RICE UNIVERSITY

Separation and characterization of crude oils and investigation of their wetting properties on rock surfaces

by

Sara Rezaee

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE

Francisco Vargas, Chair
Louis Owen Jr. Assistant Professor
Chemical and Biomolecular Engineering

Sibani Lisa Biswal
Associate Professor Chemical and Biomolecular Engineering and Materials Science and NanoEngineering

James Tour
Professor of Chemistry, Computer Science, and Materials Science and NanoEngineering

HOUSTON, TEXAS
April 2019
ABSTRACT

Separation and characterization of crude oils and investigation of their wetting properties on rock surfaces

by

Sara Rezaee

The complexity of crude oil makes its compositional characterization a very challenging task. As a conventional method for characterizing crude oil, SARA fractionation is based on the differences between the solubility and polarity of the four fractions: Saturates, Aromatics, Resins, and Asphaltenes. Currently, some of the available methods for SARA separation are based on chromatographic principles that may possess some limitations, including requiring the solvent and sample in large amounts, being a time-consuming process, and providing irreproducible results. This study proposes two novel methods for maltene (SAR) and SARA analysis named the improved chromatographic technique and clay/alumina chromatography method respectively. We confirm that the new techniques require less solvent and that the amount of solvent for the desorption step does not depend on polar fractions content. Both methods are three to four times faster compared to the ASTM D2007 method. The proposed systems are practical for industrial application since the equipment is fairly inexpensive and can be easily assembled in any laboratory. Additionally, they do not require an expert operator to analyze the data, which is essential in some chromatography methods like High-Pressure Liquid Chromatography (HPLC). The improved chromatographic technique is only for maltene analysis, while this method makes it possible to collect the separated fractions and use them
for further analysis. The clay/alumina chromatography method is for SARA analysis and does not require prior separation of asphaltene for maltene fractionation.

As the most complex and heavy organic fraction of crude oil, asphaltenes are one of the major contributors flow assurance issues. It can significantly affect oil field production by depositing and blocking wells and flowlines. In this study, asphaltenes are fractionated into four parts based on their solubility in n-pentane, n-hexane, n-heptane, and n-octane. Asphaltene composition and structure are determined by elemental analysis and Fourier-transform infrared (FTIR) spectroscopy. Spectroscopy shows the functional groups in different asphaltene fractions (C₅-₆, C₆-₇, C₇-₈, C₈+) to be the same. The aromaticity of C₅-₆ asphaltene is the lowest among the four fractions, however highest in C₈+, which is the heaviest fraction, has the highest aromaticity. A new approach to aromaticity calculation is proposed based on elemental analysis, and the validity of the method is verified by comparing the results to aromaticity based on FTIR. Also, to investigate the polydispersity of asphaltene fractions, the molecular weight distribution is measured by gel permission chromatography (GPC).

In the following part of the study, the effect of crude oil properties on wettability properties of calcium carbonate is studied. The tilting plate method was chosen as an appropriate method for contact angle measurement because it involves the formation of a rigid film instead of the use of the oil withdrawal method or a moving needle. The contact angle measurement method has some limitations; for instance, sometimes data is not reproducible. In this study, we propose a method of calcite preparation that involves controlling the brine layer on the surface calcite during the oil aging step. Additionally, the contact angle measurement procedure is simulated in a way designed to establish a
wettability condition as close as possible to the reservoir condition. Moreover, the standard deviation of the method has been improved from 30° to 15°. We observe that the calcite tends to be more oil-wet when the water layer thins. In addition, this study also shows the importance of aging time in oil in the presence of brine and equilibration time of calcite in brine before contact angle measurement. It has been shown that low salinity NaCl brine alters the wettability from an oil-wet condition toward a more water-wet condition by contact angle measurement.

Different approaches are presented in the literature to discuss the controlling mechanism of low-salinity brine flooding in improving oil recovery. In this part, we focus on crude oil compositions and properties including “water micro-dispersion formation,” “asphaltene stability,” “interfacial tension,” and their correlation with oil recovery by low-salinity brine flooding. We observe that increasing the water micro-dispersion formation leads to an increase in additional oil recovery, except for one crude oil which does not contain any asphaltenes. There is no direct correlation between the asphaltene onset of precipitation (vol. % heptane) and total oil recovery since as expected, not all of the asphaltenes are surface active. Additionally, we confirm that the most important and effective parameter is interfacial tension. It is correlated to the total\(^1\)/additional\(^2\) oil recovery with the highest R\(^2\) in comparison with the other parameters.

\[\text{Total oil recovery in this dissertation is corresponded to oil recovery amount in high salinity brine (5M NaCl brine) plus the additional oil recovery in low salinity brine (0.164M NaCl).}\]
\[\text{Additional oil recovery in this dissertation is corresponded to only oil recovery amount in low salinity brine (0.164M NaCl brine).}\]
Acknowledgments

I would like to express my sincere and deepest gratitude to my supervisor, Dr. Francisco Vargas for his excellent guidance, encouragement and valuable advice during my studies; there are no words to describe his enormous unconditional support.

I would like to thank Dr. Hirasaki and Dr. Biswal for their continuous collaborations and insightful discussions on multiple projects. This work is evaluated in a broader view and becomes much stronger under their valuable suggestions.

Many thanks to Maura Puerto for showing me there is always something to discover and look forward to in science. Thank you for your great support for the report writing and correction, teaching me many of the experimental techniques and your helpful discussion.

I would like to thank Dr. Mohammad Tavakoli for all his academic help during my whole PhD experience and his contribution toward the completion of this thesis.

I also want to thank Dr. Rocio Doherty for all of her assistance, help, and support.

Thanks to the undergraduate students that contributed to this work, Brianna Hernandez, Jose Cavalcante De, and Morgan Glose.

I would like to thank my thesis assessment committee members Dr. Tour and Dr. Biswal taking your precious time to read my thesis and their helpful advice. I also thank Dr. Verduzco for allowing me to use equipment in his lab to complete my experiments.
Also, I would like to thank all of the other Vargas group members, especially my lab mates Shayan Enayat, Aisha Khaleel and Jun Kuang for accompanying me on this journey and always providing positive lab environment. I especially thank Jin Song for great discussion and helping with Spontaneous imbibition test result and implementing the procedure for contact angle measurement.

My sincere thanks also go to Dr. Tony Spratt and Elijah Kempton who provided me internship opportunities in their groups and leading me working on diverse exciting projects.

Lastly, I would like to thank my family for their support throughout my career as nothing would be possible without their love. Also, I want to thank my supportive friend, Shaghayegh Agah, who stayed by my side through thick and thin.
# Contents

Acknowledgments ........................................................................................................... v

Contents .......................................................................................................................... vii

List of Figures .................................................................................................................... xi

List of Tables ..................................................................................................................... xvii

List of Equations .............................................................................................................. xix

Nomenclature ................................................................................................................... xx

Introduction ...................................................................................................................... 1
  1.1. Thesis motivation ...................................................................................................... 1
  1.2. Objective .................................................................................................................. 3
  1.3. Thesis structure ....................................................................................................... 3

Crude Oil fractionation, quantification, and characterization ........................................... 6
  2.1. Conventional methods for crude oil fractionation .................................................... 6
  2.2. Improved chromatographic technique for SAR (Maltene)\textsuperscript{22} fractionation .... 11
    2.2.1. Materials and methods ...................................................................................... 11
    2.2.2. Procedure ........................................................................................................ 13
      2.2.2.1. SARA analysis using the ASTM D2007 method ........................................ 13
      2.2.2.2. Maltene analysis using the proposed methodology ................................. 14
    2.2.3. Results and discussion ..................................................................................... 18
    2.2.4. Summary of results ......................................................................................... 22
  2.3. Clay/Alumina chromatography technique for SARA fractionation\textsuperscript{28} .................. 23
    2.3.1. Materials and methods .................................................................................... 23
    2.3.2. Procedure ......................................................................................................... 24
      2.3.2.1. Adsorption Step ....................................................................................... 26
      2.3.2.2. Desorption Step ...................................................................................... 27
    2.3.3. Quantification of SARA fractions\textsuperscript{28} .................................................. 29
    2.3.4. Summary of results ......................................................................................... 33
  2.4. Chapter summary .................................................................................................... 34

Asphaltene fractionation and characterization .................................................................. 36
3.1. Asphaltene and its properties .............................................................. 36
3.2. Materials and methods ........................................................................ 47
3.3. Results and discussion ......................................................................... 50
  3.3.1. Fractionation based on solubility ..................................................... 50
  3.3.2. Study of asphaltene structure by FTIR .......................................... 55
  3.3.3. Asphaltene properties ..................................................................... 58
   3.3.3.1. Aromaticity ................................................................................. 58
   3.3.3.2. Molecular Weight ................................................................. 62
3.4. Chapter summary .................................................................................... 66

Effect of crude oil fractions on wettability properties of calcium carbonate reservoirs ................................................................................................................. 68
4.1. Investigating the wettability properties of carbonate reservoirs .......... 68
4.2. Materials and methods ......................................................................... 73
  4.2.1. Crude oil ....................................................................................... 73
  4.2.2. Preparation of samples ................................................................. 75
  4.2.3. Contact angle measurement ......................................................... 76
  4.2.4. Structural analysis ......................................................................... 77
   4.2.4.1. NMR spectroscopy ................................................................. 77
   4.2.4.2. FTIR spectroscopy ................................................................. 77
4.3. Results and discussion ......................................................................... 78
  4.3.1. Improvement of contact angle measurement procedure ................ 78
    4.3.1.1. Appropriate method for contact angle measurement ............... 78
    4.3.1.2. Controlling water layer thickness on calcite surface .............. 82
    4.3.1.3. Contact angles measurement for model oil on calcite plates with a
              controlled water layer thickness .................................................. 88
    4.3.1.4. Summary of the results ......................................................... 96
  4.3.2. Investigating the effect of different variables on the contact angle .. 97
    4.3.2.1. Effect of salinity ................................................................. 97
    4.3.2.2. Effect of aging time ........................................................... 100
    4.3.2.3. Effect of asphaltene concentration and its solvent ............... 102
    4.3.2.4. Effect of different asphaltene fractions .................................. 103
    4.3.2.5. Comparing the effect of resin and asphaltene ...................... 104
    4.3.2.6. Summary of results ........................................................... 106
4.3.3. Effect of low salinity brine aging on wettability properties of calcite plates by CA measurement at room temperature ................................................................. 108

4.3.3.1. Procedure of calcite preparation, oil aging step, and smart water aging ................................................................................................................................. 108

4.3.3.2. Comparing the result of contact angle for mode oil and crude oil samples before and after low salinity brine aging ........................................................................ 110

4.3.4. Characterization of adsorbate fractions on calcite surface ....................... 112

4.3.4.1. Adsorption of surface active components on to the calcite surface during the oil aging ........................................................................................................ 112

4.3.4.2. Desorption of surface active components from the calcite surface .... 114

4.3.4.3. Determination of the chemical structure of adsorbate .......................... 117

4.3.4.4. Summary of results .................................................................................. 125

4.4. Chapter summary ............................................................................................ 126

Investigating the correlation between crude oil properties and oil recovery .......... 129

5.1. Investigating the mechanism of enhanced oil recovery by low salinity brine .... 129

5.2. Materials and methods .................................................................................... 132

5.2.1. SARA analysis .............................................................................................. 133

5.2.2. Spontaneous imbibition test ......................................................................... 135

5.2.3. Water micro-dispersion formation measurement .......................................... 136

5.2.4. Asphaltene onset point of precipitation (vol. % of Heptane) ......................... 137

5.2.5. IFT measurement .......................................................................................... 138

5.3. Result and discussion ....................................................................................... 138

5.3.1. Effect of water micro dispersion formation .................................................. 138

5.3.2. Effect of asphaltene stability by measuring asphaltene onset point of precipitation (vol. % of Heptane) ............................................................... 145

5.3.3. Effect of Interfacial tension ......................................................................... 147

5.4. Chapter summary ............................................................................................ 157

Conclusions and recommendations ........................................................................ 159

6.1. Conclusion .......................................................................................................... 159

6.2. Recommendation ................................................................................................ 161

6.2.1. Effect of crude oil and low salinity brine aging on wettability properties of calcite by CA measurement at high temperature ............................................. 161
6.2.2. Asphaltene deposition tendency on surfaces with different wettability properties ............................................................... 165
6.2.3. Asphaltene fractionation based on their surface activity ......................... 170

References ........................................................................................................................................................................ 171
List of Figures

Figure 2-1 Column details: a. PTFE column, b. Detail of Nylon straight connector.22

Figure 2-2. Improved chromatographic technique; Adsorption step5 (From Doherty et al. CRC Press, 15-73, 2018)22

Figure 2-3. Improved chromatographic technique; Desorption step.

Figure 2-4. FTIR results of saturate fraction when the pump flow rate is: a) 1 ml.min⁻¹, b) 3 ml.min⁻¹ and c) 5 ml.min⁻¹.

Figure 2-5. FTIR spectra of aromatic fraction when the pump flow rate is a) 1 ml.min⁻¹, b) 3 ml.min⁻¹, and c) 5 ml.min⁻¹.

Figure 2-6. SARA analysis of four crude oils22

Figure 2-7. Comparison of SARA analysis based on the improved chromatographic technique and ASTM D200722

Figure 2-8. Clay and alumina chromatographic columns28

Figure 2-9. FTIR spectra of alumina column effluent.

Figure 2-10. Adsorption and desorption process in clay and alumina columns.

Figure 2-11. Fractionation of eight crude oils by clay/alumina chromatography technique28

Figure 2-12. Comparison of SARA analysis result based on ASTM D2007 and clay/alumina chromatography methods28

Figure 2-13. Comparison of SARA fractions determined by the third party laboratory and Clay/Alumina Chromatography method28

Figure 3-1 Schematic of a basic gel chromatography system5,5,74

Figure 3-2 Asphaltene sample diluted by THF.

Figure 3-3 Solution filtered and placed in GPC vials.

Figure 3-4 C₅-₆ and C₆-₇ asphaltenes separated from crude oil A5.
Figure 3-5 C7-8 and C5+ to C8+ asphaltene separated from crude oil A5.......................... 51
Figure 3-6 Asphaltene fractionation; Aging time=48 hrs5................................................. 53
Figure 3-7 Asphaltene separation by soxhlet extraction5..................................................... 54
Figure 3-8 FTIR of C5+ asphaltene of crude oil C................................................................. 58
Figure 3-9 Aromaticity based on elemental analysis and FTIR............................................. 60
Figure 3-10 aromaticity based on elemental analysis and FTIR for asphaltene from
a. Crude SA9 and b. Crude SA6.......................................................................................... 62
Figure 3-11 Asphaltene molecular weight changes by concentration5............................... 63
Figure 3-12 Asphaltene molecular weight distribution in different concentration, . 64
Figure 3-13 Asphaltene molecular weight distribution for different asphaltene
fractions of crude oil SA9 with a concentration of 0.16 wt. %5............................................ 65
Figure 3-14 Average number molecular weight of asphaltene monomer versus
polydispersity index for different crude oils........................................................................ 66
Figure 4-1 Overview of chapter 4.......................................................................................... 73
Figure 4-2 a. Skin formation, a. 0.4 wt. % C5-6 asphaltene in MO / equilibration
time=5 days...................................................................................................................... 80
Figure 4-3 a. RCA, 0.05 wt. % C5-6 asphaltene in MO / equilibration time=2 days,
0.1M NaCl brine; b. ACA, 0.05 wt. % C5-6 asphaltene in MO / Time=0, ......................... 81
Figure 4-4 Comparison of Contact Angles determined without controlling thickness
of water-layer left on calcite plate during oil aging and thereafter rinsing aged plate
with brine. MO Standard Deviation ±30°.......................................................................... 83
Figure 4-5 Example of water film with and without wiping for two calcite plates. 85
Figure 4-6 Effect of water layer thickness on wettability alteration of calcite plate,
RCA and ACA for MO in 5M NaCl brine........................................................................... 91
Figure 4-7 RCA/ACA measurement for MO in 5M NaCl brine when plate is
equilibrated with brine at 120°C (Dry 2).......................................................................... 91
Figure 4-8 RCA/ACA measurement for MO and n-C12 in 5M NaCl brine, equilibration time in brine before contact angle measurement = 2hrs, wiping method was used to control water layer thickness. ................................................................. 93

Figure 4-9 Effect of calcite equilibration in brine before contact angle measurement. .................................................................................................................................................. 94

Figure 4-10 Effect of temperature during calcite plate equilibration in 5M NaCl brine on wettability alteration. ...................................................................................................................................... 95

Figure 4-11 Effect of temperature during calcite plate equilibration in 0.1M NaCl brine on wettability alteration. ...................................................................................................................................... 96

Figure 4-12 RCA and ACA, 0.05 wt. % C5+ asphaltene in MO, 0.1M and 5M NaCl, 1 week aging at 120°C. ....................................................................................................................................................... 98

Figure 4-13 RCA and ACA, 0.05 wt. % C5+ asphaltene in MO, aging of 3 and 1 week in 0.1M and 5M NaCl. ....................................................................................................................................................... 99

Figure 4-14 RCA and ACA for 0.05 wt. % C5+ asphaltene in MO at (a) time zero (a) and (b) after 4 days. Calcite plate aged for one week at 120°C in test fluids. ........ 100

Figure 4-15 RCA and ACA, 0.05 wt. % C5+ asphaltene in MO, 0.1M NaCl, 1 and 3 weeks aging at 120 °C. ............................................................................................................................................... 101

Figure 4-16 RCA and ACA for 0.05 wt. % C5+ in MO at (a) time zero and (b) after 4 days. Calcite plate aged for three weeks at 120 °C in test fluids; C5+ in MO and 0.1M NaCl. ............................................................................................................................................... 101

Figure 4-17 Effect of asphaltene media on wettability alteration, RCA and ACA in 5M NaCl after 2 weeks aging. .............................................................................................................. 102

Figure 4-18 RCA and ACA, 0.05 and 2.10 wt. % C5+ asphaltene in Toluene. Calcite plates aged for 2 weeks at 120 °C in test oil and 5M NaCl. .................................................. 103

Figure 4-19 RCA and ACA of C5-6 and C5+ asphaltene in MO at 0.05 wt. % (Test fluid). Calcite plates aged for one week at 120°C in test fluid and 0.1M NaCl brine. ........................................................................................................................................ 104

Figure 4-20 Effect of SA6 oil and its surface active fractions (asphaltene and resin) on wetting alteration. ................................................................................................................... 105
Figure 4-21 RCA and ACA measured at ambient conditions in oil-aged calcite plates, Oil aged + 5M NaCl aged, Oil aged + 0.164M NaCl aged. ....................................... 111

Figure 4-22 AOP of 2.1 wt. % C₅+ in toluene and SA6 oil by using the indirect method. .................................................................................................................. 112

Figure 4-23 Calcite plates after aged in test oils in the presence of 5M NaCl and : 114

Figure 4-24 Calcite plates after rinsing by DCM, toluene and acetone: a is 8 wt. % resin in Toluene, b is C₅+ in MO, c is C₅+ in toluene, d is SA6 crude oil and e 2.1 wt. % C₅+ in toluene. ........................................................................................................... 114

Figure 4-25 Adsorption capacity versus RCA/ACA. .............................................. 116

Figure 4-26 FTIR spectra; a. clean calcite, b. aged calcites in different oil samples. .............................................................................................................................. 120

Figure 4-27 SEM images of a. clean calcite, b. calcite aged in 2.1 wt. % C₅+ in toluene, ......................................................................................................................... 122

Figure 4-28 SEM images of a. clean calcite, b. calcite aged in 2.1 wt. % C₅+ in toluene, ......................................................................................................................... 123

Figure 4-29 Surface compositional analysis of clean calcite plate. ..................... 123

Figure 4-30 Surface compositional analysis of calcite aged in SA6 oil............... 124

Figure 4-31 Surface compositional analysis of calcite aged in SB4 oil............... 124

Figure 4-32 Surface compositional analysis of calcite aged in 2.1 wt. % C₅+ asphaltene in toluene......................................................................................................................... 125

Figure 5-1 Is oil recovery correlated with …?.......................................................... 132

Figure 5-2 SARA analysis of Crude A-H................................................................. 134

Figure 5-3 Oil recovery based on spontaneous imbibition test.......................... 136

Figure 5-4 Micro dispersion experiment procedure............................................ 137

Figure 5-5 a Crude oil G, b Crude oil B and c Crude oil E. Number 1 contains 5M NaCl brine and 2 is related to 0.164M brine. ........................................................................... 140

Figure 5-6 Additional oil recovery versus micro dispersion ratio....................... 141
Figure 5-7 Additional oil recovery versus micro dispersion ratio................................. 142

Figure 5-8 Effect of “asphaltene + resin” on “micro dispersion ratio” @ 0.164M NaCl.......................................................... 143

Figure 5-9 Effect of asphaltene on micro dispersion formation @ 0.164M NaCl.. 144

Figure 5-10 Effect of asphaltene/resin ratio on micro dispersion formation ........ 145

Figure 5-11 Total oil recovery and asphaltene onset point of precipitation......... 147

Figure 5-12 IFT of different oils against 0.164 and 5M NaCl brine....................... 148

Figure 5-13 Total oil recovery versus IFT of Crude A-H and MO I in 0.164M NaCl brine. ........................................................................................................ 149

Figure 5-14 Additional oil recovery versus IFT of Crude A-H and MO I in ........ 150

Figure 5-15 Total oil recovery versus IFT of Crude A-F (without crude G) and MO I in 0.164M NaCl brine. .............................................................. 152

Figure 5-16 Additional oil recovery versus IFT of Crude A-F (without crude G) and MO I in 0.164M NaCl brine. .............................................................. 153

Figure 5-17 IFT versus micro dispersion @ 0.164M NaCl brine. ....................... 153

Figure 5-18 IFT versus time in 0.164M NaCl brine (not equilibrated with calcium carbonate powder). .......................................................... 155

Figure 5-19 Comparison IFT in 0.164M before and after equilibration with calcium carbonate powder. pH_{Eq}=9.5 and pH_{Neq}=7.1........................................... 155

Figure 5-20 IFT in 0.164M NaCl brine versus asphaltene + resin content......... 156

Figure 5-21 IFT in 0.164M NaCl brine versus asphaltene content. ................. 157

Figure 6-1 Measuring RCA/ACA of MO in 5M NaCl at 120 °C............................... 164

Figure 6-2 Effect of changing brine from 5M to 0.164M on calcite wettability properties @ 120 C. ................................................................. 165

Figure 6-3 Hamaker constant and asphaltene deposition tendency.................... 167

Figure 6-4 Asphaltene sticking tendency on 32 different solid surfaces........... 170
List of Tables

Table 2-1. Crude oil sample properties................................................................. 11
Table 2-2. Materials needed for the ASTM D2007 method and the improved chromatographic technique. ....................................................................................... 12
Table 2-3. Crude oil properties................................................................................. 24
Table 2-4. Chromatography columns characteristic .............................................. 25
Table 3-1 Crude oil properties................................................................................ 47
Table 3-2 Preparing samples with different asphaltene concentration ................. 49
Table 3-3 Asphaltene fractionation result by the addition of different precipitants 55
Table 3-4 Infrared absorption frequencies assigned to a typical FTIR spectrum\textsuperscript{24,39,42}. ........................................................................................................ 56
Table 3-5 Aromaticity index of C\textsubscript{5+} asphaltene based on FTIR and elemental analysis........................................................................................................... 60
Table 3-6 Elemental analysis of C\textsubscript{5+} asphaltene of different crude oils. .......... 61
Table 4-1 SA6 crude oil properties........................................................................... 74
Table 4-2 Total Acid Number; C\textsubscript{5+} asphaltene and crude oil SA6 and SB4........ 75
Table 4-3 Different methods to control water layer thickness on the calcite surface. ......................................................................................................................... 86
Table 4-4 Summary of the ACA and RCA result. ...................................................... 106
Table 4-5 Adsorption capacity of calcite plates in case of aging in four different samples.................................................................................................................. 116
Table 4-6 Aromaticity based NMR analysis.......................................................... 118
Table 5-1 Crude oil properties............................................................................... 133
Table 5-2 Water content of test oils before and after mixing with 0.164M or 5M NaCl brine.................................................................................................................... 139
List of Equations

Equation 2-1 ........................................................................................................... 30
Equation 2-2 ........................................................................................................... 30
Equation 2-3 ........................................................................................................... 30
Equation 3-1 ........................................................................................................... 43
Equation 3-2 ........................................................................................................... 43
Equation 3-3 ........................................................................................................... 58
Equation 4-1 ........................................................................................................... 115
Equation 4-2 ........................................................................................................... 117
Equation 6-1 ........................................................................................................... 168
Equation 6-2 ........................................................................................................... 169
Equation 6-3 ........................................................................................................... 169
### Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>PIONA</td>
<td>n-Paraffin, Isoparaffin, Olefin, Naphthene and Aromatic</td>
</tr>
<tr>
<td>TLC-FID</td>
<td>Thin-Layer Chromatography with Flame Ionization Detection</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-Pressure Liquid Chromatography</td>
</tr>
<tr>
<td>AMD-HPLC</td>
<td>Automated multi-dimensional high-performance liquid chromatography</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permission chromatography</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>VPO</td>
<td>Vapor Pressure Osmometry</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectroscopy</td>
</tr>
<tr>
<td>MALDITOF-MS</td>
<td>Matrix-Assisted Laser Desorption Ionization-Time-of-Flight</td>
</tr>
<tr>
<td>TAN</td>
<td>Total Acid Number</td>
</tr>
<tr>
<td>CA</td>
<td>Contact Angle</td>
</tr>
<tr>
<td>ACA</td>
<td>Advancing Contact Angle</td>
</tr>
<tr>
<td>RCA</td>
<td>Receding Contact Angle</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1. Thesis motivation

Identifying and quantifying the main compounds or pseudo-components of crude oil mixture is important for predicting crude oil behavior in different conditions. Due to the complex composition of crude oils, performing the elemental analysis is not possible. Therefore, in place of this analysis, hydrocarbon group type analysis is preferred\(^1\). One approach to hydrocarbon group type analysis is SARA separation. It separates the crude oil components into four parts based on their solubility and polarity: Saturates, Aromatics, Resins, and Asphaltene. Most available chromatography techniques used for SARA analysis suffer from some limitations, such as using large amounts of solvent or sample and yielding irreproducible results. It is worthwhile to develop an easy method that is fast, repeatable, uses a small amount of solvent, and is applicable for industrial uses.
Among the crude oil fractions, asphaltenes are the heaviest and most problematic fraction of crude oil; it causes damages to the flowlines. Asphaltenes are the least understood issue among the flow assurance problem because of the complexity of its structure, aggregation, precipitation, and deposition processes. A better understanding of asphaltene structure and properties is essential to predicting their tendency to deposit or precipitate under different conditions. Also, in order to provide a model for determining asphaltene stability and characteristic, it is necessary to assess the physical properties of asphaltene such as aromaticity and molecular weight.

