simplified to the van der Waals’ mixing rule for non-polar compounds by setting the non-randomness parameter and the energy parameters as follows (Huron and Vidal, 1979),

$$\alpha_{ji} = 0$$ [7-11a]

$$g_{ii} = -\frac{a_i}{b_i} \lambda$$ [7-11b]

$$g_{ji} = -2 \frac{\sqrt{b_i b_j}}{b_i + b_j} \sqrt{g_{ii} g_{jj}} \left(1 - k_{ij}\right)$$ [7-11c]

Since the aforementioned feature of the Huron-Vidal mixing rule allows it coherent with the van der Walls’ mixing rule, it can be applied to multicomponent mixtures including both polar and non-polar components. As such, the former is
employed for polar components, while the latter is used for non-polar components. In this study, the Huron-Vidal mixing rule is adopted for the interaction of DME/water pair, while the classical mixing rule is applied for the interaction of water/heavy oil and DME/heavy oil pairs.

As for the water/DME pair, the Huron-Vidal mixing rule parameters are obtained by matching the DME solubility in water (Pozo and Streett, 1984; Sheng et al., 2018). The non-randomness parameters for components of water and DME are 0.131, i.e., $\alpha_{ij} = \alpha_{ji} = 0.131$, where $i$ is water and $j$ is DME. The energy parameters for water and DME are listed as follows,

$$g_{12} - g_{22} = (-1000 - 0.570T) \times R$$  \[7-12a\]

$$g_{21} - g_{11} = (1370 + 1.290T) \times R$$  \[7-12b\]

where $R$ is the universal gas constant.

7.3.4 Swelling factor

Oil swelling effect is closely related to the DME partition coefficient (i.e., the ratio of the amount of DME dissolved in oleic phase to that of in aqueous phase), imposing a significant effect on oil viscosity reduction. It has been well recognized that a larger oil swelling factor results in diluted oil with better mobility, higher connectivity of isolated oil ganglia, and eventually higher oil production (Chahardowli et al., 2016). Thus, it is essential to accurately quantify swelling behaviour and then design and optimize the
hybrid thermal-DME heavy oil recovery process. The swelling factor is defined as (Teja and Sandler, 1980),

$$ SF = \frac{V_1}{V_2 (1 - S)} \quad [7-13] $$

where $SF$ represents the swelling factor, $V_i$ represents the molar volume of DME-heavy oil mixtures at saturation state, $V_2$ denotes the molar volume of dead heavy oil at saturation temperature and atmospheric pressure, and $S$ denotes the DME solubility in heavy oil.

Since the original PR EOS has its deficiency in predicting mixture volumes (Whitson and Brulé, 2000), a volume-translation strategy proposed by Péneloux et al. (1982), which has shown accuracy in predicting liquid phase volumes/densities and swelling factors (Péneloux et al., 1982; Li et al., 2013a; 2017b; Lopez-Echeverry et al., 2017), is adopted in this work. It should be noted that the volume-translation technique does not affect the calculation of isothermal flash and DME partition coefficient. The corrected molar volume is expressed as follows (Péneloux et al., 1982),

$$ V_c = V_{EOS} - \sum_{i=1}^{N_c} y_i C_i \quad [7-14] $$

where $V_c$ and $V_{EOS}$ are the corrected molar volume and the original molar volume obtained by Equation [7-14] and the Equation [3-1], respectively, and $C$ is the volume-shift parameter, which is expressed as,

$$ C = 0.40768 \left( \frac{RT}{P_e} \right) (0.29441 - Z_{RA}) \quad [7-15] $$
where $Z_{RA}$ denotes the Rackett parameter, which is given by (Rackett, 1970; Spencer and Danner, 1972; 1973),

$$Z_{RA} = 0.29056 - 0.08775\omega$$  \[7-16\]

It is common to characterize heavy oil as a single pseudocomponent in PVT modeling because of the computational expenses of multicomponent thermodynamic models. The Lloydminster heavy oil is considered as a single component and four pseudocomponents in this study, while the detailed characterization procedure and formulations can be found in elsewhere (Li et al., 2013b; Huang et al., 2020b). The thermodynamic properties of DME, water, and heavy oil are provided in Table 7-3 (API, 1983).

In this work, the root-mean-squared relative error (RMSRE) is employed to evaluate the performance of the proposed theoretical model, while it is defined as,

$$RMSRE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}} \right)^2} \times 100\%$$  \[7-17\]

where $N$ is the total number of data points, $X_i^{cal}$ and $X_i^{exp}$ are theoretically calculated and experimentally measured data.

7.4 Results and Discussion

7.4.1 Multiphase boundaries

The phase behaviour equilibrium experiments are performed with DME/water/heavy
<table>
<thead>
<tr>
<th>Component</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (bar)</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>400.05</td>
<td>52.92</td>
<td>0.2000</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>647.30</td>
<td>220.89</td>
<td>0.3440</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>933.66</td>
<td>12.65</td>
<td>1.0288</td>
</tr>
</tbody>
</table>
oil mixtures at different pressures and temperatures. The thermodynamic model developed in this study is employed to reproduce the experimentally measured two-phase LV and three-phase ALV phase boundaries (also known as saturation pressures) of Feeds #11-12 and #13-15, respectively. It should be noted that Equations [7-11a]–[7-11c] are utilized in the new model for Feeds #11-12 that are in the absence of water. More specifically, the phase boundary is determined by performing two-phase LV or three-phase ALV equilibrium calculation where the vapour phase just vanishes from the system. It is worthwhile pointing out that the measured saturation pressures of Feed #11 at five different temperatures are used to tune the BIP between DME and heavy oil (denoted as $BIP_{DME-HO}$), while the measured ones of Feed #12 are utilized to verify the obtained $BIP_{DME-HO}$. Subsequently, the optimized $BIP_{DME-HO}$ is directly applied to perform phase equilibrium calculations for Feeds #13-15.

