Full Length Article

Application of Peng-Robinson equation of state for modelling the multiphase equilibrium properties in Athabasca bitumen/ethane mixtures

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ABSTRACT

Phase behavior of (bitumen + solvent) mixtures and their properties are essential for surface upgrading methods and enhanced oil recovery applications. The objective for this work is to systematically model the phase partitioning and component distribution in the (bitumen + solvent) mixtures. To perform equation of state modelling, compositional analysis of bitumen is utilized to characterize the bitumen sample and its components up to C\textsubscript{100}. The full range of components is utilized in Peng-Robinson equation of state (PR-EOS) to predict the equilibrium phase properties, such as composition and density, in vapor-liquid and liquid-liquid regions. Based on the results, PR-EOS accurately captures the composition of phases, component distribution in each phase, and phase properties. Thereafter, an algorithm is proposed to lump the components on the basis of two-phase envelope generation. The results indicate that Athabasca bitumen and its phase behavior in (bitumen + solvent) mixtures can be well represented in multi-phase regions by four pseudo-components.

1. Introduction

Determining phase behavior and estimating the thermodynamic properties for complex fluid systems or ill-defined fluids, such as (bitumen + solvent) mixtures, present significant challenges. Despite the importance of phase behavior data for production, pipeline transportation, upgrading, and refining of such fluids, limited experimental data for bitumen-containing mixtures have been reported in the literature. This is due to the fact that experimental measurements for these systems are usually expensive and time-consuming. This issue is even more pronounced when multiple phases form at equilibrium conditions. Modelling is a credible alternative for studying the phase behavior and the interaction of (bitumen + solvent) systems.

The thermodynamic modelling of (bitumen + solvent) systems is limited compared to simple hydrocarbon systems and conventional oil. This might be due to complex nature and lack of a known characterization method for heavy oil and bitumen. Although different characterization schemes, as stated by Kumar and Okuno\textsuperscript{1}, have been proposed for different reservoir fluids\textsuperscript{2–6}; for example, gas condensates\textsuperscript{7–10}, volatile oils\textsuperscript{11,12}, near-critical fluids\textsuperscript{13–16}, the methods for heavy oil and bitumen characterizations are limited\textsuperscript{1,17–18}. This led to variety of models in literature for pseudo-component determination in the phase behavior study of (bitumen + solvent) mixtures.

Mehrotra et al.\textsuperscript{19} utilized Bishnoi et al.\textsuperscript{20} characterization method to develop five pseudo-component in order to study the phase behavior and solubility of carbon dioxide and ethane in Athabasca and Peace River bitumens using Peng-Robinson equation of state (PR-EOS). The critical properties calculated from Kesler and Lee\textsuperscript{21} correlation provided a good agreement with the experimental solubility data. Fu and Puttagunta\textsuperscript{22} and Fu et al.\textsuperscript{23} considered a pseudo-component in the vapour-liquid equilibrium calculations of (bitumen + solvent) systems for the sake of simplicity. They developed a temperature-dependent correlation for binary interaction parameters to represent the vapour-liquid data. Mehrotra and Srceck\textsuperscript{24,25} and Mehrotra et al.\textsuperscript{26} utilized PR-EOS along with Kesler and Lee\textsuperscript{21} correlation for calculating critical properties to estimate the nitrogen, carbon monoxide, methane, carbon dioxide, and ethane solubility in Athabasca, Cold Lake, and Wabasca bitumen at the temperatures up to 110 °C and at the pressures up to 10 MPa. The bitumen was characterized using three pseudo-components which represent distillable maltene, undistillable maltene, and asphaltene that could adequately match the experimental data. Frauenfeld et al.\textsuperscript{27} estimated the methane, ethane, propane, and carbon dioxide solubility in Lloydminster Aberfeldy oil and a blended Cold Lake/Lloydminster oil using PR-EOS. The binary interaction parameters were adjusted to tune the model.
Kariznovi et al. [28] modelled the phase behaviour of (bitumen + solvent) mixtures using PR-EOS for four bitumens (Athabasca, Peace River, Wabasca, and Cold Lake) mixed with four different solvents (nitrogen, carbon dioxide, methane, and ethane). They used the lab data of Mehrorova and Srnvcek [24,25,29] and Srnvcek and Mehrorova [30,31] and considered three, five and six pseudo-components which were defined on the basis of different fractions of bitumen. A universal set of pseudo-components was also proposed applicable for different Alberta bitumens.