Since approximately 60-70% of the oil cannot be produced by conventional methods, Enhanced oil recovery (EOR) processes are gaining importance. EOR methods are applied to the reservoir to increase the ability of the oil to flow to a well by injecting water, chemicals, or gases into the reservoir. In order to provide a reliable and commercial method for enhanced oil recovery, it is crucial to study the wettability properties of rock surfaces and effective parameters for wettability alteration. Currently, the contact angle measurement is one common technique used to investigate the wettability properties of rock surfaces. Nevertheless, this method suffers from several limitations caused by the effects of surface roughness, geometry, and surface heterogeneity. Therefore, it is crucial to have a reliable procedure that simulates the wettability properties as the reservoir condition, with a reproducible result.

Low-salinity brine flooding is one common and emerging technique for EOR. Crude oil fractions, and specifically asphaltene as the heaviest and most polarizable fraction impact on the wettability properties of rock reservoirs. Nevertheless, there is no general agreement on how crude oil properties can describe the mechanism of enhanced oil recovery through
low-salinity brine injection. Finding a correlation between crude oil characteristic and improved oil recovery in the presence of low-salinity brine is a research area of great interest.

1.2. Objective

The following objectives have been achieved by the work presented in this dissertation:

- Develop an improved chromatography technique for maltene analysis.
- Propose a novel method for SARA fractionation without prior separation of asphaltene.
- Fractionate asphaltene based on solubility and investigate the structure and polydispersity of each fraction by Fourier Transform Infrared Spectroscopy (FTIR), aromaticity calculation, and molecular weight distribution measurement.
- Improve the contact angle measurement procedure for evaluating the effect of crude oil on wettability properties of calcium carbonate reservoir.
- Investigate the mechanism of enhanced oil recovery by low salinity brine flooding based on crude oil properties.

1.3. Thesis structure

This dissertation introduces a novel improved chromatography technique for crude oil fractionation, based on the solubility and polarity of each fraction. The asphaltene characteristic is also investigated in terms of polydispersity based on molecular weight distribution and aromaticity. The effect of different crude oils on the wettability properties
of calcite plates are presented. In addition, the impact of crude oil fractions and properties on total/additional oil recovery based on imbibition test is evaluated.

In Chapter 2, two different methods for crude oil fractionation based on chromatography technique are developed. The purity of separated fractions is verified by FTIR spectroscopy, the test is repeated for each sample four times to ensure the repeatability of the result, and the reproducibility of the data is verified by comparing the result to a third party laboratory.

In Chapter 3, a new method for asphaltene fractionation is discussed. In addition, the functional groups of different asphaltene fractions are investigated using FTIR. The aromaticity of asphaltene fractions is calculated based on a new approach using elemental analysis data, and the results are compared to the aromaticity found using the FTIR method.

In Chapter 4, an improved method for contact angle measurement procedure is developed to acquire more reproducible results and simulate the wettability properties for the calcite plate as close as possible to the reservoir condition. The importance of water layer thickness on the wettability properties of calcite is discussed. In order to attain a better understanding of the mechanism of wettability change in the calcite plate after aging in different crude oil fractions, the characteristic of the calcite plate surface is studied before and after the aging process.

In Chapter 5, the relationship between the crude oil properties (water micro-dispersion formation, asphaltene onset point of precipitation [vol. % heptane] and interfacial tension and total/additional oil recovery by low-salinity brine injection are
explored. Moreover, a hypothesis is proposed to describe the mechanism of enhanced oil recovery by low-salinity brine flooding.

In Chapter 6, a summary of the thesis is provided, and future work is suggested.
Crude Oil fractionation, quantification, and characterization

2.1. Conventional methods for crude oil fractionation

Crude oil contains different hydrocarbon molecules ranging from very light components to very heavy ones, such as highly asphaltenic crudes. The study of the crude oil components, species by species, is not feasible because of the large number of hydrocarbon types. Instead, a hydrocarbon group type analysis is commonly employed.

Crude oil fractionation is essential because there is a wide variation in the properties of the lightest crude oil to the heaviest one. For example, heavy oil has higher viscosity, asphaltene content, and metals in comparison with conventional oil.

There are three main methods of crude oil fractionation; based on the boiling point, the chemical structure and the polarity.

The most common and oldest way to separate the crude oil into its fractions is based on the different boiling temperatures of its components. This process is known as fractional distillation. In a distillation tower, the crude oil is heated up until the least volatile components are evaporated. At the top of the column, the lighter products such as butane,
liquid petroleum gasses (LPG), gasoline blending components, and naphtha are recovered. The components with a mid-range boiling point stay in the middle of the distillation tower such as jet fuel, kerosene, and distillates. At the bottom of the column, at a temperature of 537.8 °C (1000°F), the heaviest products such as residual fuel oil are recovered. The characterization based on the type of hydrocarbons is known as PIONA (n-paraffin, isoparaffin, olefin, naphthene and aromatic) analysis. Since olefins usually are not present in crude oil; this analysis for crude oil is known as PNA analysis. In this approach, the separation is based on gas chromatography systems.

SARA analysis is one of the hydrocarbon group type separation methods conducted by identifying the main or pseudo-components of oil mixture based on the solubility and polarity of the four fractions. Crude oil fractionation based on the polarity and solubility is the focus of this chapter.

The three main and basic chromatography methods for SARA fractionation are (1) Thin-Layer Chromatography with Flame Ionization Detection (TLC-FID) or Iatroscan, (2) clay-silica gel adsorption chromatography (ASTM D2007), and (3) High-Pressure Liquid Chromatography (HPLC).

The fractionation in the TLC-FID method is based on the thin layer chromatography (TLC) with quartz rods that are coated with sintered silica particles. The amount of SARA fractions is defined based on the peak areas in the FID response factor. The advantages of using TLC-FID method are using a small amount of sample (about 10 μL) and quantifying asphaltene as well as maltene fractions (In the HPLC and ASTM methods, asphaltene needs to be separated before maltene analysis). However, one of the limitations of this method is the potential loss of volatile fractions of saturates and aromatics during the
analysis. This implies that this method is not appropriate for analyzing light and medium oils. Another limitation is that overloading and channeling at the origin of the silica-coated rods may happen while loading the sample into a small spot. Additionally, it is occasionally a challenge to differentiate between resin and asphaltene signals since resins have polar substituents like asphaltene.

The oldest chromatography method is the ASTM D2007, which uses a system of two columns filled with clay and silica gel, respectively. The separation in this method is based on the affinity of maltene fractions (saturate, aromatic and resin) to be adsorbed into the clay and silica gel columns. Resins are adsorbed onto attapulgus clay while the aromatics are adsorbed onto the silica gel. The remaining saturates elute directly and are collected in a flask. This method has a few limitations, and four of those are addressed here. It requires large quantities of solvent and crude oil sample (about 1.5 L and 10 g respectively), and it is time-consuming (up to 2 weeks per test). It is also difficult to automate, and the results are not always reproducible because of light component losses.

Silica and alumina were used in the early HPLC technique while in the improved method amino-bonded silica columns are used to fractionate saturates, aromatics, and resins. The result of this technique is reproducible and uses the very minimum amount of sample. However, one of the limitations of this method is its higher operational costs in comparison with the simple chromatography method. HPLC also needs to be calibrated for all of the hydrocarbons since each of them has a specific HPLC response. This response depends on column characteristic, the calibration curve, retention time and peaks area (Each peak represents the detector response for a different compound.) for known compounds. Calibration curve needs to be tested to verify that column properties have not changed.
because of aging time or some irreversible adsorption of incompletely precipitated asphaltene and polar compounds.

Based on the three main methods available for SARA analysis, different procedures have been proposed to improve SARA separation and quantification of crude oil. Microfluidic SARA (MF-SARA) method was developed by J. Sieben et al. 2017. In this approach, after topping process the crude oil with a temperature of 260 °C, asphaltene is separated by ASTM D7996. Next is a separation of maltene by a miniaturized chromatographic column. As the maltene passes through a column, saturate is determined by refractometer and aromatic, and resin content is measured by a spectrometer.

Automated multi-dimensional high-performance liquid chromatography (AMD-HPLC) crude oil analysis, which is based on chromatography technique, contains two columns alkyl nitrile (cyano column) and silica column. The oil is injected through the cyano column followed by a silica gel column. Based on the polarity of fractions, the asphaltene and resins are selectively adsorbed onto the cyano column while the aromatics are adsorbed onto the silica gel of the second column and saturates pass through two columns. Quantification of each fraction is done using gravimetry or evaporative relative light scattering detection (ELSD) after desorption process with appropriate solvent. Raki et al. proposed a method based on flash chromatography and Iatroscan methods. In this method, after asphaltene separation, the maltene is fractionated by Iatroscan method.

There are still some general limitations related to available techniques. Some of the methods follow the oil topping procedure; heating the oil samples until 260-343 °C. In these procedures, not only the volatile component but semi-volatiles from the oil are separated. Since the volatile separated by this process is not only related to saturate
fractions, it will cause some discrepancy in analyzing result by using different heating
temperature for light to heavy oils. Also, one of the disadvantages of automated and fast
methods for asphaltene quantification is that sometimes there is not enough aging time
(less than 12 hrs) for separating the total asphaltene fraction. When the asphaltene aging
time in precipitant (n-alkane) is not enough (less than 16-24 hrs), it causes some errors on
asphaltene content measurement which depends on the stability of the asphaltene in oil\textsuperscript{20}.

Taking into account some of the advantages and disadvantages of the described methods,
a new methodology for maltene analysis “improved chromatography technique” is
proposed in the first part of this study that aims to overcome some of the limitations of
previous methods. The proposed method is based on a chromatography technique by using
less sample and solvent in comparison with ASTM D2007. The time of the process is
shorter in comparison with other chromatographic systems, and the purity of separated
fractions is verified by FTIR analysis. This method is easy to operate, and it does not
require a skilled operator to analyze and interpret the results.

In the second part, we propose a different methodology, “\textit{clay/alumina chromatography
method}” for crude oil fractionation and quantification which does not require prior
separation of maltene fraction. Asphaltene content is quantified based on the modified IP-
143 (ASTM D6560)\textsuperscript{21}. To quantify SAR fractions, in the first step oil is added into the clay
and the alumina columns. Among the SARA fractions, saturate and aromatic fractions pass
through the clay column while only saturate fraction is not adsorbed by the alumina
column. In the second step, these components are desorbed and recovered with the
appropriate solvent, and each fraction is quantified. The new proposed method uses less
sample and solvent in comparison to the available chromatography methods, and there are
fewer losses of volatile components. This method is simple and easy to perform and does not need an experienced operator to analyze the result.

2.2. Improved chromatographic technique for SAR (Maltene)\textsuperscript{22}

fractionation

2.2.1. Materials and methods

The experimental procedure was conducted on four different crude oils from the Middle East and the Gulf of Mexico. The properties of these crude oils at ambient condition are presented in Table 2-1. The crude oils were first centrifuged to remove any sediment, sand particles, or water present in the system prior to asphaltene separation. Density and viscosity were measured using an Anton Paar DMA 4500 digital vibrating U-tube densitometer and a Cannon-Fenske glass capillary viscometer, respectively.

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>Density (g.ml(^{-1}); 20 °C)</th>
<th>Viscosity (cP; 20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.884</td>
<td>56.0</td>
</tr>
<tr>
<td>C</td>
<td>0.885</td>
<td>22.0</td>
</tr>
<tr>
<td>S6</td>
<td>0.834</td>
<td>4.8</td>
</tr>
<tr>
<td>S9</td>
<td>0.836</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 2-1. Crude oil sample properties.

The materials needed for the experiment were clay, 500 to 250 μm (30 to 60 mesh), silica gel (>200 sieve size), n-pentane, n-hexane, n-heptane (purity: 99%), dichloromethane (DCM) or toluene (purity: 99.5%), and acetone (purity: 99.9%). Table 2-2 presents the amounts of clay and silica gel needed for both the ASTM D2007 and improved chromatographic technique.
Table 2-2. Materials needed for the ASTM D2007 method and the improved chromatographic technique.

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer/Reference No.</th>
<th>Particle size (µm)</th>
<th>ASTM D2007 (g)</th>
<th>Improved chromatographic technique (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attapulgus Clay</td>
<td>Forcoven Products Inc.</td>
<td>250-500</td>
<td>200</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Catalog No. NC9027284</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica gel</td>
<td></td>
<td>90-710</td>
<td>200</td>
<td>8</td>
</tr>
</tbody>
</table>

Clay and silica gel were used to fill in two separate Polytetrafluoroethylene (PTFE) columns. Figure 2-1 shows the details of the chromatography columns. The inlet and outlet of each column were connected using 5 pieces including straight connector (Nylon tube fitting, $\frac{1}{2}$” OD), black O-rings (Buna N, $\frac{1}{2}$” OD), Teflon rod, ferrule, and nut (Teflon, $\frac{1}{8}$”) to provide sealing protection against leakages. Since the liquid flow may wash the silica or clay, a 0.2 micron filter paper (PTFE, $\frac{1}{2}$”) was placed in the straight connector to keep them inside the column.
2.2.2. Procedure

2.2.2.1. SARA analysis using the ASTM D2007 method

SARA analysis based on ASTM D2007\textsuperscript{23} was performed initially to obtain reference data. This data is used to evaluate the results obtained using the proposed new method. Additionally, the outcome of this experiment has provided a further understanding of the limitations of using a chromatography method and has aided us in developing ideas for improving the new chromatography method used for SARA analysis. After asphaltene separation, the filtered solution went through the maltene (saturates, aromatics, and resins) separation. Maltenes were fractionated based on liquid chromatography by the ASTM D2007 procedure,\textsuperscript{23} while asphaltene is quantified based on ASTM D6560.\textsuperscript{21} In this study, toluene, as the solvent of resin and aromatic fractions, was replaced by DCM due to its
faster evaporation time. The boiling point of DCM is 40 °C, while the boiling point of the lightest aromatic fraction is 80 °C, so there was minimal loss of aromatic fractions during the process of evaporation. Also, DCM has higher solubility parameter 20.2 MPa\(^{1/2}\) in comparison with toluene (18.3 MPa\(^{1/2}\)) which makes it a better solvent for washing resin fraction with the solubility parameter reported in the range 21.1-21.8 MPa\(^{1/2}\).\(^{24}\)

2.2.2. Maltene analysis using the proposed methodology

The heart of the new system, as depicted in Figure 2-2, consists of two chromatographic columns, one containing silica gel and one containing clay (Attapulgus). The additional equipment required to achieve the separation includes an HPLC pump and a distillation system, a round-bottom flask, a distillation column, a thermometer, and a condenser. A set of two- and three-way valves to control the direction of the flow is also required. The process was carried out in two steps: adsorption and desorption. During the first step, saturates, aromatics and resins were separated based on their affinity to be adsorbed by the clay or the silica gel column. During the second step, these components were desorbed by washing the columns with the appropriate solvent then being recovered. Both steps are further described below.

**Adsorption Step\(^{22}\):**

During this step, 1A, 2A, 3A, 4A and 5A valves (Figure 2-2) were open, while the rest remained closed throughout the adsorption process. Therefore, the flow of the solution followed the brown path indicated in Figure 2-2.

1 g of maltene, the filtrate of the asphaltene separation process that was diluted with 200 ml of precipitant (n-pentane or n-heptane), was placed into a solution container. The
solution was pumped at 1 ml.min$^{-1}$ through valve 1A and fed into the clay column in which only resins were adsorbed. Thereafter, the solution passed through valves 2A and 3A and was fed into the silica column, which adsorbed the aromatic components. The solution continued on its path, passing through the 4A and 5A valves and collecting in the effluent container. After the entire solution passed through the column, the effluent containing the saturate fraction was collected. To separate saturates fraction, n-pentane or n-heptane (the precipitants of asphaltene) was evaporated from the solution at approximately 36.1 °C or 98 °C respectively, and the saturates were dried and weighed. The purity of saturate was checked using FTIR to confirm that there was no aromatic or resin present in the saturate fractions. The amount of saturate is quantified by subtracting the amount of oil from the sum of aromatic, resin and asphaltene amounts. The difference between the measured and calculated saturate fractions was less than 3 wt. %. Therefore, it is accurate enough and much more time efficient to calculate the saturate as a difference between the oil and the sum of aromatic, resin and asphaltene fractions, assuming a 100 % recovery.
Desorption Step:\n
After completing the adsorption process, the columns were washed separately with a solvent to recover the resins and aromatics fractions. 200 ml of a mixture of DCM (50 vol. %) and acetone (50 vol. %) were used to wash the clay column to desorb the resins fraction. In this step, as depicted in Figure 2-3a (solid line), valves 1A, 2B, and 5B were open, and the rest remained closed. The silica gel column was washed with 200 ml of a mixture of DCM (62 vol. %) and hexane (38 vol. %) to desorb the aromatic fraction. The amount of solvent (200 ml) and pump flow rate (1 ml.min⁻¹) during desorption step was optimized in
such a way that a certain level of liquid is always present in the solvent container. As Figure 2-3b (solid line) indicates, for washing, silica gel column valves 1B, 3B, 4B, and 5B were open, and the remaining valves were closed. When the solvent passed through the columns, it dissolved resins and aromatics from the clay and the silica gel media, respectively. The solution continued to the distillation system.

Figure 2-3. Improved chromatographic technique; Desorption step,

a) Washing clay column, b) Washing silica gel column (From Doherty et al., CRC Press, 15-73, 2018).
Distillation Process:

The solution of solvent, DCM (50%) + acetone (50%), and resins leaving the clay column was fed into the distillation column from the top and was collected in a round-bottom flask. The temperature of the heating mantle was fixed in such a manner that the solvent evaporated without burning the resins. The temperature of the distillation column was monitored using a thermometer at the top of the column to ensure that the vapor was pure solvent. The pure solvent was collected in a solvent container after passing through the condenser. For the aromatic fractions, the process of distillation was exactly the same, with the exception that the solvent used for washing the silica was DCM (62 vol. %) and hexane (38 vol. %). Once the solvents leaving the clay and silica gel columns became clear, the desorption process was stopped, and both resins and aromatics were dried in an oven and subsequently weighed.

2.2.3. Results and discussion

To determine the optimum pump flow rate and maximum adsorption efficiency, three different pump flow rates (1, 3, and 5 ml.min\(^{-1}\)) were tested. The purity of the effluent was checked using FTIR to ensure that there is no aromatic or resin in the saturate fraction. Figure 2-4 presents the IR results of the saturate fraction while the pump flow rates were 1, 3, and 5 ml.min\(^{-1}\). The peak at 1600 cm\(^{-1}\) corresponds to the aromatic C=C bonds, and the shoulder at 3050 cm\(^{-1}\) corresponds to aromatic C—H stretching. The peaks in the wavelength range of 2800-3000 cm\(^{-1}\) are related to CH\(_2\) and CH\(_3\) in aliphatic chains. The peaks in the range 1350-1500 cm\(^{-1}\) are related to the CH\(_3\) functional groups.\(^{25}\) Based on
these results, it can be concluded that the flow rates of 3 and 5 ml.min\(^{-1}\) were not acceptable, as the IR spectra, Figure 2-4b, and c, indicate some peaks related to the aromatic fraction at 1600 and 3050 cm\(^{-1}\). Therefore, 1 ml.min\(^{-1}\) was chosen as an appropriate flow rate during the adsorption step in order to prevent impurities in the effluent.

**Figure 2-4.** FTIR results of saturate fraction when the pump flow rate is: a) 1 ml.min\(^{-1}\), b) 3 ml.min\(^{-1}\) and c) 5 ml.min\(^{-1}\).

Figure 2-5 depicts the FTIR spectra of aromatic fractions by testing three pump flow rates (1, 3 and 5 ml.min\(^{-1}\)). In Figure 2-5b and c, the peak at 1700 cm\(^{-1}\) belonged to the carboxylic functional group,\(^{26}\) which indicates the presence of some resin fractions in the silica gel column. Therefore, it can be concluded that 3 and 5 ml.min\(^{-1}\) are not appropriate flow rates for the adsorption process. At 1 ml.min\(^{-1}\), the FTIR spectra indicate that there is no more
carboxylic acid in the silica gel column, and the resin fraction was entirely adsorbed by the clay column.