(1) **DME/heavy oil P-T phase boundary**

A total of five measured saturation pressures of Feed #11 at temperatures from 348.15 to 408.15 K are used to tune the BIP of DME/heavy oil pair which is equal to 0.013. Then, the tuned $BIP_{DME-HO}$ is utilized to regenerate the experimentally measured saturation pressures of Feeds #11-12, while their comparison against the measured ones versus temperature is shown in Figure 7-2. As expected, the saturation pressure is increased
with temperature as the attraction forces between molecules in oleic phase decrease with temperature, lowering the solubility of DME in oleic phase (Haddadnia et al., 2018). Overall, the thermodynamic model is able to reproduce all the measured saturation pressures of Feeds #11-12 with a high accuracy (RMSRE within 3.07%), illustrating that the tuned $BIP_{DME-HO}$ is appropriate. A relatively larger deviation at the last temperature point (i.e., 408.15 K) is observed, owing to the fact that the test temperature is near the critical temperature of DME. Also, another point needs to be noted is that the saturation pressure of the DME/heavy oil mixture increases with an increase of DME fraction in a given mixture at constant temperature. For example, the measured saturation pressure of Feed #11 with a DME concentration of 21.2 mol% at 348.15 K is 412 kPa, whereas it is 776 kPa of Feed #12 with a DME concentration of 41.6 mol% at the same temperature.

In addition, the comparison between the experimentally measured and theoretically calculated saturation pressures for DME/heavy oil mixtures by treating heavy oil as one pseudocomponent and four pseudocomponents is shown in Table 7-4. Also, the BIPs between DME and the four pseudocomponents are obtained by the method proposed in Li et al. (2013b), which are listed in Table 7-5. It is found that similar results are obtained by treating heavy oil as one pseudocomponent and four pseudocomponents, with an overall RMSRE of 2.88% of the former compared to
### Table 7-4

Experimentally measured and theoretically calculated saturation pressures for DME/heavy oil mixtures at different temperatures

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>$T, \text{ K}$</th>
<th>Measured</th>
<th>Calculated$^a$</th>
<th>$RMSRE, %$</th>
<th>Calculated$^b$</th>
<th>$RMSRE, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>348.15</td>
<td>412</td>
<td>391</td>
<td>4.61</td>
<td>393</td>
<td>5.10</td>
</tr>
<tr>
<td></td>
<td>363.15</td>
<td>521</td>
<td>505</td>
<td>2.69</td>
<td>507</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>378.15</td>
<td>630</td>
<td>636</td>
<td>1.11</td>
<td>637</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>393.15</td>
<td>758</td>
<td>784</td>
<td>3.43</td>
<td>784</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>408.15</td>
<td>885</td>
<td>945</td>
<td>6.67</td>
<td>944</td>
<td>6.78</td>
</tr>
<tr>
<td>12</td>
<td>348.15</td>
<td>776</td>
<td>806</td>
<td>3.87</td>
<td>803</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td>363.15</td>
<td>1071</td>
<td>1057</td>
<td>1.31</td>
<td>1048</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>378.15</td>
<td>1329</td>
<td>1351</td>
<td>1.66</td>
<td>1334</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>393.15</td>
<td>1675</td>
<td>1687</td>
<td>0.72</td>
<td>1659</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>408.15</td>
<td>1991</td>
<td>2046</td>
<td>2.76</td>
<td>2021</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td><strong>Overall</strong></td>
<td></td>
<td></td>
<td><strong>2.88</strong></td>
<td></td>
<td><strong>2.78</strong></td>
</tr>
</tbody>
</table>

Note:

$^a$denotes the saturation pressure calculated by characterizing the heavy oil as one pseudocomponent; and

$^b$denotes the saturation pressure calculated by characterizing the heavy oil as four pseudocomponents.
<table>
<thead>
<tr>
<th>Component</th>
<th>DME</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME</td>
<td>0</td>
<td>0.0086</td>
<td>0.0130</td>
<td>0.0164</td>
<td>0.0177</td>
</tr>
<tr>
<td>PC1</td>
<td>0.0086</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PC2</td>
<td>0.0130</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PC3</td>
<td>0.0164</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PC4</td>
<td>0.0177</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
PC denotes pseudocomponent
Figure 7-2 Comparison between the measured and calculated saturation pressures for DME/heavy oil mixtures
2.78% of the latter. Thus, it is appropriate to characterize the heavy oil as one pseudocomponent in this study.

To further validate the suitability of treating the heavy oil as one pseudocomponent, DME compositions in vapour and oleic phase are calculated and compared with those obtained by treating the heavy oil as four pseudocomponents, while the results are provided in Table 7-6. The test pressures are respectively set at 400 and 800 kPa for Feeds #11 and #12 to ensure both vapour and oleic phase coexist in the system in a temperature range of 360-400 K. It is clear that the prediction results of DME compositions in both vapour and liquid phases are very similar by characterizing heavy oil as single pseudocomponent and four pseudocomponents with RMSRE of 0.09% and 1.01% for vapour and liquid phases, respectively, indicating that very close prediction results are obtained by treating heavy oil as one pseudocomponent and four pseudocomponents.