Saber and Shaw [32] and Saber et al. [33] used a group contribution method to estimate the critical properties of bitumen pseudo-components for equation of state phase behaviour modelling of (Athabasca bitumen + n-decane) mixtures. Diaz et al. [34] studied the phase behaviour for the mixtures of Athabasca bitumen, propane, and carbon dioxide using different characterization methods. They utilized simulation distillation (SimDis) data along with six characterization approaches to predict the saturation pressures and liquid-liquid phase boundaries of pseudo-ternary systems.

Agrawal et al. [35] modelled the saturation pressure of live Peace River bitumen at different condensate concentrations with PR-EOS using the characterization method proposed by Diaz et al. [34] through the adjustment of binary interaction parameters. They fitted the saturation pressure and asphaltene onset data with temperature-dependent binary interaction parameters. The developed model reasonably predicted the saturation pressures of methane/bitumen, ethane/bitumen, carbon dioxide/bitumen, and n-pentane/bitumen. Li and Yang [36] modelled the phase behaviour of propane/n-butane/heavy-oil systems at the temperatures up to 123 °C and the pressures up to 5030.0 kPa with a volume-translated PR-EOS coupled with a modified alpha function. The experimental data was accurately matched with the binary interaction correlations and the volume-translated equation of state, while prediction accuracy was decreased near the pure solvent critical temperature.

Badamchi-Zadeh et al. [37] proposed a bitumen characterization method with an equation of state model for the carbon dioxide, propane, and Athabasca bitumen mixtures. Four pseudo-components were defined for bitumen based on conversion of the SimDist data of asphaltene free bitumen to a normal boiling point distribution. Then, the binary interaction parameters were tuned to match the saturation pressure. Yang et al. [38] modelled the phase behavior of methane/propane/heavy-oil (Lloydminster) mixture using the volume-translated PR-EOS along with a modified alpha function at the pressures up to 10 MPa and the temperature range of 22–50 °C. A new correlation for the binary interaction parameter was proposed in order to match the measured swelling factors and saturation pressures. Ghasemi and Whitson [39] proposed a systematic approach to model the phase behaviour of the mixtures containing light solvents (nitrogen, carbon dioxide, carbon monoxide, methane, and ethane) and Athabasca bitumen using cubic equations of state. Gamma distribution was used to fit the bitumen distillation data; then, single-carbon-number (SCN) fractions were defined, and Twu [40] correlation was used to calculate the critical properties of fracious. Finally, SCN fractions were lumped into five pseudo-fractions.

Gao et al. [41] observed the multiphase behavior for (bitumen + n-butane) mixtures in their phase behavior studies at pressures up to 10 MPa and temperatures up to 160°C. Eghbali and Dehghanpour [42] presented experimental and modelling study for multiphase behavior of (Clearwater bitumen + butane) and (Clearwater bitumen + CO₂) mixtures. They calibrated PR-EOS to predict (bitumen + solvent) phase behavior. Kumar and Ōkuno [43] proposed a method for characterization of bitumen by improving the fluid characterization method which was developed based on perturbation from n-alkanes (PnA). The authors showed that LLE data needed positive interaction coefficients between (bitumen + solvent) while VLE was not sensitive to the interaction coefficients used. Azifar et al. [44] fractionated Athabasca bitumen to four cuts by using modified vacuum distillation. The PR-EOS was then tuned to match solubility data of propane in each bitumen cut. The bitumen was also characterized using the boiling point or carbon number distribution and the generalized model was then proposed to obtain the solubility of propane in the bitumen samples.