![FTIR spectra of aromatic fraction](image)

**Figure 2-5.** FTIR spectra of aromatic fraction when the pump flowrate is a) 1 ml/min, b) 3 ml/min, and c) 5 ml/min.

Four crude oils (S9, S6, C, and A) were fractionated using an improved chromatographic technique in order to conduct the maltene analysis. Asphaltene content was determined based on ASTM D6560,\textsuperscript{21} using n-pentane as the precipitant. The results are provided in Figure 2-6. The maltene analysis was obtained after 2 days, and the maximum standard deviation for this method was approximately 4 wt. %.
Maltene analysis was also performed using the ASTM D2007 method. Figure 2-7 presents the SARA fractionation based on both improved chromatographic technique and ASTM D2007 methods. The reported result is the average of four measurements. The percent relative standard deviations in the values of SARA determined by ASTM D2007 methods are 6, 7, 3, and 0.1 wt. %, respectively, whereas the percent relative standard deviations in the SARA values determined by the “improved chromatographic technique” are 4, 3.5, 2, 0.1 wt. %. The process of ASTM D2007 method was time-consuming; it took approximately 10 days to complete the SARA analysis which includes the separation of asphaltene and maltene fractionation, while the improved chromatographic technique took only 5 days.

Furthermore, the ASTM D2007 method required large amounts (500 ml pentane, 2000 ml DCM, and hexane for the S6 or S9 analysis) of solvent, while, in the proposed method, the efficiency of separation was increased by solvent recirculation. Pure solvents washed the
adsorbed resins and aromatics in each cycle. Additionally, the solvent can be recovered at the end of the process, thus decreasing the costs associated with using large amounts of solvent. Also, it reduces the risk of exposure to the chemical to laboratory personnel.

Data from several sources have identified that the ASTM D2007 method has some limitations, such as being time-consuming, using a large amount of solvent and sample, and generating larger standard deviation in comparison with the other methods.\textsuperscript{12,17,27} These limitations are consistent with the findings of this study.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-7.png}
\caption{Comparison of SARA analysis based on the improved chromatographic technique and ASTM D2007\textsuperscript{22}.}
\end{figure}

\textbf{2.2.4. Summary of results}

In this study, a new method for maltene analysis is proposed that boasts several unique advantages. In our new method, not only 1/10 of ASTMS DS2007 solvent is required, but it is also fully recovered at the end. The time needed for maltene analysis, once the asphaltene is removed, is reduced to 2 days from the 7 days required with the ASTM D2007 column. The collected data are found to be more reproducible since the volatile components are not separated and are measured as a part of saturates and aromatics.
Another advantage of our method is that it relies upon low-cost, readily available equipment and easy to perform and analyze the data.

Furthermore, in TLC-FID, it is impossible to collect the extracted fractions due to the small amounts of the sample used. Although in HPLC method it is possible to collect the separated maltene fractions, it is needed to run the test several times to get a significant amount of each fraction, depending on the intended application. However, by using the new proposed analysis appropriate amount of maltene fractions for further analysis can be separated.

2.3. Clay/Alumina chromatography technique for SARA fractionation

2.3.1. Materials and methods

The experimental procedure was conducted on eight different crude oils from the Middle East and the Gulf of Mexico. Table 2-3 shows some of the physical properties of the crude oils used in this part of the study. The crude oils were first centrifuged to remove any sediments and sand particles or water present in the system prior to use in the experiments. Densities were measured by using an Anton Paar DMA 4500 digital vibrating U-tube densitometer with a measuring range of 0-3 g/cm³. Viscosity was measured at ambient conditions using a Cannon-Fenske glass capillary viscometer. The water content was then measured by a Metrohm Karl Fischer titration apparatus (model 870 KF Titrino plus).
### Table 2-3. Crude oil properties

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>Density (g/ml; 20 °C)</th>
<th>Viscosity (cP; 20 °C)</th>
<th>Water content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6</td>
<td>0.834</td>
<td>4.8</td>
<td>0.06</td>
</tr>
<tr>
<td>S9</td>
<td>0.836</td>
<td>6.0</td>
<td>0.05</td>
</tr>
<tr>
<td>P7</td>
<td>0.876</td>
<td>15.3</td>
<td>0.03</td>
</tr>
<tr>
<td>P1</td>
<td>0.878</td>
<td>21.3</td>
<td>0.04</td>
</tr>
<tr>
<td>C</td>
<td>0.885</td>
<td>22.0</td>
<td>0.03</td>
</tr>
<tr>
<td>A</td>
<td>0.884</td>
<td>56.0</td>
<td>0.07</td>
</tr>
<tr>
<td>C2</td>
<td>0.910</td>
<td>136.3</td>
<td>0.09</td>
</tr>
<tr>
<td>P60</td>
<td>0.930</td>
<td>338.9</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The materials needed for the experiment were clay; 500 to 250 μm (32 to 60 mesh), alumina; 60-200 μm (65 to 250 mesh), n-pentane (purity: 99%), dichloromethane (DCM), toluene (purity: 99.5%) and acetone (purity: 99.9%).

### 2.3.2. Procedure

In this method, there is no prior separation of light component. Since for each fractionation step, oil is used without separating asphaltene or light component; there are less losses of volatile components. Asphaltene content is quantified based on modified IP-143 standard methods\textsuperscript{21,23}. Briefly, a precipitant (usually n-pentane or n-heptane) is added to the oil with the ratio of 40:1 (ml precipitant: g oil). The mixture is aged for one day before filtration by 0.2 μm Nylon filter paper. The filter paper containing asphaltene is washed in a Soxhlet by hot precipitant first to remove the non-asphaltenic materials: maltene and wax. Then the filter is washed with toluene to extract all the precipitated asphaltene. In the last step, asphaltene content is quantified by evaporating the toluene.
The proposed chromatographic system consists of two columns, one of them containing alumina and the other one containing clay (Attapulgus) as shown in Figure 2-8. The columns characteristics are mentioned in Table 2-4.

<table>
<thead>
<tr>
<th>Column Characteristic</th>
<th>Chromatographic columns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attapulgus Clay amount</td>
<td>8 g</td>
</tr>
<tr>
<td>Alumina amount</td>
<td>8 g</td>
</tr>
<tr>
<td>Clay particle size</td>
<td>250-500 μm</td>
</tr>
<tr>
<td>Alumina particle size</td>
<td>60-200 μm</td>
</tr>
<tr>
<td>Column length</td>
<td>210 mm</td>
</tr>
<tr>
<td>Column diameter</td>
<td>9.5 mm</td>
</tr>
<tr>
<td>Column material</td>
<td>Teflon</td>
</tr>
</tbody>
</table>

Figure 2-8. Clay and alumina chromatographic columns.  

The process is carried out in two steps. In the first step, saturates, aromatics, resins, and asphaltene are separated by selective adsorption into the clay and the alumina columns. In
the second step, these components are desorbed and recovered. Both steps are described below.

**2.3.2.1. Adsorption Step**

A known amount of crude oil (0.2-0.3 g) which is diluted in an n-alkane with a ratio of a 40:1 ml/g (40 ml of n-alkane per 1 g of oil) – usually n-pentane or n-heptane – is prepared. The diluted oil sample is added to each column separately. In the clay column, asphaltene, and resin fractions are adsorbed, and the saturate and aromatic fractions pass through the column. While in the alumina column, asphaltene, resin, and aromatic fractions are adsorbed by the alumina particles and only saturate fraction passes through the column. The sample beaker is washed with the precipitant (n-pentane or n-heptane) and added to the column. In the end, more alkane (n-pentane or n-heptane) is charged to the column to make sure there is no more saturate and aromatic in the clay column and no more saturate in the alumina column. To control the purity of separated saturate fraction, n-pentane or n-heptane (the precipitants of asphaltene) was evaporated from the effluent of the alumina column at approximately 36.1 °C or 98 °C respectively, and the saturates were dried and weighed. The saturate fraction is analyzed by FTIR spectroscopy to verify the purity of saturate fraction. An example of saturate IR spectra is shown in Figure 2-9. The absence of peaks other than CH₂ and CH₃ shows that the saturate fraction is pure. In saturate fraction, the peaks in the range 2800-3000 cm⁻¹, 1457 cm⁻¹, and 1375 cm⁻¹ are assigned to the C-H stretch of alkanes, C-H scissoring vibration, and the C-H rocking vibration, respectively²⁹.
The process of adsorption is fast. It takes less than 30 minutes to transfer all the diluted sample to the columns. The next step is to wash the columns with the appropriate solvent to desorb the adsorbed materials.

### 2.3.2.2. Desorption Step

After completing the adsorption process, the clay and alumina are transferred to two thimbles and washed in two Soxhlet apparatuses separately. In the first washing step, dichloromethane (DCM) is used as a solvent for removing the fractions adsorbed by the clay or alumina particles. After the first washing step (time of washing process is mostly dependent on polar fractions content), Soxhlet extraction is stopped and the clay/alumina dry over the next several hours. It is necessary to mix the dried clay/alumina thoroughly in thimbles to make sure that the adsorbed fractions are washed thoroughly. If any adsorbate remained unwashed on the clay/alumina particles, it could be detected in this step by checking the color of adsorbent. Finally, each column is washed with toluene and acetone.

![FTIR spectra of alumina column effluent](image)

**Figure 2-9. FTIR spectra of alumina column effluent.**
separately to dissolve the remaining adsorbed fractions. 75 ml of each solvent is needed in this method to remove all the adsorbed material from clay or alumina. The reported solubility parameter of asphaltene, resin, and aromatic are in the range 24.3-26.4, 21.1-21.8, and 19.2-19.4 MPa$^{1/2}$, respectively. Therefore, the chosen solvent should cover these ranges of solubility parameter and polarity. DCM (solubility parameter of 20.2 MPa$^{1/2}$ and polarity index of 3.1), acetone (solubility parameter of 19.7 MPa$^{1/2}$ and polarity index of 5.1), and toluene (solubility parameter of 18.3 MPa$^{1/2}$ and polarity index of 2.4) were chosen as solvents.

The heating rate, condenser cooling rate, and fluid level of the solvent in the Soxhlet apparatus are adjusted to maintain the appropriate level of solvent in the Soxhlet and flask. To increase the rate of separation, a motor was installed on top of the condenser column to vertically move the thimble containing the clay or alumina particles. Using this technique, the diffusion rate of adsorbed fractions into the washing solvent increases, and therefore, the efficiency of extraction improves. The washing process had been continued until the solvent in contact with the thimble in the Soxhlet was almost colorless.

After washing the columns properly, the solution of solvent and adsorbate is transferred to a beaker and was placed on a hot plate. When all the solvent was evaporated, and the weight of the beaker plus adsorbate was almost constant, the adsorbate weight was calculated.

Figure 2-10 shows the flowchart of two steps of adsorption-desorption processes for SARA analysis.
2.3.2.3. Quantification of SARA fractions$^{28}$

The three following steps were applied to determine the amount of SARA fractions:

**Step 1.** Calculating the asphaltene weight percent based on modified IP-143 (ASTM D6560)$^{21,23}$.

**Step 2.** Calculating resin plus asphaltene content ($m_{\text{Asphaltene+Resin}}$), which was extracted by washing clay columns.

**Step 3.** Calculating aromatic plus resin plus asphaltene content ($m_{\text{Asphaltene+Resin+Aromatic}}$), which was extracted in the desorption process of washing alumina columns.

Asphaltene content is quantified as mentioned in Step 1. The amount of saturate, aromatic and resin can be quantified based on the three below formulas.

---

**Figure 2-10. Adsorption and desorption process in clay and alumina columns.**
\[ Resin \text{ wt.\%} = \frac{m_{Asphaltene+Resin}}{m_{oil}} \times 100 - \text{Asphaltene wt.\%} \]

\textbf{Equation 2-1}

\[ Aromatic \text{ wt.\%} = \frac{m_{Asphaltene+Resin+Aromatic}}{m_{oil}} \times 100 - \text{Asphaltene wt.\%} - \text{Resin wt.\%} \]

\textbf{Equation 2-2}

\[ Saturate \text{ wt.\%} = 100 - \text{Asphaltene wt.\%} - \text{Resin wt.\%} - \text{Aromatic wt.\%} \]

\textbf{Equation 2-3}

\textbf{2.3.3. Results and discussion}

Asphaltene was extracted prior to the maltene analysis in most of the chromatographic techniques\textsuperscript{12,31}. There may be some losses of the light component during the process of asphaltene separation. In order to decrease the number of steps of the SARA separation, crude oil was added to each column separately in the proposed method. In this way, losses of the light component during the asphaltene separation process does not affect the final result. SARA fractionation of 8 different crude oils ranging from 20° to 40° API by the clay/alumina chromatography method is summarized in Figure 2-11.
Figure 2-11. Fractionation of eight crude oils by clay/alumina chromatography technique\textsuperscript{28}.

Also, SARA fractionation was done with ASTM D2007 to compare the results of the two separation methods. Analysis based on ASTM D2007 provided further explanation about the limitation of this method. Fractionation results based on ASTM D2007 and clay/alumina chromatography method are shown in Figure 2-12 for two different crude oils (C and A).

The major differences between the two techniques are the required time, amounts of sample, and solvent. The new procedure requires only about two days per sample, compared to 10 days for the ASTM D2007 for the analysis. Only 0.2-0.3 g of oil is needed for the new method while more than 5 g of oil is required for the ASTM D2007 test. The solvent -- which is needed for washing clay or alumina column -- is 75 ml of each of DCM, toluene, and acetone. The amount of solvent is not dependent on the polar fraction content in this method since the desorption process is taking place in soxhlet. While for the ASTM D2007 method more than two liters of solvents are needed during the process of washing.
resin or aromatic from clay or silica gel. Additionally, the amount of solvent depends on the aromatic and resin content, which was approximately between 2.5 and 4 L in these experiments.

Also, the standard deviation (SD) in this method is 2.1 wt. % for saturate, 1.2 wt. % for aromatic, 1.1 for resin and 0.05 wt. % for asphaltene fractions. The reported SD is in an acceptable range in comparison with ASTM D2007. Based on the ASTM D2007 result the repeatability (the difference between two test results) is 2.1 wt. % for saturate fractions, 2.3 wt. % for aromatic fractions and 1.2 wt. %, 0.81 wt. %, 0.24 wt. % for polar fractions while polar content is greater than 5%, between 1 to 5 % and less than 1 % respectively\textsuperscript{23}.

![Figure 2-12. Comparison of SARA analysis result based on ASTM D2007 and clay/alumina chromatography methods\textsuperscript{28}](image1.png)

By using ASTM D2007, the reproducibility (The difference between the two test results by a different operator) is 4 wt. % for saturate, 3.3 wt. % for aromatic and 1.8 wt. %, 1.3 wt. % and 0.4 wt. % for polar fractions while the polar fraction content is higher than 5%, between 1 to 5% and less than 1% respectively\textsuperscript{23}. In order to evaluate the reproducibility of the new proposed system, SARA analysis of three oil sample was done by a third party laboratory. Figure 2-13 compares SARA analysis based on clay/alumina chromatography technique of the third party laboratory result. The values reported by the third party
laboratory was in the same range as SARA analysis by the proposed method, and the maximum difference between test results is related to saturate fraction which is 4.1 wt. %.

Figure 2-13. Comparison of SARA fractions determined by the third party laboratory and Clay/Alumina Chromatography method\textsuperscript{28}.

2.3.4. Summary of results

Compositional analysis of crude oil is a crucial step in the oil characterization process. Although there are different methods proposed for SARA analysis, all of them have some limitations. In order to enhance the efficiency and repeatability of the results of SARA quantification, the new method of the clay/alumina chromatography system is proposed. Our method reduces the time of analysis from the 10 days necessary to complete the ASTM D2007 analysis to 2 days, and the amount of solvent and sample used are reduced by 90\% of what the ASTM D2007 method requires. Moreover, the proposed system is inexpensive, easier to operate and analyze the data, and small enough to fit inside a laboratory fume
hood. The repeatability and reproducibility of the result are verified by comparing the result to the ASTM D2007 method.

2.4. Chapter summary

In this study, we present two different methods for maltene and SARA fractionation; “improved chromatographic technique” for maltenes fractionation and “clay/alumina chromatography method” for SARA analysis.

Both new techniques require less solvent and the amount of solvent for desorption step does not depend on the polar fractions content in comparison with the available chromatography technique. Both methods are three to four times faster compared to ASTM D2007 method; the time for fractionation by the “improved chromatographic technique” is 5 days and 2 days by clay/alumina chromatography method while in ASTM D2007 is 10 days. The proposed systems are practical for industrial application since the equipment are reasonably inexpensive and could be easily assembled in any laboratory. Additionally, these methods do not require any expert operator to analyze the data which is needed in some chromatography methods like High-Pressure Liquid Chromatography (HPLC).

Furthermore, in TLC-FID, it is impossible to collect the extracted fractions due to the small amounts of the sample used. Although in the HPLC method it is possible to collect the separated maltene fractions, it is needed to run the test several times to get a significant amount of each fraction, depending on the intended application. However, by using the “improved chromatographic technique” appropriate amount of maltene fractions for further analysis can be separated.
Chapter 3

Asphaltene fractionation and characterization

3.1. Asphaltene and its properties

Asphaltenes are the least soluble part of the oil that can be precipitated in n-alkanes. N-alkane was identified by Boussingault in 1837 from an ether-insoluble fraction of asphalt. The actual chemical structure of asphaltene is challenging to be defined using current analytical tools, and it is still the subject of ongoing researches. Asphaltene contains condensed aromatic and naphthenic molecules with molar masses ranging from 100-10000 g/mol. They also consist of carbon, hydrogen and polar molecules containing most of the heteroatoms (N, S, O) and metal (nickel and vanadium) content of heavy oils. Heteroatoms are mostly related to aromatic sheets. Asphaltene has higher aromaticity, polarity, molecular weight, and heteroatom content in comparison with other crude oil fractions (Saturate, aromatic and resin). There are two proposed structure for asphaltene;
Archipelago structure and Island structure. In archipelago structure, asphaltene has several aromatic cores that are attached by aliphatic chains. The other structure is Island or Yen-Mullins model which the asphaltene has one polyaromatic core with aliphatic chains.

Elemental formula of asphaltene is $\text{C}_{420}\text{H}_{496}\text{N}_{6}\text{S}_{14}\text{O}_{4}\text{V}$, an H/C ratio of 1.18, N/C 0.014, O/C 0.010, S/C 0.033, and a molecular weight of 6191 g/mol. The composition is about 81 % C, 8 % H, 7.3 % S, 1.4 % N, 1 % O and 0.8 % V.

Asphaltene stability depends on factors including the composition, pressure, and temperature of the oil$^{35}$. The effect of composition and, by inference, pressure on asphaltene precipitation is generally believed to be stronger than the effect of temperature. However, several disagreements regarding this point still exist in the literature. Pressure depletion alone can destabilize asphaltenes, and it is likely the primary reason for asphaltene deposition in wellbore tubular. These observations are consistent with various experimental studies showing that the bulk of asphaltene precipitation from undersaturated crude oils occurs close to bubble-point pressures.

The loss of light ends implies better solubility of the asphaltene components. Low hydrogen-to-carbon ratios, high aromaticities, and high condensation of aromatic rings were the main characteristics of the asphaltenes from unstable crude oils. According to these results, the stability behavior of crude oils is strongly influenced by the structural characteristics of their asphaltenes$^{36}$. Also, some physical properties of crude oil are being determined based on asphaltene$^{37}$. 
Asphaltene can refer to the polydisperse distribution of a broad range of molecules, with different sizes and molecular characteristics. Therefore, it is essential to analyze the distribution of the different types of asphaltenes in this chapter.

A common strategy to study asphaltene characterization is asphaltene fractionation based on their solubility. The advantages of this strategy are reducing the complexity of the material to study and provide a distribution of properties for the asphaltenes. Rogel et al. 2015 fractionated asphaltene into 4 parts: fraction no. 1, extracted with 15/85 CH₂Cl₂/n-heptane at room temperature; fraction no. 2, extracted with 30/70 CH₂Cl₂/n-heptane at room temperature; fraction no. 3, extracted with 100% CH₂Cl₂ at room temperature; fraction no. 4, extracted with 90/10 CH₂Cl₂/methanol. They showed that there was a decrease in the hydrogen-to-carbon molar ratio (H/C) from fraction no. 1 to no — 3 which is inconsistent with a lower solubility. There was an increase for fraction no. 4 which was caused by the low solubility of this fraction due to the presence of polar functionalities. Also, IR spectra showed that there is an increase in the carbonyl signal for fraction no. 4. Also, their results of IR spectroscopy showed that low amount of hydrogen would cause an increase in aromaticity and the size of the polyaromatic rings in the molecules. Aromaticity is defined as the number of aromatic carbon to the total carbon using 13C NMR. Different studies showed that by increasing the solubility of precipitant the H/C ratio of the extracted asphaltene fractions decreased and the aromaticity increased.

Davarpanah et al. 2015 fractionated the asphaltene into two C₅⁺ and C₇⁺ asphaltenes based on their solubility in n-alkanes. They showed that the aromaticity of the C₇⁺ fraction is higher than the one for C₅⁺. Also, the number of carbons for the C₅⁺ fraction is higher than the C₇⁺ fraction based on 1H NMR results.
Strausz, Peng, and Murgich, separated Athabasca asphaltenes into five fractions using gel permeation chromatography fractionation by separating them with different solvent (Benzene) to sample ratios. The gel permission chromatography (GPC) results showed that, by diluting the sample, the retention time of the asphaltene in GPC response increases and MW decreases from 17000 to below 12000. Also, they showed that increasing the ratio of solvent to sample reduces the aromaticity from 48% to 35. Nitrogen, oxygen, and sulfur contents are the same in different fractions.

Ostlund et al. 2004 fractionated asphaltenes based on their different polarities using binary mixtures of dichloromethane (DCM) and n-pentane. In the first step the asphaltene is dissolved in DCM, and it is mixed thoroughly. In the second step, pentane is added and mixed for 30 min. Then the mixture is centrifuged, and the undissolved asphaltene is separated. This process is repeated three more times, and the asphaltene of each step is separated. They showed that the asphaltene separated in the first step has the highest tendency to flocculate and the highest molecular weight. The heteroatoms content was approximately the same for the four asphaltenes fractions.

Tojima et al. 1998 developed a new method of fractionation by using heptane-toluene and separating the light and heavy C$_7$+ asphaltene fraction. In their method the C$_7$+ asphaltene is separated first, then a toluene/heptane with a ratio of 65/35 is added to the C$_7$+ asphaltene. In this step, the undissolved asphaltene is separated and named the lowest soluble portion of C$_7$+ asphaltene. As the next step, the soluble asphaltenes remained in toluene solution are recovered by evaporation of the solvent. To separate the most soluble fraction of C$_7$+, the process is repeated two more times with a toluene/heptane ratio of 25/75 and 18/82.
Finally, the most soluble fraction of C$_7$+ asphaltene is separated by evaporation of toluene. They showed that the aromaticity of heavier asphaltenes is higher than for the lighter asphaltenes and it has the most highly condensed polynuclear aromatics. As a result, they concluded that the heavy asphaltenes are considered as peptized material and the light ones are peptizing material$^{44}$.

The molecular weight is one of the critical parameters that can be used for developing correlations for the physical properties of asphaltenes $^{45}$. Asphaltenes are a polydisperse distribution of a broad range of molecules, with different sizes and molecular characteristics. Therefore the distribution of molar masses is expected for its molecular weight$^{46}$. The average monomer asphaltene molecular weight goes from 500 to 1000 g/mol depending on the source of sample $^{47}$. The average molecular weight of the aggregates varies from 3000 to 10000 g/mol, and some of the aggregate sizes can reach as high as 50000 g/mol $^{46}$.