(2) DME/water/heavy oil P-T phase boundary

As for hydrocarbon systems including water or other polar substances, non-classical mixing rules are required to quantify their phase behaviour. The experimentally measured and theoretically calculated saturation pressures for Feeds #13-15 by implementing the PR EOS associated with the van der Waals’ mixing rule and Huron-Vidal mixing rule are tabulated in Table 7-7. Figure 7-3 plots the measured
Table 7-6 DME compositions in vapour and oleic phases at 400 and 800 kPa for Feed #11 and Feed #12, respectively

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>T, K</th>
<th>DME compositions (V)</th>
<th>RMSRE, %</th>
<th>DME compositions (L)</th>
<th>RMSRE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>One PC</td>
<td>Four PCs</td>
<td>One PC</td>
<td>Four PCs</td>
</tr>
<tr>
<td>11</td>
<td>360</td>
<td>0.9999999983</td>
<td>0.9996757671</td>
<td>0.03</td>
<td>0.1765266197</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>0.9999999947</td>
<td>0.9994390855</td>
<td>0.06</td>
<td>0.1513854823</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>0.9999999847</td>
<td>0.9990664005</td>
<td>0.09</td>
<td>0.1312477806</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>0.9999999585</td>
<td>0.9984984571</td>
<td>0.15</td>
<td>0.1149282869</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.9999998939</td>
<td>0.9976581628</td>
<td>0.23</td>
<td>0.1015630684</td>
</tr>
<tr>
<td>12</td>
<td>360</td>
<td>0.9999999986</td>
<td>0.9998230114</td>
<td>0.02</td>
<td>0.3389858603</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>0.9999999958</td>
<td>0.9996885782</td>
<td>0.03</td>
<td>0.2910604551</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>0.9999999880</td>
<td>0.9994772386</td>
<td>0.05</td>
<td>0.2527377910</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>0.9999999682</td>
<td>0.9991563753</td>
<td>0.08</td>
<td>0.2216862769</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>0.9999999204</td>
<td>0.9986840333</td>
<td>0.13</td>
<td>0.1962395179</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>0.09</td>
<td></td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>Feed No.</td>
<td>$T$, K</td>
<td>Measured</td>
<td>Calculated</td>
<td>RMSRE, %</td>
<td>Calculated</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
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<td></td>
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<td>2289</td>
<td>12.40</td>
<td>2720</td>
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<td>Overall</td>
<td></td>
<td>17.87</td>
<td>5.08</td>
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</table>
Figure 7-3 The measured and predicted saturation pressures for DME/water/heavy oil mixtures (Note: vdW denotes van der Waals, HV denotes Huron-Vidal, and WS denotes Wong-Sandler)
saturation pressures and predicted ones by implementing the PR EOS associated with the van der Waals’ mixing rule as well as the Huron-Vidal mixing rule for DME/water/heavy oil mixtures. Similar to the DME/heavy oil mixtures, it is found that the saturation pressure of DME/water/heavy oil mixtures increases with temperature, indicating that the amount of DME dissolved in oleic phase is reduced with an increment of temperature. Compared the saturation pressures of Feed #13 with those of Feed #12, it can be observed that adding water to the DME/heavy oil mixture leads to an increase in saturation pressure. This is because water molecules evaporate into the vapour phase at high temperature and low pressure conditions (Pedersen et al., 2014). It can also be found that the system saturation pressures increase with the DME concentration in the mixture.

As also seen from Figure 7-3, a good agreement is observed between the measured saturation pressures and calculated ones obtained by the Huron-Vidal mixing rule, while there exist large deviations for the van der Waals’ mixing rule, implying that the PR EOS and the non-classical mixing rule can reproduce the saturation pressures with an acceptable accuracy for the DME/water/heavy oil mixtures. This is because the random distribution of molecules in mixtures is assumed by the van der Waals’ mixing rule (Pedersen et al., 2014), which is not appropriate for the DME/water/heavy oil mixtures since water and DME have a polar structure. As for the Huron-Vidal mixing rule, however, a modified non-random two-phase liquid (NRTL)
activity coefficient model is employed to describe the interaction between water component and DME as it takes the extent of the distribution deviation of different molecules in an actual phase into account (Pedersen et al., 2014).

To further validate the predictability and reliability of the Huron-Vidal mixing rule for DME/water/heavy oil mixtures, the comparison of calculating saturation pressures of the aforementioned systems is made with another commonly used mixing rule for non-ideal mixtures containing polar components, i.e., the Wong-Sandler mixing rule. In brief, the excess Helmholtz free energy ($\Delta F$) at infinite pressure is equated from an equation of state to that from an activity coefficient model (Wong and Sandler, 1992). As such, the correct quadratic composition dependence of the second virial coefficient is obtained, making it possible to use a single equation of state to model phase behaviour of mixtures containing polar, aromatic, and associating components. The details of the Wong-Sandler mixing rule can be found elsewhere (Wong and Sandler, 1992; Wong et al., 1992).

Figure 7-3 and Table 7-7 also compare the saturation pressures obtained from the experimental measurements and theoretical calculations by using the Huron-Vidal and Wong-Sandler mixing rules, respectively. It is found that the saturation pressures obtained from the Wong-Sandler mixing rule are good but not as accurate as those of the Huron-Vidal mixing rule, especially at relatively higher pressures. For DME/water pairs, the ratio $b_1/b_2 = (T_{c1}P_{c2})/(T_{c2}P_{c1}) = 2.35$, which is pretty large between the two
molar covolumes \( b_1 \) and \( b_2 \), indicating that the mixture is very asymmetric. This explains the large deviations between the experimental data and the ones obtained from the Wong-Sandler mixing rule because it is less suitable to model highly asymmetric systems at high pressures, due to the fact that the matching between \( G^E \) and \( A^E \) is less accurate (Coutsikos et al., 1995).

