January 2017

Study Of Pore-Dependent Petroleum Fluid Properties In Tight Shale Plays: Bakken Formation

Agustinus Zandy

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STUDY OF PORE-DEPENDENT PETROLEUM FLUID PROPERTIES IN TIGHT SHALE PLAYS: BAKKEN FORMATION

by

Agustinus Zandy

Bachelor of Science, Bandung Institute of Technology, 2007

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

December

2017
This thesis submitted by Agustinus Zandy in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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Dean of the School of Graduate Studies

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Title     Study of Pore-Dependent Petroleum Fluid Properties in Tight Shale Plays: Bakken Formation
Department Petroleum Engineering
Degree    Master of Science

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Agustinus Zandy
December 2, 2017
# TABLE OF CONTENTS

LIST OF FIGURES ................................................................................................................................. v  
LIST OF TABLES ................................................................................................................................. ix  
ACKNOWLEDGEMENT ............................................................................................................................... ix  
ABSTRACT .................................................................................................................................................. xi  

CHAPTER  
I. INTRODUCTION .................................................................................................................................... 1  
   Background ............................................................................................................................................... 1  
   Statement of Problem ................................................................................................................................. 5  
   Research Objectives ................................................................................................................................. 6  
   Method Overview ...................................................................................................................................... 6  
   Thesis Outline ......................................................................................................................................... 7  

II. BAKKEN FORMATION SHALE PLAY ..................................................................................................... 9  
   Background: Unconventional Resources ................................................................................................. 9  
   Geology and Mineralogy ........................................................................................................................... 11  
   Nanoscale consideration and parameters in the Bakken Formation ..................................................... 15  

III. NANO-SCALE EFFECTS ON PETROLEUM FLUID PROPERTIES ....................................................... 19  
   Pore Size Distribution in Middle Bakken Formation ............................................................................... 20  
   Nuclear Magnetic Resonance ................................................................................................................ 24  
   Molecular Simulation on Confined PVT .................................................................................................... 27  
   Equation of State ..................................................................................................................................... 30  
   Adsorption Effect on Pore Volume with Molecular Simulation .............................................................. 33  
   Experimental Work on Nano-PVT ........................................................................................................... 39  
   Analytical Work on Peng-Robinson EOS ............................................................................................... 45  

IV. RESULT AND ANALYSES ................................................................................................................... 53  
   NMR Analysis ....................................................................................................................................... 53
Analysis and Comparison of Analytical Work and Literature Data............... 57

V. CONCLUSIONS AND RECOMMENDATIONS ........................................... 66
   Conclusions .................................................................................. 66
   Recommendations ......................................................................... 67

NOMENCLATURE .................................................................................. 68

APPENDICES ....................................................................................... 70
   APPENDIX A  NMR T₂ Distribution Curves ........................................... 71
   APPENDIX B  Analytical Process In Deriving The Critical Properties From The Pressure Tensor ........................................................................ 76

REFERENCES ...................................................................................... 80
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Decline curve analysis of Bakken: showing ten-year probabilistic-type curve (PTC) for all horizontal wells in the Bakken Formation (Cook, 2013)</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>The Bakken Formation Map – Bakken-Lodgepole total petroleum system (TPS) and major structural elements within the province in the United Stated (Pollastro et al. 2010)</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>Extent of the Williston Basin (Langton, 2008)</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>Stratigraphic column of the Bakken Formation with Lodgepole as overlying and Three-Forks as underlying formations (modified from Kuhn et al., 2012 and Pollastro et al., 2010)</td>
<td>12</td>
</tr>
<tr>
<td>5.</td>
<td>Approximate limits of Bakken members in the United States area, determined from data compilation from studies of Webster (1984), Hester and Schmoker (1985), Smith and Bustin (2000), and lefever (2008). (Pollastro et al., 2010)</td>
<td>13</td>
</tr>
<tr>
<td>6.</td>
<td>Lithologic column depicting lithofacies and sedimentologic characteristics of the Middle Bakken Formation (Pitman et al., 2001)</td>
<td>14</td>
</tr>
<tr>
<td>7.</td>
<td>Slabbed sandstone is displaying reticulated fracture network on a wet surface. Note that the permeable nature and distribution of fractures are not apparent when the surface is dry. (Pitman et al., 2001)</td>
<td>17</td>
</tr>
<tr>
<td>8.</td>
<td>Pore size distribution of the Middle Bakken Formation (Ramakrishna et al. 2010)</td>
<td>18</td>
</tr>
<tr>
<td>9.</td>
<td>MICP analysis of Bakken Formation on a histogram showing porosity versus pore-throat diameter for Upper (blue), Middle (yellow), and Lower (red) Bakken members. (Anyanwu, 2015)</td>
<td>22</td>
</tr>
<tr>
<td>10.</td>
<td>Pore size distribution analysis on Middle Bakken samples using nitrogen adsorption (Liu et al., 2017)</td>
<td>23</td>
</tr>
<tr>
<td>11.</td>
<td>Relationship between pore size, NMR signal and relaxation time or T2 distribution (Coates et al., 1999 and Magritex)</td>
<td>25</td>
</tr>
<tr>
<td>12.</td>
<td>NMR porosity partitioning correlation to T2 cutoff (Al-Marzouqi et al., 2010)</td>
<td>26</td>
</tr>
<tr>
<td>13.</td>
<td>Molecular model (perspective view) for the alkane-organic slit system. Black molecules are graphite while red-grey molecules are n-octanes. (Modified from Wang et al., 2015)</td>
<td>34</td>
</tr>
<tr>
<td>14.</td>
<td>Mass density profile for n-C8H18 in a 4.43 nm carbonaceous slit at 353 K (Wang et al., 2015)</td>
<td>35</td>
</tr>
<tr>
<td>15.</td>
<td>Effect on single-component fluid on the continuous mass density profiles for alkanes in a 4.54 nm carbonaceous slit. (Wang et al., 2015)</td>
<td>36</td>
</tr>
</tbody>
</table>
16. Effect of multi-component mixtures on the continuous mass density profiles for alkanes in a 4.54 nm carbonaceous slit. (Wang et al., 2015) ......................................................... 37
17. Bubble point pressure profile of the multicomponent mixture with different compositions (Dong et al., 2016) .................................................................................. 38
18. Typical pore size distribution (solid red line) for the Middle Bakken obtained from high-pressure MICP (Nojabaei et al., 2013). The orange marked area represents the volume of adsorbed layers while the blue-shaded area shows the amount of recoverable oil. (Wang et al., 2015) .......................................................................................... 39
19. Optical micrograph of the microfluidic and nanofluidic chip ............................................. 40
20. Three consecutive images during the vaporization of n-pentane in the nanofluidic device. Left: n-pentane in two micro-channels vaporized entirely, leaving the nano-channels full of liquid; Middle: n-pentane inside the nano-channels started to evaporate; Right: n-pentane vaporized completely (Wang et al., 2014) .............................................................................. 41
21. The evaporation process of a ternary mixture stopped in one of the micro-channels at 345 K (Wang et al., 2014) ............................................................................................................. 42
22. Top view of nanofluidic device (Liu et al., 2014) ................................................................... 43
23. Optical flow pattern under time sequence for water displacing oil (fading out). Green color is the oil phase while the black color is the water phase (Liu et al., 2014) ............... 44
24. Residual oil saturation (green) measurements on three layers (Liu et al., 2014) ................. 44
25. Schematic Diagram of Pore Model ............................................................................................ 48
26. Procedure for deriving the equation of critical properties (critical volume, temperature, and pressure) .................................................................................................................. 50
27. Digital, 3D representation of sample #16433 ......................................................................... 54
28. T2 distribution profile of core sample #17351 ....................................................................... 55
29. The fraction of micro-, meso-, and macro-porosity from five core samples using NMR analysis .................................................................................................................................. 56
30. Critical temperature of methane in confined condition .......................................................... 59
31. Critical temperature of ethane in confined condition .............................................................. 60
32. Critical temperature of butane in confined condition ............................................................. 61
33. Effect of pore size on the discrete mass density profiles for n-octane in carbonaceous slits (modified from Wang et al., 2015) ......................................................................................... 62
34. T2 distribution and corresponding data for the Middle Bakken core sample of NDIC #16068 ........................................................................................................................................ 71
35. T2 distribution and corresponding data for the Middle Bakken core sample of NDIC #16433 ........................................................................................................................................ 72
36. T2 distribution and corresponding data for the Middle Bakken core sample of NDIC #16652........................................................................................................................................... 73
37. T2 distribution and corresponding data for the Middle Bakken core sample of NDIC #16841........................................................................................................................................... 74
38. T2 distribution and corresponding data for the Middle Bakken core sample of NDIC #17351........................................................................................................................................... 75
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Summary of the petrophysical parameters of the Middle Bakken Formation</td>
<td>18</td>
</tr>
<tr>
<td>2.</td>
<td>Average Pore Size of Middle Bakken Formation</td>
<td>23</td>
</tr>
<tr>
<td>3.</td>
<td>Critical properties of confined methane in different pore sizes (Pitakbunkate et al., 2016)</td>
<td>28</td>
</tr>
<tr>
<td>4.</td>
<td>Critical properties of confined ethane in different pore sizes (Pitakbunkate et al., 2016)</td>
<td>28</td>
</tr>
<tr>
<td>5.</td>
<td>Critical temperatures of bulk and confined fluids of some hydrocarbons (Singh and Singh, 2011; Xiong et al., 2013)</td>
<td>29</td>
</tr>
<tr>
<td>6.</td>
<td>Critical Pressures of Bulk and Confined Fluids of Some Hydrocarbons (Singh and Singh, 2011; Xiong et al., 2013)</td>
<td>30</td>
</tr>
<tr>
<td>7.</td>
<td>Total porosity from NMR Analysis</td>
<td>57</td>
</tr>
<tr>
<td>8.</td>
<td>Critical Temperature (in °R) of Propane in Confined Pore</td>
<td>63</td>
</tr>
<tr>
<td>9.</td>
<td>Critical Temperature (in °R) of Pentane in Confined Pore</td>
<td>63</td>
</tr>
<tr>
<td>10.</td>
<td>Critical Temperature (in °R) of Hexane in Confined Pore</td>
<td>64</td>
</tr>
<tr>
<td>11.</td>
<td>Critical Temperature (in °R) of Heptane in Confined Pore</td>
<td>64</td>
</tr>
<tr>
<td>12.</td>
<td>Critical Temperature (in °R) of Decane in Confined Pore</td>
<td>64</td>
</tr>
<tr>
<td>13.</td>
<td>Critical Temperature (in °R) of methane to decane in bulk condition</td>
<td>65</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT

I would like to thank my graduate committee members, Dr. Hadi Jabbari, Dr. Minou Rabiei, and Dr. Hui Pu. Their thought provoking discussions and editorial comments were greatly appreciated in the development of this thesis. I would especially like to thank my advisor, Dr. Hadi Jabbari for invaluable discussion, unwavering support, and guidance throughout this work. A special thank you also goes out to Dr. Xiaodong Hou for his guidance in understanding nuclear magnetic resonance system and help in setting up and operating the equipment.

I would like to express my gratitude to the Energy and Environment Research Center (EERC) for providing training and access to their state of the art sample preparation equipment. I would especially like to thank Steve Smith for the assistance in functioning the equipment, Lonny Jacobson, and other EERC colleagues for their support on my work. I would like to also thank the entire core library staff for the access to core.

I would like to thank my graduate colleagues and friends, especially Alex Monk and Sai Wang for their support, assistance during experiments, and the constructive discussion. Finally, I would like to thank my Mom and Dad for unfailing support and encouragement throughout this challenging process.
To my mom Ratna N. and my dad Antonius H.,

The world’s best parents and my motivators!
ABSTRACT

In 2013, the United States Geological Survey (USGS) released an estimate of 7.38 billion barrels of oil held within the Bakken Formation, one of the most significant discoveries. However, the Bakken Formation, a tight shale play, is also known for its ultra-low permeability and nano-scale pore size (1 – 100 nm). A nano-scale pore size can impact the petroleum fluid properties when compared to its bulk properties. This study utilized a theory-based analytical method and compares the results with those from experiments conducted under the simulated conditions.