Asphaltene molecules tend to self-associate into nano-aggregates which causes some trouble in the molecular weight measurement $^{48}$. One of the critical concepts in asphaltene self-association modeling, developed by Agrawala and Yarranton, is that asphaltene molecules may contain multiple active sites that can act as propagators or single active sites that can act as terminators $^{49}$. In a mixture of asphaltenes and resins, asphaltenes are considered as propagators which serve as links for other similar molecules and form a chain. Resins serve as the terminators and end the chains $^{48}$. Molecular dynamic simulations have shown that the primary driving force for the association is the interaction between the aromatic cores of the asphaltene molecules. Also, the heteroatoms attached to the aromatic cores have more influence on the association in comparison with the ones attached to the
aliphatic chain. Also, the length and number of chains are not as effective on the aggregation of asphaltenes as the aromatic cores; this last one will affect the aggregation size of asphaltenes. Better solvents (such as tetrahydrofuran (THF) in comparison with chloroform and benzene), and higher temperature decrease asphaltene self-association and aggregation.

The measured molar mass depends on the solvent, temperature, and concentration. By increasing the concentration and decreasing the temperature and aromaticity of the solvent, asphaltene molar mass increases.

There are three most common methods for molecular weight (MW) measurement; gel permeation chromatography (GPC), vapor pressure osmometry (VPO) and mass spectroscopy (MS).

GPC can determine several important parameters including number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity which is the ratio of $M_w/M_n$- the most fundamental characteristic of a polydisperse system. $M_n$ is affected mainly by the low molecular weights of nonassociated molecules in the sample.

$M_W$ is affected mainly by the weight of the aggregates and the molecular weights of the biggest monomers, and it will influence the physical properties of asphaltenes. $M_W$ is always higher than $M_n$ unless the asphaltene aggregates are completely monodisperse. The ratio of $M_W$ to $M_n$ is used to calculate the polydispersity index (PDI) of a polymer, which indicates the aggregation tendency of the asphaltene molecule. The broader the molecular weight distribution, the larger the PDI. If the polydispersity value is close to 1.0, the distribution is narrow while larger values correspond to a broader distribution.
The GPC methodology has limitations with the most important one being the use of polystyrene as standard in the analysis of asphaltenes. According to Sato, Takanohashi, and Tanaka (2005), hydrocarbons with a peri-condensed polyaromatic structure tend to elute later than linear polymers with similar $MW$; therefore, the number-averaged $MW$ determined for asphaltenes is lower than expected. It is considered that the $MW$ of asphaltenes determined by this method is not the actual value, but rather a polystyrene equivalent $MW^S$.

Another method to measure asphaltene molecular weight is Vapor Pressure Osmometry or VPO. It is a conventional method for the determination of asphaltene molecular weight, though it cannot measure an accurate molar mass of asphaltene in a solvent because of the self-association of the asphaltene molecules. This is considered its major drawback. The main advantage in comparison with the GPC method is that the molar mass of the asphaltene samples with different concentration can be measured by VPO $^{54}$.

The repeatability of the asphaltene molecular weight measurements based on the VPO method is approximately ±15%. This method is based on the different vapor pressure created by adding a small amount of solute to a solvent. In this method, two separate thermistors contained a pure solvent, and a drop of solute-solvent are placed in a chamber. Each thermistor shows different temperature because of the different vapor pressure caused by the various components of the solute. The difference between the temperatures causes the resistance or voltage to change in proportional relation to the molecular weight of the solute $^{55}$. 
\[ \frac{\Delta V}{C_2} = K \left( \frac{1}{MW} + A_1 C_2 + A_2 C_2^2 + \cdots \right) \]

Equation 3-1

Where \( \Delta V \) is the voltage difference between the thermistors, \( C_2 \) is the solute concentration, \( K \) is a proportionality constant, \( A_1 \) and \( A_2 \) are coefficients arising from the non-ideal behavior of the solution and \( MW \) is the molecular weight of the sample. The equation at low concentration becomes:

\[ \frac{\Delta V}{C_2} = K \left( \frac{1}{MW} + A_1 C_2 \right) \]

Equation 3-2

For an ideal system, the second term is zero, and \( \Delta V/C_2 \) is constant \(^5^6\). VPO shows higher molecular weight in comparison with GPC result since GPC is calibrated based on polystyrene which does not have the same retention time as crude oil. Therefore, the VPO results are more reliable for lower molecular weights \(^5^6\).

Barrera et al. 2013 compared the molecular weight of two asphaltene fractions by VPO; a light cut and a heavy cut. They defined the light cut of asphaltene as the soluble part in a Heptol (n-heptane and toluene) solution, and a heavy cut as the precipitated part in the Heptol solution. They showed that the molecular weight of lighter cuts increases less than the heavier cuts by increasing the asphaltene concentration. This is caused by the fact that the lighter cuts contain less self-association while the heaviest cuts have more \(^5^5\).

In addition to VPO and GPC methods, mass spectroscopy is also one of the most commonly used methods for measuring molecular weight. This method is mainly based on the
volatilization/ionization of the sample. This is a powerful method to measure the mass-to-charge ratio (m/z) of ions to identify and quantify molecules in simple and complex mixtures. In this method, the sample (asphaltene) is vaporized and then ionized by an ion source which creates molecular ions. These ions will be deflected by electric and magnetic fields. Then, the deflected ions will hit a detector of ions. Based on the strength of the magnetic field, different ions (different m/z) will be detected by the ion detector at different times. The computer connected to the mass spectrometer analyzes the data from the detector and produces a plot of m/z (on the x-axis) against the relative abundance (on the y-axis) of the ions. Assuming that the charge of the ions is +1 (one electron is lost), it is possible to find the weight percent of each of the ion fractions (based on the relative abundance on the y-axis) \(^{57}\).

MS results can be misleading in two conditions; incomplete volatilization because of low laser power or fragmentation because of excessive power. Controlling laser energies can solve the problem of fragmentation. It is possible to control the laser energy by the use of a MALDITOF-MS (Matrix-Assisted Laser Desorption Ionization-Time-of-Flight) method which is mainly used to analyze biopolymers and synthetic polymers \(^{58}\). In this method, because asphaltenes are dissolved in a diluted solution, it is not necessary to measure the distribution of molecular weight \(^{59,60}\).

Shinya Sato et al. 2005 compared the data of MW obtained by mass spectroscopy (MS) and gel permeation chromatography. They reported that the values of MW (MS) is almost the same as MW by GPC (standard was polystyrene) for MW greater than 900 amu. For the molecular weight less than 900 amu, the difference between the MW (MS) and MW (GPC) increases \(^{53}\). One of the limitations for GPC is that the sample needs to be filtered through
a 0.2 μm filter paper in the GPC method, therefore the aggregates bigger than 0.2 μm are removed.

There is still a debate on the accuracy of the MS method, although most of the studies prove that the MALDI measurements, with the asphaltene diluted in a matrix, give more reliable results.

The other important parameter in terms of asphaltene is its aromaticity. The study of the asphaltene structure and its aromaticity is necessary to understand their self-association and aggregation behavior. Also, aromaticity is one of the important parameters to investigate the stability of crude oil. Asphaltene aromaticity range is reported from 0.7 to 0.4\textsuperscript{61}.

It is proved that when the aromaticity of crude oil decreases, the oil becomes more stable\textsuperscript{29,62}. Therefore, if the aromaticity of asphaltene is high, there is more tendency for the asphaltene to aggregate and precipitate. Leon et al. found a relation between the aromaticity and the degree of condensation and the stability of the crudes\textsuperscript{63}. Besides, the aromaticity of maltenes affects the stability of crude oil; if the aromaticity of the maltene is high, it can be a suitable solvent for the asphaltene\textsuperscript{64}.

When the asphaltene aromaticity is high, the aggregation of the asphaltene molecule happens in lower concentration in comparison with the asphaltene with lower aromaticity\textsuperscript{63}.

Temperature and molecular weight changes affect the asphaltene aromaticity. By increasing the temperature and molecular weight of the sample, the aromaticity increases\textsuperscript{65}. At high temperature, the rheology of asphaltene can be changed which increases the
asphaltene aromaticity (Sharma and Yen 1994). By increasing the temperature, some of the long alkyl functional groups in asphaltene structure are separated from the molecule. Also, because of the polymerization and condensation, some products such as carben–carboids and coke will form which cause a higher degree of aromaticity.

There are different ways to calculate the aromaticity index; based on elemental composition, and by FTIR and NMR spectroscopy. The aromaticity index (or relative aromaticity) (McLean and Kilpatrick 1997) can be calculated based on the elemental analysis results as a ratio of C/H. Another method is based on NMR spectroscopy; this method can provide very accurate values (McLean and Kilpatrick 1997). In this method, the aromaticity is defined as the number of aromatic carbon to the number of total carbon based on the $^{13}$C NMR spectrum. The peaks in the 100-170 ppm region are related to aromatic bands and the ones in 10 to 70 ppm region are related to aliphatic bands. The aromaticity index is calculated by the number of aromatic carbons divided by the amount of aromatics plus the amount of aliphatic carbons. $^{13}$CNMR shows that the asphaltene molecule contains 40% aromatic carbon and 90% of hydrogen is in methylene and methyl groups. Aromatic compounds have a higher carbon to hydrogen (C/H) ratios than naphthenes, which in turn have higher C/H ratios than paraffin. The heavier (denser) the crude oil, the higher its C/H ratio.

Since asphaltenes, the heaviest part of the crude oil, is responsible for the million dollar losses caused by their deposition on wells and pipes, this chapter is dedicated to exploring more closely their properties, structure, and composition. Other properties, such as aromaticity, molecular weight, and polydispersity that help to understand, predict, and prevent asphaltene deposition are described as well. In order to compare the asphaltene
fractions molecular weight and finding the distribution for the molecular weight, GPC was chosen as the reference method for molecular weight measurement.

### 3.2. Materials and methods

Asphaltene studied in this chapter are extracted based on ASTM D6560\textsuperscript{21} from different crude oils shown in Table 3-1. The method is entirely described in section 3.3.

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>Density (g/ml; 20 °C)</th>
<th>Viscosity (cP; 20 °C)</th>
<th>Water content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6</td>
<td>0.834</td>
<td>4.8</td>
<td>0.06</td>
</tr>
<tr>
<td>S9</td>
<td>0.836</td>
<td>6.0</td>
<td>0.05</td>
</tr>
<tr>
<td>P7</td>
<td>0.876</td>
<td>15.3</td>
<td>0.03</td>
</tr>
<tr>
<td>P1</td>
<td>0.878</td>
<td>21.3</td>
<td>0.04</td>
</tr>
<tr>
<td>C</td>
<td>0.885</td>
<td>22.0</td>
<td>0.03</td>
</tr>
<tr>
<td>A</td>
<td>0.884</td>
<td>56.0</td>
<td>0.07</td>
</tr>
<tr>
<td>P60</td>
<td>0.930</td>
<td>338.9</td>
<td>0.06</td>
</tr>
</tbody>
</table>

GPC was used to find the molecular weight distribution. GPC consists of three PSS-SDV (Styrene-divinylbenzene) columns with 100, 1000 and 10000 Angstrom pore sizes. These pores can vary from small to quite large, and act as the molecular filters. The larger size molecules will not fit into the smaller pores. Conversely, the smaller particles will fit into most of the pores and will be retained longer\textsuperscript{52}. Figure 3-1 illustrates how the sample is injected into the mobile phase and the path that the sample takes to the detector. The mobile effluent frequently being used in a
GPC method is THF, because of its low refractive index and viscosity, and the calibration standard is polystyrene\textsuperscript{73}.

Inside the GPC, the dissolved sample is injected into a continually flowing stream of solvent (mobile phase). The mobile phase (THF) flows through millions of highly porous, rigid particles (stationary phase) tightly packed together in a column. Data acquisition accessories control the test automatically, record the results, and calculate the average molecular weight. The most widely used detector today for GPC analysis is the differential refractometer. It is a concentration sensitive detector that merely measures the difference in refractive index (dRI) between the eluent in the reference side and the sample + eluent on the sample side. Since the refractive index of polymers is usually constant above molecular weights of about 1,000 g/mol, the detector response is directly proportional to the sample concentration\textsuperscript{73}.

![Figure 3-1 Schematic of a basic gel chromatography system\textsuperscript{5,5,74}.](image-url)
Extracted asphaltene is dissolved in THF in order to prepare the different sample concentration (Shown in Table 3-2 and Figure 3-2). Then the solutions are filtered using 0.2 μm filter paper (PTFE) and added to small GPC vials shown in Figure 3-3.

**Table 3-2 Preparing samples with different asphaltene concentration**

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration (mg/ml)</strong></td>
<td>1.5-2</td>
<td>0.5-1</td>
<td>0.2-0.5</td>
<td>0.1-0.2</td>
<td>~ 0.05</td>
<td>~ 0.01</td>
<td>~ 0.001</td>
</tr>
<tr>
<td><strong>Weight percent (wt. %)</strong></td>
<td>~ 0.2</td>
<td>~ 0.1</td>
<td>~ 0.06</td>
<td>~ 0.01</td>
<td>~ 0.006</td>
<td>~ 0.001</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

![Figure 3-2 Asphalten sample diluted by THF.](image)
3.3. Results and discussion

3.3.1. Fractionation based on solubility

In this study, we fractionated asphaltene based on their solubility using 4 precipitants: n-pentane, n-hexane, n-heptane, and n-octane. Asphaltene separation was performed based on the method IP-143 (ASTM D6560-IP 143), and the separated asphaltene fractions are shown in Figure 3-4 and Figure 3-5. The C$_{5-6}$ and C$_{6-7}$ asphaltenes are shown by Figure 3-4 are viscous liquids. While Figure 3-5 shows that C$_{7-8}$ and C$_{5+}$ to C$_{8+}$ asphaltenes are powder-like solids. Based on this observation, it is clear that different asphaltene fractions have different chemical compositions and structures. Based on the results described in this chapter, C$_{5-6}$ asphaltene has the lowest aromaticity and molecular weight, while the C$_{8+}$ has the highest molecular weight and aromaticity$^5$. 
In this method, the chosen precipitant (n-pentane, n-hexane, n-heptane, and n-octane), is added to the crude oil at a 40:1 volume-to-weight ratio (40 cm$^3$ of precipitant per 1 g of oil). The oil is mixed with the precipitant in a glass vial, and the vial is sealed to prevent the evaporation of the solvent. The mixture is sonicated once a day for 30 minutes to enhance the mixing of the oil and the precipitant, and the subsequent precipitation of asphaltenes. The aging process of the asphaltene aggregates occurs at ambient temperature. After two days, the aging process is completed, and the solution is filtered using a 0.2 μm
Nylon filter. The filter cake, containing the asphaltenes fraction, is placed inside a Soxhlet apparatus (Figure 3-7) using a paper thimble and refluxed with the corresponding asphaltene precipitant (\(n\)-C5, \(n\)-C6, \(n\)-C7, and \(n\)-C8) for two days to purify the asphaltene fraction and remove any co-precipitated material. The solvent plus the impurities are then added to the maltene fraction. The heating rate, condenser cooling rate, and fluid level of the solvent in the Soxhlet apparatus have to be adjusted to maintain the appropriate level of solvent in the Soxhlet and flask. To increase the rate of asphaltenes purification, a motor is installed on top of the condenser column to vertically move the thimble containing the filtered asphaltenes. Using this technique, the diffusion rate of impurities into the washing solvent increases, and therefore, the efficiency of extraction improves. In the next step, the filter papers containing the purified asphaltenes are washed with toluene to dissolve all asphaltenes. The end point of this step is determined by the color of the toluene in contact with the thimble; the process will stop when toluene is colorless. In the final stage, the solutions of toluene and asphaltenes are transferred to evaporation plates to allow the complete evaporation of toluene at a temperature of 378 K–393 K. The samples are taken to constant weight, and the weights of \(C_{5+}\), \(C_{6+}\), \(C_{7+}\), and \(C_{8+}\) asphaltenes are calculated.

Finally, by subtracting the \(C_{6+}\) asphaltene content from the \(C_{5+}\) asphaltene content, the amount of \(C_{5-6}\) asphaltene is quantified. With the same methodology, the amounts of \(C_{6-7}\) and \(C_{7-8}\) asphaltenes are obtained. In order to separate \(C_{5-6}\), \(C_{6-7}\), \(C_{7-8}\), and \(C_{8+}\) asphaltene fractions for further analyses, it is needed to wash the \(C_{5+}\), \(C_{6+}\), \(C_{7+}\), and \(C_{8+}\) fractions with \(n\)-C6, \(n\)-C7, \(n\)-C8, and toluene, respectively. The final step is to remove the added solvent by evaporation. The residue is the corresponding asphaltene fraction. The summary of the method is shown in Figure 3-6.
Figure 3-6 Asphaltene fractionation; Aging time=48 hrs⁵.
Table 3-3 shows the results of the asphaltene fractionation of seven light crude oils. Based on the results, the asphaltene distribution is not the same for the crude oils. Different asphaltene fractions have different chemical compositions and structures. Not only asphaltene structure varies from one crude oil to the other, but also the asphaltene sub-fractions look different.
Table 3-3 Asphaltene fractionation result by the addition of different precipitants 
(*n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane).

<table>
<thead>
<tr>
<th>Asphaltene fractions form crude oil</th>
<th>C5-6 (wt. %)</th>
<th>C6-7 (wt. %)</th>
<th>C7-8 (wt. %)</th>
<th>C8+ (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S6</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>S9</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>A</td>
<td>5.0</td>
<td>0.3</td>
<td>0.1</td>
<td>8.7</td>
</tr>
<tr>
<td>C</td>
<td>0.4</td>
<td>0.7</td>
<td>0.4</td>
<td>3.4</td>
</tr>
<tr>
<td>P7</td>
<td>0.6</td>
<td>0.2</td>
<td>0.6</td>
<td>2.9</td>
</tr>
<tr>
<td>P60</td>
<td>0.8</td>
<td>0.2</td>
<td>0.1</td>
<td>7.5</td>
</tr>
<tr>
<td>P1</td>
<td>1.0</td>
<td>0.3</td>
<td>0.1</td>
<td>5.6</td>
</tr>
</tbody>
</table>

3.3.2. Study of asphaltene structure by FTIR

Fourier Transform InfraRed (FTIR) spectroscopy is an analytical technique used to identify organic and some inorganic materials. It is based on the absorption of mid-IR radiation, located between the wavelengths of 2.5 µm (4000 cm⁻¹) and 25 µm (400 cm⁻¹) of the light spectrum. When sample exposed to infrared radiation, the different bonds in the molecule selectively absorb radiation of specific wavelengths which changes their dipole moment and, therefore, the excited vibrational state. The wavelength of light absorbed by a specific bond is a function of the energy difference between the basal and excited vibrational states. Therefore, the wavelengths absorbed by the sample are a characteristic of its molecular structure. The result, the FTIR spectrum, is a plot of absorbance (or transmittance) of radiation versus wavenumber in cm⁻¹, where wavenumber is the reciprocal of the wavelength. For studying asphaltene structure, FTIR gives information about the different functional groups that can be found in the asphaltene molecule. In addition, the paraffinicity and aromaticity of asphaltenes, the existence and relative proportion of heteroatomical functional groups versus aliphatic compounds,
and the degree of condensation in the polyaromatic compounds can be determined by FTIR spectra\textsuperscript{78,79}. These parameters have been used to characterize the geochemical evolution and the correlation of oils from different locations as well as to model the behavior of asphaltenes in crude oil\textsuperscript{78–80}. Table 3-4 shows the main adsorption peak for the component of crude oils.

Table 3-4 Infrared absorption frequencies assigned to a typical FTIR spectrum\textsuperscript{5,38,41}.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Frequency range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>C-H (stretch)</td>
</tr>
<tr>
<td></td>
<td>C-H (bend or scissoring)</td>
</tr>
<tr>
<td></td>
<td>C-H (Rock)</td>
</tr>
<tr>
<td></td>
<td>CH(_3)</td>
</tr>
<tr>
<td></td>
<td>CH(_2)</td>
</tr>
<tr>
<td>Alkenes</td>
<td>=C-H (stretch)</td>
</tr>
<tr>
<td></td>
<td>C=C (bend)</td>
</tr>
<tr>
<td></td>
<td>=C-H (out of plane bend)</td>
</tr>
<tr>
<td>Alkynes</td>
<td>-C≡C- stretch</td>
</tr>
<tr>
<td></td>
<td>-C≡C- bend</td>
</tr>
<tr>
<td>Amides/Amines</td>
<td>N-H bend</td>
</tr>
<tr>
<td></td>
<td>C-N stretch, aromatic amines</td>
</tr>
<tr>
<td></td>
<td>C-N stretch, aliphatic amines</td>
</tr>
<tr>
<td>Aromatic</td>
<td>C-H (stretch)</td>
</tr>
<tr>
<td></td>
<td>C=C (stretch)</td>
</tr>
<tr>
<td>Alcohols</td>
<td>O-H (stretch)</td>
</tr>
<tr>
<td></td>
<td>C-O (stretch)</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>H-C=O</td>
</tr>
<tr>
<td></td>
<td>C=O (stretch)</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>O-H (stretch)</td>
</tr>
<tr>
<td></td>
<td>C=O (stretch)</td>
</tr>
<tr>
<td></td>
<td>C-O (stretch)</td>
</tr>
<tr>
<td></td>
<td>O-H (bend)</td>
</tr>
</tbody>
</table>
In this study, the spectrum is recorded in a Nicolet FTIR Infrared Microscope with 64 scans and a 4 cm\(^{-1}\) resolution. Not all absorption bands are visible due to the small proportion of some functional groups in the asphaltene molecule. Low intensities of asphaltene spectrum in the wavelength region of 3600-3000 cm\(^{-1}\) show that there are a small amount of OH and NH groups. The peaks in the range 2800-3000 cm\(^{-1}\) are attributed to the –C-H stretch of an alkane. Carbonyl groups (1750-1600 cm\(^{-1}\)) has weak intensities in IR region for asphaltenes\(^{68,81}\).

Figure 3-8 shows an example of the FTIR spectrum of C\(_{5+}\) asphaltenes from crude oil C. FTIR analysis was done for different asphaltene fractions: C\(_{5-6}\), C\(_{6-7}\), C\(_{7-8}\), C\(_{8+}\), the result shows that all the fractions contain the same functional group. Based on the results it can be seen that there is a peak around 1735 cm\(^{-1}\) that demonstrates the carbonyl stretch C=O esters. The peak in the range 1585-1600 cm\(^{-1}\) is attributed to C-C stretching vibration of aromatic rings. Also, there are several peaks in the region 1300-1000 cm\(^{-1}\) which shows the C-O stretches. The peak at 1457 cm\(^{-1}\) is related to the C-H scissoring vibration. There are some peaks in the region 1250-1300 which can be attributed to the C-N stretching of aromatics amines. The peak at 1375 cm\(^{-1}\) corresponds to the C-H rocking vibration. The peak at 810 cm\(^{-1}\) is attributed to =C-H bends. The peak at 720 cm\(^{-1}\) shows the C-H rocking vibration.
3.3.3. Asphaltene properties

3.3.3.1. Aromaticity

In this study, we proposed a new approach for calculating aromaticity and verified it by comparing the result to the aromaticity based on FTIR method. Aromaticity is defined as the ratio of Unbonded Carbon/Total Carbon or Unbonded Carbon/Total Hydrogen. The unbonded carbons are the carbons in the aromatic rings, and it is assumed that the aromatic carbons do not have any bonding with hydrogen. Therefore, the un-bonded carbons are calculated based on the below equation:\(^5\)

\[
UC = TC - \frac{TH}{2}
\]

Equation 3-3

Where \(UC\) is the unbonded carbon, \(TC\) is the total carbon and \(TH\) is the total hydrogen.
Aromaticity can be defined based on the FTIR spectrum as well. It is defined as the ratio of absorbance at the 1600 cm$^{-1}$ band (which corresponds to the aromatic C=C bonds) to the absorbance at 1400 cm$^{-1}$ band (which corresponds to aliphatic C–H bonds). In addition, there is an indirect aromaticity index which is defined based on the ratio of absorbance at the 1600 cm$^{-1}$ band to the absorbance at 2900 cm$^{-1}$ band (which corresponds to aliphatic C–H bonds).