Most of the above-mentioned studies have focused on the modelling of the vapor-liquid equilibrium and solubility data. The phase behavior of (bitumen + solvent) mixtures is still challenging when the multiphase equilibrium occurs at specific conditions. The objective of this study is thus to develop a characterization method for heavy oil and bitumen. The method is applicable for both the multiple-phase equilibrium conditions, and the development of PVT models for the purpose of simulation study. In addition, it tests the applicability of equation of state for phase behavior modelling study of (bitumen + solvent) mixtures. The characterization is based on the simulated distillated data and physical properties of bitumen coupled with available correlations for the calculation of critical properties. WinProp software from Computer Modelling Group (CMG) version 2017 was used to model the phase behaviour of the (bitumen + solvent) mixtures. The phase behavior predictions were examined with the available literature data for bitumen/ethane mixtures including vapor-liquid (VLE) and liquid-liquid equilibrium (LLE) data. The compositional analysis, phase compositions, and phase densities are compared against the experimental data and the phase diagrams are generated. These information are extremely important for surface upgrading, production, pipeline transportation, and refining.

### 2. Equilibrium calculation

State of the system is determined by fugacity of each component in each phase at equilibrium conditions. The equilibrium condition for species i in phase I and II is presented as,

\[ f_i^I = f_i^{II} \]

(1)

In terms of the fugacity coefficients, Eq. (1) can be re-written as,

\[ y_i \hat{\beta}_i^I P = x_i \hat{\beta}_i^{II} P, \]

where the partial fugacity coefficients are calculated using,

\[ \ln \hat{\beta}_i = \frac{\int_0^\infty \left( \frac{\nu P}{\ln \nu P} - \frac{RT}{\nu} \right) dv}{RT} - \ln Z, \]

(3)

where \( P \) is pressure, \( T \) is temperature, \( v \) is volume, \( R \) is gas universal constant, and \( Z \) is compressibility factor. Equation of state (EOS) is typically utilized to express the relationship between the pressure, temperature and volume. Peng-Robinson (Peng and Peng [45]) EOS, a cubic EOS, provides acceptable results for the hydrocarbon mixtures and petroleum systems and thus, it was employed in this study to calculate the equilibrium properties of bitumen containing mixtures. The general form of Peng-Robinson EOS is shown as,

\[ P = \frac{RT}{v - b} - \frac{a\lambda(T)}{v(v + b) + b(v - b)}, \]

(4)

where,

\[ a = \frac{0.45724RT^2T_c^2}{P_c^2} \]

(5)

\[ b = \frac{0.07780RT_c}{P_c}, \]

(6)

\[ \lambda(T) = \left[ 1 + x(1 - T_c^{(1/2)}) \right]^2, \]

(7)

\[ x = \frac{0.379642 + 1.48503 - 0.164423\omega^3 + 0.016666\omega^3}{0.379642 + 1.48503 - 0.164423\omega^3 + 0.016666\omega^3}, \]

(8)

where \( P \) is pressure, \( T \) is temperature, \( v \) is volume, \( a \) represents the attractive forces between molecules, \( b \) accounts for the volume of molecules, \( T_c \), and \( P_c \) are the critical temperature and pressure. \( a \) and \( b \) are
calculated from the critical properties of the component for a single component system. However, for multicomponent mixtures, \( a \) and \( b \) are defined based on the individual components’ \( a \) and \( b \) using the van der Waals mixing rules:

\[
a_n = \sum_i x_i D_i, 
\]

\[
D_i = \sqrt{a_i} \sum_j x_j (1 - \delta_{ij}) \sqrt{a_j}, 
\]

\[
b_n = \sum_i x_i b_i, 
\]

(9, 10, 11)

where \( \delta_{ij} \) represents the binary interaction between the hydrocarbons in the mixture, which is typically defined as a function of the critical properties. In WinProp, the binary interaction parameters are related to critical volume of components through the following equation [46,47],

\[
\delta_{ij} = 1 - \left( \frac{2^{1/6} v_{ij}^{1/6} v_{ij}^{-1/6}}{v_{ij}^{1/3} + v_{ij}^{1/3}} \right)^2 
\]

(12)

Oellrich et al. [48] showed that a value of 1.2 for \( n \) provides an acceptable match with the experimental results for the paraffin-paraffin interaction coefficients. This equation satisfactorily reproduces the methane interaction coefficients reported by Katz and Firoozabadi [49] (Mehra [46]). In this study, \( n \) was considered as a tuning parameter to fit the experimental VLE and LLE data. Worth to mention that, Diaz et al. [34] defined the binary interaction parameters as a function of components’ critical temperatures to match the saturation pressure data of (Athabasca bitumen + solvent) mixtures.