Peng-Robinson Equation of State (PR-EOS) was modified to calculate the critical properties of individual hydrocarbon component in confined conditions. The modification was deduced from the Helmholtz free energy function with Lennard-Jones potential for particles interaction. The modified PR-EOS became a function of molecule-to-pore-size ratio. The value of pore size was obtained using nuclear magnetic resonance (NMR) and from related experiments. NMR measurements were conducted on five-Middle Bakken core samples and provided the pore size distribution and porosity. The results from the analytical method and experiments were compared with the data from the literature to examine the theory and for comparison purposes.

Suppression effect on critical temperature was calculated on eight hydrocarbons (from methane to decane) and compared with the experimental results. The total porosity from five-
NMR experiments, is within the range of 2.73 to 9.38 % with an average of 5.4 %. A close match was found between the model and experiments with a deviation of 14% for pore sizes within 1 – 3 nm and of 1.02% for pore sizes larger than 3 nm. The pore size of 3 nm seems to work as a cutoff due to the adsorption layers on the vicinity of the pore wall. Also, the bulk critical properties were estimated using the equations and presented similar results to the literature, with a maximum deviation of 0.03%.
CHAPTER I

INTRODUCTION

Background

Across the United States and North America, shale oil reservoir developments are a growing source of natural oil and gas reserves. However, they cannot be produced at commercial rates without successful application of some specific recovery processes due to the shales ultra-low permeability. Despite its poor petrophysical properties, shale rocks have proven to be an excellent source of oil and gas, capable of producing at commercial rates when completed with multistage hydraulic fractured horizontal wells (Ayers, 2005). In 2013, The United States Geological Survey (USGS) released an estimate of 7.38 billion barrels of oil held within the shale oil reservoir (the Bakken formation) while the North Dakota Department of Mineral Resources reported a production of 32,473,305 bbl at an average of 1,047,525 bbls per day as of July 2017. The fact of a huge reserve made the Bakken petroleum system one of the most significant discoveries, a crucial unconventional play in the US petroleum production and helped the US to become energy independent. However, despite producing millions of barrels of oil per day, the North Dakota Bakken recovery factor is approximately 7% while typical oil fields produce over 20% to 40% of the oil in place (Myths of Bakken: Bismarck Tribune Nov 17th, 2014). The low recovery factor has led to several studies on how to improve recovery by understanding fluid flow inside the rocks.
Hydrocarbon production from shale plays is technically and economically challenging. The primary economic challenge that industry is facing is the high cost of new wells combined with low recovery factor and high initial decline rate. The high production decline rate requires either drilling new wells or optimizing production of old wells by conducting re-stimulation to maintain the overall production levels. Without newly drilled wells or any re-stimulation work, the production of the Bakken formation declines rapidly in the first several months after the first production (Figure 1), and it was hypothesized due to the topology and specifically the pore structure (geometry and topology) within the matrix (Anyanwu, 2015).

Figure 1 Decline curve analysis of Bakken: showing ten-year probabilistic-type curve (PTC) for all horizontal wells in the Bakken Formation (Cook, 2013)
The Bakken Formation is an interbedded sequence of black shale, siltstone, and sandstone that underlies large areas of northwestern North Dakota, northeastern Montana, southern Saskatchewan, and southwestern Manitoba. Figure 2 illustrates the area of the Bakken Formation in United States’ perspective.

Figure 2 The Bakken Formation Map – Bakken-Lodgepole total petroleum system (TPS) and major structural elements within the province in the United Stated (Pollastro et al. 2010)

The Bakken Formation was deposited as part of the Williston Basin. Its age is between Late Devonian to Early Mississippian. The Bakken Formation comprises three distinct members. The upper and lower members are black, organic-rich shales and widely recognized as world-class source rocks (type II Kerogen). These members are called Upper Bakken and Lower Bakken which serve as very effective seals, owing to their very low permeability ranges from...
0.01–20 mD. The middle member is the primary oil-producing member and predominantly composed of siltstones and sandstones, which has low porosity (1%-15%) and low permeability (0-20 millidarcies), particularly low for a reservoir rock. The middle member is commonly called Middle Bakken (LeFever et al., 1991; Pitman et al., 2001; Pollastro et al., 2010; Kuhn et al., 2012).

The Middle Bakken Formation, an unconventional reservoir, is considered to be self-sourced from the Upper and Lower Bakken members. Although considered as the source rock of the Middle Bakken, the Upper Bakken has also been produced since late 1970's to the early 1990's around the southwest part of the basin in North Dakota (LeFever et al., 1991). Sonnenberg (2014) reported that the Upper Bakken has recently been targeted with multistage hydraulically fractured horizontal drilling in areas where the Middle Bakken pinches out. Thus, studying the reservoir potentials of the Bakken formation focusing on pore size distribution becomes an interesting topic.

The pore size of the Bakken Formation varies between 0.5 - 100 nm (Ambrose et al. 2010). This range is comparable to the size of hydrocarbon fluid molecules being four to six Ångström for straight-chain hydrocarbons (Mitariten, 2005). Such nanoscale pore throats and pore size distribution are believed to be the source of differences between the real oil production behavior and the fluid phase behavior (Pressure – Volume – Temperature or (PVT)), data from laboratory test (Curtis et al., 2011). Conducting PVT tests in nanoscale pore throats (or commonly called confined PVT), requires the consideration of additional aspects of pore-fluid interrelations, such as adsorbed gas volume (Ambrose, 2011), pore pressure effects (Sigal, 2013),
pore wall interaction (Ambrose, 2011; Michel et al., 2011; Didar, 2012), rock compaction (Nelson and Batzle, 2006), and capillary pressure. These factors influence the PVT properties, such as decreasing the critical pressure and the critical temperature (Singh and Singh 2011 and Xiong et al. 2013).

The fluid phase behavior is interpreted by comparing results from PVT experiments to equations of state (EOS). PVT experiments are tools to study the characteristic of a specific fluid. It yields fluid parameters, such as bubble point pressure ($P_b$), oil formation volume factor ($B_o$), and the gas-oil ratio (GOR). All of which are required for reserve calculations, field reservoir management, and production forecasts. Indeed, experimental data collected from routine PVT tests are inadequate for the characterization of fluids in a nanopore environment. To characterize the fluid properties, one can modify the EOS using analytical models which are used in this research.

**Statement of Problem**

Besides having a nanoscale pore size, the Middle Bakken oil production has a behavior of a long-lasting flat producing gas-oil ratio or GOR, deviates from the predicted GOR profile from PVT analysis (Dong et al., 2016). According to Firincioglu et al. (2012), the petroleum fluid properties under confinement deviate from that of bulk properties because of an increased capillary, structural, electrostatic, Van der Waals and adsorptive forces. Devegowda et al. (2012) emphases on intramolecular and molecules – pore surface under confined environment alters the fluid properties. For that reason, understanding the pore size distribution in the Middle Bakken
and the effect on petroleum fluid properties is essential. A specific petroleum fluid properties are important as primary parameters in production forecasting and field development strategy. The alteration in petroleum fluid properties will be estimated through modifying Peng-Robinson equation of states (PR-EOS) by taking pore size into account while the pore size distribution will be obtained through nuclear magnetic resonance (NMR) experiments and literature review.

**Research Objectives**

The primary objective of this study is to modify Peng-Robinson equation of state (PR-EOS) to predict the suppression on critical properties due to the confinement effect. Other objectives sought in this study, include:

- Obtaining pore size distribution (PSD) of Middle Bakken samples through nuclear magnetic resonance (NMR) experiment
- Comparing the experimental results from experiments and literature to the tuned Peng-Robinson EOS

**Method Overview**

To fulfill the objectives of this study, the following methods were conducted:

- Literature review to investigate modifications in Equations of State (i.e., Van der Waals and Peng-Robinson Equation of States)
- Literature review to compile experimental results of hydrocarbons’ critical properties in confined environment
- NMR analysis on PSD of the Middle Bakken samples
- Modifying Peng-Robinson EOS to predict the suppression on critical properties due to nano-pore environment
- Making comparison to validate the tuned Peng-Robinson EOS with the results from experiment and literature

**Thesis Outline**

This thesis consists of five chapters. The outline of this thesis is as follows:

- Chapter I presents the introduction, the overview of unconventional reservoirs, especially the Middle Bakken Formation (shale oil), the statement of problem, as well as research objectives and methodologies
- Chapter II explains the overview of the Bakken Formation as an unconventional resource in the United States, includes its geology, mineralogy information, and nano-scale consideration and parameters in the Bakken Formation
- Chapter III presents a comprehensive literature review in the adsorption effect on pore volume using molecular dynamics (MD) simulation, EOS-modification (focused on Peng-Robinson EOS), and experimental results of confined PVT involved hydrocarbons. The fundamentals of nuclear magnetic resonance (NMR) to measure pore size distribution and literature data of the Middle Bakken Formation's PSD are also presented in this chapter.
- Chapter IV discusses the results of the Middle Bakken pore size distribution from NMR experiment, the analytical result of modifying PR-EOS to predict
suppression of critical properties in confined environment, and the comparison of critical properties using tuned PR-EOS to experimental results from literature.

Chapter V presents the conclusions of this study including the recommendations for future work related to this topic.
CHAPTER II

BAKKEN FORMATION SHALE PLAY

Background: Unconventional Resources

The Upper Devonian and Lower Mississippian Bakken Formation, known as the Bakken Formation, is a thin (as much as 160 ft) widespread unit within the central and deeper portions of the Williston Basin, a large, roughly circular intracratonic sedimentary basin located on the North American Craton occupying a geographic area of about 300,000 square miles across portions of North Dakota, South Dakota, Montana, Saskatchewan, and Manitoba (Figure 3). The basin has a complex tectonic history due to deformed underlying basement rocks and two major bounding structural fault systems. These fault systems are responsible for much of the basin’s interior faults and lineaments, block-fault movements, sedimentation patterns, salt dissolution, fluid movement and thermal history (Pollastro et al., 2010).
The first oil discovery in the Bakken Formation was in the early 1950s at Antelope field in McKenzie County, North Dakota (LeFever, 1991) on the Nesson anticline, one of the Williston Basin's largest and most productive structures. In this field, the oil was produced from fractured Bakken state on a secondary and oblique structure along the east flank of the Nesson anticline where there is thick, tight, porous sandstone within the middle sandstone member which is commingled with the Upper Devonian Three Forks formation.

For the first time in 1995, the Bakken Formation continuous accumulation was assessed by USGS and resulting in an estimated for undiscovered technically recoverable reserves of 151 million barrels of oil (MMBO). Level of Bakken exploration, production, and resource potential had greatly intensified by two significant discoveries – the Elm Coulee field, Richland County,
Montana, in 2000, and the Parshall field, Mountrail County, North Dakota, in 2006. The Middle Bakken Formation within those areas has moderate- to high-matrix-porosity and both vertical and horizontal vertical fractures. The presence of these reservoirs, combined with the advancement of long-lateral and multi-stage fracture technology in horizontal well completions, have allowed a rapid development of the Bakken formation and resulted in wells with estimated ultimate recoveries (EUR) up to about 2 MMBO (Pollastro et al., 2010).

**Geology and Mineralogy**

The Bakken Formation is an Upper Devonian through Lower Mississippian unit of the Williston Basin, Montana and North Dakota. The Bakken Formation is overlain by the Mississippian Lodgepole Formation and overlies the Devonian Three-Forks Formation (Figure 4). The Bakken Formation is a highly organic-rich and siliciclastic rock, classified as a world-class petroleum source and reservoir rock with the potential to produce exceedingly large volumes of undiscovered hydrocarbons (Pollastro et al., 2008a, b, b; Anna et al., 2008).
The Bakken Formations informally consists of three members: lower shale member, known as Lower Bakken; middle sandstone member, known as Middle Bakken; and the upper shale member, known as Upper Bakken. The Lower Bakken is the smallest in the geographic extent (black dotted line in Figure 5) with a well-defined depocenter along the east flank of the Nesson anticline. It is a dark-brown to black, quartz-rich, fissile, organic-rich shale (LeFever, 2008) with average total organic carbon (TOC) content of the Lower Bakken is about ten weight percent (Price et al., 1984; Schmoker and Hester, 1983; Smith and Bustin, 1998).
The Middle Bakken is the thickest (as much as 90 ft.) member of the Bakken Formation. Its lithology varies and consists of a light-gray to medium-dark-gray, interbedded sequence of siltstones and sandstones with lesser amounts of dolomite, shale, and limestones rich in silt, sand, and oolites (Webster, 1982; Hayes, 1984; Thrasher 1985; Smith and Bustin, 1996, 2000; LeFever et al., 1991; LeFever, 2007a, b). There are at least three studies identified and mapped lithofacies of The Middle Bakken to predict matrix and fracture porosities. Smith and Bustin (1998, 2008)
recognized six lithofacies and three sub-units while LeFever (2007a) correlated log-core then identified and mapped seven lithofacies and Canter et al. (2008) defined five main lithofacies. Figure 6 depicting LeFever’s lithofacies and sedimentologic characteristics of the Middle Bakken Formation.