Figure 3-9 shows the correlation between the result of the aromaticity of C$_{5+}$ asphaltene fractions for seven crude oils (A, P60, P7, P1, C, SA9 and SA6) by FTIR and elemental analysis methods. The aromaticity calculated by elemental analysis is the ratio of UC/TC, UC/TC, and C/H. The result shows that there is a good correlation between the aromaticity calculated by the three methods, therefore, they can be used as an index to compare the asphaltene fractions structure. The trend of changing aromaticity based on elemental analysis versus FTIR is the same for all three methods of aromaticity calculation. Also, the complete results of aromaticity and its corresponded crude oils are shown in Table 3-5. In addition, the result of the elemental analysis is presented in Table 3-6. Based on the obtained aromaticity factors, one can conclude that the polycyclic aromatic core for the asphaltenes in the crude oil SA6 contains least aliphatic chains and most aromatic rings among all available asphaltenes.
Figure 3-9 Aromaticity based on elemental analysis and FTIR.

Table 3-5 Aromaticity index of C_5+ asphaltene based on FTIR and elemental analysis.

<table>
<thead>
<tr>
<th>C_5+ asphaltene of crude oil</th>
<th>FTIR</th>
<th>UC/TC</th>
<th>UC/TH</th>
<th>C/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.22</td>
<td>0.40</td>
<td>0.34</td>
<td>0.84</td>
</tr>
<tr>
<td>P60</td>
<td>0.23</td>
<td>0.41</td>
<td>0.35</td>
<td>0.85</td>
</tr>
<tr>
<td>P7</td>
<td>0.31</td>
<td>0.47</td>
<td>0.45</td>
<td>0.95</td>
</tr>
<tr>
<td>P1</td>
<td>0.33</td>
<td>0.48</td>
<td>0.46</td>
<td>0.96</td>
</tr>
<tr>
<td>C</td>
<td>0.33</td>
<td>0.48</td>
<td>0.46</td>
<td>0.96</td>
</tr>
<tr>
<td>SA9</td>
<td>0.44</td>
<td>0.49</td>
<td>0.47</td>
<td>0.97</td>
</tr>
<tr>
<td>SA6</td>
<td>0.45</td>
<td>0.51</td>
<td>0.52</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 3-6 Elemental analysis of C₅+, asphaltene of different crude oils.

<table>
<thead>
<tr>
<th>C₅+ Asphaltene from crude oil</th>
<th>C, wt. %</th>
<th>H, wt. %</th>
<th>S, wt. %</th>
<th>N, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>78.83</td>
<td>7.83</td>
<td>7.28</td>
<td>0.87</td>
</tr>
<tr>
<td>P60</td>
<td>80.16</td>
<td>7.81</td>
<td>7.5</td>
<td>1.05</td>
</tr>
<tr>
<td>P7</td>
<td>86.59</td>
<td>7.62</td>
<td>2.07</td>
<td>1.16</td>
</tr>
<tr>
<td>P1</td>
<td>87.74</td>
<td>7.61</td>
<td>1.43</td>
<td>1.18</td>
</tr>
<tr>
<td>C</td>
<td>87.97</td>
<td>7.66</td>
<td>1.97</td>
<td>1.24</td>
</tr>
<tr>
<td>SA9</td>
<td>84.84</td>
<td>7.27</td>
<td>3</td>
<td>0.72</td>
</tr>
<tr>
<td>SA6</td>
<td>86.1</td>
<td>7</td>
<td>3.32</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Also, the aromaticity is defined for three different asphaltene fractions; C₅-6, C₅+, and C₈+ based on FTIR and elemental analysis method. As it is shown in Figure 3-10, the aromaticity for C₅-6 asphaltene which is the most soluble fraction of asphaltene is the lowest while C₈+ which is heaviest among these three fractions has the highest aromaticity index.
3.3.3.2. Molecular Weight

GPC (also called size exclusion chromatography, SEC) separates molecules by their size, similarly to a molecular sieve process\textsuperscript{52}.

Figure 3-11 shows how the molecular weight of asphaltene is affected by the concentration, by increasing the concentration of asphaltene, the bigger aggregate particles are form and the molecular weight of asphaltene increases. Based on the result the aggregate number molecular weight changes between 1000-2000 g/mol for a different kind of asphaltene samples. While the number molecular weight of monomer asphaltene is approximately between 600-800 g/mol.
Figure 3-11 Asphaltene molecular weight changes by concentration$^5$.

Figure 3-12 shows the $Mn$ distribution for C$_{5+}$ asphaltene fractions of crude oil S9 and C by GPC at different concentration. As noticed, the distribution changes dramatically by the asphaltene concentration. Based on the result the distribution is broader for higher asphaltene concentration and as the concentration decreases the curves become narrower$^{49}$. By increasing the concentration, the molecular weight increases due to the aggregation of the asphaltene molecules$^{72}$, therefore the molecular weight shown in the plot is related to the molecular weight of small asphaltene particles and aggregates. As it is clear from Figure 3-11, the asphaltene molecular weight of crude oil C is greater than crude oil SA9. Also, based on Figure 3-12, the distribution of $Mn$ for crude oil C is broader in comparison with crude oil SA9 which shows that asphaltene $Mn$ of crude oil C is higher than crude oil SA9.
Figure 3-12 Asphaltene molecular weight distribution in different concentration, a) Crude oil S9, b) Crude oil C5.

Figure 3-13 shows the *Mn* distribution for different asphaltene fractions of SA9 crude oil (the procedure of fractionation is described in section 3.3). As it is expected the molecular weight of the C8+ fraction is the highest, and the distribution is the broadest. The
distribution of the molecular weight for C_{5-6} asphaltene is the narrowest among the asphaltene fractions since the structure of C_{5-6} asphaltene fraction is more resinous, and its aromaticity is less than a C_{8+} fraction.

![Figure 3-13 Asphaltene molecular weight distribution for different asphaltene fractions of crude oil SA9 with a concentration of 0.16 wt. %.](image)

Most of the distributions in Figure 3-12 and Figure 3-13 are bimodal which shows that, at least, there are two different species in the solution. The number of low molecular weight molecules increases in the first peak for the lowest concentration of asphaltene in Figure 3-12 and Figure 3-13. Mansoori et al. 2007 showed the same trend for the molecular weight changes for C_{5+} and C_{7+} asphaltene.

In addition to the distribution of molecular weight, it is possible to find the average molecular weight of each distribution. The average Mn and PDI measured at 1.9 mg/ml concentration for the C_{5+} asphaltene from the crude oil in this example are 1443 g/mol and
3.4, respectively, while the average Mn and PDI measured at 0.001 mg/ml concentration are 710 g/mol and 2.1. The Mn reported for the C$_{5+}$ asphaltene at 1.9 mg/ml is an aggregate weight but not the actual Mn for an asphaltene molecule because of the asphaltene self-association.

The result of the average number molecular weight of C$_{5+}$ asphaltene of crude oils is shown in Figure 3-14. The average molecular weight and polydispersity are different for the asphaltene samples. This result is inconsistent with Figure 3-11 results which indicates that each asphaltene molecular weight changes differently with concentration.

![Figure 3-14](image)

**Figure 3-14** Average number molecular weight of asphaltene monomer versus polydispersity index for different crude oils.

### 3.4. Chapter summary

The asphaltene properties are studied in order to have a better understanding of asphaltene behavior and prevent or mitigate the deposition issues. The most critical
parameters for understanding the asphaltene behaviors are its structure, composition, aromaticity and molecular weight. The structure of asphaltene and its functional group was studied using FTIR, which these results are used for calculating the aromaticity of different asphaltene fractions. Aromaticity and molecular weight are the input parameters that are used in PC SAFT model to define and predict the asphaltene onset of precipitation. As a summary of the results, in this part of the study, a method was proposed for asphaltene fractionation based on the solubility of asphaltene in different n-alkanes. Aromaticity is a crucial property to understand the stability of crude oil, and it varies for different fractions in the asphaltene polydispersed distribution. Different alkanes can be used to separate different asphaltene fractions from this distribution. Light paraffinic solvent, such as \( n \)-pentane, precipitate a larger fraction of the distribution. The results obtained by different methods show that fractions might vary in their heteroatoms content and molecular weight.

Asphaltene polydispersity characteristic is shown by using GPC for molecular weight measurement. It is shown that asphaltene molecular weight increases by increasing the asphaltene concentration. The distribution of molecular weight for different asphaltene fraction is compared with each other. \( C_{8+} \) asphaltene which is the heaviest fraction has the broadest distribution while \( C_{5-6} \) asphaltene has the narrowest distribution as the most soluble fraction of asphaltene.
4.1. Investigating the wettability properties of carbonate reservoirs

Wettability of rock/crude control the flow and distribution of fluids in a reservoir and affects oil recovery\textsuperscript{86}. Therefore, it is a crucial concept in the oil industry. Wettability of mineral surfaces is highly dependent on the micro-topography, physical and chemical properties of minerals, crude oil quality (acidic and basic groups), brine composition (ionic strength, pH), and ambient conditions (e.g., temperature, pressure and dissolved CO\textsubscript{2})\textsuperscript{87–89}. Three different methods are available for measuring wettability of a system: contact-angle measurement, the Amott 6 method (imbibition and forced displacement), and the USBM
method\textsuperscript{90}. The last two are based on rock/brine/oil displacement behavior. The contact angle (CA) is a direct measurement of surface wettability and the best method for measuring the wettability of crude and brine on the polished mineral surfaces. Amott and USBM methods are used mostly to measure the average wettability of a core sample\textsuperscript{90}.

The contact angle is the best wettability measurement method for a system consisting of pure fluids and artificial cores. This method can also be used to study the wettability alteration by crude oil fractions. There are different methods available for contact angle measurement including the tilting plate method, sessile drops or bubbles, Wilhelmy balance method, capillary tube, tensiometric method, and capillary rise at vertical plate method\textsuperscript{91}. Contact angle measurement results can show how the surface energy changes in various conditions. These changes can result from the adsorption of the surface active fractions (asphaltenes+resins) in the crude oil and electrostatic and structural components due to the formation of the double layer. Based on the contact angle measurement results, the substrate is water wet if the contact angle is in the range of 0 to 70°, mix wet (neutral) if the contact angle is 70°-110° and oil wet if the contact angle is between 110°-180\textsuperscript{92,93}. The range of contact angle mentioned above as the oil wet/intermediate wet/water wet may vary in different studies. But the difference is not significant enough to change the final result.

Contact angle is one of the most common methods to study the wettability alteration although it is facing several limitations including reproducibility issues and hysteresis (difference between advancing and receding contact angle)\textsuperscript{94}. Hysteresis is one of the challenges that can be caused by three factors:
(1) Surface roughness, and pore geometry effect on CA$^{90}$, 

(2) Surface heterogeneity effect on CA measurement, and

(3) Surface immobility on a macromolecular scale$^{90,95}$. 

Chemistry of the rock surfaces plays an important role in the wettability properties. The most common sedimentary rock types are shale, sandstone, and carbonate which are water wet before adsorbing organic compounds. The wettability of the rock reservoirs can be altered by adsorption of a polar compound or the deposition of organic material from the crude oil$^{86}$. Carbonate rock is naturally oil-wet, and this is why the average oil recovery from carbonate rock is less than sandstone$^{86,96,97}$. Carbonate reservoirs are more prone to adsorb polar fractions (asphaltene + resin) from the crude oil onto their positive calcium sites and become oil wet$^{98,99}$. Approximately about 80% of carbonate reservoirs are oil wet while 15% of them are strongly oil wet$^{93,97}$. Therefore; it is possible to increase the oil recovery by changing the oil wet surfaces to water wet$^{93}$. 

Among the crude oil fractions, asphaltene and resins have an acidic group in their structure which are mostly responsible for wettability alteration$^{86,95}$. Although asphaltene and resins are the surface active components of crude oil, their stability is affected by the amount of other fractions (saturate and aromatic). For example, Morrow and Tang determined that changing the amount of light components fractions in the oil affect the wettability alteration and water flood efficiency$^{100}$. They showed that the Berea sandstone became oil wet by addition of light components$^{100}$. Asphaltene has a greater effect on wettability alteration$^{101,102}$ in comparison with the resin fraction. Morrow et al. 1986 showed that the wettability alteration toward more oil wet condition in Berea sandstone caused by
deposition of a monolayer of asphaltene using contact angle measurement\(^\text{94}\). Asphaltene has a greater negative charge than resin and a tendency to aggregate and separate from the oil fractions\(^\text{95}\). It can alter wettability by four different mechanisms: (or including) polar interaction, ionic interaction, acid/base interactions, and surface precipitation. In the absence of water, the polar interaction is most likely to happen between oil components and the solid substrate\(^\text{103}\). The polar interaction is between the polar atoms (N, S, O) of the crude oil and polar surface sites of the rocks\(^\text{104}\). Ion binding exists due to the presence of divalent or multivalent ions in brine which can bind to both oil and solid/water interfaces\(^\text{104}\). Ionic interactions depend on the compositions of oil, brine, and solid surface, as well as the temperature and aging time. Acid base interactions affect surface charge at both oil/water and solid/water interfaces. Ionized acidic or basic sites at the interfaces will influence the adsorption behavior by which polar crude oil components may alter wettability. The acidic compounds like naphthenic acid and phenols in the crude oil are responsible for wettability alteration of carbonate reservoirs\(^\text{105}\). Carboxylic acid groups are the main functional groups responsible for the acidity of the polar fractions in oil\(^\text{106}\). Xie et al. 2010 showed that by increasing the acidic components of the sample, the water wetness of volcanic rock decreased\(^\text{107}\). Surface precipitation happens in case that the oil media is a poor solvent for asphaltene. If the oil is the poor solvent, the asphaltene tendency to wet the surface increases.

Changing the wettability properties of carbonate reservoir from oil wet to water wet helps to increase the mobility of oil which results in increasing the amount of recoverable oil\(^\text{87}\). In this work, a study of the effect of crude oil fractions on wettability properties of rock reservoirs is conducted by measuring the contact angle of different oil samples and the
model oil in 0.1M (low salinity) and 5M (high salinity) NaCl brine. Also, we developed an appropriate contact angle measurement procedure to simulate the reservoir condition with reproducible results.

The main motivation in this study is changing the wettability properties of reservoir surfaces from oil-wet to water-wet for enhancing oil production. In this chapter first the appropriate method for contact angle measurement is introduced. The second step is improving the procedure of calcite plate preparation and contact angle measurement by controlling water layer thickness on the calcite surface. Third, the effect of different variables such as brine concentration, oil aging time and asphaltene fractions are investigated by contact angle measurement. Then the effect of low salinity brine aging after the oil aging step is determined in different model oil and crude oil systems. Finally, the characteristic of the adsorbate is studied by measuring the adsorption capacity of each calcite aged in different oil samples. Also, the structure of the adsorbate is studied by SEM and EDAX analysis. The below diagram (Figure 4-1) shows the overview of the works that is presented in this chapter.
In the next chapter, the focus is on understanding the mechanism of wettability alteration which helps us to investigate how low salinity brine can alter the wettability from oil wet to water wet in some of the crude oil systems.

**4.2. Materials and methods**

**4.2.1. Crude oil**

SA6 crude oil samples from the Middle East were used in this experiment. The physical properties of the oil are listed in Table 4-1. The crude oils were first centrifuged to remove any sediment, sand particles, or water present in the system prior to asphaltene separation. Density and viscosity were measured using an Anton Paar DMA 4500 digital...
vibrating U-tube densitometer and a Cannon-Fenske glass capillary viscometer, respectively. SARA analysis was done by clay-alumina chromatography method described in chapter 2.

Table 4-1 SA6 crude oil properties

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>Density (g/cc)</th>
<th>Viscosity (cP; Tamb)</th>
<th>Saturate (wt. %)</th>
<th>Aromatic (wt. %)</th>
<th>Resin (wt. %)</th>
<th>C₅+ asphaltene (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA6</td>
<td>0.836</td>
<td>4.8</td>
<td>70.9</td>
<td>19.0</td>
<td>8.0</td>
<td>2.1</td>
</tr>
<tr>
<td>SB4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Iceland spar samples (pure calcite, from WARD’S Natural Science) were used as substrates in order to simulate the calcium carbonate reservoir rock surface.

0.1M and 5M NaCl brine solutions were used as the low and high salinity simulated-sea-water. The pH of the prepared synthetic brines is 9.4±0.1. All brine solutions were pre-contacted with calcium carbonate powder in order to reach equilibrated pH.

Also, total acid number (TAN) was measured since it is a crucial factor for wettability alteration in carbonate reservoir as they adsorb organic acids\textsuperscript{86}. TAN shows the presence of carboxylic acid groups which adsorb strongly onto the carbonate surface by displacement of water\textsuperscript{108}.

TAN of the crude oil and its asphaltene and resin as the largest and most polar components of the crude oil were measured based on the Fan and Buckley 2007\textsuperscript{109} method (Spiking method).
TAN for the SA6 crude oil was around 0.06 mg KOH/g oil while TAN for the C$_5$+ asphaltene and resin fractions were 0.86 and 0.54 mg KOH/g sample.

Based on the SARA fractionation and TAN number of the resin and asphaltene, it is possible to calculate the TAN of oil:

$$\text{TAN}_{\text{SA6}} = \text{R wt. } \% \times \text{TAN}_\text{R} + \text{Asph wt. } \% \times \text{TAN}_\text{Asph} = 0.079 \times 0.54 + 0.021 \times 0.84 = 0.06$$

Thus, TAN calculation result was consistent with the experimental data. The TAN of SA6 and SB4 oil, resin and asphaltene fraction are shown in Table 4-2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TAN (mg KOH/g sample), SA6</th>
<th>TAN (mg KOH/g sample), SB4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_5$+ asphaltene</td>
<td>0.86 ± 0.10</td>
<td>-</td>
</tr>
<tr>
<td>Resin</td>
<td>0.54 ± 0.08</td>
<td>-</td>
</tr>
<tr>
<td>Crude oil</td>
<td>0.06 ± 0.01</td>
<td>0.1 ± 0.01</td>
</tr>
</tbody>
</table>

### 4.2.2. Preparation of samples

Asphaltenes separation was done based on modified IP-143 procedure\textsuperscript{21}. In this work, two asphaltene fractions were separated; C$_5$+ and C$_5$-6. N-pentane with the ratio of a 40:1 ml/g (40 ml of precipitant per 1 g of oil) was used to extract the maximum amount of asphaltenes from crude oil (C$_5$+ asphaltene). After two days (aging time) each solution was filtered separately. The filtered asphaltenes (C$_5$+) were then refluxed with its precipitant (n-pentane) to wash all the impurities that co-precipitated with asphaltenes by using soxhlet.
In order to have C\textsubscript{5-6} asphaltenes, it was needed to wash the C\textsubscript{5} with n-hexane in soxhlet. The final step was to remove the added solvent by evaporation. The residue is the C\textsubscript{5-6} asphaltene fraction. In order to prepare the solution the appropriate amount of asphaltene was dissolved in Model Oil (MO). MO contains 87 vol. % n-C12 and 13 vol. % Toluene. Also, resin solution was prepared by extracting resin from crude oil SA6 by ASTM D2007 method\textsuperscript{23}.

4.2.3. Contact angle measurement

The contact angle was measured by “KRUSS Drop Shape Analyzer DSA100” device in this study.

In the sessile drop method, a drop of crude oil was formed at the end of a fine capillary tube and brought into contact with the flat mineral surface. The droplet was allowed to age on the surface. The water-advancing and water-receding contact angles were measured by using the capillary tube to expand and contract the volume of the crude-oil drop\textsuperscript{91}.

Also, in this study, the moving needle was used instead of moving plate method (dual-drop dual-crystal technique\textsuperscript{110}). In this method, the advancing angle, ACA, was measured by pulling the periphery of a drop over a surface, while the receding contact angle, RCA, was measured by pushing it back\textsuperscript{91}.

Tilting plate method was based on tilting the system slowly until the pendant drop on it begins to move in the uphill direction. At that time, the downhill contact angle was the advancing angle and the uphill angle was the receding contact angle. It is necessary to wait for enough time to reach equilibrium. It is necessary to wait for enough time to reach equilibrium.
The rest of the procedure for the calcite preparation and oil aging step are explained in result and discussion.

4.2.4. Structural analysis

4.2.4.1. NMR spectroscopy

Quantitative $^1$H and $^{13}$C NMR spectroscopy analyses were performed by a Bruker AVANCE III HD 600 MHz high-performance digital spectrometer operating at 600 MHz for proton and 150.9 MHz for carbon.

The spectra were obtained with deuterated chloroform (CDCl3) as the solvent and tetramethylsilane (TMS) as an internal reference. The sample was prepared with the concentration of approximately 1-15 mg diluted in 0.5 mL CDCl3 in a 5 mm tube.

The proton data were acquired using a 2.5 s acquisition time, a 12019 Hz sweep width, a 30° pulse flip angle, and no recycle delay. The spectra resulted from 128 scans and were referenced to the CDCl3 resonance at 7.3 ppm. The carbon spectra were collected with a 2.7 s acquisition time, a 36231 Hz sweep width, 30° pulse flip angle, and a recycle delay of 1 s. The spectra resulted from 3000 scans and were referenced to the CDCl3 resonance at 77 ppm.

4.2.4.2. FTIR spectroscopy

FTIR analysis is a technique used to check the availability of organic material. The sample absorbance was measured at different wavelengths. Different peaks at specific wavelength showed the molecular structure. Nicolet FTIR Infrared Microscope was used to study the structure of the adsorbate. The infrared and near-infrared analysis was performed on the
original crude oil samples at 25°C. The wave numbers region was set to 4000-400 cm\(^{-1}\), and the total number of scans per spectra set to 256. Total path length was 2 mm. Analysis of FTIR results was done based on the description in the handbook of infrared standards\(^{111}\).

### 4.3. Results and discussion

#### 4.3.1. Improvement of contact angle measurement procedure

##### 4.3.1.1. Appropriate method for contact angle measurement

Contact angle experiments are often used for investigations of wettability behaviors. At the first step, the captive-drop technique was followed to measure both angles; RCA was measured from the oil droplet deposited and left to equilibrate, detached from the needle, on the surface of calcite plate while ACA was determined by withdrawing the oil from the same equilibrated droplet. When withdrawing the oil, a rigid film or prune-like skin formed gradually around the oil droplet at the oil-brine interface. Different tests of measuring contact angle had been done trying to solve the problem of having a rigid film that impedes measurement accuracy.

For the first measurement, C\(_{5-6}\) asphaltene, the most soluble fraction of asphaltene, was extracted and dissolved in the Model Oil (MO). The contact angle of the asphaltene in MO and calcite surface immersed in 0.1M NaCl was measured by “DSA100”. The test was done with a solution of 0.4 wt. % C\(_{5-6}\) asphaltene in MO at ambient condition.

RCA at time zero is approximately 20° and monotonically increased until it reaches equilibrium 38° after five days. For measuring the ACA, the volume of the droplet was
decreased. During the process of measuring ACA, the rigid film is formed and remained on the surface of calcite. Figure 4-2.a discloses the rigid film formation in the process of ACA measurements.

In order to prevent the rigid film, the concentration of asphaltene was decreased to 0.1 wt. % and the solution media was changed from MO, n-dodecane + toluene, to only toluene that is a better solvent for the asphaltene. However, the test result shown in Figure 4-2.b indicates the skin is still developed, even after dropping asphaltene concentration from 0.4% to 0.1% and changing the solvent to a more aromatic one.