3. Density calculation

EOS can also be utilized to determine the volumetric properties of petroleum/hydrocarbon mixtures. Peneloux et al. [50] proposed a volume translation technique to be applied to Peng-Robinson EOS in order to improve the volumetric calculations without impacting the other properties. In the volume shift technique, the volume is corrected by the following relation,

\[
v_{cor} = v - c, 
\]

(13)

where \( v_{cor} \) is corrected molar volume and \( v \) is translation parameter. For multi-components systems, \( c \) is defined as,

\[
c = \sum_{i=1}^{N} x_i c_i, 
\]

(14)

where \( x_i \) is the mole fraction of component \( i \) in the mixture and \( c_i \) is defined as

\[
c_i = \Omega_i v_{i,(RT/P)} 
\]

(15)

where \( \Omega_i \) is a constant specific to the EOS (for Peng-Robinson EOS, it is 0.077796), \( v_{i} \) is the volume translation, \( T_c \) is the critical temperature, and \( P_c \) is the critical pressure. \( v_i \) is also considered as a tuning parameter that commonly obtained through matching the lab volumetric data (e.g. densities, relative volumes, and etc.). Thus, the volume translation technique is available to modify the calculated volumetric and also to match the bitumen and equilibrium phases’ densities.

In WinProp, three methods are available for the volume shift: constant volume shift, temperature dependent volume shift correlation, and linear temperature dependent volume shift. Using constant volume shift option, the densities of the equilibrium phases are inaccurately modeled with the EOS particularly when a wide range of temperatures is considered. Thus, it is essential to define temperature-dependent volume shifts. Pedersen et al. [51] proposed the following equation to calculate the temperature-dependent volume shifts for each component,

\[
S = S_o + S_i (T - T_{ref}) 
\]

(16)

Component volume shifts can be evaluated by finding the difference between the saturated liquid molar volume of a pure component obtained from the EOS and the saturated liquid molar volume calculated using a modified Rackett’s Z-factor equation at any specific temperature [52],

\[
v_i = (RT_i/P_i)Z_{bk} \left[ 1 + (1 - T_i/T_c)^{2/7} \right] 
\]

(17)

Rackett’s compressibility factors are back-calculated from the specific gravity and critical properties with the assumption that the specific gravity is roughly equal to the saturated liquid density at 60°F.

4. Viscosity calculation

In WinProp, Pedersen viscosity correlation [53] is used to calculate the viscosity of high viscous fluids such as heavy oil and bitumen. This correlation is based on the corresponding state method, and it calculates the viscosity of mixtures with respect to a reference substance at the same reduced temperature and pressure using the following relation,

\[
\frac{\mu_{mix}(T, P)}{\mu_{ref}(T_{ref}, P_{ref})} = \left( \frac{T_{mix}}{T_{ref}} \right)^{1/6} \left( \frac{P_{mix}}{P_{ref}} \right)^{2/3} \left( \frac{MW_{mix}}{MW_{ref}} \right)^{1/2} \left( \frac{\beta_{mix}}{\beta_{ref}} \right). 
\]

(18)

where \( T_c \) and \( P_c \) are the critical temperature and pressure. The molecular weight (MW) is calculated using both weight and molar averaged values as,

\[
MW_{mix} = d_i (MW_{w}^{di} - MW_{w}^{di}) + MW_n 
\]

(19)

The rotational coefficient (\( \beta \)) represents the deviation from simple corresponding states, and it is defined as,

\[
\beta = 1 + d_i (\rho_{c}/\rho_{c})^{1/3} \left( MW_{w}^{di} \right) 
\]

(20)

where \( \rho_{c} \) and \( \rho \) are the critical density and mixture density. The viscosity of a mixture calculated using the Pedersen model is dependent on the critical pressures, critical temperatures, molecular weights of each component, and the coefficients \( d_i \) (as shown in the above equations). A modified version of Pedersen correlation for methane viscosity gives a better correlation of the viscosity data [54].