Figure 6 Lithologic column depicting lithofacies and sedimentologic characteristics of the Middle Bakken Formation (Pitman et al., 2001)

The Upper Bakken, the largest in geographical extent (black solid line in Figure 5), is organic rich and exhibits laminated to the massive bedding of silt-size material (Meissner, 1978;
Schmoker and Hester, 1983; Price et al., 1986; Smith and Bustin, 2000). It is lithologically similar to the Lower Bakken and consists of dark grey to brownish-black to black, fissile, noncalcareous, bituminous and carbonaceous shale (Meissner, 1978; LeFever, 1991) with organic contents as much as 35 weight percent TOC.

The Bakken Formation can easily be identified through an open hole log. Gamma ray (GR), resistivity, and sonic logs are the vital logging tools in determining the Bakken Formation. The Bakken Formation has characteristics of abnormally high gamma-ray reading, above 200 API; high sonic transit times, between 80 to 120 μs/ft; low resistivity readings, lower than 100 ohm-m in the shallower, thermally immature part, and higher than 100 ohm-m in the deeper, thermally mature part of the basin (Meissner, 1978; Webster, 1982, 1984; Hester and Schmoker, 1985). The Middle Bakken has typical log characteristics of clastic and carbonate rocks.

**Nanoscale consideration and parameters in the Bakken Formation**

The Middle Bakken Formation has measured core porosity within the range of 1 to 16 percent, averaging about five percent. Ropertz (1994) reported an order of three percent of porosity with high-pressure mercury injection measurements. When the porosity is associated with burial depth, thermal maturity and sedimentary section correspond to the porosity value. At burial depth less than 9,840 ft., porosity value of sandstones and siltstones lays between 5 to 7 percent while in deeper depth and high level of thermal maturity, it ranges between three to six percent.
In addition to a low porosity value, the Middle Bakken Formation is known for its ultra-low permeability or poor petrophysical properties. The measured permeability ranges from 0 to 20 millidarcies (mD), averaging 0.04 mD. In immature shales, the permeability in sandstones is ranging from 0.06 to 0.01 mD. The permeability decreases as burial depth increase to the range of < 0.01 to 0.01 mD where shales are mature. The decrease in permeability is associated with carbonate precipitation in response to the generation of CO$_2$ during kerogen maturation of the shales. Permeability values greater than 0.01 mD is revealed in the Middle Bakken Formation contained open, natural hydraulic fractures. (Pitman et al., 2001).

Open horizontal fractures are associated with three factors, source-rock thickness and level of thermal maturity, the extent of hydrocarbon generation in shales bounding the reservoir unit, and proximity to source facies. Reservoir rocks adjacent to mature to over-mature source-rocks has the best developed and most extensive fracture network. The fractures are highly permeable with excellent fluid-retention properties, which is indicated by being easily visible when the rock is wet (Figure 7), while the rock matrix has a very high capillary resistance to fluid flow.
Figure 7 Slabbed sandstone is displaying reticulated fracture network on a wet surface. Note that the permeable nature and distribution of fractures are not apparent when the surface is dry. (Pitman et al., 2001)

Equally crucial to petrophysical properties is pore size distribution (PSD). There are limited publications on the pore size distribution of the Middle Bakken Formation. Ramakrishna et al. (2010) examined the PSD of the Middle Bakken Formation using the Winland $R_{35}$ technique (Kolodzie, 1980) and $R_{inflex}$ technique (Katz and Thompson, 1986). The experiment yielded an $R_{35}$ value of 27.2 nanometers and an $R_{50}$ value of 20 nanometers (Figure 8). Comparatively to Ramakrishna et al. (2010), Anyanwu (2015) completed PSD experiments using mercury injection capillary pressure (MICP) to the Middle Bakken Formation and measured the
average pore size of 6.8 nanometers. Table 1 summarizes some petrophysical parameters reported in the literature.

![Pore size distribution of the Middle Bakken Formation (Ramakrishna et al. 2010)](image)

**Figure 8** Pore size distribution of the Middle Bakken Formation (Ramakrishna et al. 2010)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average Value</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix Ø (%)</td>
<td>3.7 – 8.0</td>
<td>Pitman et al. (2001)</td>
</tr>
<tr>
<td>Fracture Ø (%)</td>
<td>0.02 – 12.8</td>
<td>Pitman et al. (2001)</td>
</tr>
<tr>
<td>Matrix $k$ (mD)</td>
<td>0 – 0.2</td>
<td>Pitman et al. (2001); Ramakrishna et al. (2010); Kuhn et al. (2012); Anyanwu (2015)</td>
</tr>
<tr>
<td>Fracture $k$ (mD)</td>
<td>0.6 – 54.5</td>
<td>Pitman et al. (2001)</td>
</tr>
<tr>
<td>Pore size distribution</td>
<td>6.8 – 27.2</td>
<td>Pitman et al. (2001); Anyanwu (2015)</td>
</tr>
<tr>
<td>(nanometer)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER III

NANO-SCALE EFFECTS ON PETROLEUM FLUID PROPERTIES

Understanding fluid phase behavior in the confined environment, known as confined PVT, has become the main interest for scientists and researchers. One of the essential aspects of fluid phase behavior in a confined environment is to consider the pore size effect in the PVT equation. A strong pore size dependency to the deviations in critical temperature of many chemical compounds is experimentally verified (Morishige et al., 1997; Morishige and Shikimi, 1998).

Accordingly, the review of the pore size distribution, the properties of the Bakken Formation used in the calculations, and confined PVT properties estimation are discussed in the first section of this chapter. The pore size distribution is measured using mercury injection capillary pressure (MICP) (Ramakirishna et al., 2010 and Anyanwu et al., 2015). Another way to determine pore size measurement is by utilizing a nuclear magnetic resonance (NMR), discussed in the second section of this chapter.

The Middle Bakken Formation pore size of 0.5 to 100 nm (Ambrose et al., 2010) is comparable to the chain diameter of straight-chain hydrocarbons, ranging in four to six Ångström (Mitariten, 2005). A similar pore size affects the intermolecular interaction and the interaction between the molecules and the pore surface that altered the fluid properties. The alteration in fluid properties is studied through experiment, simulation, and analytical works.
The simulation utilizes molecular dynamics simulation (MDS) and Grand Canonical Monte Carlo (GCMC) to explain the intermolecular interaction and molecules – pore surface interaction. The literature data on simulation results is explained in the third section.

The simulation results should be expressed through the analytical works and proved through experiments. Zarragoicoechea and Kuz (2002) modified the Van der Waals equation of state to consider the pore size effect. Wang et al. (2014) and Liu et al. (2014) studied the fluid properties in nanoscale pore size utilizing nanofluid devices. The method of analytical and experimental works are discussed in the fourth and fifth sections of this chapter. The ideas obtained from the literature are utilized to modify the analytical work and compare the results with the literature data.

**Pore Size Distribution in Middle Bakken Formation**

To make distinct comparisons between the modified Peng-Robinson EOS and experimental results, a good understanding of pore size distribution (PSD) in the Middle Bakken Formation is necessary. The PSD data works as reference data while modifying Peng-Robinson EOS. Since suppression of critical properties happens in smaller pore sizes, knowing the smallest value of pore size is critical.

There are limited publications on the pore size distribution of the Middle Bakken Formation. Ramakrishna et al. (2010) examined PSD of the Middle Bakken Formation using the Winland R₃₅ technique (Kolodzie, 1980) and R_inflex technique (Katz and Thompson, 1986). Winland R₃₅ technique is an empirical relationship between porosity, permeability, and pore
throat radius proposed by H. D. Winland. \( R_{35} \) is well described as the modal class of pore throat size where the pore network becomes interconnected forming a continuous fluid path through the sample (Spearing et al., 2001; Hartmann and Beaumont, 1999). The \( R_{\text{inflex}} \) technique refers to the point of inflection of the pore throat size profile against mercury saturation plot from mercury injection capillary pressure (MICP) experiment. The experiment yielded an \( R_{35} \) value of 27.2 nanometers and an \( R_{50} \) value of 20 nanometers (Figure 8).

Comparatively to Ramakrishna et al. (2010), Anyanwu (2015) measured pore size distribution using mercury injection capillary pressure (MICP) to all Bakken members; the Upper, Middle, and Lower Bakken. Mercury, a non-wetting phase, is injected into the sample at different pressures. Washburn’s equation was utilized to calculate pore-throat radius from the recorded pressures (Equation 1).

\[
\Delta P = \frac{-2 W \alpha \cos \theta}{R} 
\]

(1)

With known surface tension (485 dynes/cm for Hg) and the contact angle between mercury and porous medium (130° in most solids), the equation is expressed as:

\[
\Delta P = \frac{90.4}{R} 
\]

(2)

Figure 9 illustrates the pore size distribution of the Bakken samples with average pore size of 7.8, 6.8, and 17.6 nanometers for the Upper, Middle, and Lower Bakken, respectively (Anyanwu, 2015).
Figure 9 MICP analysis of Bakken Formation on a histogram showing porosity versus pore-throat diameter for Upper (blue), Middle (yellow), and Lower (red) Bakken members. (Anyanwu, 2015)

In addition, Liu et al. (2017) measured pore size distribution of Middle Bakken using nitrogen adsorption. The average pore size is 12.98 nanometers from five samples, with minimum pore size diameter was 2.5 nanometers. Figure 10 illustrates the experiment results.
Figure 10 Pore size distribution analysis on Middle Bakken samples using nitrogen adsorption (Liu et al., 2017)

In conclusion from Ramakrishna et al. (2010), Anyanwu (2015), and Liu et al. (2017) experiments, the average pore size of the Middle Bakken ranges from 6.8 to 27.2 nanometers (Table 2). The lowest value of 2.5 nanometers is the smallest pore size while modifying Peng-Robinson EOS.

Table 2 Average Pore Size of Middle Bakken Formation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sources</th>
<th>Average Value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size</td>
<td>Ramakrishna et al. (2010)</td>
<td>20 – 27.2</td>
</tr>
<tr>
<td>Average pore size</td>
<td>Anyanwu (2015)</td>
<td>6.8</td>
</tr>
<tr>
<td>Average pore size</td>
<td>Liu et al. (2017)</td>
<td>12.98</td>
</tr>
</tbody>
</table>
Nuclear Magnetic Resonance

Besides MICP, pore size distribution (PSD) data can be obtained using nuclear magnetic resonance (NMR). Dunn et al. (2002) lay out the basic theory behind NMR. NMR is a phenomenon that can be found in systems of nuclei that have both angular momentum and magnetic moments. For example, hydrogen nuclei which have a spin with a non-zero angular momentum and an intrinsic magnetic moment.

On its application in petrophysics, NMR not only extracts information on pore size distribution from different rock types but also information on the saturating fluids (Dunn et al., 2002). For example, the signal detected from the hydrogen in oil decays faster than the hydrogen in free water (Green and Veselinovic, 2010). Brownstein and Tarr (1979) provided the original framework for obtaining pore sizes from NMR analysis by measuring the diffusive motion. Latour et al. (1992) found a direct relationship between a fluids relaxation time and the pore's surface-to-volume ratio, which is given by Kenyon (1997) as:

\[ T_2^{-1} = \rho \left( \frac{S}{V} \right) \]  

(3)

where \( T_2 \) is the longitudinal relaxation time (ms), \( \rho \) is the surface relaxivity or the ability of the surface to cause relaxation of proton magnetization (µm/ms), and \( S/V \) is the pore’s surface to volume ratio (µm²/µm³). When the magnetic field is introduced to the sample, the small pore will exhibit a short relaxation time due to its strong interaction with the surrounding and fast approach to equilibrium while a large pore will exhibit a long relaxation time. Figure 10 illustrates the relationship between pore size, relaxation time, and NMR signal.
The smallest pores or micropores, expressed with the fastest $T_2$, contain capillary bound fluid or known as the bulk volume irreducible index (BVI). The largest pores or macropores, expressed with the slowest $T_2$, contain free fluid or known as the free fluid index (FFI). The industry standard $T_2$ values are 33 ms and 3 ms for immobile fluid and free fluid, respectively (Dunn et al., 2002). These cutoffs were calibrated on conventional reservoirs and could not directly be applied in unconventional reservoir (Romero and Montoya, 2001; Green and Veselinovic, 2010). In unconventional reservoir, the increasing percentages of micropores
increase the surface relaxivity and shift the T2 distribution to smaller values (Kenyon, 1992). For unconventional reservoir, the cutoffs of 10 ms and 1 ms for long and short T2 respectively are more appropriate (Green and Veselinovic, 2010).

