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Investigation of Different Reference Fluids for Viscosity Prediction of Raw Bitumen and Bitumen Mixture Using Corresponding-States Method

by

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Abstract

Bitumen consists of different alkane and aromatic compounds and has a greater viscosity than conventional oils. Due to its high viscosity, the mobility of bitumen and, thus, oil should be increased significantly using methods such as solvent-based and thermal recovery oil production processes. Extraction techniques, such as steam-assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS), play an important role in recovering unconventional oil, such as bitumen. A thermal and solvent based method such as expanding solvent steam-assisted gravity drainage (ES-SAGD) technique has been developed to reduce the amount of steam consumed in this process. In all of the aforementioned methods, viscosity plays an important role in the design of the processes. Viscosity is a key transport property in well-designed pipeline and process simulations and also in prediction of production rates.

In this research, the focus is on the prediction of viscosity for raw Athabasca bitumen and bitumen mixtures with solvents, such as toluene, xylene and n-decane. In the literature, viscosity corresponding states methods have been used for the prediction of viscosity, with the bitumen characterized into different pseudo-components.

Methane has been used as a reference fluid, which is quite inappropriate for bitumen viscosity calculations. This study investigates different reference fluids, such as alkane, cycloalkane and aromatic hydrocarbons. Aromatic hydrocarbons show a closer trend to bitumen viscosity. Higher molecular weight aromatics, such as 1,1 diphenylheptane, can predict Athabasca bitumen viscosity without much deviation.
The effects of temperature, pressure and solvent concentration on the prediction of viscosity are examined. The model is tested for the prediction of the viscosity of bitumen mixtures with toluene, xylene and n-decane; and, the resulting absolute deviations from the experimental data are 8.40, 8.05 and 8.54%, respectively. The Lindeloff corresponding states model is also investigated with different reference fluids for the prediction of bitumen viscosity; and, again, 1,1 diphenylheptane results in less deviation from the experimental data than the other studied reference fluids.
Acknowledgements

The author wishes to express his gratitude to Dr. Jalal Abedi for his invaluable support, guidance, encouragement and insight throughout the course of this research. I also wish to thank him for his patience during this work.

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<td>a, b</td>
<td>Adjustable parameters in eq. 3-3 and 3-4</td>
</tr>
<tr>
<td>AARD</td>
<td>Average absolute relative deviation in eq. 3-8</td>
</tr>
<tr>
<td>A, B, C</td>
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<tr>
<td>( A_p )</td>
<td>Size shape factor correction coefficient in eq. 5-14</td>
</tr>
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<td>( A_t )</td>
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<td>B, C</td>
<td>Virial coefficients in eq. 4-19 and 4-20</td>
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<td>( B_T, C_T )</td>
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</tr>
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<td>D, E, F, G</td>
<td>Adjustable parameters in eq. 5-18</td>
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<tr>
<td>( f_{\alpha,0} )</td>
<td>Parameter in eq. 4-87</td>
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<td>H</td>
<td>Hamiltonian function in eq. 4-23</td>
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<td>( h_{\alpha,0} )</td>
<td>Parameter in eq. 4-88</td>
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<tr>
<td>k</td>
<td>Adjustable parameters in eq. 3-7</td>
</tr>
<tr>
<td>( K_w )</td>
<td>Watson characterization factor in eq. 3-15</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>P</td>
<td>Absolute Pressure, bar</td>
</tr>
<tr>
<td>( P_c )</td>
<td>Critical pressure</td>
</tr>
<tr>
<td>( P_v )</td>
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</tr>
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<td>Q</td>
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<td>Universal gas constant</td>
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<td>S</td>
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<td>T</td>
<td>Absolute temperature</td>
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<tr>
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<tr>
<td>( T_b )</td>
<td>Boiling temperature</td>
</tr>
<tr>
<td>( T_c )</td>
<td>Critical temperature</td>
</tr>
<tr>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>
\( T_0 \)  
Corresponding temperature in eq. 4-72

\( T_r \)  
Reduced temperature

\( V \)  
Volume

\( V_\alpha^+ \)  
Parameter in eq. 4-92

\( V_c \)  
Critical volume

\( V_r \)  
Reduced volume

\( Z_c \)  
Critical compressibility factor

**Greek Letters**

\( \alpha \)  
Adjustable parameters in eq. 3-24

\( \alpha(T) \)  
Adjustable parameters in eq. 3-5

\( \theta \)  
Aspherical factor

\( \theta_{\alpha,o} \)  
Energy shape factor in eq. 4-89

\( \epsilon, \sigma \)  
Characteristic constants in eq. 4-21

\( \rho \)  
Density

\( \rho_o \)  
Corresponding density in eq. 4-71

\( \psi_{ij} \)  
Interaction coefficient in eq. 4-101

\( \varphi_{\alpha,o} \)  
Size shape factor in eq. 4-90

\( \mu \)  
Viscosity

\( \omega \)  
Acentric factor

**Subscripts**

ATM  
Atmospheric

\( \alpha, \beta \)  
Components

\( \alpha\beta \)  
Binary pair in mixture

calc  
Calculated

exp  
Experimental

i, j  
Components

ij  
Binary pair in mixture

mix  
Mixture

noq  
Non-spherical molecule
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>Reference fluid</td>
</tr>
<tr>
<td>q</td>
<td>Spherical molecule</td>
</tr>
<tr>
<td>x</td>
<td>Mixture</td>
</tr>
</tbody>
</table>

**Superscripts**

- **r**: Heavy reference fluid in eq. 4-94
- **o**: Simple reference fluid in eq. 4-94
Chapter 1. Introduction

1.1 General Introduction

As conventional oil reserves are being depleted, other sources of energy, such as oil sands and heavy oil, are in greater demand. Alberta’s oil sands are the second largest oil reserves in the world (approximately 175 billion barrels), after the Saudi Arabian oil reserves (estimated 250 billion barrels) (Canada. Government of Alberta, Treasury Board, 2009).

The oil sand reservoirs in Alberta typically have horizontal permeability of 5000 mD and vertical permeability of 2500 mD. The porosity of such reservoirs is around 0.32, initial oil saturation 0.85, initial water saturation 0.15 and gas saturation can be ignored. The initial temperature of the reservoir is around 10 °C and bitumen API gravity is smaller than 10 °API (Azad and Chalaturnyk, 2011).

The viscosity of bitumen can be as high as 3.5 x 10^6 cP for Christina Lake or 2 x 10^6 cP for MacKay River at 10 °C (Report Prepared for AERI Paramount Resources Ltd. 2005), which is quite high for conventional recovery processes such as waterflooding. Due to the extremely viscous behaviour, there should be special measures for bitumen production and recovery. With high viscosity, the mobility of oil is also significantly reduced; therefore, the viscosity of the oil needs to be decreased in order for it to be producible.
Oil sands consist of sand, water and bitumen. The bitumen is extracted and then further refined to produce oil. The extraction of bitumen from oil sand is performed by using hot water and caustic soda (NaOH). The mixture of oil sand, hot water and caustic soda is agitated and the bitumen can be skimmed from the top of the mixture. The oil sands have been mined since the 1960s, but since most of the bitumen in the region cannot be extracted by surface mining, the use of in situ techniques has increased. These techniques usually include the drilling of several wells, injection of high-pressure steam and recovery of the bitumen to the surface (Canada. Government of Alberta, Treasury Board, 2009).

There are different oil sands extraction techniques, including surface mining and in situ processes, such as steam-assisted gravity drainage (SAGD). These methods have different environmental and technical problems (Bushey 2011). One technical problem in SAGD and other in situ methods is the high viscosity of oil sands. Due to this issue, the mobility of oil is reduced significantly; however, with the use of thermal methods, such as steam flooding and cyclic steam stimulation, the viscosity decreases with increases in the temperature of oil sands, in order to recover the oil to the surface.

Viscosity is, therefore, a key factor in the design of such processes; and, the effects of different parameters, such as pressure, temperature and solvent concentration, should be investigated. In order to quantify the viscosity, a prediction method for different operating parameters and also different types of heavy oils is needed (Canada. Government of Alberta, Treasury Board, 2009).
In recent years, there have been developments in the SAGD process for improving the production rate, optimizing the oil-to-steam ratios, decreasing energy consumption and minimizing environmental impacts. Hydrocarbon solvents are added to the SAGD process, taking advantage of both steam and solvent for bitumen and heavy oil production. In this process, a low concentration of a hydrocarbon solvent in the vapour phase is injected with steam in a way similar to the SAGD process. The condensed solvent dissolves in the oil, causing a decrease in the viscosity of the oil (Nasr et. al. 2002). This method has been found to be feasible in field-scale projects and leads to lower heat and water consumption than with the use of steam only.

Viscosity plays an important role in the design and simulation of such processes; therefore, there should be a reliable mathematical model to predict the viscosity of the bitumen or heavy oil at different temperatures, pressures and solvent concentrations. There are different ways for determining heavy oil viscosity. One approach is the use of empirical correlations and experimental data for tuning the parameters. Experimental data on a variety of oils should be collected, since the correlation is not reliable in the absence of data. The correlation parameters need to be tuned for both dead and live oil, and experimental data for the specified ranges of pressure or temperature are needed.

To address these challenges, a corresponding states model that is more complicated but more reliable has been developed. This method shows a good ability for viscosity prediction of light oils; however, as the oil becomes heavier, the prediction capability decreases (Lindeloff et. al. 2004).
Viscosity corresponding states methods have a theoretical background and can be used for different pure substances and mixtures. These approaches usually use methane as the reference fluid, because the viscosity of methane can be determined with good approximations for wide ranges of pressures and temperatures. The use of a heavier reference fluid may be more convenient; however, the viscosity of other fluids cannot be calculated as precisely for wide ranges of pressures and temperatures. In some cases, their use may lead to a solid state of that reference fluid and the viscosity would be meaningless.

Another problem is the pressure effect on the viscosity of heavy oil: the viscosity data of most heavy components has been found at atmospheric pressure. The viscosity corresponding states model needs a pressure correction for higher pressures (Lindeloff et. al. 2004).

In order to model the viscosity of extra heavy oils, such as bitumen, the corresponding states model should be modified; and, an appropriate reference fluid should be selected. A pressure correction should also be considered for pressures higher than atmospheric. Moreover, the effect of the solvent concentration needs to be studied with bitumen/solvent mixtures.

1.2 Research Objective

The purpose of this research was the derivation of a viscosity prediction method for bitumen and bitumen/solvent systems. The main focus was on Athabasca bitumen. The method of viscosity
corresponding states was used, and the effects of different reference fluids were investigated. The effects of pressure and solvent concentration of bitumen/solvent mixtures were also studied.

Bitumen is a complex substance that contains different types of hydrocarbons, both polar and non-polar. In order to predict bitumen viscosity, it should be characterized into different pseudo-components. In the literature, there are different methods for bitumen characterization; and, each of them leads to different results; therefore, a better characterization scheme should be found for viscosity prediction.

1.3 Thesis Organization

This thesis is divided into seven chapters. The main purpose of the first chapter is a general introduction to the subject of this project. The motivation for this study and the research objective are also presented in this chapter.

In Chapter 2, the existing literature is reviewed; and, topics relevant to this project are discussed, in order to provide an appropriate foundation for this research.

In Chapter 3, bitumen characterization is examined based on literature data. There are different methods for bitumen characterization, significantly affecting the calculated model viscosity.

Chapter 4 describes the corresponding states principles theory, which provides the theoretical background for this report.
Chapter 5 includes the mathematical modeling for raw bitumen viscosity based on corresponding states principles. The effects of different reference fluids on the viscosity calculation are investigated, and the best reference fluid is selected.

In Chapter 6, bitumen mixtures with aromatic solvents, such as toluene and xylene, are investigated. Pressure and concentration corrections are considered for the corresponding states model. The mathematical model is compared with the previously published experimental data in the literature, and deviations are analyzed (Guan et al., 2013; Nourozieh et al., 2013).

Finally, Chapter 7 presents the conclusion and recommendations for improving the mathematical model to be able to predict viscosity of raw bitumen and bitumen mixtures.
Chapter 2. Literature Review

The transport properties, such as viscosity, of raw bitumen and bitumen mixtures have been studied and are reported in different research papers in the literature. Due to the wide area of viscosity studies, this review is concentrated on the correlations and corresponding states model for bitumen and heavy oil viscosity. Different experimental research works on the physical properties of bitumen, such as viscosity, density and solubility, have been conducted by Alberta Research Council’s (ARC) Heavy Oil and Oil Sands (HOOS) research department (Canada. Government of Alberta. Treasury Board 2009).

2.1 Viscous Behaviour of Bitumen Rheological Properties

Ward and Clark (1950) investigated the viscosity of bituminous samples. They reveal that oils in bituminous sands of different reservoirs and even in different layers of a reservoir are different in viscosity and specific gravity. They also mentioned that there was no approach to bring the oil sample to the surface without changing its properties. They proposed a standardized extraction procedure to measure the properties of extracted oil sand and then modified the data for the changes to the oil. The extraction of oil from a bituminous sample was done by vaporization of benzene. They claimed that bitumen showed Newtonian behaviour in their measurements.
Dealy (1979) investigated the rheological properties of oil sands from Alberta’s Athabasca, Cold Lake and Lloydminster reservoirs and showed that these bitumens exhibited mildly non-Newtonian behaviour at a very low shear rate. He mentioned that parameters, such as solvent concentration, asphaltene content and dispersed water, had strong influences on the viscous behaviour of bitumen.

Jacobs et al. (1980) studied the viscosity of Athabasca bitumen and the influence of carbon dioxide, methane and nitrogen. For achieving this purpose, they designed an experimental apparatus to investigate the viscosity of gas saturated bitumen. They observed that the viscosity decreased drastically, especially at low temperatures. By increasing the pressure and temperature, the viscosity decreased. The influence of methane was less than that of carbon dioxide; and, the alteration of viscosity can be ignored with nitrogen. It is worth mentioning that, for some temperatures above 100 °C, pressure changes did not significantly influence viscosity.

Schramm and Kwak (1988) studied the rheological behaviour of Athabasca bitumen. They observed that bitumen itself was a Newtonian substance, in which viscosity is very sensitive to temperature variation. It was found that moieties could dramatically change the behaviour of bitumen, in that bitumen froth that consisted of air, water and solids had very complicated non-Newtonian behaviour.

Poon and Kisman (1992) studied a number of heavy oils and bitumens from Alberta and Saskatchewan and reported a mixture of bitumen and a small amount of sand showed non-
Newtonian behaviour. They proposed an analytical dilatant (shear thickening) model for viscosity modeling of bitumen.

Zhao and Machel (2009) investigated Upper Devonian Grosmont Formation bitumen in Alberta and observed that it was substantially non-Newtonian, showing a distinctive shear thinning behaviour at low temperatures.

2.2 Different Mathematical Modeling and Prediction Methods for the Viscosity of Bitumen

Jacobs et al. (1980) developed a simple correlation for carbon dioxide saturated bitumen. The relationship was in terms of temperature in the following form:

\[
\log(\mu) = \frac{A}{T} + B
\]

Where \(A\) and \(B\) are empirical parameters that are determined based on experimental data and are functions of temperature.

Khan et al. (1984) studied the viscosity of Athabasca bitumen and conducted two different viscosity correlations. They modified Eyring and Hildebrand’s equations for dead-bitumen viscosity. The two double logarithm empirical models (one linear and the other nonlinear) are as follows:
\[
\ln(\ln(\mu)) = C_1 \ln(\mu) + C_2 \quad 2 - 2
\]
\[
\ln(\ln(\mu)) = [1 + b_1 T + b_2 (b_1 T)^2] e^{b_1 T} \quad 2 - 3
\]

The coefficients in the above correlations are determined based on experimental data using the least squares method. Khan et al. (1984) reported minimum and maximum average deviation ranges of 3.6 to 10.7% and showed that Equation 2-3 leads to better results in most cases. They did not consider the effect of pressure.

Mehrotra and Svrcek (1982) conducted an analysis of the solubility of the bitumen mixture with synthetic combustion gas. The viscosity and density of the mixture were also measured. They developed a pressure dependent correlation for bitumen mixture with carbon dioxide (CO\(_2\)), methane (CH\(_4\)) and nitrogen (N\(_2\)) as follows:

\[
\log \log(\mu + 0.8) = a_1 + a_2 T + \left( a_3 - \frac{a_4}{T} \right) P \quad 2 - 4
\]

They reported average deviations of 6.5, 12.2 and 1.3% for CO\(_2\), CH\(_4\) and N\(_2\) saturated bitumen, respectively. Other correlations they proposed are demonstrated in the following formulas:

\[
\log \log(\mu) = a_1 + a_2 T + \left( a_3 + \frac{a_4}{T + 273.16} \right) P \quad 2 - 5
\]
\[
\mu = (b_1 + b_2 T + b_3 P) (MW)^{(c_1 + c_2 P + c_3 T)} \quad 2 - 6
\]
Mehrotra and Svrcek (1986, 1987) studied the viscosity of pressurized bitumen. The temperature ranged from 43 to 120 °C, and the maximum pressure was 10 MPa. They discovered a substantial influence of pressure on bitumen viscosity. Based on experimental data, they developed two different correlations for bitumen viscosity:

\[
\ln(\mu) = \exp[a_1 + a_2 \ln(T)] + a_3 P_g
\]  
\[2-7\]

\[
\ln\ln(\mu) = [a_1 + a_2 \ln(T)] + a_3 P_g
\]  
\[2-8\]

Where \(P_g\) is the gauge pressure in MPa.

The reported average deviations of Athabasca bitumen were 2.8 and 1.8\% for Equation 2-7 and 2-8, respectively; and, the reported average deviations of Cold Lake were 2.2 and 2.1\%, respectively. They also revealed that, for lower density bitumen, increasing the pressure had less effect on bitumen viscosity.