5. Bitumen characterization

Before applying an EOS for a phase behavior study, the fluid samples should be thoroughly characterized. The characterization of heavy fractions such as heavy oil and bitumen is generally on the basis of the boiling point distribution from atmospheric and vacuum distillation. Crude oils and distillate fractions contains thousands of components with complex molecular structures that typically show a continuous boiling point distribution. Two commonly used approaches for oil characterization are the characterization of the crude oil or its fractions: (i) in terms of pseudo-components that are defined by hydrocarbon type, e.g., paraffinic, olefinic, naphthenic or aromatics; or an average boiling point (ii) the continuous mixture approach, in which the oil is represented by a continuous distribution function with respect to boiling point, molecular mass, and/or some other measurable properties. The continuous mixture approach is adequate when the oil consists of one type of hydrocarbon groups, such as paraffins or naphthenic;

### Table 1

<table>
<thead>
<tr>
<th>Bitumen properties [58].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mol)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SARA Fraction (wt%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>11.76</td>
</tr>
<tr>
<td>Aromatics</td>
<td>57.00</td>
</tr>
<tr>
<td>Resins</td>
<td>21.61</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>9.62</td>
</tr>
</tbody>
</table>

\[\text{Table 1} \]

\[\text{Molecular Weight (g/mol):} \quad 512.5 \pm 6.9 \]
however, heavy oil and bitumen are a complex mixture composed of different hydrocarbons types (e.g. saturates, aromatics, etc.). In this study, the pseudo-component approach is employed for the bitumen characterization. The pseudo-components are primarily defined, and their critical properties are estimated and along with the component’s composition are applied into the Peng-Robinson EOS. The multi-phase equilibrium is then calculated by a flash method combined with a phase stability check. In this study, WinProp software from Computer Modelling Group (CMG) was used to model the phase behaviour of the bitumen containing mixtures. The tangent-plane stability criterion is used in WinProp\[55\]. This method is on the basis of a stage-wise procedure in which the number of phases gradually increases. The equilibrium equation (Eq.(3)) is solved with Quasi-Newton Successive Substitution (QNSS)\[56\].

The compositional analysis of Athabasca bitumen sample was already reported by Kariznovi et al.\[57\], and was used to define the pseudo-components and characterize the bitumen. Table 1 summarizes the bitumen properties\[58\]. Based on the lab distillation data, components were defined for the distillable fraction of Athabasca bitumen, which accounts for about 80 percent (in mass) of the fluid, and also matches the component distribution. Riazi \[59\] developed the following correlation to relate the component’s boiling point to corresponding carbon number,

\[ T_b = 1090 - \exp(6.9955 - 0.11193 N_c^{1/3}) \]  

(21)

where \( T_b \) is the boiling point in Kelvin, and \( N_c \) is carbon number. Riazi \[59\] showed that the data of Katz-Firoozabadi \[49\] is represented by this equation with an average absolute deviation (AAD) of 0.2%.

Riazi \[59\] also utilized the physical properties of hydrocarbons (\( C_{6-22} \)) to develop correlations for the estimation of molecular weight as a function of normal boiling point, and the prediction of specific gravity as a function of molecular weight.