In the next test, the equilibration time of measuring RCA decreased from 6 hrs to 1 hr to examine the effect of time duration on the film formation. The skin is formed again in the ACA measurement, see Figure 4-2.c.

The last test for prevention of skin formation was done with a sample that had the three fractions of crude oil; asphaltene, resin, toluene as the aromatic fraction. The test results indicated that the skin was formed in measuring ACA, see Figure 4-2.d.
The test result indicated that skin formation is unrelated to the concentration of asphaltene or presence of n-Dodecane as a precipitant in MO (87% Dodecane +13% Toluene). The only difference is that at higher concentration of asphaltene the skin is thicker and produces irregular shape after oil withdrawal. As a result, we decided to change the method of measuring ACA in a way that the droplet volume remained constant during the measuring process. In this way, the interfacial tension remains constant, and the accumulation of asphaltene at the water-oil interface is prevented simultaneously. Thus, this method is followed to prevent skin formation consisted of dragging the drop of oil attached to needle throughout the calcite plate; however, after dragging the oil drop, it is needed to wait for enough time to reach equilibrated values, which was between 2-3 days while needle must remain in contact with the drop. The idea of moving needle from the dual drop dual crystal was proposed by Rao et al. 1996\textsuperscript{110}. In the process of validating the dragging method, it is observed that volume of the droplet is still decreasing during the equilibration time; thus,
the dragging method is also unacceptable. Our hypothesis is that the volume change is caused by evaporation inside the needle.

The following example is showing one of the results which has the skin formation problem because the drop volume constantly decreases during the test: In this test, the sample contains 0.05 wt. % C_{5-6} asphaltene in a mixture that contains 87% n-dodecane + 13% toluene (MO). The calcite plate was aged in 0.05 wt. % C_{5-6} asphaltene in MO, with 0.1M NaCl brine present, for one week at 120°C. The equilibrated RCA measured ~ 37° after two days of aging on calcite plate, see Figure 4-3.a. To measure the ACA, the drop was dragged on the surface of calcite. When the contact line moved the ACA at time zero was 46.7°, see Figure 4-3.b. Then the droplet was monitored during the test time to measure an equilibrated ACA value and after three days, it is clearly observed that a skin is formed and the volume of the droplet decreased, see Figure 4-3.c.

![Figure 4-3](image)

Figure 4-3 a. RCA, 0.05 wt. % C_{5-6} asphaltene in MO / equilibration time=2 days, 0.1M NaCl brine; b. ACA, 0.05 wt. % C_{5-6} asphaltene in MO / Time=0, c. Volume decreasing; Skin formation / equilibration time=3 days.
The process of ACA measurement lasts longer than one day, the skin forms gradually, but interfacial tension decreases rapidly causing accumulation of asphaltene at the water-oil interface\textsuperscript{112} for the wrinkled skin to become visible around the oil drop.

To clearly demonstrate that volume of droplet decreases over time, the interfacial tension (IFT) of a mixture contained 50 vol% toluene and 50 vol % n-dodecane was measured, against 0.1M NaCl brine; the IFT decreases from 40.1 to 35.2 mN/m during 38 hours while the volume of droplet decreases from 52.5 to 46.8 μl. The conclusion is that the consequence of the droplet volume changes is only significant in crude oil samples that require more than 2 hours of equilibration time.

Finally, a successful method was found by depositing the drop, leaving it detached from the needle and then tilting the calcite plate for keeping the volume of droplet constant which prevents skin formation. Also based on lander et al. 1993 study tilting method is more precise, and its results are more reproducible in comparison with the sessile drop method\textsuperscript{113}.

### 4.3.1.2. Controlling water layer thickness on calcite surface

Effect of water layer thickness (WLT) on the surface of calcite before starting the oil aging step is discussed in this part of the study.

The CA was measured for MO and other oils containing crude oil fractions such as asphaltene or resin as the surface active components. For both cases, calcite plates were aged at 120°C for two weeks in test oils in the presence of 5M NaCl brine; a small amount of 5M NaCl brine was added to the aging vessels and then filled with test oil. RCA was measured by slowly depositing a sessile drop from a needle under the aged calcite immersed in brine, this pre-equilibrated with test oil. After RCA equilibration, the needle
was reinserted into the drop and ACA was measured for MO by dragging the drop while moving the needle. However, for other oils, ACA was measured by tilting the cuvette for keeping the volume of droplet constant which prevented skin formation. CA measurement was repeated 3 times for each sample and results are presented in Figure 4-4.

RCA & ACA measurements has produced test results with large standard deviations (±30°) for the MO sample (Figure 4-4a). It is doubtful that oils with fully distinct properties could produce the same range of wettability alterations as shown in Figure 4-4.b.

MO without any surface-active materials makes calcite mix-wet with large standard deviation as shown in Figure 4-4. Due to this high uncertainty, the validity of the followed procedure is questioned.

![Figure 4-4](image-url)

**Figure 4-4** Comparison of Contact Angles determined without controlling thickness of water-layer left on calcite plate during oil aging and thereafter rinsing aged plate with brine. MO Standard Deviation ±30°.
From experimental test results, it has been found that one of the most important parameters for accuracy in contact angle measurements is the thickness of water layer left on the surface of an aged calcite plate. The process of aging a calcite plate consists of immersing a cleaned plate in brine first and then drops it into an aging vessel containing test oil and some brine. Stability of the water film that resides between the surface of calcite plates and oil affect the wettability alteration of the rock. Also, the amount of water which is left on the surface of calcite plate before starting oil aging process plays an important role in wetting condition of a reservoir rock\textsuperscript{107}. Buckley et al. 1997 reported that a thick water film on the surface of substrate could be stable or unstable which can affect the surface forces balances\textsuperscript{114}. The water film stability on the surface of the calcite plate is as important as asphaltene adsorption on the surface. Having a thin water layer on the surface of calcite plate before aging may cause some rupture on the water film which provides access of substrate for asphaltene precipitation or adsorption\textsuperscript{115}. If the water film is stable on the substrate, there is less adsorption of polar components to the solid surfaces\textsuperscript{116}. Based on the water film stability there are two main mechanisms controlling the wettability properties: Surface active molecules diffuse through the water film, or they adsorb directly to the surface of the substrate from the organic phase.

In order to study the effect of water layer thickness on wettability alteration, calcite plate was prepared by these four proposed approaches:

**Vertical-gravity drainage, Spin coating, Wiping and Dry (1 and 2)**

From our experimental test results, it has been found that one of the most important parameters for accuracy and reproducibility in contact angle measurements is the thickness
of water layer left on the surface of a calcite plate to be aged. Aging a calcite plate consisted of immersing a cleaned plate in test brine first at a constant temperature for a fixed time and then immersing it into an aging vessel containing test oil with some brine or test oil only. The amount of water which was left on the surface of calcite plate before starting the oil aging process plays an important role in how the substrate wettability is altered.

Figure 4-5 is for disclosing pictures of how “wet or dry” calcite plates appear under normal viewing. Calcite is not optically clear because the manner is polished for conducting the test; polishing is done with 600 (3 min) and 1200 (3 min) paper grit.

Figure 4-5 Example of water film with and without wiping for two calcite plates.

A summary of different methods followed to control WLT is shown in Table 4-3. Cartoon of calcite plates is just to indicate the comparative thickness of the water layer for each method.
To study the effect of WLT on wettability alteration, Calcites were prepared by wiping, spin coater and vertical gravity drainage methods. In case of the dry method, Dry 1 and Dry 2, were submitted to below steps. The test brine is 5M NaCl, and the aging vessel contains appropriate amounts of pre-equilibrated MO and test brine. Dry 1 was equilibrated in test brine at room temperature as the others while Dry 2 was done at 120°C. However, plates for Dry 1 and Dry 2 were similarly aged in MO only; the aging vessel was free of brine; thus, the only difference in procedure was the temperature during initial 5M NaCl brine equilibration. Below are the calcite preparation and contact angle measurement procedure that was followed in this study.

1. Polished calcite plate with 600 (3 min) and 1200 (3 min) paper grit.
2. Rinsed it with DI water and test brine.

<table>
<thead>
<tr>
<th>Method</th>
<th>Calcite plate</th>
<th>Control of water layer thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td></td>
<td>Depends on the humidity of the air</td>
</tr>
<tr>
<td>Wiping</td>
<td></td>
<td>Manual Control</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Depends on the moisture of tissue paper and how hard is pressed</td>
</tr>
<tr>
<td>Spin Coater</td>
<td></td>
<td>Machine Control</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Layer thickness is controlled by speed and time of spinning</td>
</tr>
<tr>
<td>Vertical gravity drainage</td>
<td></td>
<td>No control, undetermined time</td>
</tr>
</tbody>
</table>
3. Equilibrate calcite for a day with test brine at room temperature (for Dry 2 at 120°C).

4. Transferred calcite from test brine to the aging vessel (for Dry 1 and Dry 2 with MO but not brine) after weighing WLT by the following approaches:

   - **Vertical gravity drainage:** The visible water film left on the calcite surface was not removed. In this method, the water layer thickness is controlled only by gravity.
     - Took calcite out of test brine and insert it into age vessel.

   - **Spin coating:** The WLT was controlled by using a spin coater (By controlling speed and time the water layer thickness is different).
     - Took calcite out of test brine and use spin coater to control the water layer thickness on the plate.
     - Inserted, as fast as possible, calcite into the aging vessel.

   - **Wiping:** The WLT was aimed to be controlled by wiping the water from the surface.
     - Took calcite out of test brine and wiping both sides immediately with a squeegee; this was made of a glass slide wrapped in tissue paper soaked, not dripping, in test brine.
     - Inserted, as fast as possible, squeegeed calcite into the aging vessel.

   - **Dry 1:** The WLT depends on the air humidity.
     - Took calcite out after 1 day in test brine at room temperature and dry it by blowing air parallel to its surface and leave it in a desiccator for 1 hour.
o Inserted, as fast as possible into an aging vessel containing only MO (not brine).

- Dry 2: The WLT depends on the air humidity.
  
o Took calcite out after 1 day in test brine at 120°C and dry it by blowing air parallel to its surface and leave it in a desiccator for 1 hour.
  
o Inserted, as fast as possible into an aging vessel containing only MO (not brine).

5. Aged calcite plates with controlled WLT at 120°C for 2 weeks in the hermetically closed aging vessel.

6. Removed plate from the aging vessel and get rid of bulk oil by soaking for 10 min in Cyclohexane previously pre-equilibrated with test brine.

7. Evaporated cyclohexane by leaving calcite in the humidity-controlled chamber.

8. Left the calcite plate in test brine (pre-equilibrated with CaCO₃) for 5 min and immediately start measuring contact angle.

4.3.1.3. Contact angles measurement for model oil on calcite plates with a controlled water layer thickness

After immersing the aged calcite plate for 5 minutes in brine previously pre-equilibrated with CaCO₃, RCA and ACA were measured by depositing MO drop, which still attached to the needle, and moving the needle. The test was done with calcite plates from the four preparation methods of “Vertical gravity drainage”, “Wiping”, “Spin Coater” and “Dry 1-and-Dry 2”. The test results are shown in Figure 4-6. Each measurement was repeated 5 times to find the standard deviation (SD). Also, two speeds of 500 and 50 rpm for 20
seconds were chosen for spin coating aiming to reach a WLT thinner than in the “Vertical gravity drainage” but thicker than in the “Wiping” methods.

The MO in the presence of 5M NaCl brine makes the calcite intermediate or oil wet based on the different water layer thickness on the calcite surface. The test result shows that the calcite plate becomes more oil wet by decreasing the water layer thickness. When preparing plate by “Vertical gravity drainage” method, a thick layer of water remained on the surface of calcite plate. After the oil aging process, patches of water remained on the surface of calcite. This is due to the rupture on the water layer. Therefore, the surface of calcite is not uniformly water wet or oil wet after removing the bulk oil from the surface, which causes a large standard deviation in the result.

Based on the test result presented in Figure 4-6 by decreasing the WLT on the calcite surface, the surface is more oil wet. The thin layer of water remaining on the surface of calcite provides access for the MO to be in contact with the substrate. As a result, calcite become more oil wet; it is observed that the ACA increased by decreasing the water layer thickness.

By using spin coater, with different speed more control on water layer thickness is possible, and the standard deviation of the test result is smaller in comparison with the vertical gravity drainage method.

In case of Dry 1, the calcite plate was first equilibrated with 5M NaCl brine at room temperature and then was dried. Then, the dried calcite plate was aged in MO at 120°C for 2 weeks. After the bulk of oil was removed from the calcite surface, the calcite was placed in 5M NaCl brine (which is equilibrated with MO and calcium carbonate), and after 5 min,
the RCA/ACA were measured. As it is shown in Figure 4-6, the calcite equilibrated with 5M NaCl brine at room temperature remained water wet.

All three cases, vertical gravity drainage, spin coater, and wiping, have a water layer during oil aging. Thus, the calcite surface was equilibrated with brine at 120 °C.

In case of Dry 2, the calcite plate was first equilibrated with 5M NaCl brine at 120°C and then it was dried. Then, the dried calcite plate was then aged in MO at 120°C for 2 weeks. After the bulk of oil was removed from the calcite surface, the calcite is placed in 5M NaCl brine (which is equilibrated with MO and calcium carbonate), and after 5 min, the RCA/ACA was measured by moving needle. It is observed that the drop is pinned to the surface and it was impossible to move the droplet by dragging drop attached to the needle. Also, the test was repeated and ACA was measured by withdrawing the oil. The results are shown in Figure 4-7. For the Dry cases to be comparable with the other three cases, it was necessary to equilibrate the calcite first with 5M NaCl brine at 120°C. Therefore, the test result of Dry 2 should be more comparable than Dry 1 with the other cases (Vertical gravity drainage, spin coater, wiping). The results presented in the next part helps to understand the effect of equilibrating calcite on 5M NaCl brine at room temperature, and elevated temperature is 120°C.
MO in the presence of 5M NaCl brine makes the calcite intermediate or oil wet based on different water layer thickness on the calcite surface. We have two hypotheses to answer why the MO without surface active components made the calcite oil wet.

First hypothesis: Aging the calcite in the presence of 5M NaCl at 120 °C for 1 day makes the surface positively charged while the MO is negatively charged at water/oil.
interface\textsuperscript{118}. Therefore, the MO is attracted to the positively charged surface by electrostatic interaction. This hypothesis is proven by measuring zeta potential of calcite and MO which based on results calcite is positively charged and MO is negatively charged which results in the attraction between MO and calcite plate.

Second hypothesis: Toluene might adsorb to the calcite by $\pi$-bond interactions\textsuperscript{119}. In order to verify this hypothesis in the next step, the CA results for only n-dodecane is shown in Figure 4-8.

To validate the hypothesis, the RCA and ACA were measured for pure n-dodecane in 5M NaCl brine. The calcite was prepared based on the wiping method to control the WLT on the surface of calcite. The test result is shown in Figure 4-8; pure n-C12 makes the calcite intermediate wet which shows that even n-C12 could change the wettability properties of calcite. Therefore, it is concluded that $\pi$-bond interaction between aromatic ring (toluene) and the cation is not responsible for wettability alteration in case of MO.
Effect of equilibration in brine before contact angle measurement for “aged-in oil” calcite on wetting properties with controlling WLT

Figure 4-9 is presented to compare the test results of different equilibration time in brine before contact angle measurement for various methods. After removing the bulk oil by cyclohexane, the aged calcite was equilibrated in a cuvette filled with 5M NaCl for 5 minutes and 2 hours. In case of wiping method, 1-day equilibration in brine was also tested. Increasing the equilibration time in brine, before contact angle measurement, promotes water wet conditions indicating that it takes some time for the calcite plate to be equilibrated at room temperature after the oil aging process at 120 °C.
Figure 4-9 Effect of calcite equilibration in brine before contact angle measurement.

By increasing the time of rehydration of calcite with brine, the surface becomes more water wet. After 2 hours in brine at room temperature, the aged calcite becomes more water wet. It can be speculated that after 5 min, the calcite surface charges are more similar to that at elevated temperature.

Effect of temperature and brine salinity on calcite equilibration before the oil aging step with controlling WLT

To independently elucidate the effect of equilibrating calcite plate in 5M NaCl brine before oil aging two experiments by aging at RT and 120°C on the clean calcite were done. RCA and ACA were measured for MO in test 5M NaCl brine. The test results are shown in Figure 4-10. Equilibration with 5M NaCl after 1 day at 120 °C produced intermediate-wet calcite while it remained water wet after 1 day equilibration at room temperature.
One day equilibration in 5M NaCl brine is not enough to reach the same equilibration at 120°C.

The effect of salinity during the calcite equilibration is also determined, results are shown in Figure 4-11. To study the effect of brine salinity the same test was conducted with 0.1M NaCl brine. Undoubtedly in case of having 0.1M NaCl brine, the calcite equilibration at room temperature and 120°C for 1 day produced any changes on water wettability properties of calcite.

**Figure 4-10** Effect of temperature during calcite plate equilibration in 5M NaCl brine on wettability alteration.
When the calcite is equilibrated at 120 °C in 5M NaCl brine, the surface has more positive-surface charges complexes (CaOH$^{0.75}$ ... Na$^+$)$^{120,121}$ in comparison with 0.1M NaCl brine$^{122}$ which causes stronger electrostatic interactions between oil and solid. In this way, oil has a higher tendency to be retained by the solid surface.

4.3.1.4. Summary of the results

For the contact angle measurement method, the tilting plate was adopted aiming to keep the droplet volume constant and prevent skin formation. Also, in order to decrease the standard deviation of the CA result, the method was modified by controlling the water layer thickness as explained below.

- The standard deviation of the contact angle measurements for MO in 5M NaCl brine has been improved from 30° (Vertical gravity drainage) to 15° (Spin coater,
V=50 rpm for 20 s) by controlling the water layer thickness of 5M NaCl brine deposited on the calcite before its aging for two weeks at 120°C with oil in the presence of brine.

- Calcite tends to be more oil wet when the WLT becomes thinner.
- MO, without any surface active material, in 5M NaCl brine produces intermediate to oil wet condition as a function of WLT.
- Re-hydration or equilibration of calcite before contact angle measurement in brine affects the wettability properties of the surface. By increasing the equilibration time in the cuvette filled with brine, the aged calcite becomes more water wet. Equilibration of calcite surface charges at room temperature will take longer than elevated temperature.
- The π-bond interactions between toluene and positive ions on the calcite surface are not responsible for wettability alteration since it is determined that even pure n-dodecane makes the plate intermediate wet.

4.3.2. Investigating the effect of different variables on the contact angle

4.3.2.1. Effect of salinity

In this test, the calcite plate was aged in test fluids, 0.05 wt. % C₅⁺ asphaltene in MO for one week at 120°C in two different NaCl concentrations; 0.1 and 5M NaCl brine. Increasing the brine concentration from 0.1M to 5M made the calcite plate more oil wet, see Figure 4-12, such result is inconsistent with the Mahani et al. 2015 and Ibrahim and Nasr-al-Din.123,124 While Aslan et al. 2016 showed that by increasing the NaCl
concentration, contact angle decreases initially (the calcite plate became more water wet) and then increases (The calcite became more oil wet). Adhesion of surface active component in the test oil (asphaltenes fraction in MO) occurred more readily on the surface of calcite when in the presence of 5M NaCl brine; under this condition, the calcite has more positive surface charge. Song et al. 2019 showed that calcite in the presence of 5M NaCl brine has a significantly higher surface charge in comparison with 0.1M brine which causes the attraction of negatively charged oil. The result is consistent with Al-Shalabi et al. 2013. When the brine concentration decreases the electric double layer force (Which is repulsive between crude oil and mineral surfaces.) increases which are caused by increasing the electrostatic repulsion. Also, Lee et al. 2010 investigated that the water layer thickness decreases by increasing the salinity of brine. These two explanations can be the cause of changing wettability properties by low salinity water injection.

Figure 4-12 RCA and ACA, 0.05 wt. % C₅⁺ asphaltenes in MO, 0.1M and 5M NaCl, 1 week aging at 120°C.
Also, it was concluded the wettability alteration is the same for 0.05 wt. % C₅⁺ in MO, by using 5M NaCl in 1-week aging and 0.1M NaCl in 3 weeks aging, see Figure 4-13. This result is an indication of the importance of aging time which will be further discussed.

![Figure 4-13 RCA and ACA, 0.05 wt. % C₅⁺ asphaltene in MO, aging of 3 and 1 week in 0.1M and 5M NaCl.](image)

The CA test results are the equilibrated CA and as an example, the RCA/ACA for C₅⁺ asphaltene in MO in 5M NaCl brine after 1 week aging in test oil is shown in Figure 4-14. The RCA and ACA are 149° and 153.5° at time zero, see Figure 4-14.a. The equilibrated RCA and ACA are 139° and 145° after 4 days, see Figure 4-14.b.
Effect of aging time

Aging time is one of the important factors that may affect the wetting alteration of the calcite plate. Two calcite plates were aged in test fluids, 0.05 wt. % C₅⁺ asphaltene in MO and 0.1M/5M NaCl brine, for two weeks at 120°C; aging vessels were filled with brine (¼) and test oil. RCA and ACA were measured by depositing the drop and tilting the plate. As it is shown in Figure 4-15, the aging of the calcite plate for 3 weeks makes it more oil wet.

Figure 4-14 RCA and ACA for 0.05 wt. % C₅⁺ asphaltene in MO at (a) time zero (a) and (b) after 4 days. Calcite plate aged for one week at 120°C in test fluids.
The CA test results are the equilibrated CA and as an example, the RCA/ACA for C₅⁺ asphaltene in MO in 0.1M NaCl brine after 3 weeks aging in test oil is shown in Figure 4-16. The RCA and ACA are 139° and 162° at time zero, see Figure 4-16.a. The equilibrated RCA and ACA are 135° and 142° after 4 days, see Figure 4-16.b.

![Figure 4-15 RCA and ACA](image)

**Figure 4-15 RCA and ACA, 0.05 wt. % C₅⁺ asphaltene in MO, 0.1M NaCl, 1 and 3 weeks aging at 120 °C.**

![RCA and ACA](image)

**Figure 4-16 RCA and ACA for 0.05 wt. % C₅⁺ in MO at (a) time zero and (b) after 4 days. Calcite plate aged for three weeks at 120 °C in test fluids; C₅⁺ in MO and 0.1M NaCl.**
4.3.2.3. Effect of asphaltene concentration and its solvent

Two samples containing 0.05 wt. % C$_{5+}$ asphaltene were tested, one dissolved in Toluene and the other in MO. Two calcite plates were aged in test fluids, 0.05 wt. % C$_{5+}$ asphaltene in MO or toluene and 5M NaCl brine, for two weeks at 120°C; aging vessels were filled with brine (¼) and test oil. RCA and ACA were measured by depositing the drop and tilting the plate. Based on the test results, Figure 4-17, and as it was expected, asphaltene in MO make the calcite plate more oil wet in comparison with the asphaltene in toluene. Toluene is a better solvent for asphaltene in comparison with the mixture of n-C12 and toluene. In case of using MO, precipitation of asphaltene may happen due to the presence of 87 vol. % n-C12 in addition to the adsorption by the ionic attraction.

![Figure 4-17](image.png)

Figure 4-17 Effect of asphaltene media on wettability alteration, RCA and ACA in 5M NaCl after 2 weeks aging.

Since the C$_{5+}$ asphaltene content of the actual crude oil was 2.1 wt. %, in the next test the asphaltene content was increased from 0.05 wt. % to 2.1 wt. %. The CA was measured for
two samples; 0.05 wt. % C₅⁺ asphaltene in toluene and 2.1 wt. % C₅⁺ asphaltene in toluene; in 5M NaCl brine after 2 weeks aging at 120 °C. Based on Figure 4-18, by increasing the asphaltene concentration, the calcite is more oil wet since more asphaltene adsorbed into the calcite surface.