Overall, the Huron-Vidal mixing rule is chosen in this work owing to its capability of dealing with polar components as well as the convenience of reverting to the classical van der Waals’ mixing rule in the absence of polar components (Pedersen et al., 2014). In addition, the number of parameters required for the Huron-Vidal mixing rule is less than that of other similar non-classical mixing rules, e.g., the Wong-Sandler mixing rule (Epelle et al., 2020).

(3) H-T phase boundary

Figure 7-4 plots the LV two-phase boundary for Feed #12 and ALV three-phase boundary for Feed #13 in the \( H-T \) phase diagram at 1500 kPa, respectively. The detailed procedures to construct the \( H-T \) phase diagram can be found in CHAPTER 4. As can be seen in Figure 7-4(a), the LV two-phase boundary of Feed #12 is located in a wide temperature range of 385.01 to 880.10 K, while the phase transition enthalpies
Figure 7-4 $H$-$T$ phase diagrams at 1500 kPa for (a) Feed #12 (41.6 mol% DME, and 58.4 mol% heavy oil), and (b) Feed #13 (7.4 mol% DME, 82.2 mol% water, and 10.4 mol% heavy oil)
are determined to be \(-20089\) and \(476832\) J/mol at 1500 kPa by use of the previously
developed enthalpy determination algorithm. Also, it is observed that enthalpy is
increased with temperature in the two-phase region for Feed #12. With respect to Feed
#13, however, the three-phase boundary is determined to be 369.85 to 441.95 K and
\(-33372\) to \(-9565\) J/mol in terms of temperature and pressure, respectively. In addition
to the observation that enthalpy increases with temperature in the three-phase region,
the enthalpy is found to increase at a faster rate at the phase boundary between ALV
and LV phases. This phenomenon is also known as the narrow-boiling behaviour, i.e.,
a small change in temperature resulting in a significant change in enthalpy (Zhu and
Okuno, 2015).

7.4.2 Phase volumes

According to the \(P-T\) phase diagram of the DME/water/heavy oil mixtures in Figure
7-3, the ALV three phase volumes are measured below the saturation pressure to
ensure ALV three phases are all present in the system. As aforementioned, the interface
between oleic and aqueous phase cannot be clearly identified. Thus, the volumes of
vapour phase as well as liquid phases consisting of both oleic and aqueous phases at
various pressures and constant temperatures are recorded. Figure 7-5 demonstrates the
measured and calculated phase volume fractions for Feed #13 at temperatures of
363.15 K and 378.15 K, respectively. More specifically, three-phase isothermal flash
Figure 7-5 Comparison of measured and predicted phase volumes for vapour phase and liquid phase (including both aqueous and oleic phases) for Feed #13 at (a) 363.15 K, and (b) 378.15 K
calculation by using the new thermodynamic model proposed in this study is performed to determine phase volumes. As can be seen, a generally good match is achieved between the experimental measurements and theoretical predictions for Feed #13 at different pressures that are lower than the saturation pressure, indicating that the new model works well for determining phase volumes for mixtures contained polar components with a reasonable accuracy. In addition, at pressures higher than the saturation pressure, only liquid phases including both oleic and aqueous phases exist in the system. With further decrease of pressure which is lower than the saturation pressure, vapour phase begins to appear, forming a three-phase ALV coexisting system. Furthermore, the vapour phase fraction increases rapidly with a small decrease in pressure, meaning that phase volumes are sensitive to pressure. For example, the vapour phase volume fraction at 1300 kPa is 33.3%, while it is 61.4% at 1200 kPa for Feed #13 at 363.15 K. A relatively larger deviation for predicting phase volumes is observed at higher pressures in the ALV three-phase region because there is only a smaller amount of vapour exists in the system, which is more likely to induce larger errors. During the experimental measurements, it is difficult to identify the interface between aqueous and oleic phases due to the oil-water emulsification, however, it has an insignificant effect on the prediction of phase volumes because the aqueous and oleic phases are measured and predicted as one liquid phase (Li et al. 2017a; Chen et al. 2020).
7.4.3 Swelling factors

Since swelling factor is an essential parameter in simulating and optimizing heavy oil recovery processes involving solvent utilization, its measurement and prediction is of important significance (Li et al., 2013b). Figure 7-6 presents the swelling factors obtained from experiments and calculations as a function of temperature for Feeds #11-12 with a DME concentration of 21.2 mol% and 41.6 mol%, respectively. As can be seen, the dissolution of DME in heavy oil results in a strong swelling effect. Under real reservoir conditions, swelling of oil is able to connect the isolated oil in porous media, increase oil relative permeability and saturation, and finally enhance oil recovery (Javanmard et al., 2019). It is found from Figure 7-6 that DME has a comparable swelling effect in comparison with propane and CO₂ (Han, 2015), illustrating that DME can be applied as a potential alternative solvent for heavy oil recovery. Also, it is found from Figure 7-6 that Feed #12 with a higher DME mole fraction in its feed has a higher swelling factor in comparison with Feed #11. For example, at a given temperature of 363.15 K, the swelling factor of Feed #12 is 1.18, whereas it is 1.06 for Feed #1. This is ascribed to the fact that more DME is dissolved into the oleic phase in terms of Feed #12. It is interesting to note that the swelling factor increases only slightly with respect to temperature, demonstrating that
Figure 7-6 Comparison of the experimentally measured and theoretically predicted swelling factors for Feeds #11-12
temperature imposes an insignificant effect on swelling factors. In addition, the swelling factors calculated by the theoretical model are larger than those from the measured ones for the total of ten experimental temperatures. This may be due to the fact that the oil expansion effect caused by heat is not considered in the theoretical model. In general, the thermodynamic model in combination with the volume-translation strategy proposed by Péneloux et al. (1982) is accurate in determining the measured swelling factors with a reasonable RMSRE of 1.86% for two feeds of the DME/heavy oil mixtures with a total of ten experimental measurements.