The T2 cutoffs were associated with the porosity cutoffs to identify the pore size distribution. Allen et al. (2001) developed a method for characterizing pore geometry by partitioning total NMR porosity into three categories based on pore size: micropores (less than 0.5 µm), mesopores (0.5 to 5 µm), and macropores (larger than 5 µm). The pore size of 0.5 µm is correlated with the short T2 cutoff, while the pore size of 5 µm with the long T2 cutoff. Figure 11 illustrates the correlation between the rock pore size distribution and the T2 cutoffs.

![Figure 12 NMR porosity partitioning correlation to T2 cutoff](Al-Marzouqi et al., 2010)

In this study, NMR was employed to measure the pore size distribution (PSD) of five Middle Bakken core samples. The discussion on NMR analysis and the pore size distribution data will be presented in Chapter IV.
Molecular Simulation on Confined PVT

The nanoscale pore size is one of many factors that alters the fluid critical properties. The alteration can be observed through simulation and experimental work. Literature data on simulation work, utilizing molecular dynamics simulation (MDS) and Grand Canonical Monte Carlo (GCMC) are presented in this section.

Pitakbunkate et al. (2014) presented simulation results on the changes of PVT properties of methane and ethane in nanopores. GCMC simulation was employed with graphite slabs to illustrate the matrix. Pore size was varied from one to ten nanometers. Lennard-Jones potential was used to describe the Van der Waals interaction between molecules. In the model, Pitakbunkate et al. (2014) assumed \( r_c \) (pore size radius) to be five times as large as molecular size \( \sigma \) for Lennard-Jones potential to take into account (equation 3).

\[
U(r_{ij}) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^6 \right]; & 5\sigma \leq r_{12} \\
0 & 5\sigma > r_{12}
\end{cases}
\]

Under that circumstance, the model may generate potential or interaction equal to zero in any pore sizes smaller than five times the molecular size, as the example is the methane's critical pressure inside one-nanometer pore of \( 5.8 \times 10^{-5} \) psi. Table 3 and 4 present the result of his simulations on properties of methane and ethane in several nanopore sizes and the estimated critical point properties.
Table 3 Critical properties of confined methane in different pore sizes (Pitakbunkate et al., 2016)

<table>
<thead>
<tr>
<th>Pore size (nm)</th>
<th>Critical temperature ($T_c$) °R</th>
<th>Critical pressure ($P_c$) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>178.2</td>
<td>$5.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>2.0</td>
<td>228.6</td>
<td>4.9</td>
</tr>
<tr>
<td>3.0</td>
<td>279.0</td>
<td>88.5</td>
</tr>
<tr>
<td>4.0</td>
<td>304.2</td>
<td>235.7</td>
</tr>
<tr>
<td>5.0</td>
<td>315.0</td>
<td>355.3</td>
</tr>
<tr>
<td>6.0</td>
<td>320.4</td>
<td>427.9</td>
</tr>
<tr>
<td>7.0</td>
<td>326.7</td>
<td>485.9</td>
</tr>
<tr>
<td>Bulk Fluid</td>
<td>342.8</td>
<td>667.2</td>
</tr>
</tbody>
</table>

Table 4 Critical properties of confined ethane in different pore sizes (Pitakbunkate et al., 2016)

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Critical temperature ($T_c$) °R</th>
<th>Critical pressure ($P_c$) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>387.0</td>
<td>4.6</td>
</tr>
<tr>
<td>3.0</td>
<td>464.4</td>
<td>84.1</td>
</tr>
<tr>
<td>4.0</td>
<td>506.7</td>
<td>242.9</td>
</tr>
<tr>
<td>5.0</td>
<td>525.6</td>
<td>355.3</td>
</tr>
<tr>
<td>6.0</td>
<td>536.4</td>
<td>442.4</td>
</tr>
<tr>
<td>7.0</td>
<td>540.0</td>
<td>493.1</td>
</tr>
<tr>
<td>8.0</td>
<td>543.6</td>
<td>529.4</td>
</tr>
<tr>
<td>9.0</td>
<td>547.2</td>
<td>551.1</td>
</tr>
<tr>
<td>10.0</td>
<td>549.0</td>
<td>565.6</td>
</tr>
<tr>
<td>Bulk Fluid</td>
<td>549.5</td>
<td>708.4</td>
</tr>
</tbody>
</table>

Singh and Singh (2011) and Xiong et al. (2013) also provided pore to critical properties relationships of pure hydrocarbons under nano-confinement condition. Grand-Canonical Transition Matrix Monte Carlo (GC-TMMC) was employed to simulate the hydrocarbon in the graphite and mica. Graphite illustrates organic kerogen pores, corresponds to adsorbing pores while mica represents inorganic pore systems, nonadsorbing pores. The intermolecular potential was described with the modified Buckingham exponential intermolecular potential of Errington
and Panagiotopoulos while wall-fluid interaction with the 9–3 Steele potential on equation 4 and 5 respectively (Singh and Singh, 2009). The results are summarized in Table 4 and Table 5.

\begin{equation}
U(r_{ij}) = \begin{cases}
\frac{4\varepsilon}{1-\alpha^2} \left[ \frac{6}{\alpha} \exp \left(\alpha \left( 1 - \frac{r}{r_m} \right) \right) - \left( \frac{r_m}{r} \right)^6 \right]; & r > r_m, \\
\infty; & r < r_m
\end{cases}
\end{equation}

\begin{equation}
\varphi_{wf}(z) = \frac{2}{3} \pi \rho_w \varepsilon_{wf} \sigma_{wf}^3 \left[ \frac{2}{15} \left( \frac{\sigma_{wf}}{z} \right)^9 - \left( \frac{\sigma_{wf}}{z} \right)^3 \right]
\end{equation}

Table 5 Critical temperatures of bulk and confined fluids of some hydrocarbons (Singh and Singh, 2011; Xiong et al., 2013)

<table>
<thead>
<tr>
<th>Component</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>NC4</th>
<th>NC5</th>
<th>C6</th>
<th>C7</th>
<th>C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>343.0</td>
<td>549.6</td>
<td>665.8</td>
<td>765.3</td>
<td>845.5</td>
<td>913.3</td>
<td>1189.0</td>
<td>1111.7</td>
</tr>
<tr>
<td>Nonadsorbing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pore 4 nm</td>
<td>355.3</td>
<td>540.2</td>
<td>644.1</td>
<td>733.2</td>
<td>805.0</td>
<td>865.6</td>
<td>1112.4</td>
<td>1043.2</td>
</tr>
<tr>
<td>6 nm</td>
<td>349.5</td>
<td>544.6</td>
<td>654.3</td>
<td>748.3</td>
<td>824.0</td>
<td>888.0</td>
<td>1148.3</td>
<td>1075.3</td>
</tr>
<tr>
<td>10 nm</td>
<td>345.7</td>
<td>547.6</td>
<td>661.0</td>
<td>758.3</td>
<td>836.7</td>
<td>902.9</td>
<td>1172.3</td>
<td>1096.8</td>
</tr>
<tr>
<td>20 nm</td>
<td>344.2</td>
<td>548.7</td>
<td>663.8</td>
<td>762.4</td>
<td>841.8</td>
<td>908.9</td>
<td>1182.0</td>
<td>1105.4</td>
</tr>
<tr>
<td>Adsorbing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pore 4 nm</td>
<td>365.6</td>
<td>532.2</td>
<td>625.9</td>
<td>706.2</td>
<td>770.9</td>
<td>825.6</td>
<td>1048.0</td>
<td>985.6</td>
</tr>
<tr>
<td>6 nm</td>
<td>356.2</td>
<td>539.5</td>
<td>642.6</td>
<td>730.9</td>
<td>802.1</td>
<td>862.3</td>
<td>1107.0</td>
<td>1038.4</td>
</tr>
<tr>
<td>10 nm</td>
<td>349.0</td>
<td>545.0</td>
<td>655.2</td>
<td>749.7</td>
<td>825.7</td>
<td>890.1</td>
<td>1151.7</td>
<td>1078.3</td>
</tr>
</tbody>
</table>

29
Table 6 Critical Pressures of Bulk and Confined Fluids of Some Hydrocarbons (Singh and Singh, 2011; Xiong et al., 2013)

<table>
<thead>
<tr>
<th>Component</th>
<th>Critical Pressure, ( P_c ) (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
</tr>
<tr>
<td></td>
<td>666.4</td>
</tr>
<tr>
<td>Nonadsorbing pore</td>
<td></td>
</tr>
<tr>
<td>4 nm</td>
<td>393.7</td>
</tr>
<tr>
<td>6 nm</td>
<td>495.4</td>
</tr>
<tr>
<td>10 nm</td>
<td>567.1</td>
</tr>
<tr>
<td>20 nm</td>
<td>657.8</td>
</tr>
<tr>
<td>Adsorbing pore</td>
<td></td>
</tr>
<tr>
<td>4 nm</td>
<td>2025</td>
</tr>
<tr>
<td>6 nm</td>
<td>2175.6</td>
</tr>
<tr>
<td>10 nm</td>
<td>1849.5</td>
</tr>
<tr>
<td>20 nm</td>
<td>989.9</td>
</tr>
</tbody>
</table>

Equation of State

In addition to experiment results, understanding the fundamentals and development of the widely-used EOS can help us to come up with improvements. Even though the focus of this study is modifying Peng-Robinson EOS, the Van der Waals EOS was considered for comparison purposes.

Peng and Robinson (1975) proposed a two-parameter EOS consisting of two forces; repulsion and attraction forces presented as repulsion pressure \( P_R \) and attraction pressure \( P_A \). They modified the attraction pressure term of the semi-empirical Van der Waals equation. The basic Peng-Robinson equation of state is given by Equation 6.

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

(6)

\[
\alpha(T) = \alpha(T_c) \alpha(T_r, \omega)
\]

(7)
\[ b(T) = b(T_c) \]  

(8)

where \( a \) is a measure of the intermolecular attraction forces and \( b \) is related to the size of the spheres. \( b \) is usually temperature independent while \( a \) is dependent upon temperature and molecular properties. By modifying the attraction pressure term of the semi-empirical Van der Waals EOS, the vapor pressures of pure substances and equilibrium ratios of a mixture can be accurately predicted (Peng and Robinson, 1975).