The molecular weight of each single carbon number, as proposed by Riazi \[59\], can be estimated by the following equation,
The specific gravity of each component is also related to molecular weight by,
\[
SG = 1.07 - \exp[3.56073 - 2.93886 \times MW^{0.1}]
\]  
where \( MW \) is the molecular weight. Eqs. (21)–(23) were used to calculate the boiling points, molecular weights, and specific gravities of SCN groups. The boiling points of the components along with their compositions reasonably represent the experimental distillation data of Athabasca bitumen. The un-distilled fraction of Athabasca bitumen was represented by a single component and assigned an average molecular weight based on Diaz et al.’s [34] work. Alboudwarej et al. [60] proposed the following equation for asphaltene fractions to relate the specific gravity and molecular weight,
\[
SG = 670 \times MW^{0.0629}
\]
Eq. (24) along with the average molecular weight of asphaltene was used to estimate the specific gravity of non-distillable fraction in this study. Thus, on the basis of the developed characterization scheme, the distillable fraction of bitumen is represented by single carbon numbers, and the non-distillable fraction by one pseudo-component (composition of \( C_{100+} \) is 18.76 mass percent). The comparison of experimental and calculated critical properties and acentric factor of components. Kesler and Lee [21] proposed the following equations,
\[
T_c = \left( 341.7 + 811SG + [0.76392 + 0.21132SG]T_b \right. \\
\left. + \left( 0.25939 - 1.81239SG \right) \times 10^2 \right) / 1.8
\]  
\[
P_c = \exp\left[ 8.3634 - 0.0566/SG - (0.24244 + 2.2898/SG + 0.11857/SG^2) \times 10^{-3}(1.8 \times T_b) + (1.4685 + 3.648/SG + 0.47227/SG^2) \times 10^{-3}(1.8 \times T_b)^2 - (0.42019 + 1.6977/SG^2) \times 10^{-10}(1.8 \times T_b)^2 \right] / 14.7
\]  
\[
\omega = \frac{\ln P_c - 5.92714 + 6.09648 T_b}{15.6875 T_b^2 - 13.4721 \ln T_b + 4.35777 T_b^2} \quad \text{for } T_b \leq 0.8
\]
\[
\omega = -7.904 + 0.1352K_n - 0.007465K_n^2 + 8.359 T_b \\
+ \left( 1.408 - 0.01063K_n \right) \quad \text{for } T_b > 0.8
\]  
Calculating the critical properties of Alberta bitumen and they concluded that the Kesler and Lee [21] correlations provided the most acceptable results for bitumen/gas systems. Kariznovi et al. [28] also examined different correlations to calculate critical properties and acentric factor of non-distillable fractions. They came into the conclusion that the phase boundaries are better predicted with Lee-Kesler correlation compared to other available methods. Thus, in this study, the Kesler and Lee [21] correlation was used to calculate the critical properties and acentric factor of the components.

Kesler and Lee [21] proposed the following equation for asphaltene fractions to relate the specific gravity and molecular weight,
\[
T_b = \left( 341.7 + 811SG + [0.76392 + 0.21132SG]T_b \right. \\
\left. + \left( 0.25939 - 1.81239SG \right) \times 10^2 \right) / 1.8
\]  
\[
P_b = \exp\left[ 8.3634 - 0.0566/SG - (0.24244 + 2.2898/SG + 0.11857/SG^2) \times 10^{-3}(1.8 \times T_b) + (1.4685 + 3.648/SG + 0.47227/SG^2) \times 10^{-3}(1.8 \times T_b)^2 - (0.42019 + 1.6977/SG^2) \times 10^{-10}(1.8 \times T_b)^2 \right] / 14.7
\]  
\[
\omega = \frac{\ln P_b - 5.92714 + 6.09648 T_b}{15.6875 T_b^2 - 13.4721 \ln T_b + 4.35777 T_b^2} \quad \text{for } T_b \leq 0.8
\]
\[
\omega = -7.904 + 0.1352K_n - 0.007465K_n^2 + 8.359 T_b \\
+ \left( 1.408 - 0.01063K_n \right) \quad \text{for } T_b > 0.8
\]
where $P$ is pressure in atm, $T$ is temperature in K, $P_{cr}$ and $T_{br}$ are reduced critical pressure and reduced boiling point temperature, respectively. As discussed earlier, the components’ critical volumes are needed in Eq. (12) to calculate the binary interaction parameters between the components. In this study, Twu’s correlation [40] was employed to calculate the critical volumes of the components using their boiling point, molecular weight, and specific gravity.