7.4.4 Partition coefficients

Not only is DME a mutual soluble solvent in both the aqueous and oleic phases, but also achieves the first contact miscibility with oil (Groot et al., 2016b). The combination of such favourable properties allows it to partition from the aqueous phase to oleic phase once contacted with reservoir fluids when co-injected with hot water/steam (Ratnakar et al., 2016). The DME partition coefficient imposes a significant impact on the oil swelling effect and viscosity reduction as it governs the extent of DME partitioning to the oleic phase. In this study, the modified PR EOS together with the Huron-Vidal mixing rule is applied to determine the DME partition coefficient.
The evolution of DME partition coefficient between the oleic and aqueous phases is plotted in Figure 7-7, which is obtained by conducting three-phase flash calculations using the new model proposed in this study. The partition coefficients of DME for the studied mixture are calculated to be in a range of high values of 18.5-26.0, which is favorable for heavy oil recovery because the preferentially partitioning of DME into the oleic phase will result in a rapid and strong oil swelling. It is interesting to note that the DME partition coefficients obtained from this study and those from Ratnakar et al. (2016) (approximately from 13.0 to 20.0) are in the same order though the oils used are different. Also, the DME partition coefficient is decreased with pressure for the same feed at a constant temperature. It can be found from Feeds #13 and #14 that the DME exhibits similar partition coefficients under the same temperature and pressure conditions, indicating that the feed composition has a negligible effect on DME partition coefficients.

Take Feed #13 as an example for further investigation, the DME concentration in both the aqueous phase and oleic phase at three different temperatures is tabulated in Table 7-8. It is found that DME concentration in the oleic phase is much higher than that in the aqueous phase, demonstrating a preferential solubility of DME in oleic phase. For a given pressure of 1000 kPa, the DME partition coefficients at 348.15 K and 363.15 K are calculated to be 19.51 and 22.77, respectively, indicating that the DME partition coefficient is increased with temperature. Overall, high partition
Table 7-8 The calculated DME concentration in aqueous phase and oleic phase of Feed #13 at three different temperatures

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Pressure, kPa</th>
<th>Aqueous phase, mol%</th>
<th>Oleic phase, mol%</th>
<th>Partition coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.15</td>
<td>1000</td>
<td>1.82</td>
<td>35.46</td>
<td>19.51</td>
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<td>19.98</td>
</tr>
<tr>
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<td>1100</td>
<td>1.12</td>
<td>25.23</td>
<td>22.51</td>
</tr>
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<td></td>
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<td>21.02</td>
<td>22.77</td>
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<tr>
<td></td>
<td>1400</td>
<td>0.84</td>
<td>21.85</td>
<td>25.99</td>
</tr>
</tbody>
</table>
Figure 7-7 Variation of DME partition coefficient of DME/water/heavy oil mixtures for (a) Feed #13, (b) Feed #14, and (c) Feed #15
coefficients of DME make it rapidly partition into the heavy oil, leading to strong oil swelling, large viscosity reduction, and high oil production.

7.4.5 DME solubility

DME has been employed as a water-soluble solvent for the traditional waterflooding process (Riele et al., 2016). To investigate whether DME is a suitable non-hydrocarbon solvent for hybrid steam-solvent processes, the DME solubility in both the oleic and aqueous phases is theoretically predicted because it plays a crucial role in modeling and designing heavy oil recovery processes. As mentioned by Lindeloff and Michelsen (2003), the Huron-Vidal mixing rule has the capacity to represent polar components as the incorporated parameters are able to correlate solubility data. As such, the PR EOS together with the Huron-Vidal mixing rule is applied to perform three-phase equilibrium calculations to obtain the DME solubility in both the oleic and aqueous phases.

The amount of DME dissolved in the aqueous phase obtained by the new theoretical model for Feed #14 at 348.15 K and 363.15 K is illustrated in Figure 7-8. As can be seen, the DME has a much higher solubility in the aqueous phase compared to CO₂ and propane (Zhu and Okuno, 2015; Li and Li, 2018) due to its characteristic of polarity. As such, its solubility in the aqueous phase cannot be neglected. In addition, the higher the solubility of a solvent is, the faster and stronger of the solvent
Figure 7-8 The predicted DME solubility of Feed #14 in the aqueous and oleic phases at (a) 348.15 K, and (b) 363.15 K, respectively.
partitioning into the oleic phase will be. Figure 7-8 also presents the DME solubility in the oleic phase calculated using the new theoretical model for Feed #14 at temperatures of 348.15 K and 363.15 K and various pressures which are within the three-phase region. It is clearly observed that there is a large amount of DME dissolved in heavy oil, leading to reducing oil viscosity as well as swelling and mobilizing the oleic phase. The DME solubility in the Lloydminster heavy oil used in this work is determined to be from 25.2 to 37.4 mol% in a pressure range of 1100-1400 kPa at 363.15 K, compared to that in Athabasca bitumen of around 40.0 to 70.0 mol% in a pressure range of 1000-1200 kPa at 373.15 K (Haddadnia et al., 2018). As can be seen, the DME solubilities in both the aqueous and oleic phases are decreased with temperature at the same pressure. For example, at a given pressure of 1200 kPa, the DME solubilities in aqueous and oleic phases are respectively determined to be 2.1 mol% and 45.3 mol% at 348.15 K, compared to 1.3 mol% and 29.4 mol% at 363.15 K. Also, it is interesting to note from Figure 7-8 that the amount of DME dissolved in oleic phase increases almost linearly with pressure at a specified temperature.