Following the growth of unconventional reservoirs and verification of a strong pore size dependency to the deviations in critical temperature of many chemical compounds (Morishige et al., 1997; Morishige and Shikimi, 1998), EOS modification is necessary by considering pore size. Zarragoicoechea and Kuz (2002) assumed the pressure for a confined fluid as a diagonal tensor \( \mathbf{P} \) with components \( P_{ii} (i = x,y,z) \). The Helmholtz free energy was utilized to obtain the axial and transversal components of the pressure tensor for understanding confined-PVT. The Helmholtz free energy of a system of \( N \) particles interacting via a pair potential \( U(r_{12}) \) (inert walls) can be written as:

\[
F = f(T) - \frac{kT N^2}{2V^2} \int \left( e^{-\frac{U(r_{12})}{kT}} - 1 \right) dV_1 dV_2
\]

(9)

where \( U(r_{12}) \) is the Lennard-Jones potential for particle interaction (Zarragoicoechea and Kuz, 2002).

\[
U(r_{12}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^6 \right]
\]

(10)
The integral was partitioned into two regions, \( r_{12} < \sigma \) and \( r_{12} > \sigma \). The integral of the first region (\( r_{12} < \sigma \)) is equal to zero since the value of \( e^{-\frac{U_{(s12)}}{kT}} \approx 0 \) at \( \frac{\sigma}{r_{12}} > 1 \) while in the second region (\( r_{12} > \sigma \)), it can be estimated as follows:

\[
e^{-\frac{U_{(s12)}}{kT}} \approx 1 - \frac{U_{(s12)}}{kT}
\]

Islam et al. (2015) improved the model from Zarragoicoechea and Kuz (2002) and obtained the pressure components as \( P_s = P_y \) and \( P_z \), given by (Islam et al., 2015):

\[
P_z = \frac{RT}{V-b} - \frac{a - 2\sigma^2 \varepsilon N^2 \sigma}{\nu^2} \left( c_1 + c_2 \frac{\sigma}{dp} \right)
\]

\[
P_x = P_y = \frac{RT}{V-b} - \frac{a - \sigma^2 \varepsilon N^2 \sigma}{\nu^2} \left( 3c_1 + 4c_2 \frac{\sigma}{dp} \right)
\]

As the direction of fluid flow is along the z-axis, \( P_z \) equation is derived with the following differential equations to estimate the critical volume, temperature, and pressure of a component.

\[
\left. \frac{dP_z}{dV} \right|_T = 0
\]

\[
\left. \frac{d^2P_z}{dV^2} \right|_T = 0
\]

Equation 16 to 18 gives the critical properties.

\[
V_c = 3b
\]

\[
T_c = \frac{8}{27bR} \left[ a - 2\sigma^3 \varepsilon N^2 \frac{\sigma}{dp} \left( c_1 + c_2 \frac{\sigma}{dp} \right) \right]
\]

\[
P_c = \frac{1}{27b^2} \left[ a - 2\sigma^3 \varepsilon N^2 \frac{\sigma}{dp} \left( c_1 + c_2 \frac{\sigma}{dp} \right) \right]
\]
A similar concept was employed by Islam and Sun (2016) to obtain the elements of pressure tensor $\mathbf{P}$, namely $P_{ii} (i = x, y, z)$. They modified Peng-Robinson EOS and developed the pressure components in three directions; $x$, $y$, and $z$, which is given by Equation 19 to 20.

$$P_z = \frac{RT}{V-b} - \frac{a - 2\sigma^3 \varepsilon N^2 \frac{\sigma}{d_p} \left(c_1 + c_2 \frac{\sigma}{d_p}\right)}{V^2 + 2Vb - b^2} \tag{19}$$

$$P_x = P_y = \frac{RT}{V-b} - \frac{a - \sigma^3 \varepsilon N^2 \frac{\sigma}{d_p} \left(3c_1 + 4c_2 \frac{\sigma}{d_p}\right)}{V^2 + 2Vb - b^2} \tag{20}$$

Once the derivation of Equation 14 and 15 is complete, the critical properties can be estimated from the modified Peng-Robinson EOS (Islam and Sun, 2016). The derivation of Peng-Robinson’s $P_z$ is more complicated than the Van der Waals because of the complexity of the denominator in the second form ($V^2 + 2Vb - b^2$). Islam and Sun (2016) proposed an assumption to simplify the derivation process. Assessment of their assumptions becomes a starting point of modifying Peng-Robinson EOS in this study. A different hypothesis is proposed to estimate the critical properties of individual hydrocarbons and compared with the literature in Chapter IV.

**Adsorption Effect on Pore Volume with Molecular Simulation**

In smaller pore size, the interaction between hydrocarbon molecules and pore surface generates adsorption layers in the vicinity of the pore surface. Various studies have been conducted to understand the adsorption of alkanes on the surface of carbonaceous materials using molecular dynamics (MD) simulation. The pore geometry is illustrated as either cylindrical
pores or slits. Song and Chen (2008) conducted a comparative study of pore geometry and indicated that no appreciable difference between those geometries.

Wang et al. (2015), utilizing MD simulation, studied adsorption behavior of n-octane within nanoscale carbonaceous slits of shale systems. The model is using optimized potentials for liquid simulation all-atom (OPLS-AA) force field, the best force field in reproducing thermodynamics and structural properties of alkanes (Jorgensen et al., 1996). The model computed long-range electrostatic terms with the particle-particle-particle-mesh (PPPM) solver instead of the Ewald summation (Luty et al., 1994).

On Wang et al. (2015) model, the organic-hosted nanopore of shale is illustrated with orthorhombic slit geometry consisting of upper and lower six-layer graphene with 0.34 nanometer interlayer spacing (Ambrose et al., 2012; Firouzi et al., 2014b; Mosher et al., 2013) with surface dimension of 2.95 × 2.56 nm². The n-octane molecules are positioned between the aperture of upper and lower layers, varied from 2 to 37.6 nanometer. Figure 12 illustrates the model configuration.

![Figure 13 Molecular model (perspective view) for the alkane-organic slit system. Black molecules are graphite while red-grey molecules are n-octanes. (Modified from Wang et al., 2015)](image-url)
The simulation run reveals that the pore size is entirely occupied by adsorbed phase and no bulk region presents on the smaller pore sizes (slit size of 1.95 and 3.8 nanometer). The adsorbed phase is indicated by the first density peak (a solid-like state) adjacent to the pore wall (Sha et al., 2008). For larger pores, the solid-liquid effect is gradually decreasing; thus, the bulk-phase portions are observed in the central region, where the mass densities are identical and conform to the predictions. Figure 13 illustrates the mass density profile inside the slit aperture of 4.43 nanometer (Wang et al., 2015)

![Figure 13 Mass density profile for n-C₈H₁₈ in a 4.43 nm carbonaceous slit at 353 K (Wang et al., 2015)](image)

Besides n-octane, the effect of chain length on alkane adsorption in the surface of carbonaceous materials is also simulated. The comparison was made on n-pentane (n-C₅H₁₂) and n-octane (n-C₈H₁₈). In the same agreement with the results from previous studies (Castro et al., 1998, Harrison et al., 2014, and Falk et al., 2015), the vicinity of the solid walls is preferentially adsorbed by longer alkanes, defined by a higher peak value in mass density profiles within the slit aperture (Figure 14) (Wang et al., 2015).
Furthermore, in the mixture systems of methane, n-pentane, and n-octane, the simulation confirms the preferential of longer alkanes being adsorbed in the vicinity of the solid walls. Figure 15 denotes the results of mixture system with different compositions. The first adsorbed layer of the blue curve is approximately 1.46 times as large as that of the bulk phase while the red curve is only 1.26 times as large. This verifies the adsorption propensity of n-alkanes with more carbon atoms per molecules (Castro et al., 1998; Harrison et al., 2014; and Wang et al., 2015).
Dong et al. (2016) simulated vapor-liquid equilibrium of a four-component mixture (\(\text{CH}_4\), \(\text{C}_4\text{H}_{10}\), \(\text{C}_5\text{H}_{12}\), and \(\text{C}_6\text{H}_{14}\)) with two different compositions of 50% - 20% - 20% - 10% and 70% - 10% - 10% - 10%. The system is isothermal at 350K with cylindrical nanopores of silicalite as the solid wall with various pore sizes of three nanometers to one micrometer. The suppression of bubble pressure in nanopore confinement is observed in both compositions (Figure 16). The bubble pressure of first composition (red dotted line) at five nanometers is reduced about 96.45 psi or 17.2% compared with the bubble pressure at bulk condition while the second composition (blue dotted line) is reduced by 46.85 psi or 7.6%. In addition, disregarding the effect of an adsorption film will overestimate the bubble pressure especially for the nanopores smaller than...
twenty nanometers. Moreover, increase in the CH₄ composition in the mixture is not only increasing the bubble pressure of mixture but also reducing the effect of nanopore confinement.

Figure 17 Bubble point pressure profile of the multicomponent mixture with different compositions (Dong et al., 2016)

Following Wang et al. (2015) and Dong et al. (2016) studies, the relationship of the thickness of the adsorbed layers and pore size should be determined and taken into account in any calculations, such as estimating petroleum fluid properties or reserves estimation in tight shale plays. As illustrated in Figure 17, the adsorbed phase in the vicinity of the pore reduces the total pore volume.
Figure 18 Typical pore size distribution (solid red line) for the Middle Bakken obtained from high-pressure MICP (Nojabaie et al., 2013). The orange marked area represents the volume of adsorbed layers while the blue-shaded area shows the amount of recoverable oil. (Wang et al., 2015)

**Experimental Work on Nano-PVT**

Besides analytical and simulation works, the alteration of petroleum fluid behavior has been experimentally verified. Wang et al. (2014) employed nanofluidic devices to visualize phase changes of pure alkane and an alkane mixture under nanoconfinement. Figure 18 illustrates Wang et al. (2014) nanofluidic design, consists of two parallel micro-channels perpendicularly connected by twenty-one nano-channels to represent the nanoscale porous rock, made of a silicon wafer (Wu et al., 2012; Wu et al., 2013). The dimensions of the micro- and nano-channels are 10 µm wide × 10 µm deep and 5 µm wide × 100 nm thick, respectively. The entire pore volume for the nanochannels is 2.56% while the microchannels’ volume is 97.44% (Wang et al., 2014).
Figure 19 Optical micrograph of the microfluidic and nanofluidic chip  
(Wang et al., 2014)

Wang et al. (2014) injected n-pentane into the nanofluidic device until it occupies all nano- and micro-channels. The experiment was done at atmospheric pressure and 298 K (76.7 °F) where the vaporization of n-pentane (boiling point of 308 K or 94.7 °F) is driven by the evaporation of the n-pentane through the open ports of the microchannels. Figure 19 illustrates the vaporization of n-pentane started in the micro-channels and then into the nano-channels once the vaporization in the micro-channels is complete. It indicates that the confinement made the boiling temperature of n-pentane in the nano-channels higher than in the micro-channels.
A ternary mixture consisting of 4.53 %-mol n-butane, 15.47 %-mol iso-butane, and 80.00 %-mol n-octane was also utilized to simulate oil behavior inside the rock. Atmospheric pressure and 345 K (161.3 °F) was applied to evaporate the liquid mixture into two phases. Instead of evaporating the entire liquid mixture, the evaporation process stopped in one of the micro-channels (Figure 20). The liberation of lighter components in the micro-channels caused this phenomenon, left the heavier components inside the channels, and made the suppression effect more severe. The experiment result verifies the molecular dynamics simulation result on the tendency of the longer chain to be adsorbed on the pore surface (Castro et al., 1998; Harrison et al., 2014; and Wang et al., 2014).
In addition to Wang et al. (2014), Liu et al. (2014) studied oil/water flow behavior in nanoscale channels. A nanofluidic device with twenty nanochannels and two microchannels was utilized. The dimensions of nanochannels and microchannels are 500 nm (depth) × 25 µm (width) × 365 µm (length) and 25 µm (depth) × 20 µm (width) × 30 mm (length), respectively, as illustrated in Figure 21.

Figure 21 The evaporation process of a ternary mixture stopped in one of the micro-channels at 345 K (Wang et al., 2014)
The oil (decane) and water (deionized water) flow behavior was visualized using a confocal microscopy. The nanofluidic device was saturated with decane and then displaced by water at a constant flow rate until a constant oil-water ratio was obtained. The water frontier started to move to the distance of about 50 µm, and then the oil phase started to fade out while water frontier remained at the same position until all the oil phase disappeared from the channel (Figure 22). The imbibition process of the water formed an extra thin layer along the wall that breaks through earlier than the frontier is a possible explanation for this phenomenon (Liu et al., 2014). Figure 23 shows the remaining oil phase (green color) with average oil saturation of 11.2%, which might be caused by the adsorption of oil to the pore surface. The experiment was completed at room temperature and pure decane. For further research, some improvements from this experiment can be done, such as: (1) conducting the experiment with various temperatures condition and (2) utilizing hydrocarbon mixtures to represent light oil characteristic of unconventional reservoirs.
Figure 23 Optical flow pattern under time sequence for water displacing oil (fading out). Green color is the oil phase while the black color is the water phase (Liu et al., 2014)

Figure 24 Residual oil saturation (green) measurements on three layers (Liu et al., 2014)
Analytical Work on Peng-Robinson EOS

The nanoscale pore size of the Middle Bakken Formation is one of the aspects that alters the petroleum fluid behavior like decreasing critical temperature and critical pressure. On the analytical work, the pore pressure effect, affected by the pore throat size, is the focus of this study. Adopting Zarragoicoechea and Kuz (2002) and Islam et al. (2015) works, explained on Subchapter III. The equation of State, the modifying continued to estimate the critical temperature and pressure of pure hydrocarbons.