6. Component lumping

Following the characterization of Athabasca bitumen, lumping or grouping of the components into fewer numbers of components is required because large number of pseudo-components is not commonly practical for modelling study. The accuracy of predictions could be reduced during lumping step while the calculation time is significantly improved. The adequate number of pseudo-components mainly depends on the mixture/system under study. Whitson [62] proposed a lumping approach that is developed originally on the basis of Sturges’ rule [63]. This scheme calculates the number of components using the following equation,

$$N_f = \text{Int} \left[ 1 + 3.3 \log_{10}(N - n) \right]$$

where $n$ and $N$ are the minimum carbon number and the maximum one in the sample, respectively. WinProp has two options for lumping into hypothetical components: default and user defined lumping scheme. The default lumping is according to components log (k) values and the k-values are calculated using Wilson’s equations. The Lee-Kesler [64] mixing rule are then used to calculate the critical properties of the components,

$$v_i = \frac{1}{8} \sum_j \sum_x x_i x_j (v_i^{1/3} + v_j^{1/3})^3$$

$$T_i = \frac{1}{8w} \sum_j \sum_x x_i x_j (v_i^{1/3} + v_j^{1/3}) \sqrt{T_i T_j}$$

$$\omega = \sum_i x_i \omega_i$$

Fig. 6. Component distribution in ethane-free liquid samples, extract (black and green) and residue (blue and red), from LLE study of (Athabasca bitumen + ethane) mixtures at 5 MPa (a) and 9 MPa (b) and a constant overall ethane composition of 40 wt%; blue and black, experimental data from Kariznovi et al. [57]; red and green, predictions by PR-EOS using full characterization scheme. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
\[ P_c = \frac{Z R T_c}{v_c} = \frac{(0.2905 - 0.085 w)}{v_c} \sum_i \sum_j x_i x_j \left( \frac{v_{ij}^{1/3} + v_{ji}^{1/3}}{v_{ij}} \right) \sqrt{v_{ij} / v_j} \]  

(34)

where \( v_c \) is the critical volume, \( T_c \) is the critical temperature, \( w \) is the acentric factor, and \( P_c \) is the critical pressure. While the modelling results with full number of components might be acceptable, the number of pseudo-components can be reduced for computational efficiency. In this study, the two-phase envelope (pressure-temperature diagram) is generated with PR-EOS using full number of components. The defined pseudo-components are then lumped into fewer number of pseudo-components using user defined method while the two-phase envelope is generated and then compared with full characterization scheme. The minimum number of pseudo-components resulting in the same two-phase envelope as full characterization scheme is the optimum number of components. As depicted in Fig. 3, the Athabasca bitumen sample can be represented by four pseudo-components. The lumped pseudo-components properties are listed in Table 2.

7. Results and discussions

As previously mentioned, the compositional analysis of Athabasca bitumen sample was used to characterize the oil. The compositions and properties of components were applied in PR-EOS. In order to fit the experimental data, the measured composition data of VLE and LLE was converted into k-values, and the exponent of binary interaction parameter equation was adjusted to match the k-values. The best fitted exponents (\( n \) in Eq. (12)) for un-lumped and lumped schemes are 0.4964 and 0.5034, respectively. Using these values, the pressure-composition (\( p-x \)) diagrams for mixtures of (Athabasca bitumen + ethane) were generated at the temperature of 22 °C as shown in Fig. 4. The VLE data are from Mehrotra and Svrcek [29] study and the LLE data from Nourozieh et al. [65] study. As depicted in the figure, the LLE was observed at overall ethane compositions greater than 18 wt% and at pressures larger than 4 MPa. Two schemes (lumped and un-lumped) accurately predict the VLE and LLE regions using the equation of state. The lumped scheme predicts the LLE separation in slightly lower overall ethane composition compared to un-lumped scheme.
Fig. 4 also demonstrates the solvent composition in the equilibrium phases at different pressures and at an overall ethane concentration of 40 wt%. As anticipated from the figure, the equilibrium compositions are reasonably predicted with two lumped and un-lumped schemes. Although the predictions show slight deviation from experimental data at higher pressures, there is a good agreement between the measured data and predicted ones.