Johnson et al. (1987) developed an extended corresponding states model for bitumen viscosity for gas-free and gas saturated bitumen. They modified the Ely and Hanley (1981) model for bitumen viscosity calculation. Instead of methane, the reference fluid in the original model was PSU # 625. The mathematical formulations are depicted in Equations 2-9 to 2-12 as follows:

\[
\mu_{\text{mix}}(\rho, T) = \mu_0(\rho_0, T_0)(h_{\text{mix,o}})^{2/3}(f_{\text{mix,o}})^{1/2}\left(\frac{M_{\text{mix}}}{M_0}\right)^{1/2}
\]  
\[2-9\]

\[
\rho_0 = \rho\left(\frac{\rho_{\text{CO}}}{\rho_c}\right), \quad T_0 = T\left(\frac{T_{\text{CO}}}{T_c}\right)
\]  
\[2-10\]
\[ f_{\alpha,o} = \frac{T_{ca}}{T_{co}} \theta_{\alpha,o}(T_{\alpha}, V_{\alpha}, \omega_{\alpha}) \quad 2 - 11 \]

\[ h_{\alpha,o} = \frac{V_{ca}}{V_{co}} \phi_{\alpha,o}(T_{\alpha}, V_{\alpha}, \omega_{\alpha}) \quad 2 - 12 \]

Where ‘c’ refers to critical condition and ‘o’ to reference fluid.

The mixing rule based on Ely and Hanley (1981) model is:

\[ h_{\text{mix},o} = \sum \sum z_{\alpha}z_{\beta} h_{\alpha\beta,o} \quad 2 - 13 \]

\[ f_{\text{mix},o} \cdot h_{\text{mix},o} = \sum \sum z_{\alpha}z_{\beta} f_{\alpha\beta,o} \cdot h_{\alpha\beta,o} \quad 2 - 14 \]

\[ f_{\text{mix},o}^{\frac{1}{2}} \cdot h_{\text{mix},o}^{\frac{4}{3}} \cdot M_{\text{mix}}^{\frac{1}{2}} = \sum \sum z_{\alpha}z_{\beta} f_{\alpha\beta,o}^{\frac{1}{2}} \cdot h_{\alpha\beta,o}^{\frac{4}{3}} \cdot M_{\alpha\beta}^{\frac{1}{2}} \quad 2 - 15 \]

\[ f_{\alpha\beta,o} = (1 - k_{\alpha\beta})(f_{\alpha,o} \cdot f_{\beta,o})^{\frac{1}{2}} \quad 2 - 16 \]

\[ h_{\alpha\beta,o} = \frac{1}{8} (1 - 1_{\alpha\beta}) \left( h_{\alpha,o}^{\frac{1}{3}} + h_{\beta,o}^{\frac{1}{3}} \right)^{\frac{3}{2}} \quad 2 - 17 \]

\[ M_{\alpha\beta} = \frac{2M_{\alpha}M_{\beta}}{M_{\alpha} + M_{\beta}} \quad 2 - 18 \]

They reported an average deviation of 6% from experimental data for Great Canadian Oil Sand (GCOS) bitumen viscosity. They also applied the Teja and Rice (1981) model for bitumen viscosity prediction. The mathematical model for the mixture viscosity prediction is presented in the following formula:

\[ \ln(\mu_{m}) = \ln(\mu_{z})^{r_{1}} + \frac{\omega_{m} - \omega_{r_{1}}}{\omega_{r_{2}} - \omega_{r_{1}}} [\ln(\mu_{z})^{r_{2}} - \ln(\mu_{z})^{r_{1}}] \quad 2 - 19 \]
Where superscripts $r_1$ and $r_2$ are the two reference fluids used in this model.

The mixing rule applied in this method is depicted in the following mathematical relationships:

\[ T_{cm} \cdot V_{cm} = \sum_i \sum_j X_i \cdot X_j \cdot T_{cij} \cdot V_{cij} \quad 2 - 20 \]

\[ V_{cm} = \sum_i \sum_j X_i \cdot X_j \cdot V_{cij} \quad 2 - 21 \]

\[ \omega_m = \sum_i X_i \cdot \omega_i \quad 2 - 22 \]

\[ M_m = \sum_i X_i \cdot M_i \quad 2 - 23 \]

\[ T_{cij} \cdot V_{cij} = \psi_{ij} \left( \frac{T_{cij}}{V_{cij}} \cdot V_{cij} \right)^{\frac{1}{2}} \quad i \neq j \quad 2 - 24 \]

\[ V_{cij} = \frac{1}{8} \left( V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}} \right)^3 \quad 2 - 25 \]

The term $\xi_m$ in Equation 2-19 can be calculated as follows:

\[ \xi_m = T_{cm}^{\frac{1}{5}} \cdot P_{cm}^{-\frac{2}{5}} \cdot M_m^{-\frac{1}{2}} \quad 2 - 26 \]

The other mixing rule considered for this method is:

\[ \omega_m \left( \frac{T_{cm}}{P_{cm}} \right)^{\frac{2}{3}} = \sum_i \sum_j X_i \cdot X_j \cdot \omega_{ij} \left( \frac{T_{cij}}{P_{cij}} \right)^{\frac{2}{3}} \quad 2 - 27 \]
\[
\left( \frac{T_{cm}}{P_{cm}} \right) = \sum_i \sum_j x_i \cdot x_j \left( \frac{T_{cij}}{P_{cij}} \right) \quad 2 - 28
\]

\[
\frac{T_{cm}^2}{P_{cm}} = \sum_i \sum_j x_i \cdot x_j \frac{T_{cij}^2}{P_{cij}} \quad 2 - 29
\]

\[
T_{cij} = \alpha_{ij} \left( T_{ci}, T_{cj} \right)^{\frac{1}{2}} \quad 2 - 30
\]

\[
P_{cij} = \frac{8 T_{cij}}{\beta_{ij} \left[ \left( \frac{T_{ci}}{P_{ci}} \right)^{\frac{1}{3}} + \left( \frac{T_{cj}}{P_{cj}} \right)^{\frac{1}{3}} \right]} \quad 2 - 31
\]

\[
\omega_{ij} = \frac{(\omega_i + \omega_j)}{2} \quad 2 - 32
\]

Johnson et al. (1987) reported that the mixing rule configured in Equations 2-20 to 2-25 led to better results for bitumen viscosity.

Mehrotra and Svercek (1987) investigated the method of Johnson et. al. (1987) for Athabasca, Peace River, Marguerite Lake and Wabasca bitumens. They used different characterizations for bitumen as 2, 3 and 4 pseudo-components. For the critical properties and acentric factor calculation, they applied the Lee-Kesler and Riedel correlation. They also used PSU # 625 as the reference fluid for the corresponding states formulation. The results were reported as satisfactory, since the average deviation was approximately 10% and the range of viscosity was between 0.5 and 271 cP. The reliability of the model can divided into two areas. For values of viscosity greater than 200 cP, the calculated results showed satisfactory deviations from
experimental data; however, values smaller than 200 cP had larger deviations, lowering the reliability of the model for this region.

Mehrotra and Svercek (1988) developed eight empirical correlations that applied to gas-free Alberta bitumen. They used about 90 experimental data and a viscosity range of 20 to 300 000 cP at temperatures from 13 to 130 ºC. They reported that seven out of 8 correlations resulted in a deviation of 10%; and, the one correlation with one parameter empirical coefficient led to an average deviation of approximately 6% from the experimental data.

The proposed correlation for bitumen viscosity is demonstrated in the following relationship:

\[
\log_{\log}(\mu + 0.7) = b_1 - 3.63029 \log(T)
\]

Where the value of \( b_1 \) changes for a variety of bitumens and the reported different values for seven types of Alberta bitumens.

Mehrotra et al. (1989) examined Cold Lake bitumen viscosity data and the influence of temperature on viscosity of bitumen cuts. They revealed that viscosity could be changed drastically for different cuts for the range of 4.3 to 430 000 cP. They developed a two-parameter correlation configuration for viscosity prediction, which they claimed to be validated based on experimental data of Alberta bitumen. The correlations are:

\[
\log_{\log}(\mu + 0.7) = b_1 + b_2 \log(T)
\]
They used the mixing rule for mixture viscosity from Reid et al. (1977):

\[
f(\mu_m) = \sum_{i=1}^{n} x_i f(\mu_i) \tag{2 - 35}
\]

Based on Equation 2-34, \(f(\mu_i)\) can be replaced with the following relationship:

\[
f(\mu_i) = \log(\mu_i + 0.7) \tag{2 - 36}
\]

Application of Equation 2-34 to the mixture leads to:

\[
\log(\mu_m + 0.7) = \sum_{i=1}^{n} x_i \log(\mu_i + 0.7) \tag{2 - 37}
\]

Equation 2-36 can be converted by mathematical operations to:

\[
(\mu_m + 0.7) = \prod_{i=1}^{n} (\mu_i + 0.7)^{x_i} \tag{2 - 38}
\]

The average deviation for different reported bitumen fractions varied between 0.9 and 6.6% for Cold Lake bitumen. To improve the deviation from experimental data, Mehrotra et al. (1989) proposed another form of \(f(\mu_i)\):
\[ f(\mu_i) = (M_i)^{0.5}\log(\mu_i + 0.7) \]  \hspace{1cm} 2 - 39

Equation 2-38 can be converted to Equation 2-40 for mixtures:

\[ (\bar{M})^{0.5}\log(\mu_m + 0.7) = \sum_{i=1}^{n} x_i (M_i)^{0.5}\log(\mu_i + 0.7) \]  \hspace{1cm} 2 - 40

Leading to:

\[ \log(\mu_m + 0.7) = \sum_{i=1}^{n} \left[ x_i \left( \frac{M_i}{\bar{M}} \right)^{0.5} \right] \log(\mu_i + 0.7) \]  \hspace{1cm} 2 - 41

Mehrotra et al. (1989) reported improvement in the average deviation of the bitumen viscosity.

Mehrotra (1991) proposed an empirical model for the mixture of bitumen and toluene based on the Walther empirical correlation. They changed Equation 2-34 to the following formula:

\[ \log(\mu_m + 0.8) = \sum_{i=1}^{n} x_i \log(\mu_i + 0.8) \]  \hspace{1cm} 2 - 42

As a result, Equation 2-41 changes to:
\[ \log(\mu_m + 0.7) = \sum_{i=1}^{n} \left[ x_i \left( \frac{M_i}{M} \right)^{0.5} \right] \log(\mu_i + 0.7) \]  \hspace{1cm} \text{Equation 2-43}

Mehrotra (1991) proposed a binary interaction parameter \( \beta_{ij} \) for Equation 2-43, based on experimental data for a bitumen/toluene mixture:

\[ \log(\mu_m + 0.7) = \sum_{i=1}^{n} \left[ x_i \left( \frac{M_i}{M} \right)^{0.5} \right] \log(\mu_i + 0.7) + \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \left( \frac{M_i M_j}{M^2} \right)^{0.5} \beta_{ij} \]  \hspace{1cm} \text{Equation 2-44}

They used viscosity experimental data for a temperature range of 20 to 120 °C with different diluents, such as benzene, toluene and a variety of xylenes. The average deviation varied from 1.2 to 4.8% for the bitumen mixtures and 0.2% for raw bitumen (GCOS syncrude).

In, Mehrotra (1992a, 1992b) developed a new empirical correlation model based on the temperature of liquid hydrocarbon mixtures. One coefficient correlation was incorporated as follows:

\[ \log(\mu_m + 0.8) = \Theta(\Phi T)^b \]  \hspace{1cm} \text{Equation 2-45}

Where empirical parameter \( b \) is different for different substances and depends on the molecular weight, the boiling temperature, critical properties and the acentric factor. The coefficients \( \Theta \) and \( \Phi \) for pure hydrocarbons are as follows:

\[ \Theta = 100, \quad \Phi = 0.01 \]  \hspace{1cm} \text{Equation 2-46}
The above model was developed for pure hydrocarbon. For bitumen mixtures with gas and liquid solvents, they combined Equations 2-45 with 2-44. They developed two empirical schemes in the following formulae:

\[
\log(\mu_m + 0.8) = \sum_{i=1}^{n} v_i \Theta (\Phi T)^{b_i} \tag{2-47}
\]

\[
\log(\mu_m + 0.8) = \sum_{i=1}^{n} v_i \Theta (\Phi T)^{b_i} + \sum_{i=1}^{n} \sum_{j=1}^{n} v_i v_j \beta_{ij} \tag{2-48}
\]

The term \( v_i \) can be found from:

\[
v_i = x_i \left( \frac{M_i}{M} \right)^{0.5} \tag{2-49}
\]

Mehrotra (1992a, 1992b) reported that Equation 2-45 can also be applied to bitumen viscosity with the following coefficients:

\[
\Theta = 160, \quad \Phi = 0.008 \tag{2-50}
\]

Parameter \( b \) for bitumen fractions can be found from the following correlations:

\[
b = -27.23 + 13.56 \log(M) - 1.886 [\log(M)]^2 \tag{2-51}
\]
\[ b = -40.95 + 58.74\rho - 1.886\rho^2 \]

Where \( M \) is molecular weight, and \( \rho \) is density of bitumen cut at 25 °C.

Mehrotra (1992a, 1992b) tested Equation 2-45 with the parameters in Equation 2-50 for Cold Lake bitumen cuts; and, the resulting average deviations for different fractions varied from 3.3 to 14.8%. They applied the correlation model in Equation 2-47 for CO2 saturated and toluene mixtures with Cold Lake bitumen and reported an average deviation of one order of magnitude from the experimental data.

The mixing rule scheme in Equation 2-48 was also tested with bitumen mixtures; and, they observed an improvement in the results compared to equation 2-47, although the interaction coefficient \( \beta_{ij} \) should found for every kind of bitumen.

Puttagunta et al. (1993) developed a pressure and temperature dependent empirical model for Canadian bitumen viscosity:

\[
\ln(\mu) = 2.30259 \left[ \frac{b}{1 + \frac{(T - 30)}{303.15} + C} \right] + B_0 P \exp(dT) + 2 - 53
\]

Where \( B_0, s \) and \( d \) are parameters depending on \( b, C \) is a constant, and \( b \) is characterization coefficient determined from the following empirical relationships:
\[ C = -3.002 \]
\[ B_0 = 0.0047424 b + 0.0081709 \]
\[ d = -0.0015646 b + 0.0061814 \]
\[ s = 0.0066940 b + 3.53641 \]
\[ b = \log(\mu_{30\degree C}) - C \]

The average deviations for Cold Lake, Athabasca and dried cold-bailed Cold Lake bitumens at different pressures and temperatures were 2.32, 4.43 and 3.85%, respectively.

Miadonye et al. (1994) presented a one-parameter empirical correlation for calculating bitumen and heavy oil viscosity. The correlation incorporated in their study was based on the curvilinear behaviour of bitumen viscosity with respect to temperature. The general model is presented in the following relationship:

\[ \log(\mu_{P=atm, x=0}) = \left[ \frac{b}{1 + \left( \frac{T - 30}{303.15} \right)^s} \right] + C \]

Where parameters \( b \), \( d \) and \( s \) can be determined from Equations 2-58, 2-54 and 2-57, respectively.

Equation 2-59 was modified for considering the effects of pressure and solvent concentration on bitumen viscosity based on the Briggs et al. correlation:
\[ \ln(\mu_{p,T,X}) = \ln(\mu_{p,T,X}) + B_T \rho - C_T X \]  
\[ B_T = B_0 \exp(-DT) \]  
\[ C_T = C_0 \exp(-ET) \]

Where \( X \) represents the mole fraction of the solvent, and \( B_T, C_T, B_0, C_0, D \) and \( E \) are empirical coefficients determined based on experimental data.

Miadonye et al. (1994) applied the model to different Alberta bitumens and reported the average deviations for Cold Lake, Peace River, Wabasca, Marguerite Lake and Athabasca bitumens as 4.41, 6.24, 5.08, 4.13 and 1.86%, respectively.

Miadonye et al. (1995) incorporated a general empirical correlation for bitumen mixture like GCOS synthetic crude, mobile solvent and naphtha. The experimental data was gathered at 30 °C and 1 atmosphere. They used 300 data points, and the reported average deviation was 8.7%. They discovered that, as the dissimilarity increases between the bitumen and the solvent, the correlation deviation also increases.

Miadonye et al. (2000) developed a new empirical model for the kinematic viscosity of raw bitumen and bitumen mixtures. The main advantage of this correlation is that no or a minimum data point is needed for an accurate viscosity prediction of bitumen mixtures. They considered the bitumen and solvent as pure substances. The correlation is:

\[ \ln(v_m) = \exp[a(1 - X_D^n)] + \ln(v_D) - 1 \]  
\[ a = \ln[\ln(v_B) - \ln(v_D) + 1] \]
\[ n = \frac{v_D}{0.9029v_D + 0.1351} \quad 2 - 65 \]

Where \( v_D \), \( v_B \) and \( v_m \) are the kinematic viscosities of pure diluent, pure bitumen and bitumen mixtures, respectively. The mass fraction of the diluent can be found from the following formula:

\[ Ln(X_D) = \frac{Ln\left\{a - Ln[Ln(v_m) - Ln(v_D) + 1]\right\}}{n} \quad 2 - 66 \]

Miadonye et al. (2000) applied the above correlation to different bitumens such as Lloydminster, Suncor and Syncrude, and diluents, such as diesel, naphtha, toluene, strachen and rimby. The average deviation was approximately 13.5%. The kinematic viscosity range of the data used in this study was between 100 to 1*10^6 cSt.

In 2004, Lindeloff et al. (2004) presented a corresponding states method for calculating heavy oil viscosities. They compared advantages and disadvantages of empirical correlations versus corresponding states principles. The main advantage of correlations was their simplicity. One disadvantage included the need for experimental data points to tune the coefficients of the model. Another disadvantage of the correlations was the risk that a correlation for dead oil would be applied to live oil, since it also contains solution gas. Pedersen et al. (1984) proposed the following equation for modeling the viscosity of mixture:

\[ \mu_{mix}(P, T) = \left(\frac{T_{C,mix}}{T_{CO}}\right)^{-1/6} \left(\frac{P_{C,mix}}{P_{CO}}\right)^{2/3} \left(\frac{M_{mix}}{M_o}\right)^{1/2} \frac{\alpha_{mix}}{\alpha_o} \mu_o(P_o, T_o) \quad 2 - 67 \]
Where the corresponding pressure and temperature, $P_0$ and $T_0$, can be found with the following formulae:

$$
P_0 = P \left( \frac{P \cdot P_{\text{co}} \cdot \alpha_0}{P_{\text{mix}} \cdot \alpha_{\text{mix}}} \right) \quad T_0 = T \left( \frac{T \cdot T_{\text{co}} \cdot \alpha_0}{T_{\text{mix}} \cdot \alpha_{\text{mix}}} \right)
$$

$$
2 - 68
$$

Where subscript $o$ in the above formula represents the reference fluid, which was methane in this case.