![Figure 4-18 RCA and ACA, 0.05 and 2.10 wt. % C₅⁺ asphaltene in Toluene. Calcite plates aged for 2 weeks at 120 °C in test oil and 5M NaCl.](image)

4.3.2.4. Effect of different asphaltene fractions

Asphaltene has the greatest effect on wettability alteration among the other crude oil fractions because it is the heaviest and most polar component in the oil and has a tendency to aggregate and separate from the oil fractions. It can be fractionated based on its solubility in different n-alkanes. In order to compare the effect of asphaltene fraction with a different structure, C₅⁺ (asphaltene precipitated by pentane) and C₅-₆ (asphaltene soluble in hexane and insoluble in pentane, considered as the most soluble fraction of asphaltene) fractions were chosen. Two calcite plates were aged in test fluids, 0.05 wt. % of C₅-₆ and
C$_5^+$ asphaltene in MO and 0.1M NaCl brine, for one week at 120°C; aging vessels were filled with brine (¼) and test oil. RCA and ACA were measured by depositing the drop and tilting the plate. Test results are shown in Figure 4-19, C$_5^+$ asphaltene made the calcite plate more oil wet; this was as expected since such fraction is heavier and more aromatic than C$_{5-6}$ fraction.

![Figure 4-19](image.png)

Figure 4-19  RCA and ACA of C$_{5-6}$ and C$_{5^+}$ asphaltene in MO at 0.05 wt. % (Test fluid). Calcite plates aged for one week at 120°C in test fluid and 0.1M NaCl brine.

4.3.2.5. Comparing the effect of resin and asphaltene

Crude oil contains different hydrocarbons which can be fractionated to 4 parts called SARA (saturate, aromatic, resin and asphaltene), based on their solubility and polarity. Among these 4 fractions, resin and asphaltene$^{102}$ are responsible for wetting alteration in the presence of carbonate reservoir because of the carboxylic acid groups$^{97}$. Resin and asphaltene are negatively charged in the crude oil sample while the calcite plate is
positively charged below a pH of about $9.5^{131,132}$. Negatively charged acidic species of resin and asphaltene adsorb to the calcite surface because of the electrostatic attractions.

Based on SARA analysis, the SA6 crude oil contains 8 wt. % resin and 2.1 wt. % C$_5$+ asphaltene. Figure 4-20 compares the result of RCA/ACA for crude oil and its fractions. The CA was measured in 5M NaCl brine and the aging time was 1 week. It is found that 2.1 wt. % C$_5$+ asphaltene in toluene altered the wettability more than the 8 wt. % resin in Toluene. This has been expected because asphaltenes as the heaviest and most polar components of oil have the greatest impact on wetting alteration$^{133}$. Also, Gonzalez and Moreira 1991 showed that asphaltene has a greater effect on wettabillity alteration in comparison with resin fraction$^{134}$.

![Figure 4-20 Effect of SA6 oil and its surface active fractions (asphaltene and resin) on wetting alteration.](image-url)
4.3.2.6. Summary of results

For contact angle measurement method, the tilting plate was adopted to keep the volume of droplet constant and prevent skin formation. Table 4-4 is a summary of the test results of contact angle measurement for asphaltene samples.

- As expected RCA < ACA

Table 4-4 Summary of the ACA and RCA result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Operating condition</th>
<th>RCA (Degree)</th>
<th>ACA (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 wt. % in MO</td>
<td>Aging 120 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaCl Brine (M)</td>
<td>Time 0</td>
<td>After equilibration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>153°</td>
<td>145°</td>
</tr>
<tr>
<td>C₅⁺ asphaltene</td>
<td>1 week 5</td>
<td>149°</td>
<td>139°</td>
</tr>
<tr>
<td></td>
<td>2 weeks 5</td>
<td>150°</td>
<td>140°</td>
</tr>
<tr>
<td></td>
<td>0.1 76°</td>
<td>140°</td>
<td>180°</td>
</tr>
<tr>
<td></td>
<td>0.1 139°</td>
<td>135°</td>
<td>162°</td>
</tr>
<tr>
<td>C₅₋₆ asphaltene</td>
<td>1 week 0.1</td>
<td>144°</td>
<td>11°</td>
</tr>
<tr>
<td></td>
<td>0.1 44°</td>
<td>11°</td>
<td>65°</td>
</tr>
</tbody>
</table>

- Calcite plate becomes more oil wet by increasing the aging time from 1 week to 3 weeks.
- Three weeks of aging time and testing with 0.1M NaCl brine produces similar wettability alteration as 1 week aging time with 5M NaCl brine.
- C₅⁺ asphaltene fraction makes the calcite plate more oil wet because it is heavier and has a higher aromaticity index than C₅₋₆ fraction.
As expected, the calcite plate becomes more oil wet by increasing the aging time from 1 week to 3 weeks in case of testing with 0.1M NaCl brine and 0.05 wt. % C$_{5+}$ asphaltene in MO.

Brine concentration have a significant effect on the wettability alteration of calcite plate. By increasing the brine concentration from 0.1M to 0.5M NaCl, the calcite plate becomes more positively charged which resulted in higher ACA and RCA for oil sample.

By changing the media of asphaltene from MO to toluene, C$_{5+}$ asphaltene in toluene wets the calcite less because toluene is a better solvent for the asphaltene than MO. Asphaltenes have more tendency to come out of the solution when in MO than when in toluene, for adsorbing into the calcite surface, because of the presence of n-dodecane in MO.

Studying the effect of crude oil fractions on wettability alteration. Test results from comparing the RCA and ACA of

- SA6 crude oil
- 8.0 wt. % Resin in toluene
- 2.1 wt. % C$_{5+}$ asphaltene in toluene
- 0.05 wt. % C$_{5+}$ asphaltene in toluene
- 0.05 wt. % C$_{5+}$ asphaltene in MO

have indicated that (a) The resin fraction of crude oil has smaller effect on wettability alteration in comparison with the C$_{5+}$ asphaltene and (b) C$_{5+}$ asphaltene in MO makes the calcite plate more oil wet in comparison with C$_{5+}$ asphaltene in Toluene; thus, when in a ‘poor’ solvent the C$_{5+}$ asphaltene fraction wets calcite more than when in a ‘good’ solvent such as toluene.
4.3.3. Effect of low salinity brine aging on wettability properties of calcite plates

by CA measurement at room temperature

After developing the CA measurement method and determining the effect of crude oil and its fraction on wettability properties of calcite plate, the effect of low salinity brine aging (0.164M NaCl) is presented in this part.

RCA and ACA were measured after calcite plates were aged at 120°C with test oil in the presence of 5M NaCl brine. Also, RCA and ACA were measured after 5M NaCl brine (control) and 0.164M NaCl brine (low salinity) aging. The process of aging is as follow:

4.3.3.1. Procedure of calcite preparation, oil aging step, and smart water aging

- Rinsed calcite plate with toluene and acetone.
- Polished calcite plate in the presence of DI water with 600 (3 min.) and 1200 (3 min.) paper grit.
- Rinsed plate with DI water and after that with test brine.

Aging calcite plate at 120°C:

- Left calcite in brine overnight at room temperature.
- Equilibrated oil and brine overnight at 120°C.
- Took calcite out of brine, controled the water layer thickness by a spin coater (V=50 rpm for 20 s) and inserted it into an aging vessel containing oil and some test brine.
• Aged calcite in oil in the presence of test brine (¼ of fluid is brine) for 2 weeks at 120°C.

**Removing the bulk oil from calcite plate:**

• Removed calcite from the vessel and soak it in cyclohexane for 10 minutes.

• Took calcite out of cyclohexane and insert in a humidity control chamber until solvent completely evaporates.

• Immersed calcite in test brine and after 5 min started the CA measurement.

**Control brine aging (5M NaCl)**

• Aged the oil treated calcite in 5M NaCl brine for two weeks at 120°C.

• Removed calcite from the vessel and soaked it in test brine and start the measurement after 5 min.

**Low salinity brine aging (0.164M NaCl)**

• Aged the oil treated calcite in 0.164M NaCl brine for two weeks at 120°C.

• Removed calcite from the vessel and soaked it in test brine and started the measurement after 5 min.

*These two steps of aging were done after the oil aging.

Six oil samples were tested as specified in the following:

1) **Model Oil** (87 vol. % n-Dodecane + 13 vol. % Toluene),
2) 0.05 wt. % C₅⁺ asphaltene in Toluene,
4) 0.05 wt. % C₅⁺ asphaltene in MO,
4) 2.1 wt. % C₅⁺ asphaltene in Toluene,
5) SA6 crude oil, and
6) SB4 crude oil.

4.3.3.2. Comparing the result of contact angle for mode oil and crude oil samples before and after low salinity brine aging

The results of contact angles after oil aging, control brine aging (5M NaCl) and low salinity brine aging (0.164M) are shown in Figure 4-21. All calcites become oil wet after being oil aged in the presence of 5M NaCl, represented by blue and grey bars. The calcites become more water wet when aging in only 5M NaCl brine after the process of oil aging, represented by purple and green bars.

For all the samples, except 2.1 wt. % C₅⁺ asphaltene in toluene, the results indicate that by aging in low salinity brines after the process of oil aging, the calcite wettability reverses from oil-wet to water-wet, represented by red and yellow bars. In case of 2.1 wt. % C₅⁺ asphaltene, the onset point of asphaltene precipitation is lower (13.3 vol. %) in comparison with SA6 (24.2 Vol. %) crude oil (means that the asphaltene is more unstable) which can be one explanation for staying oil wet even after low salinity brine aging. Asphaltene onset point (shown in Figure 4-22) was measured by an indirect method which is described in chapter 5. Additionally, it is shown in the next section that the adsorption capacity for the calcite which was aged in 2.1 wt. % C₅⁺ asphaltene in toluene was the highest among the tested samples.
Figure 4-21 RCA and ACA measured at ambient conditions in oil-aged calcite plates, Oil aged + 5M NaCl aged, Oil aged + 0.164M NaCl aged.
4.3.4. Characterization of adsorbate fractions on calcite surface

4.3.4.1. Adsorption of surface active components on to the calcite surface during the oil aging

Crude oil components, asphaltene, and resin can alter the wettability\textsuperscript{103,131} as explained below:

- Polar interactions between crude oil components and solid mineral surfaces that occur in the absence of water.

- Ionic interactions depend on the compositions of oil, brine, and solid surface, as well as on temperature and aging time. To study the oil composition, it is essential
to determine the oil acid, and base number as both of them play an important role in altering the wettability.

- Acid/base interactions are between ionized acidic and basic sites.
- Surface precipitation depends on the solvent quality (media that asphaltene is dissolved in it) and its effect on wettability alteration by asphaltene precipitation.

In order to have a better understanding of the mechanism of the calcite plate wettability changing behavior after aging in different crude oil fraction, it is decided to study the characteristic of the surface of calcite plate before and after aging process.

To study the characteristic of adsorbate for SA6 surface active fractions, five different samples were chosen, and the plates were aged in these samples at 120°C for two weeks in the presence of 5M NaCl brine.

- 8.0 wt. % Resin in Toluene
- 0.05 wt. % C₅⁺ in MO
- 0.05 wt. % C₅⁺ in Toluene
- SA6 crude oil (Asphalten content: 2.1 wt. %)
- 2.1 wt. % C₅⁺ in toluene

After two weeks the plates were taken out of the aging vessel and soaked in cyclohexane for 1 hr to remove the bulk of oil. In Figure 4-23, there are pictures of the plates after taking them out of cyclohexane.
4.3.4.2. Desorption of surface active components from the calcite surface

To enable separation of the adsorbate species from the calcite plate, the plates were rinsed with dichloromethane (DCM), toluene, and acetone. The solvent was evaporated, and the remained solid species were weighted to calculate the amount of adsorbate. In Figure 4-24 there are pictures of the plates after rinsing with the solvents.
Since the adsorbates are not washed completely from the plates, the plates were washed in soxhlet by the hot solvent. After cooled, the solvent is left to evaporate for the quantification of the amount of adsorbate in it.

Table 4-5 is for disclosing the adsorbate amount after rinsing and washing in soxhlet. It is found that the amount of adsorbate and the adsorption capacity (defined based on equation 4-1) is the highest in case that the plate is aged in 2.1 wt. % C₅⁺ asphaltene in toluene. This is expected because the sample has the highest content of surface active component (2.1 wt. % C₅⁺ asphaltene). Besides the AOP of 2.1 wt. % C₅⁺ asphaltene in toluene is lower than SA6 oil which contains the same amount of asphaltene. The lowest amount of adsorbate is related to the case that the plate was aged in 0.05 wt. % C₅⁺ asphaltene in toluene (The amount was negligible). In this case, the amount of asphaltene is small, and the solvent was toluene, therefore, the asphaltene prefers to stay in the solution rather than adsorbing to the plate.

\[
\text{Adsorption capacity} = \frac{\text{Mass of adsorbate}}{\text{Adsorbent surface area}}
\]

\textbf{Equation 4-1}

Figure 4-25 shows how the adsorption capacity of calcite is related to wettability properties after aging in test oil samples. Based on the results, there is no trend between the adsorption capacity and the wettability properties of the substrate. This result is an indication of the following fact: Although the amount of surface active components adsorbed by the substrate is important, this is not the main reason for changing the wettability properties of a surface.
Table 4-5 Adsorption capacity of calcite plates in case of aging in four different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial mass of Resin/Asphaltene (g)</th>
<th>Mass of adsorbate (g)</th>
<th>Adsorbent surface area (cm²)</th>
<th>Adsorption capacity (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0 wt. % Resin in Toluene</td>
<td>1.60</td>
<td>0.001</td>
<td>16.34</td>
<td>6.1*10⁻⁵</td>
</tr>
<tr>
<td>0.05 wt. % C₅⁺ in MO</td>
<td>0.01</td>
<td>0.0015</td>
<td>14.46</td>
<td>1.1*10⁻⁴</td>
</tr>
<tr>
<td>0.05 wt. % C₅⁺ in toluene</td>
<td>0.01</td>
<td>-</td>
<td>22.52</td>
<td>-</td>
</tr>
<tr>
<td>SA6 crude oil (A: 2.1 wt. %)</td>
<td>2.02</td>
<td>0.004</td>
<td>20.4</td>
<td>1.9*10⁻⁴</td>
</tr>
<tr>
<td>2.1 wt. % C₅⁺ in toluene</td>
<td>0.25</td>
<td>0.006</td>
<td>21.5</td>
<td>2.8*10⁻⁴</td>
</tr>
</tbody>
</table>

Figure 4-25 Adsorption capacity versus RCA/ACA.
4.3.4.3. Determination of the chemical structure of adsorbate

To gain further understanding of the mechanism of changing the wetting condition of calcite plate by aging in different oil samples, the characteristic of the surface of calcite plate before and after the aging process was studies by using CNMR, FTIR, Energy-Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscope (SEM).

NMR spectroscopy

In order to compare the adsorbate structure, $^{13}$C and $^1$H NMR were used to find the aromaticity of adsorbate. Aromaticity is defined as the amount of aromatic hydrogen/carbon band divided by the aliphatic hydrogen/carbon band. The aromaticity of each sample is calculated by Equation 4-2$^{136,137}$.

$$ f_a = \frac{A}{A + B} $$

Equation 4-2

For the aromatic hydrogen content, A and B are equal to the integrals for the aromatic hydrogen band (from 5.0 to 10.0 ppm region) and aliphatic hydrogen band (from 0.5 to 5.0 ppm region), respectively. For the aromatic carbon content, A and B are equal to the integrals for the aromatic carbon band (from 100 to 170 ppm region) and aliphatic carbon band (from 10 to 70 ppm region), respectively.

To conduct NMR spectroscopy tests, the adsorbates were first washed from the plates based on the desorption step. Then the separated solid fractions were dissolved in deuterated chloroform (CDCl₃) solution with the concentration of approximately 1-15 mg diluted in 0.5 mL CDCl₃$^{138}$. 
The summary of 13C and 1H NMR results of carbon and hydrogen aromaticity are presented in Table 4-6. Based on the result, hydrogen and carbon aromaticity of 2.1 wt. % C₅⁺ asphaltene in toluene is the highest while the aromaticity for resin in toluene is the lowest. This result can be caused by the fact that asphaltene molecules have more aromatic rings in their structure and they can make bigger aggregate molecules.

Table 4-6 Aromaticity based NMR analysis

<table>
<thead>
<tr>
<th>Test sample</th>
<th>fa (¹H NMR)</th>
<th>fa (¹³C NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 wt. % C₅⁺ in toluene</td>
<td>0.33</td>
<td>0.61</td>
</tr>
<tr>
<td>0.05 wt. % C₅⁺ in MO</td>
<td>0.28</td>
<td>0.54</td>
</tr>
<tr>
<td>SA6 Crude Oil</td>
<td>0.26</td>
<td>0.35</td>
</tr>
<tr>
<td>8 wt. % Resin in Toluene</td>
<td>0.08</td>
<td>0.18</td>
</tr>
</tbody>
</table>

FTIR spectroscopy

FTIR analysis is a technique used to check the availability of organic material. Figure 4-26 is for disclosing the FTIR spectra of fresh calcite plate and four aged plates in different samples.

Based on the results, peaks observed in the range of 2800-3000 cm⁻¹ for all the calcites samples, are corresponded to the methyl and methylene C-H stretching vibrations. For the fresh calcite, the peak in this range is related to organic compound adsorbed by the surface when the dry calcite was exposed to the air.

The peak at 1700 cm⁻¹ is attributed to the carbonyl stretch (C=O)²⁶. The peak at 1602 cm⁻¹ corresponds to the aromatic C=C stretching vibrations. In clean calcite, there is no
adsorbed compound contained oxygen, therefore, there will be no peaks at 1700 cm\(^{-1}\) and also 1100 cm\(^{-1}\). Also, for the calcite which was aged in 0.05 wt. % C\(_5^+\) in toluene, there are no peaks at 1600 and 1700 cm\(^{-1}\) which shows that there is insignificant adsorbed asphaltene on the surface of calcite after the aging process.

For all the plates, there is a peak centered at 1410 cm\(^{-1}\) which is one of the characteristic absorption bands of carbonate group (an asymmetric stretch of carbonate ion)\(^{139}\). The difference between the peak at 1410 cm\(^{-1}\) for fresh and aged calcite is that peak in the fresh is broad while it is asymmetric for the aged calcite because of the presence of the carboxylic functional group. The peak at 1170 cm\(^{-1}\) corresponds to aliphatic C-O stretch. These two peaks only appear in the spectra of aged calcite plates. The bands in the range of 700-900 cm\(^{-1}\) are attributed to CO\(_3^−\) or the C-H rocking vibration of the methyl group in alkane compound or the C-H bending in alkene compound.
Figure 4-26  FTIR spectra; a. clean calcite, b. aged calcites in different oil samples.
SEM-EDS analysis

The tested calcite samples were: clean calcite, calcite aged in 2.1 wt. % C₅⁺ in Toluene, calcite aged in SA6 oil and calcite aged in SB4 oil.

Figure 4-27 and Figure 4-28 are for disclosing the SEM images of clean calcite and three aged plates in different samples. Figure 4-29 is representative of the texture of the clean polished calcite. The SEM images of the aged calcite plates reveal the adsorption of organic compounds on the surface. Figure 4-30, Figure 4-31, Figure 4-32 and Figure 4-32 are corresponded to clean calcite, calcite aged in SA6 oil, calcite aged in SB4 and 2.1 wt. % C₅⁺ in toluene. Also based on Energy Dispersive X-ray spectroscopy or EDS analysis, the points containing S and N are indications of the organic materials adsorbed by the calcite surface after the oil aging step.
Figure 4-27 SEM images of a. clean calcite, b. calcite aged in 2.1 wt. % Cs$^+$ in toluene, c. calcite aged in SA6 oil and d. calcite aged in SB4 oil. Scale bar =1 μm.
Figure 4-28 SEM images of a. clean calcite, b. calcite aged in 2.1 wt. % C5+ in toluene, c. calcite aged in SA6 oil and d. calcite aged in SB4 oil. Scale bar =10 μm

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.14-16.52-12.37-15.97-10.68</td>
</tr>
<tr>
<td>O</td>
<td>43.10-46.16-38.90-45.24-34.84</td>
</tr>
<tr>
<td>Al</td>
<td>0.05-0.09-0.05-</td>
</tr>
<tr>
<td>Si</td>
<td>-0.12- -0.09-0.03-0.02</td>
</tr>
<tr>
<td>Ca</td>
<td>41.72-37.19-48.65-38.71-54.47</td>
</tr>
</tbody>
</table>

Figure 4-29 Surface compositional analysis of clean calcite plate.
Figure 4-30 Surface compositional analysis of calcite aged in SA6 oil.

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>77.21</td>
<td>74.55</td>
<td>52.09</td>
<td>18.16</td>
<td>40.69</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>1.43</td>
<td>0.99</td>
<td>-</td>
<td>1.01</td>
</tr>
<tr>
<td>O</td>
<td>15.69</td>
<td>18.25</td>
<td>25.18</td>
<td>29.06</td>
<td>44.9</td>
</tr>
<tr>
<td>S</td>
<td>1.92</td>
<td>1.32</td>
<td>0.81</td>
<td>-</td>
<td>0.46</td>
</tr>
<tr>
<td>Ca</td>
<td>5.18</td>
<td>4.46</td>
<td>20.93</td>
<td>52.78</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Figure 4-31 Surface compositional analysis of calcite aged in SB4 oil.

<table>
<thead>
<tr>
<th>Elements</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>86.91</td>
<td>82.26</td>
<td>29.40</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>8.84</td>
<td>6.62</td>
<td>26.54</td>
</tr>
<tr>
<td>S</td>
<td>2.02</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>2.23</td>
<td>8.93</td>
<td>44.06</td>
</tr>
</tbody>
</table>
Test results of studying the adsorption capacity of calcite by aging plates in four different samples:

- 8.0 wt. % Resin in Toluene
- 0.05 wt. % C\textsubscript{5+} in MO
- 0.05 wt. % C\textsubscript{5+} in Toluene
- SA6 crude oil (C\textsubscript{5+} Asphaltene content: 2.1 wt. %)
- 2.1 wt. % C\textsubscript{5+} in toluene

The results indicate that the adsorption capacity of calcite was the highest when the plate was aged in 2.1 wt. % C\textsubscript{5+} in toluene because the sample has the highest content of the
surface active component and in comparison with SA6 (same amount of asphaltene) has the lower AOP.

Studying the structure of adsorbate by NMR spectroscopy. NMR spectroscopy has been done to evaluate the adsorbate structural characterization. Based on 13C NMR spectroscopy the aromaticity of adsorbate in case of C₅₊ asphaltene in MO is highest among all four cases. More sophisticated test results including FTIR and 13C NMR, tend to verify that what feature of a ‘poor’ solvent make asphaltenes exert the greatest effect on substrate conversion to oil wet.

The structure of adsorbate materials is successfully being studied by FTIR. It is shown that in case of clean calcite and calcite aged in 0.05 wt. % C₅₊ asphaltene in toluene, there are no peaks in 1700, 1600, 1100 cm⁻¹. While for the calcites aged in 0.05 wt. % C₅₊ in MO, SA6 and SB4 oils, the peaks at 1700, 1600 cm⁻¹ and 1100 cm⁻¹ are related to C=O, C=C in aromatic rings and C-O were observed.

The surface structure of calcite before (no organic compound adsorbed) and after oil aging step has been studied by SEM-EDS analysis. SEM images and EDS analysis revealed the organic adsorbed particles to the surface in which spots for C, N and S concentration is higher in comparison with the points that there was any adsorbed compound.