As it was explained in the study by Nourozieh et al. [65], the solvent overall composition affects the solvent composition in equilibrium phases due to the nature of extraction process as well as the solvent affinity to extract light fractions/components. Thus, the equilibrium composition of solvent in two phases is plotted as a function of solvent overall composition at two different pressures in Fig. 5. The satisfactory predictions and similar results to experimental data were obtained for equilibrium compositions using two schemes.

It is also worth to compare the component distribution in two liquid phases excluding the solvent. This indicates how the solvent extracts the light hydrocarbon components into the lighter liquid phase, and partitions the heavy constitutes into the heavy liquid phase. Fig. 6 shows the distribution of components in two flashed-off phases taken at the equilibrium pressure of 9 MPa and a constant overall ethane composition of 40 wt%. The results indicate that the Peng-Robinson EOS coupled with the developed characterization scheme provides a good agreement not only in the solvent composition in different phases but also in the component distribution in two phases. The same plot but at a constant pressure of 5 MPa is also shown in Fig. 6. Again, the component distribution in extract and residue are well represented by the equation of state. Further investigation of results (Fig. 7) also shows that the non-distilled fractions of extract and residue are in close agreement with the lab values. The increase in overall ethane concentration or pressure leads in higher extraction of light components from the bitumen, and this results into an increase in the fraction of heavier components in the bitumen-enriched phase (L2) [65].

The proposed models (un-lumped and lumped schemes) have been examined for the solubility data over the temperature and pressure range of 20–200 °C and the pressure range of 0.1–10 MPa and they provide AARDs of 16.3% and 16.7%, respectively.

The density and viscosity of bitumen is of importance for recovery processes and their accurate predictions provide better field design and optimization. Although the density and viscosity of bitumen are usually fitted and then predicted with available correlations, the gas-saturated and solvent-diluted bitumen properties are not accurately predicted with the correlations over the wide ranges of pressures, temperatures, and solvent compositions. This is even worse when the composition of original fluid is changing with temperature, pressure, and/or solvent composition due to precipitation or formation of a second liquid phase. Thus, it is desired to model the density and viscosity of fluid or equilibrium phases while the compositional calculation is done. In WinProp, the density and viscosity of equilibrium phases were simultaneously reported with compositional calculation. Using the temperature-dependent volume shift correlation, the density of raw bitumen is well predicted over the temperature range as shown in Fig. 8 using un-lumped and lumped schemes. This indicates that the developed characterization and the defined components reasonably represent the bitumen. The viscosity of bitumen was also correlated with modified Pedersen’s correlation and the results are presented in Fig. 9. The coefficients of viscosity correlation are: $d_1 = 0.000156$, $d_2 = 2.309757$, $d_3 = 0.005902$, $d_4 = 2.216300$, and $d_5 = 0.442047$. The data is accurately modeled with this correlation over the studied temperature range.

The density of equilibrium phases with dissolved solvent is also reasonably represented by equation of state in the VLE and LLE region as shown in Fig. 10. The effect of solvent overall composition on the equilibrium densities were evaluated and compared with experimental data. The results at two pressures 5 and 9 MPa are plotted in Fig. 11. The density of light liquid phase in LLE region is slightly overestimated at higher pressure (9 MPa). This indicates that the pressure dependency of density might be not captured well in the model. Tables 3 and 4 summarize the deviation of two models from experimental data.

### 8. Conclusions

The VLE and LLE data of (Athabasca bitumen + ethane) mixtures as well as the component distribution within each phase are well represented by PR-EOS and the proposed characterization scheme. The minimum number of components to represent the multi-phase...
equilibrium was determined on the basis of two-phase envelope comparison. For the system under study, four components were found to be enough to accurately capture the equilibrium phase compositions and densities. The calibrated EOS with four components predicted multiphase equilibrium compositions, densities and viscosities within acceptable errors. The proposed models (un-lumped and lumped schemes) have been examined for the solubility data over the temperature and pressure range of 20–200 °C and the pressure range of 0.1–10 MPa and they provided AARDs of 16.3% and 16.7%, respectively. The density data were predicted with maximum AARD of 0.43%.

References