The mixing rules that Mo and Gubbins (1976) presented for the calculations of $P_{\text{mix}}$, $T_{\text{mix}}$ and $M_{\text{mix}}$ are as follows:

$$
T_{\text{mix}} = \frac{\sum \sum z_i z_j \left[ \left( \frac{T_{\text{ci}}}{P_{\text{ci}}} \right)^{1/3} + \left( \frac{T_{\text{cj}}}{P_{\text{cj}}} \right)^{1/3} \right]^3}{\sum \sum z_i z_j \left[ \left( \frac{T_{\text{ci}}}{P_{\text{ci}}} \right)^{1/3} + \left( \frac{T_{\text{cj}}}{P_{\text{cj}}} \right)^{1/3} \right]}
$$

$$
2 - 69
$$

$$
P_{\text{mix}} = 8 \* \frac{\sum \sum z_i z_j \left[ \left( \frac{T_{\text{ci}}}{P_{\text{ci}}} \right)^{1/3} + \left( \frac{T_{\text{cj}}}{P_{\text{cj}}} \right)^{1/3} \right]^3 \sqrt{T_{\text{ci}} T_{\text{cj}}}}{\left( \sum \sum z_i z_j \left[ \left( \frac{T_{\text{ci}}}{P_{\text{ci}}} \right)^{1/3} + \left( \frac{T_{\text{cj}}}{P_{\text{cj}}} \right)^{1/3} \right] \right)^2}
$$

$$
2 - 70
$$

$$
M_{\text{mix}} = 1.304 \* 10^{-4} \left( \bar{M}_W^{2.303} - \bar{M}_n^{2.303} \right) + \bar{M}_n
$$

$$
2 - 71
$$

The remaining parameters are depicted in the following formulae:
\[ \bar{M}_W = \frac{\sum z_i M_i^2}{\sum z_i M_i} \]  
\[ \bar{M}_n = \sum z_i M_i \]  
\[ \alpha_{\text{mix}} = 1 + 7.378 \times 10^{-3} \rho_r^{1.847} M_{\text{mix}}^{0.5173} \]  
\[ \rho_r = \frac{P \left( \frac{P_{\text{Co}}}{P_{\text{C,mix}}}, \frac{T}{T_{\text{Co}}} \right)}{\rho_{\text{Co}}} \]

The viscosity of methane as the reference fluid was correlated based on the Ely and Hanley (1981) method as follows:

\[ \mu(\rho, T) = \mu_0(T) + \mu_1(T) \rho + \Delta \mu'(\rho, T) \]

The density of methane is also depicted based on McCarty (1974):

\[ P = \sum_{n=1}^{9} a_n(T) \rho^n + \sum_{n=10}^{15} a_n(T) \rho^{2n-17} e^{\gamma \rho^2} \]

Lindeloff et al. (2004) proposed another correlation as an alternative method to Equation 2-67 based on Rønningersen (1993) with the formula of:

\[ \log(\mu) = -0.07995 - 0.01101 M - \frac{371.8}{T} + \frac{6.215 M}{T} \]

Where \( M \) is average molecular weight of the oil.
Different types of oil are usually moderately non-Newtonian, but this method only works in Newtonian region.

The influence of wax was ignored at temperatures more than 30 °C. They also distinguished between dead and live oil by using:

\[
\frac{M_W}{M_n} \leq 1.5 \Rightarrow M = M_n \tag{2-79}
\]

\[
\frac{M_W}{M_n} > 1.5 \Rightarrow M = M_n \left( \frac{M_W}{1.5 M_n} \right)^{0.5} \tag{2-80}
\]

Where \(M_W\) and \(M_n\) can be calculated from Equations 2-72 and 2-73.

Lindeloff et al. (2004) revealed that, for viscosities higher than 10 cP, which corresponds to a reference fluid temperature of approximately 60 K, Equation 2-67 cannot truly predict the oil viscosity. Therefore, Equation 2-78 should be used in conjunction with the corresponding states principle. The average molecular weight \(M\) in Equation 2-78 can also be found from Equation 2-79 or Equation 2-80. The effect of pressures higher than atmospheric should also be considered. They offered the following relationship for pressure correction:

\[
\frac{1}{\mu} \frac{\partial \mu}{\partial P} = 0.008 \frac{1}{atm} \tag{2-81}
\]

The summary of calculation procedure they offered is as follows:
1) \( T_{C,\text{mix}} \) and \( P_{C,\text{mix}} \) are determined from Equations 2-69 and 2-70,

2) Density of the reference fluid (methane) is determined from Equation 2-76,

3) \( M_{\text{mix}} \) and \( \alpha_{\text{mix}} \) are determined from Equations 2-73 and 2-74,

4) Corresponding pressure and temperature, \( P_0 \) and \( T_0 \), are determined from Equation 2-68,

5) For \( T_0 > 75 \), use corresponding states formula of Equation 2-67,

6) For \( T_0 < 65 \), apply Equations 2-78 to 2-80,

7) If \( 65 < T_0 > 75 \), average viscosity is determined from Equations 2-67 and 2-78, and

8) For pressures higher than atmospheric pressure, the correction in Equation 2-81 should be applied.

The above model was applied to eight types of oil, and the results showed an improvement in classic corresponding states principle of Equation 2-67. Lindeloff et al. (2004) also proposed values of 1.5 and 0.5 in Equation 2-80 as the tuning parameters. This led to better results when compared with experimental data. They reported that, for viscosities lower than 20 cP, the calculated data had a deviation of approximate 25%. For higher values, there were deviations of 200 to 300% from the experimental data points.

Cisneros and Andersen (2005) presented a viscosity model based on friction theory (f-theory) for the prediction of viscosity of heavy oil. They applied this model to oils with molecular weight up to approximately 200 gr/mole and viscosity of maximum 10 cP at reservoir condition. They applied a characterization procedure to the oil and also used a cubic equation-of-state model (van der Waals type) for calculations of the thermodynamic properties. A compressibility correction
factor was also considered in conjunction with the equation-of-state model of pressure, volume and temperature (PVT) calculations for the viscosity prediction of heavy oil.

The characterization of heavy oil was conducted based on chi-squared distribution ($\chi^2$) function and p degrees of freedom, until the C$_{7+}$ fraction is reached. Cisneros and Andersen (2005) applied this model to seven different heavy oils. The absolute average deviation (AAD) for all experimental data was approximately 7.5%. However, regarding the bias of the calculation data versus experimental data, the deviation was 1.9%, which was quite appropriate. They also considered bubble point pressure in the modeling data.

Zhang et al. (2007) measured the viscosities of the Liaohe basin in northeast China in a temperature range of 40 to 90 °C, and viscosities between 76 and 34590 cP were found at 50 °C. They developed a correlation between the viscosity and the temperature of the oil. They revealed that viscosities at different temperatures (i.e. $T = 60, 70, 80$ and $90$ °C) were strongly dependent on the viscosity at 50 °C ($\mu_{50}$). The empirical model is depicted in the following relationship:

$$\mu_T = a \cdot \mu_{50}^b$$  \hspace{2cm} 2 - 82

Where $a$ and $b$ are coefficients and are functions of temperatures as follows:

$$a = f(T)$$  \hspace{2cm} 2 - 83

$$b = f. I(T)$$  \hspace{2cm} 2 - 84
Consequently, a decent correlation was incorporated with the viscosity value at the temperature of 50 °C. Finally, using experimental data and applying curve fitting analysis, the coefficients $a$ and $b$ take the form:

\[
\begin{align*}
a &= 0.0147 \ln(T) + 0.9423, & R^2 &= 0.9998 \\
b &= 3.1613 - 0.5525 \ln(T), & R^2 &= 1.0000
\end{align*}
\]

Zhang et al. (2007) tested the above correlation with experimental data from the Liaohe Oilfield Company, and the reported error was less than 10% for most cases. They also discovered that the model depended on the region that the oil sample was collected. However, the method will be useful with different coefficients for other regions. It is worth mentioning that they did not consider the effect of pressure on oil viscosity.

Yarranton and Satyro (2009) developed an expanded fluid-based viscosity correlation model for pure hydrocarbons, hydrocarbon mixtures and bitumen. The viscosities of pure hydrocarbons were considered as a function of density. The functionality was in the following form:

\[
\mu - \mu_G = c_1 \left[ \exp(c_2 \beta) - 1 \right]
\]

Where $\mu_G$ is the viscosity of gas, $c_1$ and $c_2$ are the fitting parameters, and $\beta$ is modeled in the following relationship:

\[
\beta = \frac{1}{\exp \left[ \left( \frac{\rho_*}{\rho} \right)^n - 1 \right] - 1}
\]
Yarranton and Satyro (2009) mentioned that the form in Equation 2-87 led to satisfactory results at atmospheric pressure and moderate temperature. They made a pressure correction in parameter $\rho_s^*$ in the following formula:

$$\rho_s^* = \frac{\rho_s^0}{\exp(-c_3 \cdot P)} \quad 2 - 89$$

Where $\rho_s^0$ is the compressed state density in vacuum and $c_3$ is a fitting coefficient.

The input parameters are fluid density pressure and gas viscosity. Five coefficients (i.e. $\rho_s^0$, $n$, $c_1$, $c_2$ and $c_3$) should be determined. The typical values for pure hydrocarbons are as follows:

$$n = 0.65 \quad 2 - 90$$

$$c_1 = 0.165 \quad 2 - 91$$

$$c_2 = 0.241 \mu_{25^\circ} 0.13 \quad 2 - 92$$

$$c_3 = 1.68 \times 10^{-8} M^{0.5} \left(\frac{1}{kPa}\right) \quad 2 - 93$$

Where $\mu_{25^\circ}$ and $M$ are the viscosity at 25 °C and molecular weight, respectively.

Parameter $\rho_s^0$ is found from the least square method using the following objective function to minimize the error:

$$\text{OF} = \sum \left[ \ln \left( \frac{\mu_{\text{corr}}}{\mu_{\text{exp}}} \right) \right]^2 \quad 2 - 94$$
At least one experimental datum is needed to find $\rho_s^o$. Yarranton and Satyro (2009) tested the above model to different liquid-saturated n-alkanes, and the AAD for 1273 experimental data points was 0.019. The AAD was 0.023 for other alkanes, cycloalkanes and aromatics for 1577 data points. For hydrocarbon mixtures, the following mixing rules should be considered (volumetric basis):

\[
\rho_{s,\text{mix}}^o = \sum_{i=1}^{m} \varphi_i \rho_{s,i}^o 
\]

\[
c_{2,\text{mix}} = \sum_{i=1}^{m} \varphi_i c_{2,i} \tag{2-96}
\]

\[
c_{3,\text{mix}} = \frac{1}{\sum_{i=1}^{m} \varphi_i c_{3,i}} \tag{2-97}
\]

Where $m$ is number of components, and $\varphi_i$ is the volume fraction of each component. $n$ and $c_1$ are the same for every hydrocarbon component, so there is no need for any mixing rule.

The mixing rule for an ideal volumetric case has been developed as follows:

\[
\ln(\mu_{\text{mix}}) = \sum_{i=1}^{m} \varphi_i \ln(\mu_i) \tag{2-98}
\]

For real cases, the binary interaction coefficient $k_{ij}$ is introduced as:
\[
\ln(\mu_{\text{mix}}) = \sum_{i=1}^{m} \varphi_i \ln(\mu_i) + \varphi_i \phi_k \nu_j \quad 2 - 99
\]

For bitumen viscosity prediction, Cold Lake bitumen mixed with toluene was considered. The following correlation was applied for Cold Lake bitumen density as a function of temperature:

\[
\rho_{\text{CL}} = 1010 - 0.63T \quad 2 - 100
\]

The reported average absolute percentage relative deviation (AAPRD) and maximum absolute percentage relative deviation (MAPRD) were 17 and 47%, respectively.

Satyro and Yarranton (2010) modified the previous model for viscosity calculation. The parameter \(\rho_{s^*}\) was formulated in the following form:

\[
\rho_{s^*} = \frac{\rho_{s^0}}{1 - c_4[1 - \exp(-c_3 P)]} \quad 2 - 101
\]

Where coefficients \(c_3\) and \(c_4\) are correlated as follows:

If \(\text{MW} \leq 97\)
\[
c_4 = 0.015 + 0.00042[50 - \text{MW}] \quad 2 - 102
\]

If \(\text{MW} > 97\)
\[
c_4 = 0.035 \quad 2 - 103
\]

\[
c_3 = 1.435 \times 10^{-6} \text{MW}^{0.4267} \quad 2 - 104
\]
In previous work, Satyro and Yarranton (2009) used experimental data for density; and, in this part, the APR (advanced Peng-Robinson) model was used for liquid density prediction (Satro 2009).

Gas viscosity for each component $\mu_{G,i}$ is a function of temperature as shown in the following formula:

$$\mu_{G,i} = A_i + B_i T + C_i T^2$$  \hspace{1cm} (2 - 105)

Where $A_i$, $B_i$ and $C_i$ are curve fitting coefficients that can be determined from a Virtual Materials Group (VMGsim) database.

The mixing rules are as follows:

$$\rho_{s, mix} = \sum_{i=1}^{m} \sum_{j=1}^{m} \varphi_i \varphi_j \frac{(\rho_{s,i}^o + \rho_{s,j}^o)}{2} (1 - \beta_{ij})$$  \hspace{1cm} (2 - 106)

$$\mu_{G} = \frac{\sum_{i=1}^{m} x_i \mu_{G,i}}{\sum_{j=1}^{m} x_j \Phi_{ij}}$$  \hspace{1cm} (2 - 107)

Where:

$$\Phi_{ij} = \left[ 1 + \left( \frac{\mu_{G,i}}{\mu_{G,j}} \right)^{0.5} \left( \frac{MW_i}{MW_j} \right)^{0.25} \right]^2 \left[ 8 \left( 1 + \left( \frac{MW_i}{MW_j} \right) \right)^{0.5} \right]$$  \hspace{1cm} (2 - 108)
The application of the model to mixtures of Cold Lake bitumen and toluene was investigated for a temperature range of 20 to 120 °C. The total average absolute relative deviation (AARD) reported was 15.5%.

Motahari et al. (2011) applied the expanded fluid correlation model to dead and live bitumen and bitumen mixtures in a temperature range of 20 to 175 °C and at a maximum pressure of 10 MPa. The reported AARD for dead bitumen was 11% and for live bitumen, 20 to 28%. For bitumen mixtures with condensate for dead and live bitumen with a range of solvent concentrations of 3 to 30 wt%, the AARDs were 16 and 37%, respectively.

Zirrahi et al. (2011) developed a semi-theoretical model to predict the viscosity of mixtures of bitumen and solvents, such as methane, ethane, carbon dioxide and nitrogen. The Arrhenius mixing rule was used, and the cubic plus association (CPA) equation of state (EOS) was considered in this model. The absolute deviation they reported varied in the range of 5.4% for methane saturated bitumen to 21.2% for carbon dioxide saturated bitumen.

Guan et al. (2012) developed an experimental setup to measure the density and viscosity of mixtures of Athabasca bitumen and aromatic solvents, such as toluene and xylenes. The experimental data of the bitumen mixtures were gathered in a temperature range of ambient up to 343.15 K and in a pressure range of atmospheric up to 10 MPa. The weight fraction of the solvents was varied from 0.05 to 0.6.
Different correlation models were used in their work, and those correlations were associated with different mixing rules. The reported AARD varied from 1.7 to 2.1% for raw bitumen. For bitumen mixtures, the reported AARD was 14.8% for bitumen and toluene mixtures and 13.8% for bitumen and xylenes mixtures, based on Lederer’s correlation model. Consequently, they proposed Lederer’s correlation model for viscosity prediction of Athabasca bitumen mixtures with aromatics, such as toluene and xylenes.

Nourozieh et al. (2013) measure the density and viscosity of mixtures of Athabasca bitumen and n-decane. The temperature range was varied from ambient to 343 K and the pressure range was up to 10 MPa. The solvent weight fraction was in the range of 0.05 to 0.5. Different correlation models were tested with the gathered experimental data for different pressures, temperatures and solvent (n-decane) weight fractions. The AARDs they reported in their work were different for a variety of correlations and mixing rules. The AARDs for binary mixtures of Athabasca bitumen and n-decane were 9.6% for the Power law model, 9.9% for Arrhenius’ model, 10.8% for Lederer’s model and 15.9% for Cragoe’s model. Based on the observed deviation of the calculated results of different correlation models from the experimental data, they proposed the Power law correlation model for estimating the viscosity of Athabasca bitumen mixed with n-decane.

The above mentioned correlation models should be coupled with experimental data to find their tuning parameters. The correlations are not reliable outside the range of validity. Although The corresponding-states model are more complicated and need bitumen to be characterized into pseudo-components, they are reliable and can be used for a wide range of pressure, temperature
and solvent concentration. The purpose of this study is to develop a mathematical model for viscosity prediction of bitumen that can be valid for a wide range of operating conditions.
Chapter 3. Bitumen Characterization

Bitumen is a complicated material and contains different light, heavy, polar and non-polar components. In the literature, it usually divided into two main cuts: maltene and asphaltene. Maltene is commonly attributed to the soluble fraction and asphaltene to non-soluble part of bitumen and heavy oil. The maltene cut can also be separated into distillable and non-distillable components. Non-distillable fractions decompose at temperatures higher than 600 °C. The distillable part is composed of saturated hydrocarbons and aromatics, and the non-distillable fraction is usually called resins. The asphaltene part can be separated from bitumen by dissolution in n-heptane as a solvent (Johnson 1985).

There are two methods in the literature for oil characterization. One method defines pseudo-components for oil characterization, and the other is the continuous mixture method. The first method is usually used for bitumen characterization, since it consists of different types of hydrocarbons. The second method is suitable for oil that consists of only one type of hydrocarbon, which is not the case for bitumen. Bitumen usually separates into different pseudo-components based on a variety of hydrocarbon types, such as saturates, aromatics, resins and asphaltenes (SARA) fractions or cuts (Kariznovi et. al. 2009; Johnson 1985).