7.5 Summary

PVT experiments have been carried out to quantify the phase behaviour of DME/water/heavy oil mixtures at various conditions of pressures and temperatures. A new thermodynamic model based on the PR EOS and Huron-Vidal mixing rule has been
developed to better capture the interaction of polar components for DME and water, while it is validated against the experimental data. The theoretical model proposed in this work improves the accuracy of the phase equilibrium calculations for polar systems. Specifically, the PR EOS incorporated with the Huron-Vidal mixing rule yields RMSRE of 5.08% for predicting saturation pressures of three feeds of DME/water/heavy oil mixtures compared to that of 17.87% resulted from the van der Waals’ mixing rule. In addition, the new thermodynamic model associated with volume-translation strategy proposed by Péneloux et al. (1982) is capable of predicting phase volumes with a reasonable accuracy. Large swelling factors and DME partition coefficients are achieved as DME is a first-contact miscible solvent upon contacting heavy oil and has preferentially partitioning from aqueous phase into oleic phase, making it a viable solvent for hybrid thermal-DME heavy oil recovery processes. The upper three-phase bubblepoint is found to be increased with the addition of water to the DME/heavy oil systems. It is also found that swelling factor is not sensitive to temperature, whereas it is highly dependent on the DME concentration in a given feed.
8.1 Conclusions

The major contributions of this research are summarized as follows:

1) A modified correlation and a new enthalpy determination algorithm have been proposed and successfully applied to accurately predict ideal gas heat capacities and enthalpies for normal alkanes/alkenes and hydrocarbon fractions, respectively;

2) A robust and pragmatic WAIF model has been developed to perform multiphase isenthalpic flash calculations for solvent(s)/water/heavy oil mixtures at high pressures and elevated temperatures with the consideration of a solvent with its high solubility in the aqueous phase;

3) The proposed WAIF model and enthalpy determination algorithm have been successfully applied to accurately determine phase boundaries of $\text{C}_3\text{H}_8/\text{CO}_2/\text{water/heavy oil}$ mixtures in both the in $P-T$ and $H-T$ phase diagrams, respectively. Meanwhile, well-designed experiments have been conducted to quantify the phase behaviour of the aforementioned systems at high pressures and elevated temperatures;

4) Techniques have been developed to determine multiphase boundaries of solvent(s)/heavy oil mixtures during thermal-solvent injection processes in
A new algorithm has been proposed to determine three-phase boundaries in $P-T$ space by performing three-phase flash calculations with negative flash being allowed; and

5) A new thermodynamic model based on the modified PR EOS together with the Huron-Vidal mixing rule as well as the Péneloux volume-translation strategy has been developed to quantify the phase behaviour of solvent(s)/water/heavy oil systems including polar components.

The major conclusions of this research can be drawn as follows:

1) The newly developed correlation can be used to predict ideal gas heat capacities of hydrocarbons more accurately at high pressures and elevated temperatures compared with the traditional Kesler and Lee correlation, yielding a much smaller AARD and MARD for both normal alkanes and normal alkenes. The new enthalpy algorithm for hydrocarbon fractions can significantly improve the enthalpy prediction accuracy for both the light naphtha and Alaska naphtha. Furthermore, the enthalpy departure function used in the new algorithm is more accurate and convenient in representation of the pressure effects on enthalpy, resulting in more accurate prediction of enthalpy for hydrocarbon fractions. The new algorithm proposed in this study can be applied to predict enthalpy of ill-defined hydrocarbons such as heavy oil.
pseudocomponents both accurately and efficiently;

2) By constructing an $H-T$ phase boundary diagram first, the proposed isenthalpic flash model can be conducted directly without performing stability test for a given feed at a specified enthalpy and pressure. In comparison to the traditional isothermal flash, the new isenthalpic flash model can be applied to successfully deal with the convergence issues frequently encountered in the narrow-boiling regions. The newly developed WAIF model can be used to quantify phase behavior of solvent/water/heavy oil mixtures which are frequently encountered in hybrid solvent-steam injection processes, especially for cases where the solvents have high solubility in both the aqueous phase and the oil phase;

3) The newly developed water-associated model is found to predict the upper three-phase boundary pressures of the C$_3$H$_8$/CO$_2$/water/heavy oil mixtures with a good accuracy. In addition, the newly developed water-associated isenthalpic flash model together with the new enthalpy determination algorithm proposed in this research are applied to determine multiphase boundaries of solvent(s)/water/heavy oil systems in the $H-T$ space for the first time. Without tuning any parameters of the PR EOS, the water-associated model incorporated with the modified alpha functions for both water and non-water components is able to reproduce the experimentally measured
upper three-phase ALV boundary pressures as well as the vapour and hydrocarbon-rich liquid phase compositions of the C₃H₈/CO₂/water/heavy oil system at high pressures and elevated temperatures;