The pressure in a confined fluid is assumed as a diagonal tensor \( \hat{P} \) with components \( P_{ii} \) (\( i = x, r \)). Equation 21 gives the internal energy.

\[
dE = T \, dS - \sum_i P_{ii} \, d\varepsilon_{ii} \, V
\]

where the second term on the right-hand side represents the work done by the internal tension under a specific deformation \( d\varepsilon_{ii} \) of the volume \( V \) (Zarragoicoechea and Kuz, 2002). The Helmholtz free energy, a maximum amount of work a system can do at constant volume and temperature, has a form shown in Equation 22.

\[
F = E - TS
\]

where \( F \) is the Helmholtz free energy, \( E \) is the internal energy, \( T \) is temperature, and \( S \) is the entropy. Substituting Equation 22 into Equation 21 at constant temperature will obtain the components of \( \hat{P} \) given by Equation 24 (Zarragoicoechea and Kuz, 2002).

\[
dF = -S \, dT - \sum_i P_{ii} \, d\varepsilon_{ii} \, V
\]

\[
P_{ii} = -\frac{1}{V} \frac{\partial F}{\partial \varepsilon_{ii}}
\]
The Helmholtz free energy of a system of \( N \) particles interacting via a pair potential \( U(r_{12}) \) (inert walls) can be written as

\[
F = f(T) - \frac{kTN^2}{2V^2} \int \left( e^{-\frac{U_{(S12)}}{kT}} - 1 \right) dV_1 dV_2
\]

(25)

where \( U_{(S12)} \) is the Lennard Jones potential, given by:

\[
U_{(S12)} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^{6} \right]
\]

(26)

The standard Van der Waals (VdW) equation can be obtained from the Helmholtz free energy by integration over an infinite volume. By following the same procedure for a finite volume, the modified Van der Waals equation for confined fluid can be obtained. The integral part is divided into two regions:

a. the first region where the pore throat size is smaller than the molecule diameter \( (r_{12} < \sigma) \)

b. the second region where the pore throat size is larger than the molecule diameter \( (r_{12} > \sigma) \)

Equation 27 and 28 show the exponential value of the first and second region, respectively.

\[
e^{-\frac{4\varepsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^{6} \right]}{kT}} \approx 0 \quad \text{for } r_{12} < \sigma
\]

(27)

\[
e^{-\frac{4\varepsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^{6} \right]}{kT}} \approx 1 - \frac{U_{(S12)}}{kT} \quad \text{for } r_{12} > \sigma
\]

(28)
Then the Helmholtz free energy equation becomes:

\[ F = f(T) + \frac{kTN^2}{V} \left( \frac{2}{3} \pi \sigma^3 \right) + \frac{kTN^2}{2V^2} \int_{r_{12} > \sigma} \left( \frac{U_{(s12)}}{kT} \right) dV_1 dV_2 \]  

(29)

The double integral is solved numerically as:

\[ \frac{1}{V} \int_{r_{12} > \sigma} \left( \frac{U_{(s12)}}{kT} \right) dV_1 dV_2 = \frac{4 \varepsilon}{kT} \sigma^3 f \left( \frac{d_p}{\sigma} \right) \]  

(30)

where

\[ f \left( \frac{d_p}{\sigma} \right) = c_0 + \frac{c_1}{d_p} + \frac{c_2}{\left( \frac{d_p}{\sigma} \right)^2} \]  

(31)

The constants are given by \( c_0 = -2.7925, c_1 = 2.6275 \) and \( c_2 = -0.6743 \). Substituting it to the Helmholtz free energy equation yields (Zarragoicoechea and Kuz, 2002):

\[ F = f(T) + \frac{kTN^2}{V} b + \frac{2 \sigma^3 \varepsilon N^2}{V} \left( c_0 + \frac{c_1}{d_p} + \frac{c_2}{\left( \frac{d_p}{\sigma} \right)^2} \right) \]  

(32)

This equation is the Helmholtz free energy for a real gas. The first term, \( f(T) \), represents the ideal gas and the second and third terms represent the deviation of real gas from ideal behavior. By converting \( f(T) \) and having \( \ln(V) - \frac{N}{V} b = \ln(V - b) \), the equation is simplified as:

\[ F = -RT \ln(V - Nb) - \frac{aN^2 - 2\sigma^3 \varepsilon N^2 \sigma \left( c_1 + c_2 \frac{\sigma}{d_p} \right)}{V} \]  

(33)

As mentioned by Equation 24, the pressure tensor can be derived from the equation given by:

\[ P_{ii} = -\frac{\partial F}{\partial V} \]  

(24)
Since the pore throat is represented in two directions \((x\) and \(r\), illustrated in Figure 24\), the equation of \(P\) should also be presented in both directions, in the radial and the axial direction. The volume form should be converted into a function of the radius of the pore \((r_p,\) radial direction\) and a function of the length of the pore \((L_x,\) axial direction\) to obtain the pressure equation.

![Figure 25 Schematic Diagram of Pore Model](image)

\[
V = \pi r_p^2 L_x \left\{ \frac{\partial V}{\partial (r_p)} \right|_{L_X} = L_x \partial \left( \pi r_p^2 \right) = 2\pi r_p L_x \right. \\
\frac{\partial V}{\partial (L_x)} \right|_{r_p} = \pi r_p^2
\] (34)

Taking the derivatives and rearranging the equations yield the following terms for radial and axial pressure (Zarragoicoechea and Kuz, 2002):

\[
P_x = \frac{RT}{V-Nb} - \frac{aN^2-2\sigma^2\varepsilon N^2}{\frac{d}{\partial p} \left( c_1+c_2 \sigma \right) \frac{d}{\partial p}}
\] (35)

\[
P_r = \frac{RT}{V-Nb} - \frac{aN^2-\sigma^2\varepsilon N^2}{\frac{3c_1+4c_2 \sigma}{d^2}}
\] (36)

These equations show the modification of Van der Waals’ equation of state. The same approach was performed to Peng-Robinson EOS. The difference between these Peng-Robinson and Van der Waals EOS are the denominator of the second form, which is \(V^2 + 2Vb + b^2\) and \(V^2,\)
respectively as well as the value of $a$ and $b$. For Peng-Robinson EOS, the axial pressure and radial pressure terms are obtained as (Islam et al., 2015):

\[
P_x = \frac{RT}{V} \left( \frac{a N^2 - 2 \sigma^3 \frac{\partial N^2}{\partial p} (c_1 + c_2 \frac{\partial}{\partial p} \sigma)}{V + 2V b - b^2} \right)
\]

(37)

\[
P_r = \frac{RT}{V} \left( \frac{a N^2 - \sigma^3 \frac{\partial N^2}{\partial p} (3 c_1 + 4 c_2 \frac{\partial}{\partial p} \sigma)}{V + 2V b - b^2} \right)
\]

(38)

Hydrocarbon flows inside the pore throat in the axial direction (i.e. $x$-direction). Therefore, the equation for critical properties is derived by using the axial term ($P_x$) and applying the rule of a critical point.

The critical point is the point at which two phases of a substance initially become indistinguishable from one another. At this point, there is no phase boundary, and the heat of vaporization is zero. There is an inflection point in the constant-temperature line on a PV diagram where the derivation of pressure to the volume at a certain temperature is equal to zero. This rule is explained mathematically with equation 14 and 15, repeated below.

\[
\frac{dP}{dV} \bigg|_T = 0
\]

(14)

\[
\frac{d^2P}{dV^2} \bigg|_T = 0
\]

(15)

The derivation procedure is illustrated in Figure 25, and the output will be critical volume, temperature, and critical pressure equations.
An additional assumption is used to emphasize the effect of pore throat size \( r_p \) to the critical properties. The assumption is by modifying \( 2Vb - b^2 \) to \( k_1 + \frac{k_2}{r_p} \) (Islam et al. 2016). By having this assumption, the critical volume is no longer a constant, rather it is a function of pore throat size, \( V_c = f(r_p) \). Islam et al. (2016) indicated that the pore size effect becomes insignificant once the \( r_p \geq 100 \sigma \) which is inferred as bulk condition and becomes very significant in case of \( r_p \approx 0.8 \sigma \) with the highest nanopore effect. The Equation 39 and 40 provide Islam et al. (2016) hypothesis.

\[
\begin{align*}
  r_p \geq 100\sigma & \rightarrow 2Vb - b^2 = k_1 + \frac{k_2}{r_p} \\
  r_p \geq 0.8\sigma & \rightarrow 2Vb - b^2 = k_1 + \frac{k_2}{r_p} = 0
\end{align*}
\]
In contrast, this study has a different understanding of Islam et al. (2016). Since the pore size effect becomes very significant in case of \( r_p \approx 0.8 \sigma \), the molecule to pore size ratio \( \frac{\sigma}{r_p} \) should be taken into account and Equation 40 becomes

\[
r_p \geq 0.8\sigma \rightarrow 2Vb - b^2 = k_1 + \frac{k_2}{r_p}
\]  

(41)

Similarly, since the pore size becomes insignificant once the \( r_p \geq 100 \sigma \), the molecule to pore size ratio \( \frac{\sigma}{r_p} \) can be neglected and turns the Equation 39 as

\[
r_p \geq 100\sigma \rightarrow 2Vb - b^2 = k_1 + \frac{k_2}{\sigma} = 0
\]  

(42)

These modifications will give the following equations:

\[
k_1 = 1.01(2Vb - b^2)
\]  

(43)

\[
k_2 = -0.0101(2Vb - b^2)
\]  

(44)

For further derivation process, this form will be simplified as \((2Vb - b^2) \times D\), where

\[
D = \left(1.01 - \frac{0.0101}{\sigma}\right)
\]  

(45)

Considering the effect of pore throat size by modifying the attraction forces, the modified Peng-Robinson equation for characterizing fluids in tight formations is given by:

\[
P_x = \frac{RT}{V-b} - \frac{a-2\sigma^2\varepsilon N^2\sigma}{V^2+(2Vb-b^2)D}\left(c_1+c_2\frac{\sigma}{d_p}\right)
\]  

(46)

By applying the rule of critical point (Equation 14 and 15), the critical point properties, such as critical volume, critical temperature, and critical pressure can be derived as follows:

\[
V_c = [C]b
\]  

(47)
\[ T_c = \frac{2 \left( [C]+D \right) \left( [C]-1 \right)^2}{\left( [C]^2+2 [C]D-D \right)^2} \times \frac{(a-[X])}{Rb} \] (48)

\[ P_c = \frac{\left( [C]^2-2 [C]-D \right)}{\left( [C]^2+2 [C]D-D \right)^2} \times \frac{(a-[X])}{b^2} \] (49)

where \([C]\) is a function of \(\frac{\sigma}{d_p}\) and obtained by solving the critical volume equation, while \([X]\) is simplifying the numerator in the second form and given as:

\[ [X] = 2\sigma^3 \varepsilon N^2 \frac{\sigma}{d_p} \left( c_1 + c_2 \frac{\sigma}{d_p} \right) \] (50)

These relations show that the properties of petroleum fluid at the critical point are all dependent on a molecule-to-pore-size ratio \(\frac{\sigma}{d_p}\). Singh and Singh (2011), Xiong et al. (2013), Pitakbunkate et al. (2015), Wang et al. (2015), and Dong et al. (2016) identified the adsorption of alkanes as a function of chain length and pore size by molecular dynamics simulation. The result is the alteration of petroleum fluid properties becomes more significant in a smaller nanoscale pore size. The significance of this ratio \(\frac{\sigma}{d_p}\) in nano PVT properties is explained in Chapter V through comparison plots and a sensitivity study.
CHAPTER IV

RESULT AND ANALYSES

NMR Analysis

NMR analysis was applied to five Middle Bakken core samples to measure the pore size distribution. Since NMR measures the liquid-filled pores as transverse relaxation time, $T_2$, which represents the pore size distribution, the samples should be entirely liquid saturated. A synthetic brine of 300,000 ppm NaCl (Lampen and Rostron, 2000 and Wang et al., 2011a) was used as the saturating liquid. Prior to saturating the core samples, the 4-step sample preparation should be followed.

As the first step, the core samples are dried to remove the remaining/trapped liquid. The oven at 240 °F is introduced to the core samples for one day. During the drying process, the core sample is periodically weighed until the sample reaches a constant mass. The core samples’ volume is then measured using the 3D scanner. Figure 26 illustrates the 3D scanner measurement to the core sample #16433 with the bulk volume of 1.038563 in$^3$ (or 17.019 cm$^3$). As the third step, the core samples were vacuumed to remove the trapped air inside the pores and then introduced to the synthetic brine. The final step is placing the sample, along with the synthetic brine, into a pressure chamber at 3,000 psi for ten days.
After samples were completely saturated, pore size distributions were obtained from NMR $T_2$ analysis in Oxford Instruments Geospec 2 core analyzed coupled with Green Imager Technologies software. The instrument was calibrated with a resonance frequency of 2.458 MHz. The experiment was run until an SNR (signal-to-noise ratio) of at least 100 was achieved with the $\tau$ of 56 $\mu$s, the shortest $\tau$ allowed by the machine that still allowed the use of a short (125 kHz) bandpass filter. Short $\tau$ allows the signal to be received from small pores with very short $T_2$ and also diminishes dephasing effects (Dunn et al. 2002).