The experimental data for bitumen fractions are based on simulated distillation or true boiling point curves. These pseudo-components can be lumped to form different schemes for calculating thermodynamic properties of an unknown structured material, such as bitumen (Johnson 1985).
The physical and critical properties of hypothetical components can be calculated through different correlations, based on the specific gravity and boiling point or molecular weight found from experimental data (Johnson 1985). The Lee-Kesler correlation is able to calculate the critical temperature \( T_C \), critical pressure \( P_C \) and acentric factor based on the boiling point and specific gravity of different components (Kesler and Lee 1976).

The Cavett correlations calculate critical pressure \( P_C \) and critical temperature \( T_C \) based on the API gravity and boiling point. The Riazi-Daubert method correlates critical temperature \( T_C \), critical temperature \( P_C \), critical volume \( V_C \), molecular weight \( MW \) and boiling point \( T_b \) according to the specific gravity, with \( MW \) or \( T_b \) as input. Twu correlations are able to predict \( T_C \), \( P_C \), \( V_C \) and the specific gravity based on the \( T_b \) and \( MW \) of the components (Cavett 1962; Riazi and Daubert 1987; Twu 1984).

The number of pseudo-components is another parameter in bitumen characterization. By increasing the number of pseudo-components, the tuning parameter for fitting the experimental data points is increased, and the uncertainty in the critical and physical properties in the correlations is increased (Kariznovi et. al. 2009).

The pseudo-components represent the different bitumen fractions, which are abbreviated as SARA. As previously mentioned, bitumen can be divided into maltene and asphaltene cuts. The maltene fraction is divided into distillable and non-distillable parts according to their boiling points. Johnson (1985) proposed a 4-pseudo-component bitumen characterization for Great
Canadian Oil Sand (GCOS) bitumen, as shown in Table 3-1. As can be seen the boiling points of pseudo-components PC1 and PC2 were lower than 600 °C (873.15 K) and could be considered as saturate and aromatic parts. PC3, with a boiling point higher than 600 °C, was the resin fraction, and PC4 was the asphaltene cut. (Kariznovi et. al. 2009; Johnson 1985)

Table 3-1: GCOS Athabasca bitumen characterization (4 pseudo-component scheme) (Johnson 1985)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>8.08</td>
<td>200</td>
<td>0.9769</td>
<td>550.7</td>
<td>774.2</td>
<td>2.715</td>
<td>0.594</td>
<td>0.505556</td>
</tr>
<tr>
<td>PC2</td>
<td>31.52</td>
<td>374</td>
<td>1.0508</td>
<td>743.2</td>
<td>947.4</td>
<td>1.555</td>
<td>1.130</td>
<td>0.901369</td>
</tr>
<tr>
<td>PC3</td>
<td>41.2</td>
<td>610</td>
<td>1.0819</td>
<td>952.6</td>
<td>1103.3</td>
<td>0.752</td>
<td>2.382</td>
<td>1.389634</td>
</tr>
<tr>
<td>PC4</td>
<td>19.2</td>
<td>1089</td>
<td>1.1601</td>
<td>1421.1</td>
<td>1437.1</td>
<td>0.120</td>
<td>17.8</td>
<td>2.215240</td>
</tr>
</tbody>
</table>

Johnson (1985) also proposed one pseudo-component scheme characterization for GCOS Athabasca bitumen, as shown in Table 3-2.

Table 3-2: GCOS Athabasca bitumen characterization (1 pseudo-component scheme) (Johnson 1985)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>100</td>
<td>594.6</td>
<td>1.077</td>
<td>937.1</td>
<td>1090.9</td>
<td>0.786</td>
<td>2.271</td>
<td>1.3611</td>
</tr>
</tbody>
</table>

39
Mehrotra and Svrcek (1987) characterized Athabasca (ARC) bitumen into two, three and four pseudo-components, which are depicted in Tables 3-3, 3-4 and 3-5.

Table 3-3: ARC Athabasca bitumen characterization (2 pseudo-component scheme) (Mehrotra and Svrcek 1987)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>81.8</td>
<td>459</td>
<td>0.960</td>
<td>779.5</td>
<td>935.5</td>
<td>0.974</td>
<td>1.663</td>
<td>1.2481</td>
</tr>
<tr>
<td>PC2</td>
<td>18.2</td>
<td>1083</td>
<td>1.180</td>
<td>1459.0</td>
<td>1471.2</td>
<td>0.110</td>
<td>25.263</td>
<td>2.3209</td>
</tr>
</tbody>
</table>

Table 3-4: ARC Athabasca bitumen characterization (3 pseudo-component scheme) (Mehrotra and Svrcek 1987)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>39.3</td>
<td>360</td>
<td>0.960</td>
<td>702.0</td>
<td>882.2</td>
<td>1.365</td>
<td>1.187</td>
<td>0.9444</td>
</tr>
<tr>
<td>PC2</td>
<td>42.5</td>
<td>550</td>
<td>1.050</td>
<td>887.0</td>
<td>1045.8</td>
<td>0.872</td>
<td>2.004</td>
<td>1.3454</td>
</tr>
<tr>
<td>PC3</td>
<td>18.2</td>
<td>1083</td>
<td>1.165</td>
<td>1426.0</td>
<td>1442.8</td>
<td>0.120</td>
<td>18.066</td>
<td>2.2976</td>
</tr>
</tbody>
</table>
Table 3-5: ARC Athabasca bitumen characterization (4 pseudo-component scheme) (Mehrotra and Svrcek 1987)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>18.0</td>
<td>245</td>
<td>0.970</td>
<td>598.0</td>
<td>809.5</td>
<td>2.175</td>
<td>0.740</td>
<td>0.6317</td>
</tr>
<tr>
<td>PC2</td>
<td>21.3</td>
<td>430</td>
<td>1.035</td>
<td>785.0</td>
<td>970.3</td>
<td>1.254</td>
<td>1.384</td>
<td>1.0978</td>
</tr>
<tr>
<td>PC3</td>
<td>42.5</td>
<td>564</td>
<td>1.070</td>
<td>909.0</td>
<td>1069.2</td>
<td>0.860</td>
<td>2.069</td>
<td>1.3582</td>
</tr>
<tr>
<td>PC4</td>
<td>18.2</td>
<td>1083</td>
<td>1.160</td>
<td>1416.0</td>
<td>1434.0</td>
<td>0.123</td>
<td>16.905</td>
<td>2.2914</td>
</tr>
</tbody>
</table>

Kariznovi et al. (42) presented a 6 pseudo-component Athabasca bitumen characterization method as depicted in Table 3-6. The first 3 pseudo-components, PC1 to PC3, can be attributed as saturates and aromatics. PC4 and PC5 are resins, and PC6 can be considered as asphaltene.

Table 3-6: Athabasca bitumen characterization scheme (6 pseudo-component scheme) (Kariznovi et. al. 2009)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole %</th>
<th>MW</th>
<th>SG</th>
<th>T_b(K)</th>
<th>P_c(atm)</th>
<th>T_c(K)</th>
<th>Acentric Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>9.7</td>
<td>205</td>
<td>0.93</td>
<td>583.1</td>
<td>20.31</td>
<td>784.1</td>
<td>0.591</td>
</tr>
<tr>
<td>PC2</td>
<td>7.53</td>
<td>350</td>
<td>1.02</td>
<td>761.4</td>
<td>12.93</td>
<td>947.7</td>
<td>0.951</td>
</tr>
<tr>
<td>PC3</td>
<td>24</td>
<td>435</td>
<td>1.05</td>
<td>830.8</td>
<td>10.84</td>
<td>1008.0</td>
<td>1.085</td>
</tr>
<tr>
<td>PC4</td>
<td>33.6</td>
<td>540</td>
<td>1.08</td>
<td>897.9</td>
<td>9.21</td>
<td>1066.3</td>
<td>1.202</td>
</tr>
<tr>
<td>PC5</td>
<td>16.9</td>
<td>750</td>
<td>1.12</td>
<td>995.7</td>
<td>7.21</td>
<td>1149.2</td>
<td>1.363</td>
</tr>
<tr>
<td>PC6</td>
<td>8.27</td>
<td>1100</td>
<td>1.20</td>
<td>1128.4</td>
<td>5.75</td>
<td>1274.0</td>
<td>1.502</td>
</tr>
</tbody>
</table>
For bitumen mixture with gases like carbon dioxide, methane and ethane, Kariznovi et. al. (2009) applied the Peng-Robinson (PR) equation of state for calculating the thermodynamic properties of bitumen. They applied the following procedure:

1) Dividing the bitumen into pseudo-components,
2) Estimating the critical and physical properties of the pseudo-components using correlations, such as those of Lee-Kesler and Twu,
3) Estimating the gas solubility in bitumen using PR equation of state and applying the modification parameters using CMG WINPROP software,
4) Investigating the influence of the variety of characterization configurations and comparing the calculated results with experimental data, and
5) Finding the universal characterization scheme regardless of the type of bitumen (Kariznovi et. al. 2009).

The details of the characterization procedure of bitumen can be found in Kariznovi et al. (2009).

The average molecular weight of bitumen is calculated based on pseudo-components and can be formulated as follows:

\[
\overline{MW} = \sum_{i=1}^{N} x_i MW_{PCI} \]

Where \( x_i \) is the mole fraction of each pseudo-component, and \( MW_{PCI} \) is the molecular weight of each pseudo-component (Kariznovi et al. 2009).
The PR equation of state in the original form is as follows:

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

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

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

\[
\alpha(T) = \left[1 + k(1 - T_r)\right]^2
\]

\[
T_r = \frac{T}{T_c}
\]

\[
k = 0.37464 + 1.54226 \omega - 0.26992 \omega^2
\]

The coefficients in Equations 3-3 and 3-4 are modified by using CMG WINPROP software into \(\Omega a\) and \(\Omega b\), which are used as tuning parameters for bitumen characterization. Since bitumen consists of various complex components from non-polar and spherical molecules to polar and non-spherical molecules, the modification to PR equation of state is necessary for bitumen characterization (Kariznovi et al. 2009).

The average absolute deviation (AARD) is defined in the following mathematical formula:

\[
AARD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right|
\]
The AARD is used as a criterion of converging the mathematical modeling results to experimental data points. The universal pseudo-components are defined with fixed physical and critical properties for a variety of types of bitumen. The properties and configuration of universal scheme are shown in Table 3-7. The critical and physical properties of the pseudo-components are estimated using Lee-Kesler and Twu correlations (Kariznovi et al. 2009).

Table 3-7: Bitumen characterization for a universal scheme (Kariznovi et al. 2009)

<table>
<thead>
<tr>
<th>Component</th>
<th>MW</th>
<th>SG</th>
<th>T_b(K)</th>
<th>P_c(atm)</th>
<th>T_c(K)</th>
<th>Acentric Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>150</td>
<td>0.8</td>
<td>195.2</td>
<td>22.84</td>
<td>784.1</td>
<td>0.493</td>
</tr>
<tr>
<td>PC2</td>
<td>205</td>
<td>0.9</td>
<td>298.8</td>
<td>19.41</td>
<td>947.7</td>
<td>0.656</td>
</tr>
<tr>
<td>PC3</td>
<td>335</td>
<td>0.97</td>
<td>454.4</td>
<td>12.51</td>
<td>1008.0</td>
<td>0.999</td>
</tr>
<tr>
<td>PC4</td>
<td>510</td>
<td>1.065</td>
<td>604.3</td>
<td>9.47</td>
<td>1066.3</td>
<td>1.234</td>
</tr>
<tr>
<td>PC5</td>
<td>650</td>
<td>1.09</td>
<td>674.8</td>
<td>7.80</td>
<td>1149.2</td>
<td>1.363</td>
</tr>
<tr>
<td>PC6</td>
<td>1100</td>
<td>1.16</td>
<td>839.3</td>
<td>5.22</td>
<td>1274.0</td>
<td>1.604</td>
</tr>
</tbody>
</table>

Correlations, such as those of Lee-Kesler and Twu, can be used for the physical and critical properties estimations. The Lee-Kesler correlations are as follows (Kesler and Lee 1976):

\[
T_c = 341.7 + 811S + (0.4244 + 0.1174SG)T_b + (0.4669 - 3.2623S) \times \frac{10^5}{T_b} \\
3 - 9
\]

\[
\ln(P_c) = 8.3634 - \frac{0.0566}{S} - \left(0.24244 + \frac{2.2898}{S} + \frac{0.11857}{S^2}\right) \times 10^3T_b \\
3 - 10
\]
\[
\omega = \frac{\left(\ln(T_{br}) - 5.92714 + \frac{6.09648}{T_{br}} + 1.28862\ln(T_{br}) - 0.169347T_{br}^6\right)}{\left(15.2518 - \frac{15.6875}{T_{br}} - 13.4721\ln(T_{br}) + 0.4357T_{br}^6\right)}
\]

for \(T_{br} \leq 0.8\) \hfill 3 – 11

\[
\omega = -7.904 + 0.1352K_w - 0.007465K_w^2 + 8.359T_{br} + \frac{(1.408 - 0.01063K_w)}{T_{br}}
\]

for \(T_{br} > 0.8\) \hfill 3 – 12

Where \(T_b\) is boiling point of the pseudo-component in K and \(S\) is the specific gravity which are the input parameters coming from experimental data; and, \(K_w\) is the Watson characterization factor, which can be calculated from Equation 3-15:

\[
T_{br} = \frac{T_b}{T_c}
\]

3 – 13

\[
P_{br} = \frac{P_b}{P_c}
\]

3 – 14

\[
K_w = \frac{(1.8T_b)^{\frac{1}{3}}}{S}
\]

3 – 15

Twu correlations developed for properties estimation are as follows (Twu 1984):

\[
T_c = T_b \left(0.533272 + 0.191017 \times 10^{-3}T_b + 0.779681 \times 10^{-7}T_b^2 - 0.284376 \times 10^{-10}T_b^3 + 0.959468 \times 10^{-10}/\left(\frac{T_b}{100}\right)^{13}\right)^{-1}
\]

3 – 16

\[
P_c = \left(3.83354 + 1.19629\psi^2 + 34.8888\psi + 36.1952\psi^2 + 104.193\psi^4\right)^2
\]

3 – 17
\[ V_c = [1 - (0.419869 - 0.505839\psi - 1.56436\psi^3 - 9481.70\psi^{14})]^{-8} \quad 3 - 18 \]
\[ S = 0.843593 - 0.128624\psi - 3.36159\psi^3 - 13749.5\psi^{12} \quad 3 - 19 \]

Where parameter \( \psi \) can be found from the following relationship:

\[ \psi = 1 - \frac{T_b}{T_c} \quad 3 - 20 \]

The molecular weight of each pseudo-component can be estimated from the following implicit mathematical formula:

\[
T_b = \exp \left[ 5.71419 + 2.71579 \ln(MW) - 0.286590 \left( \ln(MW) \right)^2 - \frac{39.8544}{\ln(MW)} - \frac{0.122488}{(\ln(MW))^2} \right] \\
- 24.7522 \ln(MW) + 35.3155 \left( \ln(MW) \right)^2 \quad 3 - 21
\]

The above implicit equation (3-21) can be solved in terms molecular weight using the following recommended initial guess:

\[ MW = \frac{T_b}{(10.44 - 0.0052T_b)} \quad 3 - 22 \]

Critical volume \( V_c \) can also be estimated from the Riedel correlation based on critical temperature \( T_c \) and critical pressure \( P_c \) calculated from the aforementioned correlations:

\[ V_c = \frac{RT_c}{P_c} \left[ 3.72 + 0.26(\alpha - 7.0) \right]^{-1} \quad 3 - 23 \]
Where the unit of $P_c$ is atmosphere, $T_c$ is in K and $V_c$ is in $\frac{cm^3}{g\text{mole}}$. Parameter $\alpha$ can be calculated from the following formula (Jonson 1985):

$$\alpha = 0.9076 \left[ 1 + \frac{(T_b/T_c)\ln(P_c)}{1 - (T_b/T_c)} \right]$$

3 - 24
Chapter 4. Corresponding States Theory

4.1 Introduction

In the characterization of the macroscopic properties of materials, the microscopic behaviour should be known. The corresponding states principle is one of the microscopic theories that focuses on the molecular properties of substances (Xiang 2005).

Van der Waals developed the corresponding states principle for monoatomic materials in 1880. The general expression of this theory is that the intermolecular properties are related to the critical properties, such as the critical temperature and pressure, of a substance. This principle provides the fundamental theory for calculating thermodynamic and transport properties of materials. The corresponding states principle delineates that spherical molecules, such as methane, are compatible with van der Waals’ theory (Xiang 2005).

The equation of state developed by van der Waals correlates the molar volume of a material with the pressure, temperature and critical properties of that substance. For corresponding states, the reduced properties are defined as follows:

\[ V_r = \frac{V}{V_c} \]

\[ P_r = \frac{P}{P_c} \]
\[ T_r = \frac{T}{T_c} \]

Where \( V_c \), \( P_c \) and \( T_c \) are the critical volume, pressure and temperature of the specified substance.

The corresponding states theory can be related to statistical thermodynamics with the simpler form of a partition function. The mathematical relationships that express the properties of substances are based on the potential energy function. The form of the function is not theoretical and cannot be derived from mathematical relationships. The two-parameter corresponding developed by van der Waals states principle is appropriate for variety of substances, but is not able to predict the properties of non-spherical substances (Xiang 2005).

Substances with spherical, symmetrical and non-polar molecules show compatibility with van der Waals two-parameter corresponding states principle; however, Pitzer et al. (1955) expressed that for ordinary fluids with weakly polar and weakly non-polar molecules do not conform to van der Waals’ theory. Pitzer et al. (1955) introduced a third parameter to the corresponding states principle: the acentric factor. The three-parameter corresponding states principle is appropriate for weakly non-spherical non-polar substances. This theory is based on macroscopic behaviour from a microscopic perspective. The model of Pitzer et al. (1955) shows a significant deviation in calculating the properties of highly nonspherical and highly polar substances, but the deviation is one order of magnitude smaller than that of van der Waals’ model.

For complex polar with hydrogen-bonding molecules, there is a need for another theory to calculate the thermodynamic and transport properties. The extended principle of the
corresponding states were developed based on the deviation from a spherical molecule. The
difference of non-spherical molecules from spherical ones is observed in terms of critical
properties. This theory is not based on an empirical relationship and, thus, may be applicable to
non-polar or polar hydrogen-bonding molecules. It can be used in the calculation of
thermodynamic and transport properties for different types of materials (Xiang 2005).