4) Multiphase boundaries of solvent(s)/heavy oil systems in terms of $P-T$, $H-T$, and $P-H$ phase diagrams are respectively determined by use of isenthalpic flash algorithms at various conditions of pressures and temperatures. The PR EOS associated with the recently modified alpha function is found to be accurate in reproducing the experimentally measured VL₁L₂ three-phase boundary pressures as well as VL₁ two-phase boundaries of solvent(s)/heavy oil mixtures. For the extended $P-T$ phase diagrams of Feeds #4-6 in this study, it is found that the three-phase VL₁L₂ region of solvents/heavy oil mixtures experiences a wider area with the addition of either C₃H₈ or $n$-C₄H₁₀; and

5) The new thermodynamic model based on the PR EOS and Huron-Vidal mixing rule improves the accuracy of the phase equilibrium calculations for polar systems as it has superiority in describing the interaction of polar components such as DME and water. Large swelling factors and DME partition coefficients are achieved as DME is a first-contact miscible solvent upon contacting heavy oil and has preferentially partitioning from aqueous phase into oleic phase, making it a viable solvent for hybrid thermal-DME heavy oil recovery processes. The upper three-phase bubblepoint is found to be
increased with the addition of water to the DME/heavy oil systems. It is also found that swelling factor is not sensitive to temperature, whereas it is highly dependent on the DME concentration in a given feed.

8.2 Recommendations

The theoretical modeling and experimental measurements of the phase behaviour and physical properties for solvent(s)/water/heavy oil systems with consideration of a solvent with its high solubility in water has been systematically performed, providing accurate phase behaviour descriptions of the aforementioned systems for the hybrid steam-solvent heavy oil recovery processes. Considering the complexity of reservoir fluids and reservoir conditions, the future work of relevant research topics is recommended as follows:

1) Alkane solvents (e.g., C₃H₈ or n-C₄H₁₀) and non-hydrocarbon solvent (e.g., CO₂) have been proven to be able to reduce oil viscosity and enhance oil swelling effect. Thus, the phase behaviour and physical properties of DME/water/heavy oil mixtures with the addition of C₃H₈ or n-C₄H₁₀ and CO₂ shall be experimentally and theoretically studied, while the effect of adding other solvent(s) (e.g., N₂) to DME/water/heavy oil mixtures shall be evaluated;

2) Reservoir fluids contain a number of different salts such as NaCl and CaCl₂. The presence of salt may affect the polar interaction between DME and water.
molecules. It is necessary to incorporate the effect of salinity into phase behavior modeling as salinity has significant impact on DME solubility in brine as well as DME partitioning between brine and oil for DME/brine/heavy oil systems;

3) Asphaltene precipitation is easily occurred when alkane solvents and/or CO$_2$ are injected into a hydrocarbon reservoir (Buckley et al., 1988; Yang, 2005; Li et al., 2013a; Fang et al., 2018), leading to the appearance of a solid phase and imposing an important effect on the phase behaviour and physical properties of reservoir fluids. As such, laboratory experiments as well as robust and efficient thermodynamic models are needed to accurately quantify the phase behaviour and physical properties of solvent(s)/water/heavy oil systems with the consideration of asphaltene precipitation; and

4) Addition of light alkane solvents (i.e., C$_3$H$_8$ and $n$-C$_4$H$_{10}$) and/or CO$_2$ with DME into steam can enhance mass transfer and achieve larger swelling factors for solvent(s)/water/heavy oil systems (Ghorayeb and Firoozabadi, 2000; Etminan et al., 2010; Zheng, 2016), while the preferential mass transfer of each individual component in a solvent mixture shall be studied as it is necessary to optimize the concentrations of solvents for enhancing heavy oil recovery.
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Evaluation and Engineering, 8(6), 528-533.


Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, December 5-6.


APPENDIX A COPYRIGHT PERMISSIONS

Improved enthalpy prediction of hydrocarbon fractions with a modified alpha function for the Peng-Robinson equation of state

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Publication: Fuel
Publisher: Elsevier
Date: 1 November 2019
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BACK CLOSE WINDOW
A robust multiphase isenthalpic flash model for water/solvent/hydrocarbon systems at high pressures and elevated temperatures

Author: Desheng Huang, Deyong Yang
Publication: Fluid Phase Equilibria
Publisher: Elsevier
Date: 15 June 2019

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Determination of Multiphase Boundaries for Pressure-Temperature (P-T) and Enthalpy-Temperature (H-T) Phase Diagrams of C3H8/CO2/Water/Heavy Oil Systems at High Pressures and Elevated Temperatures

Author: Desheng Huang, Xiaoli Li, Deqing Yang
Publication: Industrial & Engineering Chemistry Research
Publisher: American Chemical Society
Date: Jan 1, 2020
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CLOSE WINDOW
### APPENDIX B SAFE OPERATING PROCEDURE (SOP) FOR PVT EXPERIMENTS

**Activity/Task/Procedure/Job/Experiment:** Safe Operating Procedure for PVT experiments using dimethyl ether (DME)

<table>
<thead>
<tr>
<th>Equipment:</th>
<th>Personal Protective Equipment (PPE):</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 500 DX syringe pump</td>
<td>Gloves</td>
</tr>
<tr>
<td>• High-pressure cylinder (volume: 500 cc; maximum pressure: 5000 psi)</td>
<td>Respirator</td>
</tr>
<tr>
<td>• Pressure gauge (2000 psi)</td>
<td>Protective Eyewear</td>
</tr>
<tr>
<td>• PVT setup</td>
<td>Face shield</td>
</tr>
<tr>
<td>• Cart</td>
<td>Appropriate Footwear</td>
</tr>
<tr>
<td>• Swagelok sampler (70 cc, 1000 psi)</td>
<td>Hearing Protection</td>
</tr>
<tr>
<td>• Regulator for DME tank: PRS 30022631510</td>
<td>Protective Clothing</td>
</tr>
<tr>
<td>• Karlez O-rings are recommended</td>
<td></td>
</tr>
</tbody>
</table>