The fraction of pore size was calculated from the $T_2$ distribution profile. The $T_2$ cutoff values of 1 ms and 10 ms are used to obtain the pore size distribution of unconventional reservoir (Green and Veselinovic, 2010). The area under the $T_2$ curve illustrates the pore size distribution of the core sample. The area below the short $T_2$ of 1 ms corresponds to microporosity or pores.
less than 0.5 microns, the area between the $T_2$ of 1 ms to 10 ms corresponds to mesoporosity or pores between 0.5 microns to 5 microns, and the area above the long $T_2$ of 10 ms corresponds to macroporosity or pores larger than 5 microns. Figure 28 illustrates the pore size distribution of well ID #17351. The pores of core sample #17351 are mainly micro- and meso-porosity. The microporosity occupies 51% of pores while the mesoporosity occupies 45% and the 4% by the macroporosity.

![Figure 28 T₂ profile of #17351](image)

Figure 28 T₂ distribution profile of core sample #17351

Figure 29 illustrates the fraction of pores from the five core samples. The mesoporosity is the main portion of the total pores, with the range of 45% to 71%. The microporosity is the second portion of the total pores, with the range of 16% to 51%. Despite having the fraction of
micro-, meso-, and macroporosity, the NMR analysis is unable to produce the pore size distribution in detail. The NMR analysis is usually combined with another experiment, like mercury injection capillary pressure (MICP) and gas (nitrogen or CO₂) adsorption or calibrated with the known pore-size-distribution sample.

Figure 29 The fraction of micro-, meso-, and macro-porosity from five core samples using NMR analysis

Besides measures the T₂ distribution time, the NMR experiment also measures the total porosity of the core samples. Table 7 presents the total porosity of each core sample, with the average of 5.4 %. These five core samples can be partitioned into two groups. The first group has
a low total porosity value of 2.73 to 4.20 % while the second group has a high porosity value of 8.04 to 9.38 %.

Table 7 Total porosity from NMR Analysis

<table>
<thead>
<tr>
<th>Well ID #</th>
<th>Total Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16068</td>
<td>9.38</td>
</tr>
<tr>
<td>16433</td>
<td>2.77</td>
</tr>
<tr>
<td>16652</td>
<td>8.04</td>
</tr>
<tr>
<td>16841</td>
<td>2.73</td>
</tr>
<tr>
<td>17351</td>
<td>4.20</td>
</tr>
</tbody>
</table>

Analysis and Comparison of Analytical Work and Literature Data

As mentioned in Subchapter III Analytical Work on Peng-Robinson EOS, the critical point properties, such as critical volume, critical temperature, and critical pressure can be estimated with the following equations:

\[ V_c = [C]b \]  

(47)

\[ T_c = \frac{2 \left( [C]+D \right) \left( [C]-1 \right)^2}{([C]^2+2[C]D-D)^2} \times \frac{\left( a-[X] \right)}{Rb} \]  

(48)

\[ P_c = \frac{\left( [C]^2-2[C]-D \right)}{([C]^2+2[C]D-D)^2} \times \frac{\left( a-[X] \right)}{b^2} \]  

(49)

where \( [C] \) is a function of \( \frac{\sigma}{d_p} \) and obtained by solving the critical volume equation, while \( [X] \) is simplifying the numerator in the second form and given as

\[ [X] = 2\sigma^3 \varepsilon N^2 \frac{\sigma}{d_p} \left( c_1 + c_2 \frac{\sigma}{d_p} \right) \]  

(50)
The applicability of the equations is examined by calculating the critical temperature of pure hydrocarbons in a confined environment. The calculated values are then compared to the experimental data. Since this study is not equipped with nanofluidic or any nano PVT equipment, others’ experiment results (Singh and Singh, 2011; Xiong et al., 2013; and Pitakbunkate, et al., 2014) are used as the reference and shown in Table 3 to Table 6 in Chapter III. In addition to experimental results, analytical results from Zarragoicoechea and Kuz (2002) and Islam et al. (2015) are also employed as a comparison. The results from this study, experiment data, and other analytical results are labeled as New Equation, Experimental, and Other Analytical, respectively.

**Critical Temperature**

In this study, the value of $\sigma/d$ is varied between 1.25 - 0.01. The $\sigma/d$ value of 1.25 has a very significant effect while the 0.01 does not alter the petroleum fluid properties. The critical temperature of pure hydrocarbons, from methane (CH$_4$) to decane (C$_{10}$H$_{22}$), is calculated with Equation 47, called as New Equation.

$$T_c = \frac{2 ((C+D) (C-1)^2)}{(C^2+2C[D-D])^2} \times \frac{(a-[x])}{Rb}$$  \hspace{1cm} (47)

As the comparison data for critical temperature of methane and ethane in confined pore, Pitakbunkate et al. (2016) data is employed representing experimental data while another analytical result is calculated using equation generated by Zarragoicoechea and Kuz (2002) and Islam et al. (2015), called as Other Analytical work and shown in Equation 17 (repeated below).
\[ T_c = \frac{8}{27bR} \left[ a - 2\sigma^3 \epsilon N^2 \frac{\sigma}{d_p} \left( c_1 + c_2 \frac{\sigma}{d_p} \right) \right] \]  

(17)

Methane has a bulk critical temperature of 343 °R. At pore size of one nanometer, the suppression of the critical temperature reaches 43.2% or 148.2°R. Figure 27 illustrates the critical temperature profile of the three results. This critical temperature profile is explained as two regions. The first region where the pore size is larger than three nanometers, both analytical works produce the same value with the Experimental data. Once the confinement effect becomes more significant, at pore size less than three nanometers (or second region), the critical temperature calculation using New Equation (red line) has a better match with the Experimental data (blue line) than Other Analytical work (green line). In the second region, the red line and green line deviate 8% and 14%, respectively, in average to the blue line shown in Figure 27.

![Figure 30 Critical temperature of methane in confined condition](image)
Figure 28 illustrates the critical temperature profile of ethane from three results. At the pore size of one nanometer, the suppression effect reaches 19.3% or 106.3 °R from its bulk critical temperature (549.6 °R). The profile of the New Equation (red line) has a similar tendency with the profile of methane. The pore size of three nanometers seems to work as a cutoff. Once the pore size is less than three nanometers, the estimated critical temperature underestimates from the Experimental data (blue line) with an average error of 13%. On bigger pore sizes (> three nanometers), the estimated critical temperature has a good match with the experimental data (average error of 2%). In contrast, the Other Analytical results (green line) overestimate the suppression effect by 12%.

Figure 31 Critical temperature of ethane in confined condition
For butane, the comparison between New Equation (red line) and Other Analytical (green line) have a similar tendency with the result displayed for methane and ethane (Figure 28). The New Equation has a perfect match with the Experimental data (Singh and Singh, 2011 and Xiong et al., 2013) with an average error of 0.21%. On the other hand, the Other Analytical results overestimate the suppression effect of the critical temperature. The trend at pore size less than three nanometer could not be established due to the experimental data only providing the suppression effect at 4, 6, 10, and 20 nanometers.

![Figure 32 Critical temperature of butane in confined condition](image)

The deviation results, shown in methane and ethane at pore sizes less than three nanometers, indicate another suppression factor needs to be taken into account. Adsorption could be a possible factor that enhances the suppression effect on the pore size less than three
nanometers (Ambrose, 2011; Michel et al., 2011; Didar, 2012). Wang et al. (2015) expressed the adsorption effect in density changing through his simulations. Figure 30 illustrates Wang et al. (2015) simulation result on density profile from wall to the middle of the pore. The model expresses the density increment at the pore size of 3.80 nanometers (green dotted line) and 1.95 nanometers (purple dotted line). The density increment in the vicinity of the pore indicates the adsorption layer that enhances the alteration of petroleum fluid critical properties.

Figure 33 Effect of pore size on the discrete mass density profiles for n-octane in carbonaceous slits (modified from Wang et al., 2015)
The New Equation is applied to other hydrocarbon components to estimate the critical temperature on nanoscale pore sizes. The suppression effect is analyzed in pore sizes within the range of 4 – 20 nm on propane, pentane, heptane, hexane, and decane as fluid samples. The New Equation results have a perfect agreement with the experiment results, with an average error within the range of 0.37% to 1.41%. The results from the New Equation are compared with the experiment result from literature and shown in Table 8 to 12.

Table 8 Critical Temperature (in °R) of Propane in Confined Pore

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>4</td>
<td>644.1</td>
<td>636.6</td>
</tr>
<tr>
<td>6</td>
<td>654.3</td>
<td>646.4</td>
</tr>
<tr>
<td>10</td>
<td>661.0</td>
<td>654.4</td>
</tr>
<tr>
<td>20</td>
<td>663.8</td>
<td>660.5</td>
</tr>
</tbody>
</table>

Table 9 Critical Temperature (in °R) of Pentane in Confined Pore

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>4</td>
<td>805.0</td>
<td>808.0</td>
</tr>
<tr>
<td>6</td>
<td>824.0</td>
<td>820.3</td>
</tr>
<tr>
<td>10</td>
<td>836.7</td>
<td>830.4</td>
</tr>
<tr>
<td>20</td>
<td>841.8</td>
<td>838.2</td>
</tr>
</tbody>
</table>
Table 10 Critical Temperature (in °R) of Hexane in Confined Pore

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>4</td>
<td>865.6</td>
<td>868.5</td>
</tr>
<tr>
<td>6</td>
<td>888.0</td>
<td>883.0</td>
</tr>
<tr>
<td>10</td>
<td>902.9</td>
<td>894.9</td>
</tr>
<tr>
<td>20</td>
<td>908.9</td>
<td>904.1</td>
</tr>
</tbody>
</table>

Table 11 Critical Temperature (in °R) of Heptane in Confined Pore

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>4</td>
<td>1112.4</td>
<td>1155.2</td>
</tr>
<tr>
<td>6</td>
<td>1148.3</td>
<td>1166.0</td>
</tr>
<tr>
<td>10</td>
<td>1172.3</td>
<td>1174.8</td>
</tr>
<tr>
<td>20</td>
<td>1182.0</td>
<td>1181.6</td>
</tr>
</tbody>
</table>

Table 12 Critical Temperature (in °R) of Decane in Confined Pore

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>4</td>
<td>1043.2</td>
<td>1036.4</td>
</tr>
<tr>
<td>6</td>
<td>1075.3</td>
<td>1060.4</td>
</tr>
<tr>
<td>10</td>
<td>1096.8</td>
<td>1080.3</td>
</tr>
<tr>
<td>20</td>
<td>1105.4</td>
<td>1095.8</td>
</tr>
</tbody>
</table>

To confirm the applicability of the New Equation, the bulk critical temperature is calculated for pure hydrocarbons (methane to decane). To calculate the bulk critical temperature using the New Equation, the effect of pore size to molecule ratio \( \frac{\sigma}{d_p} \) should be neglected. Neglecting the \( \frac{\sigma}{d_p} \) will give the value of 3.95, 0, and 1.0 for \([C]\), \([X]\), and \(D\), respectively. The
calculated critical temperature using the New Equation perfectly matches the literature data (Singh and Singh, 2011 and Xiong et al. 2013) with the average error of 0.06%. Table 13 summarizes the results of the New Equation and the literature data.