4.2 Historical Background

During the development of the kinetic theory of gases, it became known that most gases do not
follow the ideal gas law. In 1847, Regnault observed that only the hydrogen behaviour was
compatible with the Boyle gas law. He revealed that the expanding coefficient is proportional to
the pressure of the gas. In 1852, Joule and Thomson developed the Joule-Thomson effect,
through which they observed the variation of the internal energy of gas, in terms of its expansion.
They proved that intermolecular forces do not exhibit compatibility with ideal gas law (Xiang
2005).

In 1860, Mandeleev studied the proportionality of surface tension and temperature. He
discovered that, at a specified temperature, the distinction between liquid and vapour is not
possible and that the difference between these two phases was disappearing. He named this
temperature the absolute boiling temperature (Xiang 2005).
In 1869, Andrew investigated the liquefaction of carbon dioxide (CO₂) and revealed that 31.3 °C is the maximum temperature for liquefaction of CO₂. He showed that with the appropriate variation of the pressure and temperature of the gas, the material can be converted from a gaseous state to liquid one. James Thompson studied the Andrew’s work and, in 1871, revealed that the vapour phase and liquid phase isotherms intercept at some temperatures below the critical temperature (Xiang 2005).

Van der Waals studied the behaviour of real gases based on studies done by Andrews and Thompson to explain the liquid and vapour behaviour of substances. He studied the effect of intermolecular forces and considered that every molecule occupies the volume of ‘b’ and that the volume remaining for movement of molecules to move is reduced to V − b, where V is the volume occupied by the molecules. Due to molecular interaction, the pressure increases to P + a/V², where P is the internal pressure and ‘a’ and ‘b’ are van der Waals parameters in equation of states. He observed that the parameter ‘a’ has a direct relationship with the volume of molecules.

In 18th century, Bernoulli derived the following mathematical relationship for real gases:

\[ P(V - b) = RT \]

Where ‘b’ is the total volume occupied by all molecules, ‘R’ is universal gas constant and ‘T’ is the temperature (Xiang 2005).

In 1863, Hirn proposed the following formula for an equation of state:
\[(P + \psi)(V - b) = RT\]

Where \(\psi\) is related to the volume of the gas that gave the main concept of equation of states to van der Waals.

The sphere of action is a small radius around the centre of the molecule. At distances greater than this radius, the inter-molecular forces become weaker and can be ignored. Considering a uniform density of the molecules, the particles are at equilibrium if they do not pass this radius of action. If the molecules violate this radius and create a layer with the size of this radius, the inter-particle forces on these molecules are inward (Xiang 2005).

There can be considered a very thin column in the boundary layer below which each particle can absorb and affect this column. Inside this radius, if there is a particle at equilibrium and not moving, there should be a force on this particle. If this particle is moving, it will occupy the other places, and the force will vanish; and, the absorption is exerted on the particles in the places to which they move (Xiang 2005).

The absorption made by a material is proportional to the density or quantity of that substance. A similar fact also holds for particles in a column. Consequently, absorption is inversely in relationship with the square of the volume of that substance or directly proportional to the density of the material. From the above facts, van der Waals derived the following mathematical relationship:
\[(P + \frac{a}{V^2})(V - b) = RT\] 

The relationship in Equation 4-6 can also be deduced from the potential energy function. Parameter \(b\) in Equation 4-6 is related to the volume of the particles (Xiang 2005).

The van der Waals equation of state shown in Equation 4-6 can also be rearranged in the following mathematical form:

\[PV = \left[1 + \frac{(b - aRT)}{V} + \ldots\right]RT\] 

The above equation is expanded form of equation 4-6. In Equation 4-7, when the term \(1/V\) is much smaller than 1, the gas can be considered as an ideal gas. If the aforementioned term is not ignorable, the gas is a real gas and the van der Waals equation of state (EOS) should be taken into account. At higher temperatures, the van der Waals EOS is closer to the ideal gas law. Therefore, the van der Waals EOS is applicable to lower temperatures when the density of the substance is high. However, the van der Waals EOS is able to deal with critical conditions, contrary to the ideal gas law (Xiang 2005).

The van der Waals theory led to the advancement in molecular kinetic theory, which was also investigated by Maxwell in the 19th century. Maxwell criticized van der Waals’ theory for temperatures below critical point, in which the partial derivative of the pressure with respect to
volume at a constant temperature is positive \( \left( \frac{\partial p}{\partial V} \right)_T > 0 \) and stated that is meaningless from physical and thermodynamic point of views. He mentioned that the isotherm at the aforementioned state \( \left( \frac{\partial p}{\partial V} \right)_T > 0 \) was in an unstable condition and was changed by the condition which is corresponds to critical condition in which \( \left( \frac{\partial p}{\partial V} \right)_{T_c} = 0 \). Maxwell proposed the following relationship in which gas and liquid exist together, where \( P_s \) is the equilibrium pressure calculated based on Maxwell’s equal-area rule:

\[
\int_{V_L}^{V_V} (P - P_s) \, dV = 0
\]

Equation 4-8 is used to replace the van der Waals loop with the horizontal line expressed in Equation 4-7 (Xiang 2005).

Van der Waals’ theory revised by Maxwell is able to explain the phase change from vapour to liquid and vice versa. At temperatures below the critical point, vapour and liquid can exist together at equilibrium (saturated liquid and vapour) on both sides of the isotherm. However, at a critical point, the liquid and vapour phases vanish, which is also compatible with Andrews’ observation. It was also observed that the term \( \left( \frac{\partial p}{\partial V} \right)_T \) is zero at a critical condition. At a critical point, a small overpressure can lead to a large change in the density or volume of the fluid.
Van der Waals theory is also able to express supercooled and superheated fluid. As previously considered, the condition of $\left(\frac{\partial p}{\partial V}\right)_T > 0$ is meaningless; however, the two isotherms of under saturated liquid and over saturated vapour correspond to superheated liquid and subcooled vapour conditions, respectively (Xiang 2005).

The van der Waals theory can also be used to estimate the thermodynamic properties of substances at critical condition. For the determination of parameters $a$ and $b$ in Equation 4-6, the following condition at the critical point should be applied:

\[
\left(\frac{\partial p}{\partial V}\right)_T = 0 @ T = T_c, p = p_c 
\]  
\[
\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 @ T = T_c, p = p_c 
\]

Based on Equations 4-9 and 4-10, the critical properties of the substances will be found as follows:

\[
T_c = \frac{8a}{27b} 
\]

\[
p_c = \frac{a}{27b^2} 
\]

\[
V_c = 3b 
\]

Where $a$ and $b$ are parameters of the van der Waals EOS in Equation 4-6 (Xiang 2005).
Equation 4-6 can be also shown in terms of the reduced properties introduced in Equations 4-1 to 4-3 by applying the mathematical relationships presented in Equations 4-11 to 4-13 as follows:

\[
(P_r + \frac{3}{V_r^2})(3V_r - 1) = 8T_r
\]  

Equation 4-14 is the basic form of the corresponding states principle developed by van der Waals and is universally valid for every gas (Xiang 2005).

Van der Waals also derived the following relationship:

\[
P_{vr} = \frac{P_v}{P_c} = f(T_r)
\]  

Where \( P_v \) is the vapour pressure of the substance at specified temperature, and \( f(T_r) \) is determined empirically based on experimental data for each materials.

Equation 4-15 is also universally valid for every substance. In reality, most materials show more compatibility with Equation 4-15 than with van der Waals’ EOS.

The general form of the corresponding states principle is presented in the following implicit mathematical relationship:

\[
F(P_r, T_r, V_r) = 0
\]
The EOS is a specified form of the corresponding states principle in the following formula:

\[
\frac{pV}{RT} = F(T_r, V_r)
\]

In Equation 4-17, the Virial coefficients can be presented in the form of corresponding states as follows:

\[
\frac{pV}{RT} = 1 + \frac{B_r}{V_r} + \frac{C_r}{V_r^2}
\]

\[
B_r = \frac{B}{V_c} = f_B(T_r)
\]

\[
C_r = \frac{C}{V_c^2} = f_C(T_r)
\]

Where \(\frac{pV}{RT}\) is the same as the compressibility factor and is different for a variety of substances. It is worth mentioning that equation 4-7 is the Virial expansion of van der Waals equation of state (presented in equation 4-6). At critical condition, \(\frac{pV_c}{RT_c}\) is approximately constant for some gases (Xiang 2005).

4.3 Theory and Assumptions

The following assumptions have been considered:
1) The two-parameter corresponding states principle used classic statistical mechanics for its derivation.

2) The molecules of the substance are assumed to be spherical and symmetrical. The potential function between two particles has been presented as follows:

\[ u(r) = \varepsilon \phi \left( \frac{r}{\sigma} \right) \]  

Where \( r \) is the distance between two molecules, \( \phi \) is a universal function, and \( \varepsilon \) and \( \sigma \) are characteristic constants.

3) It is assumed that the vibration of the molecules is independent of the state of the substance (liquid or gas state).

4) The total potential energy of the substance is only a function of the distance between two molecules and is equal to the summation of all potential energies between each pair of molecules as follows:

\[ u = \sum \phi(r) \]  

Assumption number 3 results in the degree of freedom of particle vibration not depending on the specific volume of molecules. This assumption is not valid for highly polar and hydrogen-bonding molecules. When intermolecular radius \( r \) becomes larger, the characteristic constant \( \varepsilon \) is proportional to \( \frac{1}{r^6} \). In addition, many thermodynamic and transport properties do not depend on the exact relationship between \( \varepsilon \) and \( r \). Assumption 4 is a good estimation for non-polar substances (Xiang 2005).
If two systems have the same amount of molecules in which the equivalent dimension is proportional to the characteristic constant $\sigma$, the volume is proportional to $\sigma^3$. The vibrational energy of particles is proportional to the temperature of the substance, and the corresponding temperature is proportional to $\frac{e}{k}$ where $k$ is a Boltzman constant.

For real gases and liquids, intermolecular forces cannot be ignored. The Hamiltonian function is as follows:

\[
H = \frac{1}{2} \cdot \text{MW} \sum_{i=1}^{N} \mathbf{p}_i^2 + \Phi(\mathbf{r}^N) + \sum_{i=1}^{N} F(T, N)
\]

Where $F$ is the partition function.

In Equation 4-23, the first expression is related to the translational energy, the second term is the interaction energy between molecules, and the third term is related to the energy of the vibrational and rotational movement of particles (Xiang 2005).

Partition function $Q$ can be defined as follows:

\[
Q = \frac{1}{h^{3N}} \frac{1}{N!} \int \ldots \int \exp \left( \frac{H}{kT} \right) d\mathbf{p}_1 \ldots d\mathbf{p}_N d\mathbf{r}_1 \ldots d\mathbf{r}_N
\]

\[
d\mathbf{r}_i = dx_i \cdot dy_i \cdot dz_i
\]

\[
d\mathbf{p}_i = dp_{xi} \cdot dp_{yi} \cdot dp_{zi}
\]

Where $h$ is the Planck constant, and $N$ is the number of molecules.
The translational partition function is derived from the potential and kinetic energy of the molecules in the following form:

\[ Q_{\text{tran}} = \left( \frac{2\pi nkT}{\hbar^2} \right)^{\frac{3N}{2}} \frac{Q_{\text{conf}}}{N!} \]  \hspace{1cm} 4 - 27

Where \( Q_{\text{conf}} \) is the configurational integral, which is a function of volume and temperature, according to the following relationship:

\[ Q_{\text{conf}} = \sigma^{3N} \frac{1}{N!} \int_{\sigma^3} \cdots \int \exp \left[ -\frac{\epsilon}{kT} \sum_{i>j} \phi \left( \frac{r_{ij}}{\sigma} \right) \right] dr_1 \cdots dr_N \]  \hspace{1cm} 4 - 28

Equation 4-28 can be rewritten in the following mathematical form:

\[ Q_{\text{conf}} = \sigma^{3N} \psi \left( \frac{V}{\sigma^3}, \frac{kT}{\epsilon}, N \right) \]  \hspace{1cm} 4 - 29

Where \( \psi \) is the universal function presented in Equation 4-28, and \( \sigma \) is the corresponding value at the minimum potential energy of \( \epsilon \). If the system is diluted, \( \psi \) is close to 1 (Xiang 2005).

The Helmholtz free energy is defined as:

\[ A = -kT \ln(Q) \]  \hspace{1cm} 4 - 30
Using the Sterling relationship in combination with Equation 4-28, one can find:

\[- \frac{A}{NkT} = \frac{3}{2} \ln \left( \frac{2\pi mkT}{\hbar^2} \right) + \ln Q_{\text{ant}}(T,N) + 3\ln(\sigma) + \ln \left( \frac{\psi \left( \frac{V}{\sigma^3}, \frac{kT}{\varepsilon}, N \right)}{N} \right) \]

\[- \left[ \ln(N) - 1 \right] \]

If $A$ is not function of $N$, as can be deduced from Equation 4-30, term $\ln \left( \frac{\psi \left( \frac{V}{\sigma^3}, \frac{kT}{\varepsilon}, N \right)}{N} \right) - \ln(N)$ in Equation 4-31 must not be depend on $N$. Then, we have:

\[\ln \varphi \left( \frac{V}{N\sigma^3}, \frac{\varepsilon}{kT} \right) = \ln \left( \frac{\psi \left( \frac{V}{\sigma^3}, \frac{kT}{\varepsilon}, N \right)}{N} \right) - \ln(N) \]

Therefore:

\[Q = \left[ N\varphi \left( \frac{V}{N\sigma^3}, \frac{\varepsilon}{kT} \right) \right]^N \]

The equation of state can be derived by combining Equations 4-33 and 4-30 as follows:

\[\frac{p}{kT} = \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} = \left[ \frac{\partial \ln \varphi \left( \frac{V}{N\sigma^3}, \frac{\varepsilon}{kT} \right)}{\partial \left( \frac{V}{N} \right)} \right]_{T,N} \]

Equation 4-34 can be rewritten in the following form:
\[
\frac{p}{\varepsilon/\sigma^3} = \frac{kT}{\varepsilon} \left[ \frac{\partial L_{\mu \phi}}{\partial \left( \frac{V}{\sigma^3} \right)_{TN}} \right] 4 - 35
\]

We can define the following dimensionless groups in relationships:

\[
p^* = \frac{p}{\varepsilon/\sigma^3} 4 - 36
\]

\[
T^* = \frac{T}{\varepsilon/k} 4 - 37
\]

\[
V^* = \frac{V}{N_\sigma^3} 4 - 38
\]

Using Equations 4-35 to 4-38, we can find:

\[
p^* = f(T^*, V^*) 4 - 39
\]

Equation 4-39 depicts the pressure-volume-temperature (PVT) relationship, which can be expressed as a function of the characteristic constants \((\sigma, \varepsilon)\). At critical condition, the relationship in Equation 4-39 is as follows (Xiang 2005):

\[
p_{c^*} = f(T_{c^*}, V_{c^*}) 4 - 40
\]

\[
\left( \frac{\partial p^*}{\partial V^*} \right)_c = 0 \quad @ \ T = T_c, p = p_c 4 - 41
\]

\[
\left( \frac{\partial^2 p^*}{\partial V^*^2} \right)_c = 0 \quad @ \ T = T_c, p = p_c 4 - 42
\]
Based on the Lennard-Jones relationship, which is present at the critical condition, the following critical properties can be derived:

\[ p_c = 0.116 \frac{\varepsilon}{\sigma^3} \]  
\[ V_c = \sqrt{2} \pi N \sigma^3 \]  
\[ T_c = 1.25 \frac{\varepsilon}{k} \]

Based on the reduced properties defined by Equations 4-1 to 4-3, Equation 4-39 can be rewritten in the following form:

\[ p_r = f(T_r, V_r) \]  
\[ \frac{p^* V^*}{T^*} = \frac{pV}{RT} \]

As can be seen from Equation 4-46, the corresponding states principle is the general form of an equation of state (Xiang 2005).

The compressibility factor can be derived from the following mathematical relationships:

\[ Z = \frac{pV}{RT} = f(T_r, V_r) \]  
Or
\[ Z = f(T_r, p_r) \]
The vapour pressure of a substance can also be presented in terms of reduced properties as follows:

\[ p_{v,r} = f(T_r) \]  \hspace{1cm} 4 - 50

Where

\[ p_{v,r} = \frac{p_v}{p_c} \]  \hspace{1cm} 4 - 51

Where \( p_v \) is the vapour pressure of the substance at a specified temperature.

Transport properties, such as viscosity and thermal conductivity, can also be presented as follows:

\[ \mu_r = \frac{\mu}{\mu_c} = f(T_r, \rho_r) \]  \hspace{1cm} 4 - 52

\[ \lambda_r = \frac{\lambda}{\lambda_c} = f(T_r, \rho_r) \]  \hspace{1cm} 4 - 53

Where \( \mu \) represents viscosity, \( \lambda \) is the thermal conductivity of the substance, and \( \mu_c \) and \( \lambda_c \) are the viscosity and thermal conductivity at critical condition (Xiang 2005).
4.4 Corresponding States Parameters

The van der Waals corresponding-states model has only two parameters, as shown in Equation 4-46. The parameters are the critical temperature and the volume of the substance. This method is appropriate for monoatomic, spherical materials with a 30% error in estimation of properties of normal fluids (Xiang 2005).

For non-spherical molecules, Pitzer studied the effects of sphericity on the corresponding states model. He introduced a new parameter – the acentric factor $\omega$ – to this model. As a molecule shows greater deviation from a spherical shape, the probability of two particles to be close to each other decreases. Therefore, the minimum potential energy of spherical particles is greater than non-spherical ones. By reducing the probability of molecules approaching each other, the entropy of the system is also decreased. The entropy of spherical and non-spherical particles is as follows (Xiang 2005; Pitzer et al. 1955):

$$S_{l, q} > S_{l, noq}$$  \hspace{1cm} 4 - 54

Where $S_{l, q}$ is the entropy of spherical molecules, and $S_{l, noq}$ is entropy of non-spherical particles in liquid form.