**Specialized PPE:**

- Nitrile gloves
- Lab coat
- Long pants
- Safety boots
- Safety glasses
- Heat-resistant gloves for sample collection
<table>
<thead>
<tr>
<th>Equipment Specifications If Provided:</th>
<th>Comments / Miscellaneous Information:</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVT setup should be operated at temperature &lt; 200°C and pressure &lt; 69 MPa</td>
<td>Read PVT user manual, both this SOP and the SDS as well as handling guidelines for DME, ethanol, kerosene, and heavy oil prior to performing PVT experiments. DME hazards from its SDS: Extremely flammable gas; contains gas under pressure, may explode if heated; may cause drowsiness or dizziness; may displace oxygen and cause rapid suffocation; may form explosive mixtures with air; and may cause frostbite.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Steps</th>
<th>Hazards</th>
<th>Mitigation Strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Put on appropriate PPE</td>
<td>None</td>
<td>Wear lab coat, long pants, safety boots, safety glasses and gloves.</td>
</tr>
<tr>
<td>2. Check the snorkels/venting system if work properly (check if you can hear air flow)</td>
<td>None</td>
<td>Wear PPE. If snorkel does not seem to be working, do not proceed. Contact Faculty Safety Coordinator or Innovation Place to investigate.</td>
</tr>
<tr>
<td>3. Assemble equipment (put syringe pump on the top of the table near the PVT set up; put cylinders near the heavy oil pail and DME tank)</td>
<td>Cylinders and pumps are heavy, may cause physical injury (muscle strain, dropping on foot, dropping on fingers, etc.)</td>
<td>Use a cart to move the cylinder and pump; ask classmates for help; steel toe boots required.</td>
</tr>
<tr>
<td>4. Conduct leakage test: Inject nitrogen at 5.0 MPa to see if the system leaks</td>
<td>High pressure condition, nitrogen may leak</td>
<td>Wear safety glasses; change O-ring every three tests to avoid leakage; gradually inject high pressure nitrogen into PVT cell for leakage test; leakage on all the connections should be thoroughly checked (use of Snoop/soapy water to identify source of leaks).</td>
</tr>
<tr>
<td>Step</td>
<td>Description</td>
<td>Potential Hazards</td>
</tr>
<tr>
<td>------</td>
<td>-----------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5.</td>
<td>Prepare DME and heavy oil in transfer cylinders (inject DME from its tank to the transfer cylinder, the maximum pressure is 500 kPa and volume is 500 scc; dump 200 scc of heavy oil into another transfer cylinder)</td>
<td>Chemical exposure; DME leakage if there is uncontrolled leak</td>
</tr>
<tr>
<td>6.</td>
<td>Inject DME into the PVT cell</td>
<td>High pressure condition; DME may mix with air to form explosion if there is uncontrolled leak</td>
</tr>
<tr>
<td>7.</td>
<td>Inject heavy oil into the PVT cell</td>
<td>Oil drop; high pressure (oil is not flammable/combustible)</td>
</tr>
<tr>
<td>8.</td>
<td>Release DME remaining in the cylinder</td>
<td>DME may mix with air to form explosion (if there is uncontrolled leak)</td>
</tr>
<tr>
<td>9.</td>
<td>Increase the system to pre-specified pressure and temperature conditions</td>
<td>High pressure and temperature condition</td>
</tr>
<tr>
<td>10.</td>
<td>Decrease system pressure to measure saturation pressure</td>
<td>High pressure and temperature condition; quick pressure change may damage the glass tube</td>
</tr>
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<td></td>
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<tr>
<td>(leakage test can detect whether it is damaged or not before conducting the PVT test; no other physical injury)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Decrease system pressure further to measure phase volumes</td>
<td>High pressure and temperature condition; quick pressure change may damage the glass tube</td>
<td>Wear PPE all the time; the process should be gently operated.</td>
</tr>
<tr>
<td>12. Collect samples to perform compositional analysis</td>
<td>High pressure and temperature condition, chemical exposure, spills</td>
<td>Need heat-resistant gloves, use goggles/face shield if possibility of oil spraying; wear PPE all the time; carefully collect the gas sample with a vacuumed gas sampler (Swagelok, Canada, 1000 psi); use kerosene to clean spills if there is any.</td>
</tr>
<tr>
<td>13. Decrease the system pressure and temperature, and clean equipment</td>
<td>Oil drop; chemical exposure (no issues with flammability; wait until the system cool down to room temperature to clean the equipment)</td>
<td>Wear PPE all the time; gradually displace the sample fluid from the PVT cell; use kerosene and ethanol to clean the system several times; use snorkel to evacuate the vaporized kerosene (ethanol) in the PVT setup; ensure temperature is reduced to room temperature before cleaning the equipment.</td>
</tr>
<tr>
<td>14. Replace O-ring</td>
<td>Components may lose or damage</td>
<td>Wear PPE all the time; use wrench carefully to open and tight fittings; put all the components in a box when disassembling the system.</td>
</tr>
<tr>
<td>15. Dispose the remaining oil/kerosene in a waste jug and label it</td>
<td>Spills, chemical exposure, flammable mixtures.</td>
<td>Containment of samples in Nalgene waste jugs (from UR Stores) with waste labels; for flammable mixtures max container size is 4L, do not fill more than 75%. Contact Safety Coordinator to arrange disposal.</td>
</tr>
</tbody>
</table>