Table 13 Critical Temperature (in °R) of methane to decane in bulk condition

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Result</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>New Equation</td>
</tr>
<tr>
<td>Decane</td>
<td>1,111.7</td>
<td>1,111.6</td>
</tr>
<tr>
<td>Heptane</td>
<td>972.3</td>
<td>972.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>913.3</td>
<td>913.4</td>
</tr>
<tr>
<td>Pentane</td>
<td>845.5</td>
<td>846.1</td>
</tr>
<tr>
<td>Butane</td>
<td>765.3</td>
<td>766.9</td>
</tr>
<tr>
<td>Propane</td>
<td>665.8</td>
<td>666.7</td>
</tr>
<tr>
<td>Ethane</td>
<td>549.6</td>
<td>549.7</td>
</tr>
<tr>
<td>Methane</td>
<td>343.0</td>
<td>343.0</td>
</tr>
</tbody>
</table>

According to the results, the New Equation has a satisfactory approach in estimating the suppression effect of critical temperature in nanoscale pore sizes. The average error to the experimental data is less than 1.02% for pore size as small as four nanometers. A greater deviation is found at pore sizes less than three nanometers, and this finding will be a focus of further development of Peng-Robinson EOS for nano-PVT.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

NMR analysis indicates the pore size distribution of the Middle Bakken Formation within the micro- and meso-pore sizes. The total porosity is within the range of 2.73 to 9.38 % with an average of 5.4 % from five samples. The total porosity can be portioned to micropores of 35.5 %, mesopores of 57.1 %, and macropores of 7.4 %. The pore size of one nanometer to twenty nanometers is exercised as the nanoscale pore sizes in modifying Peng-Robinson Equation of State (PR-EOS) for confined fluid.

The modified PR-EOS for confined fluid considers the molecule-to-pore-size ratio in predicting the critical temperature of individual hydrocarbons. The calculated critical temperature, using the modified PR-EOS, has a close match with the experimental results under simulated condition. In pore sizes of one to three nanometers, the average deviation between the model and experimental is 14 % while in bigger pore sizes (larger than three nanometers), the average deviation is 1.02 %. The pore size of three nanometers acts as a cutoff for the model due to the adsorption layers in the vicinity of the pore wall. The bulk critical temperatures were also calculated using the model and presented similar results to the literature with a maximum deviation of 0.03 %.
**Recommendations**

The following works are suggested for future research:

1. Investigate the correlation of adsorption layers to pore size reduction

2. Further modification of the model to predict the suppression effect on pore size smaller than three nanometers

3. Investigate the proper equipment and experiment methods to measure the confined petroleum fluid properties

4. Investigate the proper nanofluidic device to simulate fluid flow behavior in reservoir pores

5. Integrate the NMR analysis with gas adsorption or with known pore-size-distribution sample

6. Further modification of the model to predict the suppression effect on hydrocarbon mixture
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Attraction parameter of the Equation of State</td>
</tr>
<tr>
<td>b</td>
<td>Repulsion parameter of the Equation of State</td>
</tr>
<tr>
<td>n</td>
<td>Number of moles</td>
</tr>
<tr>
<td>r</td>
<td>Radius</td>
</tr>
<tr>
<td>d</td>
<td>Diameter</td>
</tr>
<tr>
<td>E</td>
<td>Internal energy</td>
</tr>
<tr>
<td>F</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>K</td>
<td>Boltzman constant</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>N</td>
<td>Number of molecules (Avogardo number)</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>S</td>
<td>Entropy</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>T₂</td>
<td>Longitudinal relaxation time</td>
</tr>
<tr>
<td>U</td>
<td>Potential energy</td>
</tr>
<tr>
<td>U(S₁₂)</td>
<td>Lennard-Jones potential energy</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
</tbody>
</table>
Greek symbols

$\alpha$ Surface tension

$\varepsilon$ Lennard-Jones energy parameter

$\sigma$ Lennard-Jones size parameter

$\mu$ Micro

$\theta$ Contact angle

Subscripts

1, 2 Molecules id’s

b Bulk

c Critical

x Axial direction in a two dimensions

x,y,z X-, Y-, and Z-direction in a three dimensions

p Pore
APPENDIX A
NMR T$_2$ DISTRIBUTION CURVES

<table>
<thead>
<tr>
<th>Project</th>
<th>Zandy Middle Bakken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>16068 - NMR</td>
</tr>
<tr>
<td>Well</td>
<td></td>
</tr>
<tr>
<td>Sample Depth</td>
<td>0.0ft</td>
</tr>
<tr>
<td>Legal Location/Block</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heilium Porosity</th>
<th>0.0000 fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Confining Stress</td>
<td>0.00 psi</td>
</tr>
<tr>
<td>Gas Permeability</td>
<td>0.000000 md</td>
</tr>
<tr>
<td>Brine Permeability</td>
<td>0.000000 md</td>
</tr>
<tr>
<td>Bulk Volume</td>
<td>14.311 ml</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total NMR Porosity</th>
<th>0.0938 fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_2$ Log Mean</td>
<td>3.070 ms</td>
</tr>
<tr>
<td>SNR</td>
<td>100.13</td>
</tr>
<tr>
<td>NSA</td>
<td>496</td>
</tr>
<tr>
<td>Calibration</td>
<td>6.0617E-5 m/m.u.</td>
</tr>
</tbody>
</table>

**Figure 34** T$_2$ distribution and corresponding data for the Middle Bakken core sample of NDIC #16068
Figure 35 $T_2$ distribution and corresponding data for the Middle Bakken core sample of NDIC #16433
Figure 36 $T_2$ distribution and corresponding data for the Middle Bakken core sample of NDIC #16652
Figure 37 $T_2$ distribution and corresponding data for the Middle Bakken core sample of NDIC #16841
Figure 38 T₂ distribution and corresponding data for the Middle Bakken core sample of NDIC #17351
APPENDIX B

ANALYTICAL PROCESS IN DERIVING THE CRITICAL PROPERTIES FROM THE PRESSURE TENSOR

\[ F = f(T) - \frac{kTN^2}{2V^2} \iint_{r_{12} < \sigma} \left( e^{-\frac{U_{S12}}{kT}} - 1 \right) dV_1 dV_2 \]

\[ U_{S12} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^{6} \right] \]

\[ F = f(T) - \frac{kTN^2}{2V^2} \iiint_{r_{12} < \sigma} \left( e^{-\frac{U_{S12}}{kT}} - 1 \right) dV_1 dV_2 - \frac{kTN^2}{2V^2} \iiint_{r_{12} > \sigma} \left( e^{-\frac{U_{S12}}{kT}} - 1 \right) dV_1 dV_2 \]

\[ F = f(T) - \frac{kTN^2}{2V^2} \left( -\frac{4}{3} \pi \sigma^3 \times V_2 \right) - \frac{kTN^2}{2V^2} \iiint_{r_{12} > \sigma} \left( 1 - \frac{U_{S12}}{kT} - 1 \right) dV_1 dV_2 \]

\[ F = f(T) + \frac{kTN^2}{V} \left( \frac{2}{3} \pi \sigma^3 \right) + \frac{kTN^2}{2V} \iiint_{r_{12} > \sigma} \left( \frac{U_{S12}}{kT} \right) dV_1 dV_2 \]

\[ \frac{1}{V} \iiint_{r_{12} > \sigma} \left( \frac{U_{S12}}{kT} \right) dV_1 dV_2 = \frac{4\varepsilon}{kT} \sigma^3 f \left( \frac{d_p}{\sigma} \right) \]

\[ F = f(T) + \frac{kTN^2}{V} \left( \frac{2}{3} \pi \sigma^3 \right) + \frac{kTN^2}{2V} \left( \frac{4\varepsilon}{kT} \sigma^3 f \left( \frac{d_p}{\sigma} \right) \right) \]

\[ F = f(T) + \frac{kTN^2}{V} b + \frac{2\sigma^3 \varepsilon N^2}{V} f \left( \frac{d_p}{\sigma} \right) \]

\[ f \left( \frac{d_p}{\sigma} \right) = c_0 + c_1 \frac{d_p}{\sigma} + c_2 \left( \frac{d_p}{\sigma} \right)^2 \]
\[ F = f(T) + \frac{kTN^2}{V}b + \frac{2\sigma^3\varepsilon N^2}{V} \left( c_0 + \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b + \frac{2\sigma^3\varepsilon N^2}{V} \left( -\frac{a}{2\varepsilon \sigma^3} + \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b - \frac{aN^2}{V} + \frac{2\sigma^3\varepsilon N^2}{V} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b - \frac{aN^2}{V} + \frac{2\sigma^3\varepsilon N^2}{V} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b - \frac{aN^2}{V} + \frac{2\sigma^3\varepsilon N^2}{V} \left( \frac{c_1 \sigma}{d_p} + \frac{c_2 \sigma}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b - \frac{aN^2}{V} + \frac{2\sigma^3\varepsilon N^2 \sigma}{d_p} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = f(T) + \frac{kTN^2}{V}b - \frac{aN^2}{V} + \frac{2\sigma^3\varepsilon N^2 \sigma}{d_p} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ f(T) = F_0 \approx -nRT \ln(V) \]

\[ F = -kTN \ln(V) + \frac{kTN^2}{V}b - \frac{aN^2 - 2\sigma^3\varepsilon N^2 \sigma}{d_p} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]

\[ F = -RT \ln(V - Nb) - \frac{aN^2 - 2\sigma^3\varepsilon N^2 \sigma}{d_p} \left( \frac{c_1}{d_p} + \frac{c_2}{(d_p)^2} \right) \]
Derivation to obtain equation of pressure tensor

\[
P = -\frac{\partial F}{\partial V}
\]

\[
V = \pi r_p^2 L_x
\]

\[
\partial V = \partial (\pi r_p^2 L_x)
\]

\[
\partial V = L_x \partial (\pi r_p^2) = 2\pi r_p L_x \partial (r_p) \quad \text{or} \quad \partial V = \pi r_p^2 \partial L_x
\]

\[
P_x = -\pi r_p^2 \frac{\partial F}{\partial L_x}
\]

\[
P_x = - \left[ -RT \ln(\pi r_p^2 L_x - Nb) - \frac{aN^2 - 2\sigma^2 \epsilon N^2 \frac{\sigma}{d_p} (c_1 + c_2 \frac{\sigma}{d_p})}{\pi r_p^2 L_x} \right] \times \frac{1}{\pi r_p^2} \partial L_x
\]

\[
P_x = \frac{1}{\pi r_p^2} \times \frac{RT \times \pi r_p^2}{\pi r_p^2 L_x - Nb} + \frac{1}{\pi r_p^2} \times (-1) \times \frac{aN^2 - 2\sigma^2 \epsilon N^2 \frac{\sigma}{d_p} (c_1 + c_2 \frac{\sigma}{d_p})}{\pi r_p^2 L_x^2}
\]

Axial Pressure

\[
P_x = \frac{RT}{V - Nb} - \frac{aN^2 - 2\sigma^2 \epsilon N^2 \frac{\sigma}{d_p} (c_1 + c_2 \frac{\sigma}{d_p})}{V^2}
\]

\[
P_r = -2\pi r_p L_x \frac{\partial F}{\partial r_p}
\]

\[
P_r = - \left[ -RT \ln(\pi r_p^2 L_x - Nb) - \frac{aN^2 - 2\sigma^2 \epsilon N^2 \frac{\sigma}{d_p} (c_1 + c_2 \frac{\sigma}{d_p})}{\pi r_p^2 L_x} \right] \times \frac{1}{2\pi r_p L_x} \partial r_p
\]
\[ P_r = \frac{1}{2\pi r_p l_x} \times \frac{RT \times 2\pi r_p l_x}{\pi r_p ^2 l_x - Nb} + \frac{1}{2\pi r_p l_x} \times (-2) \frac{aN^2}{\pi r_p ^3 l_x} + \frac{1}{2\pi r_p l_x} \]

\[ \times (-1) \frac{-2\sigma ^3 \varepsilon N^2 \frac{\sigma}{d_p} \left(3c_1 + 4c_2 \frac{\sigma}{d_p}\right)}{\pi r_p ^3 l_x} \]

\[ P_r = \frac{RT}{\pi r_p ^2 l_x - Nb} - \frac{aN^2}{\pi ^2 r_p ^4 l_x ^2} + \frac{1}{\pi ^2 r_p ^4 l_x ^2} \frac{\sigma ^3 \varepsilon N^2 \frac{\sigma}{d_p} \left(3c_1 + 4c_2 \frac{\sigma}{d_p}\right)}{\pi ^2 r_p ^4 l_x ^2} \]

Radial Pressure

\[ P_r = \frac{RT}{V - Nb} - \frac{aN^2 - \sigma ^3 \varepsilon N^2 \frac{\sigma}{d_p} \left(3c_1 + 4c_2 \frac{\sigma}{d_p}\right)}{V ^2} \]
REFERENCES


Karimi, S. et al., 2015. Reservoir Rock Characterization using Centrifuge and Nuclear Magnetic Resonance: A Laboratory Study of Middle Bakken Cores. SPE-175069-MS.