The entropy of vapourization from a gas to liquid state can, therefore, be expressed as follows:

$$\Delta S_{l, q} < \Delta S_{l, noq}$$  \hspace{1cm} 4 - 55

Where
\[ \Delta S = S_v - S_l \] \hspace{1cm} 4 - 56

Where \( S_v \) is the entropy in the gas state, and \( S_l \) is the entropy in the liquid state (Xiang 2005).

The following formula depicts the relationship between the vapour pressure and the entropy of the vapourization of a substance:

\[ \frac{\partial \ln (p_r)}{\partial (\frac{1}{T_r})} = -\frac{T_r \Delta S}{R} \] \hspace{1cm} 4 - 57

Considering Equation 4-57 for spherical and non-spherical particles and using Equation 4-55 results in the following relationship (Xiang 2005):

\[ \left( \frac{\partial \ln (p_r)}{\partial (\frac{1}{T_r})} \right)_q > \left( \frac{\partial \ln (p_r)}{\partial (\frac{1}{T_r})} \right)_{noq} \] \hspace{1cm} 4 - 58

Equation 4-58 is valid considering the same temperature for both cases.

Pitzer observed that for noble gases, such as argon, krypton and xenon, the reduced vapour pressure is approximately 0.1 at \( T_r = 0.7 \). Based on this investigation, Pitzer defined the acentric factor in terms of the deviation of the substance from sphericity in the following mathematical relationship (Xiang 2005; Pitzer et al. 1955):
\[ \omega = -\log(p_r)_{T_r=0.7} - 1 \]

The acentric factor may also be considered as a criterion for increasing the vaporization entropy, as a result of the deviation from spherical behaviour. The vapour pressure curve is also related to vaporization entropy, as can be seen in Equation 4-57 and 4-58. Based on the above research, Pitzer modified the two-parameter van der Waals corresponding states model and developed a three-parameter corresponding states model (Xiang 2005):

\[ p_r = f(T_r, V_r, \omega) \]

The Pitzer model for the corresponding states principle improved the results for non-polar substances by one order of magnitude; however, a significant deviation is observed for highly polar materials. In the case of polar particles, the intermolecular potential of permanent dipoles with a fixed orientation is inversely proportional to the third power of intermolecular radius. Due to those dipoles, the properties of polar molecules show a significant deviation from the Pitzer model, which conforms with non-polar particles (Pitzer et al. 1955). The observed deviation indicated the need for a fourth parameter to be added to the Pitzer corresponding states theory. Dipole moments affect the properties of substance at critical condition (Xiang 2005; Pitzer et al. 1955).
The critical temperature represents the interaction energy between two molecules, and the critical volume is related to the intermolecular radius between the centres of two molecules. The compressibility factor at the critical condition is defined as follows:

\[ Z_c = \frac{P_c}{R \rho_c T_c} \quad 4 - 61 \]

Where \( Z_c \) for non-spherical particles is less than that of spherical ones and is a factor showing the deviation from sphericity. The van der Waals corresponding states model assumes the same critical compressibility factor for all the materials. In reality, \( Z_c \) for different substances is varied between 0.2 and 0.29. As previously mentioned, the following relationship is held for spherical and non-spherical molecules (Xiang 2005):

\[ Z_{c,q} > Z_{c,\text{noq}} \quad 4 - 62 \]

Where \( Z_{c,q} \) is the critical compressibility factor for spherical particles, and \( Z_{c,\text{noq}} \) represents non-spherical molecules.

Pitzer et al. (1955) proposed the following relationship between the critical compressibility factor and the acentric factor in the following form:

\[ Z_c = 0.29 - 0.08\omega \quad 4 - 63 \]

Equation 4-63 is only applicable for simple spherical molecules. For highly spherical particles, a new parameter is introduced:
\[ \theta = (Z_c - 0.29)^2 \]

Where \( \theta \) is the aspherical factor.

The aspherical factor shows the deviation from sphericity, since \( Z_c = 0.29 \) for spherical particles, such as argon. The concept of the aspherical factor is similar to that of the acentric factor introduced by Pitzer (Pitzer et al. 1955; Xiang 2005).

The new corresponding states model is proposed based on the new parameter in the following relationship:

\[ p_r = f(T_r, V_r, \omega, \theta) \]

The aspherical factor \( \theta \) for non-polar particles can be estimated as follows:

\[ \theta_{\text{nonpolar}} = 0.0064\omega^2 \]

The corresponding states model presented in Equation 4-65 can predict the properties of highly polar particles. For hydrogen-bonding molecules, such as water, the aspherical factor calculated from Equation 4-66 results in 0.263; however, the application of Equation 4-64 leads to 0.228, which is significantly different from the one calculated with Equation 4-64 and indicates that water molecules are polar. The ratio of \( \frac{\theta}{\theta_{\text{nonpolar}}} \) can be varied up to 5 for highly polar particles.
The compressibility factor based on the extended parameter $\theta$ can be found as follows (Xiang 2005):

$$Z = \frac{pV}{RT} = f(T_r, V_r, \omega, \theta) \quad 4 - 67$$

The critical compressibility factor can be modified with the following correlation:

$$Z_c = 0.29 + c_1 \omega + c_2 \theta \quad 4 - 68$$

Equation 4-68 is a modification to the Pitzer correlation presented in Equation 4-63. Coefficients $c_1$ and $c_2$ depend on the type of substance and vary from -0.055 to -11.5 for spherical, non-spherical, polar and non-polar molecules.

Substituting Equation 4-64 into Equation 4-68 with some mathematical rearrangement leads to the following relationship:

$$c_2 Z_c^2 - (1 + 0.58 c_2) Z_c + (0.0841 c_2 + 0.29 + c_1 \omega) = 0 \quad 4 - 69$$

Equation 4-69 depicts the deviation of the critical compressibility from spherical behaviour. If one considers $c_1$ and $c_2$ to be equal to zero, which is the case for spherical particles, Equation 4-69 results in $Z_c = 0.29$ (Xiang 2005).
4.5 Corresponding States Model for Viscosity Prediction

In 1981, Ely and Hanley developed a corresponding states method for the prediction of the viscosity pure fluid and mixtures. The basic formula is as follows:

$$\mu_{\text{mix}}(\rho, T) = \mu_0(\rho_0', T_0') \left( \frac{\sigma_0}{\sigma_x} \right)^2 \left( \frac{\epsilon_x}{\epsilon_0} \right)^{\frac{1}{2}} \left( \frac{M_x}{M_0} \right)^{\frac{1}{2}}$$

Where

$$\rho_0' = \rho \left( \frac{\sigma_x}{\sigma_0} \right)^3$$

$$T_0' = T \left( \frac{\epsilon_0}{\epsilon_x} \right)$$

In Equations 4-70 to 4-72, subscript x represents a mixture and o indicates the reference fluid. Characteristic constants $\sigma$ and $\epsilon$, as previously mentioned, are related to the intermolecular length and energy, respectively (Ely and Hanley 1981; Hanley and Evans 1981).

The following assumptions have been made for modeling the viscosity of pure fluid and mixtures:

1) The reference fluid and pure fluid follow van der Waals’ corresponding states model. For mixtures, the mixing rule follow van der Waals’ mixing rule.

2) The mixture of fluids is considered as a pure substance by applying the mixing rule based on van der Waals’ theory.
The potential energy of a pure substance is formulated as:

$$E_u = 2\pi N \frac{N}{v} \int u(r) g(r) r^2 dr$$ \hspace{1cm} 4 - 73

For a mixture of fluids, we have:

$$E_u = 2\pi N \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \int u_{\alpha\beta}(r) g_{\alpha\beta}(r) r^2 dr$$ \hspace{1cm} 4 - 74

Where $N$ is number of particles, $\alpha$ and $\beta$ are the components of the mixture, $u(r)$ is the potential function between two molecules, $r$ is the separation radius, and $g(r)$ is the distribution function of the separation radius.

Based on the aforementioned assumptions, components of a mixture follow van der Waals’ rule, where the force law is:

$$u(r) = \varepsilon u^* \left( \frac{r}{\sigma} \right)$$ \hspace{1cm} 4 - 75

Where $u^* \left( \frac{r}{\sigma} \right)$ is the universal function, in terms of scaled separation radius $\frac{r}{\sigma}$.

The distribution function $g(r)$ follows this rule:
\[ g_{\alpha\alpha} \left( \frac{r}{\sigma_{\alpha\alpha}} \right) = g_{\alpha\beta} \left( \frac{r}{\sigma_{\alpha\beta}} \right) = g_{\beta\beta} \left( \frac{r}{\sigma_{\beta\beta}} \right) \]

Equation 4-74 can be rewritten as:

\[ E_u = 2\pi N \frac{N}{V} \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \int u^*(r_{\alpha\beta}^*) g(r_{\alpha\beta}^*) r_{\alpha\beta}^+ r_{\alpha\beta}^+ \, dr_{\alpha\beta}^+ \]

Where

\[ r^* = \frac{r}{\sigma} \]

The following mixing rules are applied based on van der Waals’ theory:

\[ \varepsilon_x \sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \]

\[ \sigma_x^3 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta \sigma_{\alpha\beta}^3 \]

As in Equations 4-44 and 4-45, parameter \( \sigma^3 \) is proportional to \( V_c \), and \( \varepsilon \) is proportional to \( T_c \).

Equations 4-79 and 4-80 can be rewritten as:

\[ h_{x,\alpha} f_{x,\alpha} = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta h_{\alpha\beta,\alpha} f_{\alpha\beta,\alpha} \]
\[ h_{x,o} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} h_{\alpha \beta, o} \]  

4 - 82

Where \( h_{x,o} \) is the parameter related to the ratio of the critical volume of the mixture and the reference fluid, and \( f_{x,o} \) is related to the critical temperature of the mixture and reference fluid.

The mass mixing rule is depicted in the following relationship:

\[
h_{x,o}^{\frac{4}{3}} f_{x,o}^{\frac{1}{3}} M_{x}^{\frac{1}{3}} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} h_{\alpha \beta, o}^{\frac{4}{3}} f_{\alpha \beta, o}^{\frac{1}{3}} M_{\alpha \beta}^{\frac{1}{3}} \]  

4 - 83

The interaction parameters are as follows:

\[
f_{\alpha \beta, o} = (1 - k_{\alpha \beta}) (f_{\alpha, o} \cdot f_{\beta, o})^{\frac{1}{2}} \]  

4 - 84

\[
h_{\alpha \beta, o} = \frac{1}{8} (1 - l_{\alpha \beta}) (h_{\alpha, o}^{\frac{1}{3}} + h_{\beta, o}^{\frac{1}{3}})^{3} \]  

4 - 85

\[
M_{\alpha \beta} = \frac{2 M_{\alpha} \cdot M_{\beta}}{M_{\alpha} + M_{\beta}} \]  

4 - 86

Where \( \alpha \) and \( \beta \) are components, and \( f_{\alpha, o} \) and \( h_{\alpha, o} \) are as follows:

\[
f_{\alpha, o} = \frac{T_{\alpha}}{T_{co}} \theta_{\alpha, o} (T_{\alpha}, V_{\alpha}, \omega_{\alpha}) \]  

4 - 87

\[
h_{\alpha, o} = \frac{V_{\alpha}}{V_{co}} \phi_{\alpha, o} (T_{\alpha}, V_{\alpha}, \omega_{\alpha}) \]  

4 - 88

\[
\theta_{\alpha, o} = 1 + (\omega_{\alpha} - \omega_{o})(a_{1} + b_{1} \ln(T_{\alpha}^{+}) + (c_{1} + d_{1}/T_{\alpha}^{+})(V_{\alpha}^{+} - 0.5) \]  

4 - 89
\[ \varphi_{\alpha,o} = [1 + (\omega_\alpha - \omega_o)(a_2(V_\alpha^+ + b_2)) + c_2(V_\alpha^+ + d_2) \ln(T_\alpha^+)] \frac{Z_o}{Z_{o\alpha}} \quad 4 - 90 \]

\[ T_\alpha^+ = \min[2, \max(T_{ar}, 0.5)] \quad 4 - 91 \]

\[ V_\alpha^+ = \min[2, \max(V_{ar}, 0.5)] \quad 4 - 92 \]

In equations 4-89 and 4-90, \( \theta_{\alpha,o} \) and \( \varphi_{\alpha,o} \) are shape factors. Teja and Rice (1981) developed a three-parameter corresponding states principle based on the model of Pitzer et al. (1955), which is presented in the following formula:

\[ Z = Z^{(o)} + \omega Z^{(1)} \quad 4 - 93 \]

Where \( Z^{(o)} \) is the compressibility of a spherical fluid that is being considered as a reference fluid and \( Z^{(1)} \) is a complex function. (Teja and Rice 1981; Pitzer et. al. 1955)

Lee and Kesler (1975) developed a new corresponding states model that is more complicated than Pitzer model:

\[ Z = Z^{(o)} + \frac{\omega}{\omega_1} \left[ Z^{(r)} - Z^{(o)} \right] \quad 4 - 94 \]

Teja and Rice developed the following formula for viscosity prediction based on the Pitzer and Lee-Kesler models in the following form (Lee and Kesler 1975; Teja and Rice 1981):

\[ \ln(\mu_m) = \ln(\mu) + \frac{\omega_m - \omega_1}{\omega_2 - \omega_1} \left[ \ln(\mu)_2 - \ln(\mu)_1 \right] \quad 4 - 95 \]

\[ \xi_m = \frac{1}{T_{cm}} \frac{1}{P_{cm}} \left[ \frac{2}{3} \right] \frac{1}{2} M_{cm} \quad 4 - 96 \]
Equations 4-95 and 4-96 are applicable to a mixture of fluids where superscripts $r_1$ and $r_2$ are two non-spherical reference fluids (Teja and Rice 1981).

The mixing rule for this model is as follows:

\[ T_{cm} \cdot V_{cm} = \sum_i \sum_j X_i \cdot X_j \cdot T_{cij} \cdot V_{cij} \]  
\[ 4 - 97 \]

\[ V_{cm} = \sum_i \sum_j X_i \cdot X_j \cdot V_{cij} \]  
\[ 4 - 98 \]

\[ \omega_m = \sum_i X_i \cdot \omega_i \]  
\[ 4 - 99 \]

\[ M_m = \sum_i X_i \cdot M_i \]  
\[ 4 - 100 \]

\[ T_{cij} \cdot V_{cij} = \psi_{ij} \left( T_{c1} \cdot V_{c1} \cdot T_{c2} \cdot V_{c2} \right)^{\frac{1}{2}} \quad i \neq j \]  
\[ 4 - 101 \]

\[ V_{cij} = \frac{1}{8} \left( V_{c1}^3 + V_{c2}^3 \right)^{\frac{3}{2}} \]  
\[ 4 - 102 \]

Where $\psi_{ij}$ is an interaction coefficient, which can be found based on experimental data (Teja and Rice 1981).
5.1 Bitumen Viscosity Prediction using Corresponding States Principles

Ely and Hanley (1981) developed a model based on corresponding states principles for the prediction of the viscosity of hydrocarbon mixtures. The mathematical modeling is as follows:

\[
\mu_{mix}(\rho, T) = \mu_o(\rho_o, T_o) \left( h_{mix,o} \right)^{\frac{2}{3}} \left( f_{mix,o} \right)^{\frac{1}{2}} \left( \frac{M_{mix}}{M_0} \right)^{\frac{1}{2}}
\]

\[\rho_o = \rho \left( \frac{\rho_{c,0}}{\rho_c} \right), \quad T_o = T \left( \frac{T_{c,0}}{T_c} \right)\]

\[f_{\alpha,o} = \frac{T_{ea}}{T_{co}} \theta_{\alpha,o}(T_{r\alpha}, V_{r\alpha}, \omega_{\alpha})\]

\[h_{\alpha,o} = \frac{V_{ea}}{V_{co}} \phi_{\alpha,o}(T_{r\alpha}, V_{r\alpha}, \omega_{\alpha})\]

Where subscripts \(\alpha, c, o\) and mix refer to the component, critical condition, reference fluid and mixture properties, respectively.

In this model, the reference fluid is methane. The mixing rule is governed by the following relations:
\[ h_{\text{mix},o} = \sum \sum z_\alpha z_\beta h_{\alpha \beta, o} \]  
\[ f_{\text{mix},o} h_{\text{mix},o} = \sum \sum z_\alpha z_\beta f_{\alpha \beta, o} h_{\alpha \beta, o} \]  
\[ f_{\text{mix},o}^\frac{1}{2} h_{\text{mix},o}^\frac{4}{5} M_{\text{mix}}^\frac{1}{2} = \sum \sum z_\alpha z_\beta f_{\alpha \beta, o}^\frac{1}{2} h_{\alpha \beta, o}^\frac{4}{5} . M_{\alpha \beta}^\frac{1}{2} \]  
\[ f_{\alpha \beta, o} = (1 - k_{\alpha \beta})(f_{\alpha, o} - f_{\beta, o})^{\frac{1}{2}} \]  
\[ h_{\alpha \beta, o} = \frac{1}{\beta} (1 - l_{\alpha \beta})(h_{\alpha, o}^{\frac{1}{3}} + h_{\beta, o}^{\frac{1}{3}})^3 \]  
\[ M_{\alpha \beta} = \frac{2M_{\alpha} M_{\beta}}{M_{\alpha} + M_{\beta}} \] 

Ely and Hanley (1981) reported an average absolute deviation of 7% for different hydrocarbon mixtures.

Johnson (1985) introduced two correction coefficients, \( A_p \) and \( A_t \), to the work of Ely and Hanley (1981). Since the Ely and Hanley model used methane as the reference fluid, she used different reference fluids for the prediction of bitumen viscosity.

The shape factors modified by Johnson (1985) are as follows:

\[ \theta_{\alpha, o} = 1 + A_t (\omega_{\alpha} - \omega_o)(a_1 + b_1 \ln(T_{\alpha}^+) + (c_1 + d_1/T_{\alpha}^+)(V_{\alpha}^+ - 0.5) \]  
\[ \varphi_{\alpha, o} = [1 + (\omega_{\alpha} - \omega_o)(a_2 A_p(V_{\alpha}^+ + b_2 A_p)) + c_2 A_p(V_{\alpha}^+ + d_2 A_p) \ln(T_{\alpha}^+)] \frac{z_{\alpha o}}{z_{\alpha \alpha}} \]  
\[ T_{\alpha}^+ = \min(2, \max(T_{\alpha r}, 0.5)) \]  
\[ V_{\alpha}^+ = \min(2, \max(V_{\alpha r}, 0.5)) \]
$A_\alpha = 0.1, A_p = f(P_{c\alpha}, T_{b\alpha}, F_R)$

Where $F_R$ represents the reference fluid. In equations 5-11 and 5-12 $\theta_{\alpha\alpha}$ and $\varphi_{\alpha\alpha}$ are modified shape factors introduced by Ely and Hanley (1981) (presented in equations 4-89 and 4-90). The parameter $A_\alpha$ in equation 4-89 is the energy shape factor coefficient correction parameter and $A_p$ is the size shape factor coefficient correction parameter. Since there is no data for $l_{a\beta}$ and $k_{a\beta}$, they are considered to be zero (Johnson 1985).

Different reference fluids have been used for the prediction of the viscosity of bitumen. These were selected from the highly molecular aromatic hydrocarbons presented in Table 5-1 (Johnson 1985).

Table 5-1: Aromatic reference fluids used for bitumen viscosity prediction

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU # 173</td>
<td>C$<em>{31}$H$</em>{54}$</td>
</tr>
<tr>
<td>PSU # 179</td>
<td>C$<em>{26}$H$</em>{32}$</td>
</tr>
<tr>
<td>PSU # 611</td>
<td>C$<em>{20}$H$</em>{32}$</td>
</tr>
<tr>
<td>PSU # 625</td>
<td>C$<em>{14}$H$</em>{18}$</td>
</tr>
</tbody>
</table>

In this study, different types of hydrocarbons, such as aromatics, n-alkanes and cycloalkanes, were applied as reference fluids; and, the simulated results were compared with the experimental
data of GCOS Athabasca bitumen (Jacobs et al. 1980). The bitumen characterization for the GCOS bitumen presented in Table 3-1 was applied for the simulation results.

Figure 5-1 indicates the simulated results for the different reference fluids presented in Table 5-2. As can be seen from this figure, the trend of bitumen viscosity from the experimental data shows a curvilinear concave decreasing trend with increasing temperature, where the y-axis has a logarithmic scale. N-alkanes, such as n-heptane and n-hexadecane, showed linear relationships; and, cyclohexane exhibited a similar trend. Aromatics, like m-xylene and toluene, showed a trend closer to the bitumen viscosity experimental data; however, there is significant deviation from data points.

Table 5-2: Different reference fluids used in this study

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>C_7H_8</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>C_8H_10</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>C_7H_16</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>C_16H_34</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C_6H_12</td>
</tr>
</tbody>
</table>

The results indicate that aromatics were able to predict the bitumen viscosity trend; however, there was a considerable deviation from the experimental data. For this reason, higher molecular
reference fluids were applied and tested for the prediction of bitumen viscosity. Two new reference fluids and their critical properties are presented in Table 5-3. The new reference fluids (1,1 diphenyethane and 1,1 diphenyheptane) were modeled mathematically, and the results were compared with experimental data. The simulated results show good agreement with the experimental data for the prediction of GCOS bitumen viscosity prediction.

![Graph showing viscosity vs temperature for different reference fluids](image_url)

**Figure 5-1:** Application of different reference fluids and comparison with experimental data

Table 5-3. Higher molecular weight aromatics used in this study (Knovel, Yaws Handbook 2012)
The viscosity and density of 1,1 Diphenyheptane have shown in table 5-4. As can be seen viscosity is changing dramatically with temperature.

Table 5-4. Viscosity and Density of higher molecular weight aromatics at atmospheric pressure (Lowitz et al. 1958)

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>Dynamic Viscosity (cP)</th>
<th>Density (kg / m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>37.8 °C  60 °C  98.9 °C  135 °C</td>
<td>37.8 °C  60 °C  98.9 °C  135 °C</td>
</tr>
<tr>
<td>1,1 Diphenyethane</td>
<td>2.85  1.84  1.08  -</td>
<td>986.0  968.9  938.7  -</td>
</tr>
<tr>
<td>1,1 Diphenyheptane</td>
<td>7.98  4.04  1.79  1.12</td>
<td>937.5  921.6  893.8  868.4</td>
</tr>
</tbody>
</table>

Viscosity and density of 1,1 Diphenyethane and be found in Knovel, DIPPR (2012), but for 1,1 Diphenyheptane based on the model proposed by Knovel, DIPPR (2012), two correlations have been developed. Equations 5-15 up to 5-18 are showing the correlation model for viscosity and density prediction of 1,1 Diphenyheptane at atmospheric pressure (Knovel, DIPPR 2012):

\[
\ln[\mu(cP)] = A + \frac{B}{T} + C \ln(T) \tag{5 - 15}
\]
\[
A = -132.1116, \quad B = 9.0569740 \times 10^3, \quad C = 18.3045
\]

\[
\rho(\frac{\text{Knol}}{m^3}) = \frac{D}{E^{1 + (1 - T/F)^6}}
\]

\[
D = 0.2159, \quad E = 0.2155, \quad F = 1257.0718, \quad G = 0.5555
\]

The temperature ‘T’ in equations 5-15 and 5.17 is in Kelvin.

### 5.2 Pressure and Concentration Correction to Corresponding States for Bitumen Mixtures

Since the pressure is supposed to be atmospheric in the corresponding states viscosity model, a pressure correction is necessary for pressures higher than atmospheric.

Figures 5-2 up to figure 5-7 depict the viscosity variation for different pressures and temperatures at a constant concentration. As can be seen, the viscosity in the logarithmic scale showed a linear relationship with pressure. The slope of the trend line that passed through the experimental data increased with decreasing temperature.

Johnson (1985) developed a pressure correction based on the following relationship:

\[
\mu_{\text{mix}}(P, T) = \exp(\mu_{\text{mix}}(P_{\text{Atm}}, T) + B_T(P - P_{\text{Atm}}) + C_T X) \]

\[
B_T = 4.35e - 2 \times \exp((-6.49e - 3)T) \]

\[
C_T = 0
\]
Johnson (1985) ignored the concentration term. However, in this study, we also used a correction for the solvent concentration term. The pressure correction term was compatible with the experimental data from Guan et al. (2013), who have gathered a lot of data for bitumen and toluene mixtures.

As can be seen from Figure 5-2 up to figure 5-7, the viscosity of bitumen mixture with toluene showed a linear relationship. These figures have been depicted based on a fixed concentration of solvent: in this case, toluene. At a fixed temperature and solvent concentration, the viscosity trend versus pressure can be evaluated, since the other parameters have been kept constant (Guan et al. 2012). The slope of the line increased with decreasing temperature. Therefore, the pressure corrections presented in Equations 5-19 and 5-20 are compatible with these experimental data.
Figure 5-2: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.05 (Guan et. al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)
Figure 5-3: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.1 (Guan et. al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)
Figure 5-4: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.2 (Guan et. al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)
Figure 5-5: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.3 (Guan et. al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)
Figure 5-6: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.4 (Guan et. al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)
Figure 5-7: Viscosity variation for different pressures and temperatures for a bitumen and toluene mixture with a toluene weight fraction of 0.5 (Guan et al. 2013)

(Legend: + T = 344.4 K, □ T = 333.0 K, ○ T = 320.6 K, ◊ T = 309.6 K, * T = 301.5 K)

Another pressure correction method was proposed by Mehrotra and Svrcek (1982). The model, which is presented in Equation 2-4, was used as the basis for the new pressure correction. The new model can be presented in the following configuration:

$$\mu_{\text{mix}}(P, T) = \exp(\mu_{\text{mix}}(P_{\text{Atm}}, T) + (A - \frac{B}{T})(P - P_{\text{Atm}}) + C_T X)$$  \hspace{1cm} 5 - 22$$

Where A and B are coefficients, which can be found from experimental data; and, $C_T$ plays the same role as Equation 5-19 (Mehrotra and Svrcek 1982).
As previously mentioned, the slope of the regression lines in Figure 5-2 up to figure 5-7 increased with decreasing temperature; therefore, the pressure correction method presented in Equation 5-22 should correspond with this observation.

The correction for the solvent concentration was evaluated based on experimental data. The data points for the bitumen and toluene mixtures at a constant pressure and temperature were used to investigate the viscosity variation versus solvent concentration (Guan et. al. 2013).

Figure 5-8 shows the variation in viscosity with increasing solvent concentrations. As can be seen from this figure, the viscosity showed a power low relationship with the solvent weight fraction, as shown in the following equation:

$$\mu = aW^b$$  \hspace{2cm} 5 - 23

Where W represents the solvent weight fraction, a and b are coefficients that depend on pressure and temperature.

The results in Figures 5-8 and 5-9 were obtained at a pressure of 0.124 MPa and temperatures of 342.9 and 330.8 K, respectively. The results in Figures 5-10 and 5-11 were obtained at a pressure of 10 MPa. As can be seen from these graphs, coefficients a and b were not a function of temperature and could be assumed to be constant, which was not compatible with equation 5-19 up to equation 5-22.
Figure 5-8: Viscosity variation for different toluene weight fractions for bitumen and toluene mixtures at a pressure of 0.124 MPa and a temperature of 342.9 K

Figure 5-9: Viscosity variation for different toluene weight fractions for bitumen and toluene mixtures at a pressure of 0.124 MPa and a temperature of 330.8 K
In this study, Equation 5-19 up to equation 5-22 can be used for pressure and concentration corrections for the corresponding states principle at atmospheric pressure, with the modification that $C_T$ is not zero and not a function of temperature.

Figure 5-10: Viscosity variation for different toluene weight fractions for bitumen and toluene mixtures at a pressure of 10 MPa and a temperature of 342.9 K
Figure 5-11: Viscosity variation for different toluene weight fractions for bitumen and toluene mixtures at a pressure of 10 MPa and a temperature of 330.8 K

5.3 Lindeloff Model

Lindeloff et al. (2004) model is presented in section 2-2; and, Equations 2-67 to 2-75 were applied for the prediction for bitumen viscosity. As mentioned by Lindeloff et al. (2004), the use of higher molecular weight reference fluids is more suitable for heavy oils.

The mixing rules used for this model are as follows:
In Lindeloff et al. (2004) model, parameters A and B have been determined as:

\[
A = 1 \quad 5 - 26
\]

\[
B = 8 \quad 5 - 27
\]

In Lindeloff et al. (2004) model, methane was used as the reference fluid, for which the values assigned for the above parameters are valid. In this study, since different reference fluids were used, these two parameters are defined as tuning parameters for the new reference fluids. The reference fluids were chosen from a variety of hydrocarbon types, such as normal alkanes, aromatics and cycloalkanes. The list of substances used as reference fluids is presented in Table 5-5.
Table 5-5 Different reference fluids used in the Lindeloff model

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
</tr>
<tr>
<td>Benzene</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>n-Butane</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;34&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Parameters A and B in Equations 5-24 and 5-25 were used as the tuning parameters for different reference fluids. The simulation indicated that the results were not sensitive to parameter B; however, there was a significant sensitivity to parameter A. Higher molecular weight aromatics were tested with the Lindeloff model for the prediction of bitumen viscosity. The simulation results and absolute deviation are discussed in Chapter 6.
6.1 Viscosity of Raw Bitumen

Bitumen is a complex substance containing different hydrocarbon components that needs to be characterized into different pseudo-components. For GCOS bitumen, the characterization scheme in Table 3-1 was applied to its mathematical modeling. Johnson (1985) used four aromatic reference fluids (PSUs). PSU # 625 had the lowest molecular weight and PSU # 173 the highest molecular weight. PSU # 179 had the highest viscosity value and PSU # 625 the lowest. However, in terms density, PSUs # 625 and # 179 had the highest values (Johnson 1985).

The experimental data in Figure 6-1 indicates that the bitumen viscosity showed a curvilinear trend with increasing temperature. When used as the reference fluid, different PSUs also had curvilinear behaviours with increasing temperature. PSUs # 173 and # 179 showed significant deviations from the experimental data and failed to predict the bitumen viscosity: PSU # 173 underestimated the bitumen viscosity, and PSU # 179 overestimated the viscosity of bitumen. PSUs # 625 and # 611 showed closer results to the experimental bitumen viscosity: PSU # 625 resulted in less deviation, and PSU # 611 led to a slight overestimation of the bitumen viscosity. The experimental data for the GCOS bitumen were from Jacobs et al. (1980) (Johnson 1985; Jacobs et al. 1980).
In this study, two different high molecular weight aromatics (1,1 diphenyethane and 1,1 diphenyheptane) were used as the reference fluid in a, based on Figure 5-1, which showed that aromatics were able to predict the trend of bitumen viscosity, and also based on Figure 6-1, which indicated that higher molecular weight aromatics could result in decreased deviations than those of aromatics, such as toluene and m-xylene.

Figure 6-1: Prediction results of GCOS bitumen for different PSUs as reference fluids and comparison with experimental data (Johnson 1985)

The absolute average relative deviation (AARD) was used for the comparison of the predictions of the mathematical model with experimental data and is defined in the following equation:
The critical properties and acentric factors of 1,1 diphenyethane and 1,1 diphenyheptane are presented in Table 5-3, where it can be seen that 1,1 diphenyethane had lower molecular weight and boiling point values but a higher specific gravity than 1,1 diphenyheptane. On the other hand, 1,1 diphenyheptane showed a higher critical temperature and lower critical pressure.

Figure 6-2 depicts the predicted results for 1,1 diphenyethane and 1,1 diphenyheptane. As can be seen in Figure 6-2, 1,1 diphenyheptane could predict bitumen viscosity with less deviation. Table 6-1 presents the comparison of the deviation of the results. From Table 6.1, the use of 1,1 diphenyheptane as a reference fluid showed an improvement in the AARDs from the experimental data. The experimental data is from Jacobs et al. (1980) (Jacobs et al. 1980; Johnson 1985).

Table 6-1: Comparison of the predicted results of this study with those of the model in the literature

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>No. of Data Points</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1 Diphenyethane</td>
<td>13</td>
<td>21.46%</td>
</tr>
<tr>
<td>1,1 Diphenyheptane</td>
<td>13</td>
<td>5.96%</td>
</tr>
<tr>
<td>PSU#625 (Johnson 1985)</td>
<td>13</td>
<td>6.97%</td>
</tr>
</tbody>
</table>
Table 6-2 shows the predicted results versus the experimental data with 1,1 diphenyheptane as the reference fluid in the corresponding states model. As can be seen from this table, the relative deviations were lower at lower temperatures, such as 31 and 33.8 °C, than at higher temperatures, such 120 and 130 °C, at which the relative deviation was increasing. This can be attributed to 1,1 diphenyheptane as the reference fluid: as the temperature of bitumen increased the viscosity of bitumen drastically decreased; however, the rate of decreasing viscosity with increasing temperature in reference fluid was much lower than that of the bitumen viscosity.
Therefore, one may expect that the model would show higher AARDs at higher temperatures than at lower temperatures.

Table 6-2: Predicted results versus data points with 1,1 diphenyheptane as the reference fluid

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Predicted Value (cP)</th>
<th>Experimental Data (cP)</th>
<th>Relative Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.0</td>
<td>168515</td>
<td>1.68 e+05</td>
<td>-0.307</td>
</tr>
<tr>
<td>33.8</td>
<td>114762</td>
<td>1.2e+05</td>
<td>4.37</td>
</tr>
<tr>
<td>40.0</td>
<td>51541</td>
<td>5.7e+04</td>
<td>9.58</td>
</tr>
<tr>
<td>50.0</td>
<td>16146</td>
<td>1.75e+04</td>
<td>7.74</td>
</tr>
<tr>
<td>55.0</td>
<td>9536</td>
<td>1e+4</td>
<td>4.64</td>
</tr>
<tr>
<td>67.0</td>
<td>3058</td>
<td>3e+03</td>
<td>-1.93</td>
</tr>
<tr>
<td>71.2</td>
<td>2133</td>
<td>2e+03</td>
<td>-6.65</td>
</tr>
<tr>
<td>75.0</td>
<td>1564</td>
<td>1.482e+03</td>
<td>-5.53</td>
</tr>
<tr>
<td>81.0</td>
<td>984.1</td>
<td>920</td>
<td>-6.97</td>
</tr>
<tr>
<td>90.3</td>
<td>510.3</td>
<td>480</td>
<td>-6.31</td>
</tr>
<tr>
<td>96.0</td>
<td>352.7</td>
<td>360</td>
<td>2.03</td>
</tr>
<tr>
<td>120.0</td>
<td>93.85</td>
<td>100</td>
<td>6.15</td>
</tr>
<tr>
<td>130.0</td>
<td>59.34</td>
<td>70</td>
<td>15.2</td>
</tr>
</tbody>
</table>
Johnson (1985) introduced a one pseudo-component method by using Lee-Kesler correlations for the critical and physical properties of GCOS bitumen, as shown in Table 6-3. As previously mentioned, bitumen consists of different types of hydrocarbons, such as saturates, aromatics, resins and asphaltene; therefore, an aromatic is a constituent of bitumen (Johnson 1985; Kesler and Lee 1976).

As can be seen from Table 6-3, bitumen has a high critical temperature and low critical pressure. As can be observed from Table 5-5, these properties are also true for 1,1 diphenyethane and 1,1 diphenyheptane, with 1,1 diphenyheptane showing a higher critical temperature and lower critical pressure. This results in a lower deviation in the prediction of bitumen when 1,1 diphenyheptane is used as the reference fluid in the corresponding states model, as can be seen in Figure 6-2.

Table 6-3: One pseudo-component scheme for GCOS bitumen characterization (Johnson 1985)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Wt%</th>
<th>MW</th>
<th>SG</th>
<th>T_b (K)</th>
<th>T_c (K)</th>
<th>P_c (MPa)</th>
<th>V_c (m3/kmol)</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>100</td>
<td>594.6</td>
<td>1.0769</td>
<td>937.1</td>
<td>1090.9</td>
<td>0.7861</td>
<td>2.271</td>
<td>1.361125</td>
</tr>
</tbody>
</table>

6.2 Viscosity of Bitumen Mixture

6.2.1 *Bitumen/Toluene Mixture*

Based on characterization schemes in the literature, the bitumen mixture with toluene has been considered and used for our model. Athabasca Mackay River bitumen was characterized into 6
pseudo-components, with the critical properties and acentric factor presented in Table 3-6 (Kariznovi et. al. 2009).

Figure 6-3 depicts the experimental data versus the Johnson (1985) model and the model used in this study. The experimental data were gathered at a temperature of 25 °C and atmospheric pressure. As can be observed from the figure, the Johnson model showed a higher deviation at lower toluene weight fractions than the model used in this study; and, the predicted results obtained from this study exhibited an improvement in the deviation from the experimental data.

Table 6-4 compares the average deviation in this study with that of the Johnson model. As can be seen from this table, this study’s model had better predicted results in terms of AARDs.
Figure 6-3: Comparison of results of Athabasca Mackay River bitumen/toluene mixtures with experimental data, the Johnson model and this study’s model at atmospheric pressure and at temperature of 25 °C.
Table 6-4: Comparison of the models in the literature and this study with experimental data

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>No. of Data Points</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1 Diphenyheptane</td>
<td>9</td>
<td>6.99%</td>
</tr>
<tr>
<td>PSU #625 (Johnson 1985)</td>
<td>9</td>
<td>9.14%</td>
</tr>
</tbody>
</table>

Table 6-5 shows the predicted value versus experimental data for the model used in this work. As can be seen from this table at lower toluene weight percent the higher value of solvent weight percent the relative deviation is higher comparing to the other values. This is because of the fact that at low solvent weight percent the mixture behavior is close to bitumen behaviour however, at high solvent concentration the bitumen mole fraction is very low since bitumen has a very high molecular weight. At these two points the viscosity of mixture is close to bitumen (at low solvent weight percent) and toluene (at high solvent weight percent) and because of that the relative deviation from experimental data is increasing.

For pressures higher than atmospheric pressure, the experimental data in Guan et al. (2013) were used in our model. The two methods for pressure corrections introduced in Chapter 5 (Equations 5-19 and 5-22) were compared with the correlation modeling results by Guan et al. (2013).
Table 6-5: Predicted values versus experimental data for different toluene weight percent for the model used in this study

<table>
<thead>
<tr>
<th>Toluene (Wt%)</th>
<th>Predicted Value (cP)</th>
<th>Experimental Data (cP)</th>
<th>Relative Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2868.7</td>
<td>2067.5</td>
<td>-38.75</td>
</tr>
<tr>
<td>15</td>
<td>604.18</td>
<td>578.14</td>
<td>-4.504</td>
</tr>
<tr>
<td>20</td>
<td>189.26</td>
<td>184.49</td>
<td>-2.585</td>
</tr>
<tr>
<td>25</td>
<td>77.22</td>
<td>87.01</td>
<td>11.25</td>
</tr>
<tr>
<td>30</td>
<td>37.90</td>
<td>40.55</td>
<td>6.535</td>
</tr>
<tr>
<td>35</td>
<td>21.27</td>
<td>20.14</td>
<td>-5.611</td>
</tr>
<tr>
<td>40</td>
<td>13.20</td>
<td>13.75</td>
<td>4.000</td>
</tr>
<tr>
<td>45</td>
<td>8.86</td>
<td>8.77</td>
<td>-1.026</td>
</tr>
<tr>
<td>50</td>
<td>6.31</td>
<td>5.45</td>
<td>-15.78</td>
</tr>
</tbody>
</table>

Figure 6-4 depicts the predicted results versus the experimental data from Guan et al. (2013). As can be seen in this figure, the model used in this study can predict the experimental data. The number of data points used was 385; and, the resulting AARD was approximately 8.40%, which is quite acceptable.

Figure 6-5 shows that the deviation of the predicted data from experimental data increased at higher temperatures. As previously mentioned, bitumen viscosity decreases drastically with increasing temperature; and, this phenomenon is more complicated when bitumen is mixed with
a solvent. At these higher temperatures, the bitumen mixture also showed a higher deviation from the experimental data.

Figure 6-4: Comparison of the calculated viscosity versus the experimental data of Athabasca Mackay River bitumen and toluene mixture

The predicted results for different temperatures and toluene weight fractions are presented in Figures 6-5 and 6-6. Figure 6-5 shows the data points at approximately atmospheric pressure; and, Figure 6-6 presents the predicted results for different temperatures and solvent weight fractions at a pressure of 10 MPa. Increased deviation of the predicted data from experimental data at higher temperatures is also observable in Figure 6-6. At high temperatures, such as 343.7 K, the deviation from the experimental data points was significant; and, in this case, higher pressure also contributed to the deviation.
Figure 6-5: Viscosity of bitumen/toluene mixture at different temperatures and toluene weight fractions at a pressure of 0.125 MPa
Experimental data show that the viscosity of bitumen strongly depends on pressure. However, as 1,1 diphenyheptane as the reference fluid, this relationship is not as considerable as that of bitumen. The viscosity of 1,1 diphenyheptane does not change dramatically with pressure as can be observed for bitumen. Consequently, both pressure and temperature contributed to the deviation from the experimental data, which is the reason that the deviations at higher temperatures and higher pressures are more significant.
Table 6-6 depicts the comparison of the model used in this study with the correlation applied by Guan et al. (2013) to bitumen/toluene mixtures. As can be seen from this table, both pressure correction methods showed an improvement in terms of the AARD other than that of the literature model. Equation 5-22 led to better results than Equation 5-19.

Table 6-6: Comparison of our simulated data with the correlation in the literature (Guan et. al. 2013)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Case Study</th>
<th>No. of Data Point</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen/toluene</td>
<td>Eq. 5-19</td>
<td>385</td>
<td>10.5%</td>
</tr>
<tr>
<td>Bitumen/toluene</td>
<td>Eq. 5-22</td>
<td>385</td>
<td>8.40%</td>
</tr>
<tr>
<td>Bitumen/toluene</td>
<td>Guan et al. (2013)</td>
<td>385</td>
<td>14.8%</td>
</tr>
</tbody>
</table>

6.2.2 Bitumen/Xylenes Mixtures

Another solvent considered in this project was xylenes. Experimental data for Athabasca Mackay River bitumen/xylenes mixtures were gathered by Guan et al (2013). The characterization of bitumen was the same as for the bitumen/toluene mixtures.
Figure 6-7 shows the predicted results from the model in this study versus the experimental data from Guan et al (2013). The results show satisfactory predictions. The number of data points was 385, and the AARD was approximately 8.05%.

Figure 6-7: Comparison of calculated viscosity versus the experimental data for Athabasca Mackay River bitumen and xylenes mixture

Figures 6-8 depicts the modeling results compared to the experimental data gathered by Guan et al. (2013) at approximately atmospheric pressure. As with the bitumen/toluene mixtures, the deviations of the predictions from the experimental data increased as the temperature rose. The
differences of the bitumen/xylenes mixtures were more significant than those of the bitumen/toluene mixtures.

Figure 6-8: Viscosity of bitumen/xylenes mixture for different temperatures and xylenes weight fractions at a pressure of 0.125 MPa

Figure 6-9 shows the results of the bitumen/xylenes mixtures at a pressure of 10 MPa. As can be seen, the deviation from the extreme data increased at higher xylenes weight fractions.
Table 6-7 presents a comparison of the bitumen/xylenes mixture results of the model used in this study with those of the Guan et al. (2013) correlation. As can be seen, the AARDs of our model were lower than the one developed in the literature. Both the pressure correction methods (Equations 5-19 and 5-22) improved the results, and a reduction in the AARD was observable. Equation 5-22 showed better results with less deviation from the experimental data. As with the bitumen/toluene mixtures, the bitumen/xylenes mixtures also showed less deviation with Equation 5-22.
Table 6-7: Comparison of our simulated data with the correlation developed by Guan et al. (2013)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Case Study</th>
<th>No. of Data Point</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen/xylenes</td>
<td>Eq. 5-19</td>
<td>385</td>
<td>9.94%</td>
</tr>
<tr>
<td>Bitumen/xylenes</td>
<td>Eq. 5-22</td>
<td>385</td>
<td>8.05%</td>
</tr>
<tr>
<td>Bitumen/xylenes</td>
<td>Guan et al. (2013)</td>
<td>385</td>
<td>13.8%</td>
</tr>
</tbody>
</table>

6.2.3 *Bitumen and n-Decane Mixture*

The last solvent used in this project is n-Decane. Experimental data for Athabasca Mackay River bitumen/n-decane mixtures were gathered by Nourozieh et al (2013). The characterization of bitumen was the same as with the bitumen/toluene and bitumen/xylenes mixtures. Two pressure correction methods (equation 5-19 and equation 5-22) were also tested for these mixtures.

Figure 6-10 shows the modeling data versus the experimental data. As can be seen from the figure, the results showed a satisfactory deviation from the experimental data. The AARD from data points was 8.54%, and the number of experimental data points was 330.
Figure 6-10: Comparison of calculated viscosity versus experimental data for Athabasca Mackay River bitumen and n-decane mixture

Figures 6-11 depicts the comparison of the modeling results with the experimental data. As illustrated in this figure, the results were at approximately atmospheric pressure; and, the deviation from data points increased at higher temperatures and higher solvent weight fractions, as with the bitumen/toluene and bitumen/xylenes mixtures.
Figure 6-11: Viscosity for bitumen/n-decane mixture for different temperatures and n-decane weight fractions at a pressure of 0.125 MPa.

Figure 6-12 shows the viscosity results for bitumen/n-decane mixtures for different temperatures and solvent weight fractions at a pressure of 10 MPa. Again, the viscosity showed higher deviations from experimental data at higher temperatures, pressure and solvent weight fractions.
Figure 6-12: Viscosity of bitumen/n-decane mixture for different temperatures and n-decane weight fractions at a pressure of 10 MPa

Table 6-8 depicts the predicted results in terms of AARD for both of the pressure correction methods. As can be seen from Table 6-8, the pressure correction in Equation 5-22 showed better results than the literature model. Figure 6-10 shows the predicted results versus the experimental data for the pressure correction of Equation 5-22. The number of data points was 330, and the AARD was approximately 8.54%.
Table 6-8 presents the comparison of the model used in this study with one used by Nourozieh et al. (2013) correlation. As can be seen the average deviation resulted in this study has been reduced comparison with the one developed in the literature.

Table 6-8: Comparison of our simulated data with correlation developed by Nourozieh et al. (2013)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Case Study</th>
<th>No. of Data Point</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen/n-decane</td>
<td>Eq. 5-19</td>
<td>330</td>
<td>10.48%</td>
</tr>
<tr>
<td>Bitumen/n-decane</td>
<td>Eq. 5-22</td>
<td>330</td>
<td>8.54%</td>
</tr>
<tr>
<td>Bitumen/n-decane</td>
<td>Nourozieh et al. (2013)</td>
<td>330</td>
<td>9.6%</td>
</tr>
</tbody>
</table>

6.3 Bitumen Viscosity Prediction with the Lindeloff Model

As mentioned in Chapter 4, the Lindeloff corresponding states model has been developed for heavy oil. Two new parameters have been introduced, and different reference fluids have been investigated for the prediction of bitumen viscosity. GCOS bitumen was used, and the
characterization scheme in Table 5-1 with 4 pseudo-components configuration was applied. The experimental viscosity data of GCOS bitumen were from Jacobs et al. (1980).

Figure 6-13 depicts the simulation results for the viscosity of the bitumen using different alkanes as reference fluids. As can be seen from the figure, using normal alkane and cycloalkane led to significant deviations from the experimental data. Figure 6-13 indicates that the alkanes were not able to predict the trend, resulting in considerable deviations from the experimental data.
Figure 6-13: Prediction of the viscosity of GCOS bitumen based on the Lindeloff model using different alkanes as the reference fluid.

Figure 6-14 presents the simulation results for the aromatics used as the reference fluid. As can be observed from the figure, among different aromatics used for simulation, toluene showed the lowest AARD.
Figure 6-14: Predictions of the viscosity of GCOS bitumen based on the Lindeloff model using three different aromatics as the reference fluid.

Table 6-9 shows the comparison of the AARD for the different aromatics used in Figure 6-14. As can be seen from the table, toluene showed the best predicted results.
Table 6-9: Comparison of the predicted results for different aromatics as the reference fluid

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>No. of Data Point</th>
<th>AARD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>13</td>
<td>35.7%</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>13</td>
<td>130.3%</td>
</tr>
<tr>
<td>Benzene</td>
<td>13</td>
<td>158.9%</td>
</tr>
</tbody>
</table>

Figure 6-15 shows the simulation results for different types of higher molecular weight aromatics. As can be seen from this figure, 1,1 Diphenyheptane showed a better results comparing to the other one.
Figure 6-15: Predictions of the viscosity of GCOS bitumen based on the Lindeloff model using different higher molecular weight aromatics as the reference fluid.

Table 6-10 compares the predicted results in terms of the AARD for 1,1 Diphenyethane and 1,1 Diphenyheptane using as reference fluid in Lindeloff model. As can be seen, 1,1 Diphenyheptane shows the better results.
Table 6-10: Comparison of the predicted results for different higher molecular weight aromatics as the reference fluid

<table>
<thead>
<tr>
<th>Reference Fluid</th>
<th>No. of Data Point</th>
<th>AARD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1 Diphenyethane</td>
<td>13</td>
<td>44.50%</td>
</tr>
<tr>
<td>1,1 Diphenyheptane</td>
<td>13</td>
<td>5.09%</td>
</tr>
</tbody>
</table>

The Lindeloff model has two advantages over the Johnson (1985) model. One is the procedure, since the Lindeloff model does not require iteration and is faster in terms of computational time. Moreover, for some cases reported by Johnson (1985), the procedure did not converge for the case of bitumen pseudo-components.

The other advantage of the Lindeloff model is that it has only one tuning parameter, making it simpler for the user for prediction of bitumen viscosity. The Johnson (1985) model has one sizing shape factor for each component and one energy shape factor, making it more complicated, especially for bitumen with different pseudo-components.

The Lindeloff model also showed better than the Johnson (1985) model. As can be observed from Tables 6-1 and 6-10, the AARD from experimental data for Johnson model is 5.96%; however, the AARD for Lindeloff model for the same data points is 5.04%.
Chapter 7. Conclusions and Recommendations

6.2.1 Conclusions

The mathematical modeling and the results of the viscosity prediction model from the corresponding states method for raw bitumen and bitumen mixtures have led to the following conclusions:

1) The mathematical modeling for the prediction of the viscosity of raw bitumen and bitumen mixtures with toluene, xylenes and n-decane was performed, and the model could predict the bitumen mixture viscosity with acceptable deviation. The absolute average deviations (AARDs) of the viscosity prediction of bitumen mixtures with toluene, xylenes and n-decane were 8.40, 8.05 and 8.54%, respectively.

2) The effects of changing the reference fluid were investigated, and the results indicate that aromatics were able to better predict the trend of bitumen viscosity compared to normal alkanes and cycloalkanes. Bitumen showed a curvilinear trend with temperature increasing; however, normal alkanes, such as n-heptane and n-hexadecane, and cycloalkane, such as cyclohexane, exhibited a linear relationship with temperature. Although aromatics, such as toluene and m-xylene, had larger deviations from the experimental data, they were able to predict the trend of bitumen viscosity with temperature.

3) Using high molecular weight aromatics, such as 1,1 diphenyheptane and 1,1 diphenylhethane, as the reference fluid led to lower deviations from the experimental data
in the prediction of bitumen viscosity. They were also able to predict the trend of bitumen viscosity, i.e. a curvilinear relationship with temperature.

4) 1,1 diphenyheptane was proposed as the reference fluid for the prediction of the viscosity of bitumen using the corresponding states principles. It had an AARD of 5.96% from experimental data, compared to 21.46% with 1,1 diphenyethane as the reference fluid.

5) Using the Lindeloff corresponding states model is preferred, because it has only one tuning parameter that has to be found based on the experimental data, compared to the eight parameters to be tuned in the Johnson model. For Lindeloff model Using 1,1 diphenyheptane as the reference fluid in the Lindeloff model showed a lower AARD in the prediction of bitumen viscosity.

6) The modeling results showed a higher deviation at higher pressures and higher temperatures in the prediction of the viscosity of bitumen mixtures with solvents, such as xylene, toluene and n-decane. The AARD also increased at higher solvent fractions. This is attributable to the much higher trend of decreasing bitumen viscosity with increasing temperature than the trend of 1,1 diphenyheptane as the reference fluid.

7) For the prediction of the viscosity of bitumen mixtures with toluene, xylenes and n-decane, the pressure correction method presented in Equation 5-18 resulted in lower deviations from the experimental data than those of Equation 5-15. Bitumen/xylenes mixtures exhibited the lowest deviation from the experimental data.
7.2 Recommendations for Future Work

1) Different pressure methods should be examined for the prediction of the viscosity of bitumen to find one that results in lower deviations from the experimental data.

2) Bitumen characterization is an important input parameter for the prediction of viscosity. Different characterization schemes should be examined to find the one that leads to lower deviation.

3) For bitumen characterization, different correlations have been used to predict the critical and physical properties of bitumen pseudo-components. These correlations are usually coupled with equation of states. Different correlations with different equation of states should be examined to find the optimal scheme for bitumen characterization.

4) It is recommended to apply the Lindeloff corresponding states model to bitumen mixture with solvents, such as xylenes, toluene and n-decane.
References


Satyro, M.A. 2009. The role of thermodynamic modeling consistency in process simulation, in: 8th World Congress of Chemical Engineering, Palais des Congres, 23–27


Figure A-1 Flowchart for calculation of bitumen viscosity using Lindeloff Corresponding States Method

START

INPUT BITUMEN PSEUDO-COMPONENT MOLE FRACTIONS, CRITICAL AND PHYSICAL PROPERTIES AND ACENTRIC FACTOR

CALCULATE PSEUDO-CRITICAL PRESSURE AND TEMPERATURE AND MIXTURE MOLECULAR WEIGHT USING EQUATIONS 2-69, 2-70 AND 2-71

CALCULATE $\alpha_{mix}$ AND $\rho_r$ USING EQUATIONS 2-74 AND 2-75

CALCULATE CORRESPONDING PRESSURE AND TEMPERATURE USING EQUATION 2-68

CALCULATE VISCOSITY OF REFERENCE FLUID USING EQUATION 5-15 AND BITUMEN USING EQUATION 2-67

STOP