**4.4. Chapter summary**

Tilting plate method was chosen for the contact angle measurement method in order to keep the volume of droplet constant and prevent skin formation. The contact angle measurement procedure was improved by controlling the water layer thickness on the surface of calcite plate. The standard deviation of the contact angle measurements for MO
in 5M NaCl brine was improved from 30° (Vertical gravity drainage) to 15° (Spin coater, V=50 rpm for 20 s). Calcite tended to be more oil wet when the water layer thickness became thinner. By increasing and optimizing the equilibration time of calcite in brine before contact angle measurement, the calcite became more water wet.

It was shown that different parameters affect the wettability properties of a calcite plate. Calcite plate became more oil wet by increasing the aging time from 1 week to 3 weeks. Also, increasing the brine concentration caused to more oil wet condition. Between C$_{5+}$ and C$_{5-6}$ asphaltene fractions, C$_{5+}$ asphaltene produced more oil wet condition since it had higher aromaticity and heavier molecule. Comparing the effect of asphaltene and resin showed that asphaltene had greater effect on wettability properties. Since asphaltene was more stable in toluene, C$_{5+}$ asphaltene in toluene made the calcite more water wet in comparison with C$_{5+}$ asphaltene in MO.

Low salinity brine (0.164M NaCl brine) aging resulted in water wet condition for MO, C$_{5+}$ asphaltene in toluene/MO, SA6 and SB4 oil except for 2.1 wt. % C$_{5+}$ asphaltene in toluene which stayed oil wet after aging in 0.164M NaCl brine. Although SA6 has 2.1 wt. % asphaltene but the AOP for the SA6 oil was 24.2 vol. % heptane while for 2.1 wt. % C$_{5+}$ asphaltene in toluene was 13.3 vol. % heptane. Lower AOP in 2.1 wt. % C$_{5+}$ asphaltene which means more unstable asphaltene caused the oil wet condition for this case.

The surface characterization of adsorbate on the calcite after aging in 4 different samples (8 wt. % resin in toluene, 0.05 wt. % C$_{5+}$ in MO, 0.05 wt. % C$_{5+}$ in toluene and SA6 oil) was studied. The result indicated that the adsorption capacity of calcite was the highest
when the plate was aged in 2.1 wt. % C₅⁺ asphaltenes in toluene because the oil has the highest content of the surface active component.
Investigating the correlation between crude oil properties and oil recovery

5.1. Investigating the mechanism of enhanced oil recovery by low salinity brine

Low salinity water flooding is a common technique in enhanced oil recovery (EOR) processes which was first reported by Tang and Morrow 1997\textsuperscript{100,140}. Low salinity brine injection is preferred in different operating conditions since it does not require transferring the chemicals or any mixing processes like the other EOR technologies; chemical flooding technologies and thermal recovery\textsuperscript{141,142}.

Different hypotheses have been proposed to show the mechanism of low salinity water injection. There is no general agreement on the EOR primary mechanism by low salinity water flooding. Lager et al. 2008 showed that the main mechanism of enhanced oil recovery by low salinity flooding is cation exchange between the brine and mineral
surfaces and desorption of polar compound from the surfaces. McGuire et al. 2005 observed that the increase in alkalinity (pH increased from 7 to 9) is the controlling mechanism for improving the oil recovery by injecting low salinity brine. They showed that elevated pH could increase oil recovery by reducing the interfacial tension due to the decrease in the influence of capillary forces. Also, they stated that the other mechanism is the migration of clay particles from the core walls. Pu et al. 2010 tested sandstone and dolomite cores in spontaneous imbibition experiment and suggested that the dissolution of anhydrite is the controlling mechanism for increasing oil recovery with low salinity brine injection. While Zhang et al. 2018 showed that the main EOR mechanism is a detachment of clay particles and alkaline flooding may weakly affect EOR. Amirian et al. 2017 used clean and clay-coated glass model and found that increasing oil recovery by injecting low salinity brine can be explained by the expansion of the electrical double layer. In their argument, the electrical repulsion between the clay particles and oil increases once brine is added to the reservoir. When the clay-oil repulsion forces become higher than the binding forces the oil desorbs from clay particles. But they did not recognize any significant effect from fine migration. Song and Kovscek 2015 found that releasing the kaolinite particles from pore surfaces is the reason for the improved oil recovery in the clay coated glass micromodels. They injected low salinity NaCl brine especially when the concentration is less than 6000 ppm. In this condition desorption of clay particles help to increase the microscopic sweep efficiency by blocking the pore throats. This blocking finally resulted in increasing oil recovery. Emadi and Sohrabi 2013 investigated that the formation of water micro-dispersion at the oil-water interface in the presence of low salinity brine causes the increasing of oil recovery. They did not observe water micro emulsion formation in the
presence of high salinity brine. Their proposed hypothesis is that the formation of water micro dispersion in the presence of low salinity brine is caused by the release of surface active components at the interface of water/oil and coalescence of micro dispersion at the interface of oil/brine\textsuperscript{148}. They have used the FTIR spectroscopy and ESEM images to detect the water in oil micro dispersion formation. Also, they showed that at an elevated temperature of 90 °C there is slightly more chance of water micro dispersion formation\textsuperscript{149}. Alhammadi et al. 2017\textsuperscript{150} studied the effect of low salinity brine and formation of micro dispersion with two different crude oils in core flooding test. They observed the same mechanism; formation of water micro dispersion in the presence of low salinity brine for both carbonate and sandstone systems which caused the improved oil recovery\textsuperscript{150,151}. Micro dispersion formation hypothesis was tested and verified by Tetteh et al. 2017 as well \textsuperscript{152}. Sohrabi et al. 2012 and Mosavat and Torabi 2013 reported that viscosity reduction in oil/water system resulted in increasing oil recovery\textsuperscript{153,154}. Honarvar et al. 2017 stated that the main mechanisms for improving oil recovery in case of using carbonated water injection (CO\textsubscript{2} is dissolved in water before injection) are interfacial tension (IFT) reduction and oil swelling\textsuperscript{155}.

The focus of this chapter is investigating the mechanism of enhanced oil recovery by low salinity brine flooding in Indiana Limestone cores. The goal is to find if there is a correlation between intrinsic or extrinsic properties of crude oils and the recovered amount by low-salinity water. Figure 5-1 indicates relevant aspects considered for this study. Different studies have shown the importance of crude oil components on wettability alteration of mineral surfaces\textsuperscript{156,157}. In general asphaltene and resin play an important role in wettability properties due to their tendency to diffuse to water-oil interface. Also, they
can form stable water-oil emulsion\textsuperscript{103}. In order to study the effect of stability of asphaltene and its effect on oil recovery, the asphaltene onset point (AOP) (vol. % heptane) was measured. Micro-dispersion ratio in the presence of 0.164M and 5M was calculated to study the effect of water micro-dispersed emulsion on improving the oil recovery. In addition, the surface activity of the oil sample was defined by measuring interfacial tension in low salinity (0.164M) and high salinity (5M) brine.

**Figure 5-1 Is oil recovery correlated with …?**

### 5.2. Materials and methods

Density, water content and the total acid number of the crude oils tested in this study at ambient conditions are shown in Table 5-1. The crude A-H are real crude oil samples and MO I is a model oil which contains 0.05 wt. % C\textsubscript{5+} asphaltene in [87 vol. % n-dodecane + 13 vol. % toluene]. The crude oils were first centrifuged to remove any sediments and sand particles or water present in the system prior to their use. Then, the water content was measured by a Metrohm Karl Fischer titration apparatus (model 870 KF Titrino plus).
Densities were measured by Anton Paar DMA 4500 digital vibrating U-tube densitometer with a measuring range of 0-3 g/cm$^3$.

The total acid number of crude oil, as defined by American Society of Testing Materials (ASTM), is the quantity of base and it is expressed as the milligrams of KOH required neutralizing the acidic components in one gram of oil. The total acid numbers were determined by Fan and Buckley 2007\textsuperscript{109} method. Based on this method (Spiking method), it is possible to find the clear carboxylic acid inflection point. The acid number shows the amount of carboxylic acid groups present in the oil\textsuperscript{158}.

**Table 5-1 Crude oil properties**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>Density g/cm$^3$</th>
<th>Water content ppm</th>
<th>Total acid number mg KOH/g oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude A</td>
<td>Middle East</td>
<td>0.899</td>
<td>1300</td>
<td>0.57</td>
</tr>
<tr>
<td>Crude B</td>
<td>Malaysia</td>
<td>0.925</td>
<td>600</td>
<td>0.41</td>
</tr>
<tr>
<td>Crude C</td>
<td>Middle East</td>
<td>0.858</td>
<td>600</td>
<td>0.33</td>
</tr>
<tr>
<td>Crude D</td>
<td>Middle East</td>
<td>0.836</td>
<td>600</td>
<td>0.06</td>
</tr>
<tr>
<td>Crude E</td>
<td>-</td>
<td>0.874</td>
<td>500</td>
<td>0.15</td>
</tr>
<tr>
<td>Crude F</td>
<td>Middle East</td>
<td>0.852</td>
<td>700</td>
<td>0.11</td>
</tr>
<tr>
<td>Crude G</td>
<td>Middle East</td>
<td>0.836</td>
<td>900</td>
<td>0.17</td>
</tr>
<tr>
<td>Crude H</td>
<td>Middle East</td>
<td>0.807</td>
<td>400</td>
<td>0.15</td>
</tr>
<tr>
<td>MO I</td>
<td>Model oil</td>
<td>0.766</td>
<td>500</td>
<td>0.04</td>
</tr>
</tbody>
</table>

### 5.2.1. SARA analysis

SARA analysis was done based on the clay/alumina chromatography method which is described in chapter 2\textsuperscript{28}. In this method, asphaltene separation is based on modified IP-
143\textsuperscript{21} and maltene fractionation is based on a chromatography method\textsuperscript{28}. SARA analysis of the test oils is reported in Figure 5-2. The standard deviation (SD) in this method is 2.1 wt. \% for saturate, 1.2 wt. \% for aromatic, 1.1 wt. \% for resin and 0.05 wt. \% for asphaltene fractions.

![Bar chart showing SARA analysis of Crude A-H.](image)

**Figure 5-2 SARA analysis of Crude A-H.**
5.2.2. Spontaneous imbibition test

In the spontaneous imbibition tests, the effects of brine salinity, oil composition and the brine/oil/rock pre-equilibration on wettability alteration were investigated. The cores (Indiana Limestone) were initially saturated with high salt brines and then saturated with the crude oil sample, following by oil aging in 120 °C aiming to restore the oil-wetness. The oil-wet cores were first put into dry Amott imbibition cells. Then the cells were initially filled with the brines (5M NaCl) and transferred into a water bath at 90 °C. The skinny part of each Amott cell was left out of the hot water and further elongated by connecting a long and skinny glass pipette that acts as a condenser and minimize the evaporation of recovered oil in the cell. The recovered oil was read every day through the graduated part of the Amott cell. The initial brine was switched to the low salinity brine (0.164M NaCl) after the oil reading was stable for at least 5 days. The oil recovery data in 5M NaCl and additional oil recovery after changing brine from 5M to 0.164M are shown in Figure 5-3.

---

3 This experiment was done by Jin Song at Rice University.
5.2.3. Water micro-dispersion formation measurement

Water micro-dispersion formed after the oil sample was mixed or put in contact with low salinity brine. The following procedure was followed to measure the water content in the oil sample after mixing with low and high salinity brine to investigate the formation of micro dispersion. Samples were prepared in 10cc borosilicated pipettes with their tips first sealed by an oxygen-acetylene torch. After filled pipettes with test oils and brines at Water/Oil=1, they were torch sealed at their tops and mounted in a rotisserie-type mixer for gently mixing their content, end-to-end for 24 hours at ~ 6RPM. The schematic for the micro dispersion test procedure is shown in Figure 5-4.
5.2.4. Asphaltene onset point of precipitation (vol. % of Heptane)

To study the effect of stability or instability of asphaltene on the oil recovery, asphaltene onset point (AOP) of precipitation (vol. % of C7) was measured. AOP was measured by an indirect method proposed by Tavakkoli et al. 2015. In this method, a different amount of heptane is added to the oil; then oil is aged (1 day was chosen as the aging time). After one day of aging the samples are centrifuged to remove the asphaltene particles of 100 nm and above. After the centrifugation, the supernatant is withdrawn and diluted by toluene. Then the absorbance of the solution is measured by a spectrometer with the wavelength range of 700-1100 nm. The measured absorbance values were corrected to remove the effect of dilution.
5.2.5. IFT measurement

Oil-brine IFT measurements were conducted by DSA100 from KRUSS at room temperature. IFT of crude oils against 0.164M and 5M NaCl brine was measured. The brines were equilibrated with calcium carbonate powder, and the pH of both was 9.5. After oil drop was created, IFT changes were recorded until reaching a steady value after about 1 hour.

5.3. Result and discussion

Crude A-H and MO I are being studied for finding what is the reason for different oil recovery and what is the mechanism of improving oil recovery by changing brine from high to low salinity. To investigate the mechanism three different parameters “micro dispersion ratio”, “asphaltenes onset point of precipitation” and “interfacial tension” were measured.

5.3.1. Effect of water micro dispersion formation

The potential of forming “water-micro dispersion” in oil sample has been studied for the Crude A-H and MO I (0.05 wt. % C₃₅ asphaltene in n-dodecane + toluene). The water content in the test oil, after mixing it with 0.164M and 5M NaCl brine, and micro dispersion ratio is disclosed in Table 5-2. Micro dispersion ratio is defined as the ratio of water content in oil after being mixed with brine to the water content of original oil sample.

As depicted in Table 5-2, there were significant changes in water content for crude oil B, A and C when mixed with 0.164M NaCl brine while the water-content differences were
insignificant when these oils were mixed with 5M NaCl brine. In case of crude B and G and MO I there was insignificant changes in water content when they were mixed with either 0.164M or 5M.

Table 5-2 Water content of test oils before and after mixing with 0.164M or 5M NaCl brine.

<table>
<thead>
<tr>
<th>Test oil</th>
<th>Water Content in Oil ppm</th>
<th>Micro dispersion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>“As is.”</td>
<td>After mixing with</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5M NaCl</td>
</tr>
<tr>
<td>Crude A</td>
<td>1300</td>
<td>2100</td>
</tr>
<tr>
<td>Crude B</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Crude C</td>
<td>600</td>
<td>1400</td>
</tr>
<tr>
<td>Crude D</td>
<td>600</td>
<td>1100</td>
</tr>
<tr>
<td>Crude E</td>
<td>500</td>
<td>900</td>
</tr>
<tr>
<td>Crude F</td>
<td>700</td>
<td>900</td>
</tr>
<tr>
<td>Crude G</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>Crude H</td>
<td>400</td>
<td>750</td>
</tr>
<tr>
<td>MO I</td>
<td>500</td>
<td>500</td>
</tr>
</tbody>
</table>

Shown in Figure 5-5 is an example of the test results: a, b and c corresponds to crude oil G, B, and E after mixing with 5 and 0.164M brine, respectively.
The test result of additional oil recovery by spontaneous imbibition and micro dispersion ratio is disclosed in Figure 5-6. This is constructed to determine a potential correlation among studied variables. As it is shown the oil recovery increases by increasing micro-dispersion ratio (Increasing micro-dispersed water content). Highest oil recovery corresponds with the highest micro dispersion ratio (Crude A). The only exception is crude oil B that has no asphaltene content. Since there is not any asphaltene present in the crude B the water emulsion formed in oil is unstable (too short-lived) which may be the reason for crude B to be an outlier for this test.
As shown in Figure 5-7, there is a correlation between the amounts of micro dispersed water in the oil and additional oil recovery.

Sohrabi et al. 2017 in Heriot-Watt University have previously proposed the oil recovery by low salinity brine can be related to the formation of water micro-dispersions in oil. Micro-dispersion formation plays an important role in how much the low salinity brine can increase the oil recovery. This is due to the interaction between polar components of the oil with brine. They demonstrated that the crude oils which have the potential of forming water-oil micro-dispersion have higher additional oil recovery by low salinity brine flooding\textsuperscript{147,150,151}. Sohrabi et al. 2016\textsuperscript{159} showed that the wettability alteration toward more water wet condition by low salinity water flooding is caused by the micro dispersion formation in the oil which is in contact with low salinity brine. Also, they mentioned that the micro dispersion formation causes desorption of surface active components from the
rock surfaces. Our hypothesis is that when the micro dispersed water content is greater than in “as is” oil, it is interpreted as the formation of water micro-dispersion in the oil phase. The micro-dispersion formed as a water molecule which is surrounded by surface active components of the oil (asphaltene and resin). As a result of micro dispersion formation, there is a higher tendency for the surface-active components (polar group) to stay in the oil media or at the interface of water/oil rather than diffusing to the rock surfaces.

![Figure 5-7](image-url)

**Figure 5-7 Additional oil recovery versus micro dispersion ratio.**

Among crude oil fractions, asphaltene and resin are responsible for wettability alteration and formation of micro dispersion. The effect of asphaltene and resin on the micro dispersed water ratio is showed in Figure 5-8.

Based on these results, there is no trend between the “micro dispersion ratio” and the “asphaltene + resin” content, while there is a correlation between the asphaltene content and micro dispersion ratio (Figure 5-9). Asphaltene molecules in crude oil have higher
influence in the oil/brine molecular interactions since they have a greater dipole moment (3.3-6.9 D) in comparison with the resin fraction (2.4-3.2 D). Therefore, in the presence of resin fractions, the micro dispersion is not stable. Also, this can be an explanation for crude oil B to be an outlier in the correlation between micro dispersion ratio and additional oil recovery.

Figure 5-8 Effect of “asphaltenes + resin” on “micro dispersion ratio” @ 0.164M NaCl.
Since resin fractions stabilize the asphaltene in oil and keep the asphaltene dispersed in the oil sample\textsuperscript{160}. Therefore in the relationship between asphaltene/resin ratio and micro dispersion ratio is shown Figure 5-10. Approximately the correlation found between asphaltene versus micro dispersion formation and asphaltene/resin ratio versus micro dispersion ratio is the same. The results confirm that asphaltene has greater effect on water micro dispersion formation in comparison to the resin.

**Figure 5-9 Effect of asphaltene on micro dispersion formation @ 0.164M NaCl.**
5.3.2. Effect of asphaltene stability by measuring asphaltene onset point of precipitation (vol. % of Heptane)

Asphaltene deposition on the rock reservoirs plays an important role in altering wettability properties of the rock surfaces. The beginning point of asphaltene separation from the oil media is called asphaltene onset point (AOP) of precipitation. In the reservoir when the pressure is higher than the AOP, asphaltene is soluble in the oil phase while the pressure drops below the AOP, asphaltene precipitates out of the oil solution. The precipitated asphaltenes molecules aggregate and deposit on the surface\textsuperscript{161}. It has been reported in different studies that asphaltene deposition can change the wettability properties of the rock surfaces from water wet toward oil wet condition. Uetani 2014 observed that when the pressure in the system dropped below the AOP pressure, asphaltene molecule aggregate and diffuse to the water layer on the silica surface. The water film becomes unstable, and
a rupture happens in the water film. As a result, more asphaltene adsorbs to the surface and makes the silica surface oil wet\textsuperscript{162}.

The AOP of the test oil and total oil recovery are shown in Figure 5-10. It is concluded that there is no direct correlation exists between the oil recovery and asphaltene onset point of precipitation. In this experiment, crude D and F are the outliers. AOP is an indication of the precipitation point of asphaltene which is necessary but not sufficient for asphaltene deposition. Asphaltene deposition is a complex process controlled by different parameters such as compositions of reservoir fluid (oil and brine), temperature, pressure, rock surface properties, and particle size\textsuperscript{161}. Therefore, it is important to investigate the stability of asphaltene by AOP, but it is not the controlling parameter in changing the wettability properties.
5.3.3. Effect of Interfacial tension

IFT results of crude oils against 0.164M and 5M NaCl brine are reported in Figure 5-12. IFT in high salinity brine (5M) is lower than IFT in low salinity brine (0.164M). Several studies have confirmed that by increasing brine concentration IFT decreases. Serrano-Saldana et al. 2004 showed that in n-dodecane/brine system the IFT decreases by increasing surfactant concentration\textsuperscript{163}. Increasing the salt concentration decreases the thickness of electrical double layer and weakens the charges of polar head groups at the interface\textsuperscript{127}. As a result more surface active components adsorb at the oil brine interface that decreases the IFT\textsuperscript{93,164–166}. 

**Figure 5-11 Total oil recovery and asphaltene onset point of precipitation, (vol. % C7)**
IFT between oil and brine played an important role in oil recovery amount\textsuperscript{155}. In order to characterize and understand the effect of IFT on wettability alteration, the IFT changes versus total/ additional oil recovery are shown in Figure 5-13 and Figure 5-14. The reported IFT in the following figures is related to IFT in 0.164M NaCl brine which was equilibrated with calcium carbonate with a pH of 9.5. Based on the result shown in Figure 5-13, a decent correlation exist between the total oil recovery and IFT changes. The results presented in Figure 5-13 and Figure 5-14 show that the samples with lower IFT have higher oil recovery. By increasing IFT which is equal to decreasing the surface active components at the oil/brine interface the total oil recovery decreases. Also, it has been shown by the other studies that decreasing the interfacial tension between oil and water results in decreasing the capillary forces and increasing the oil recovery\textsuperscript{167}.

\[\text{Figure 5-12 IFT of different oils against 0.164 and 5M NaCl brine.}\]
Figure 5-13 Total oil recovery versus IFT of Crude A-H and MO I in 0.164M NaCl brine.
Figure 5-14 Additional oil recovery versus IFT of Crude A-H and MO I in 0.164M NaCl brine.

Crude oil G and H show significantly higher oil recovery in 5M NaCl brine in comparison with the other oil samples. This can be caused by the fact that the cores are water wet from the starting point of spontaneous imbibition test. In order to study the effect of low salinity water flooding on oil recovery, it is expected to have oil wet or mixed wet cores. Therefore, the points for crude oil G and H are removed in Figure 5-15 and Figure 5-16 in order to have a fair comparison between oil recoveries in different crude samples. Based on these result a consistent relationship can be drawn from IFT and additional/total oil recovery. We have two hypotheses to describe the correlation between the additional oil recovery and IFT.

Hypothesis 1: Different amount of interfacially active components result in different IFT values. When the amount of surface active components increases at the interface of oil/brine the IFT decreases. Samples with lower IFT have more surface active...
components (asphaltene and resin) at the oil/brine interface while samples with higher IFT have a lower amount of surface active components at the oil/brine interface. In crude oil samples with lower IFT in the presence of low salinity brine, natural surface active components prefer to be adsorbed by the oil/brine interface rather than being attracted by the core surface, leading to higher oil recovery. Besides, in the oil samples with higher IFT, the oil recovery is lower which means that more surface active components are adsorbed by the substrate.

**Hypothesis 2:** In oil sample with lower IFT, there are surface active components with bigger polar head groups. Therefore, the adsorbed components can detach from the oil/brine interface because of the strong repulsion between the polar head groups. During the detachment of polar groups from the interface, the water micro dispersion will form in oil. However, the repulsion between the head groups is reduced in samples with higher IFT. For oil with higher IFT, the adsorbed components at the interface have a longer tail that causes positive tail-tail interactions. This attractive forces causes the surface active material to remain at the oil-brine interface.

To examine the validity of the above hypothesis, the IFT versus micro dispersion formation ratio at 0.164 M NaCl brine is shown in Figure 5-17. There is a correlation between formation of micro dispersion and IFT at 0.164M NaCl brine. Which this result confirms the previously mentioned hypothesis. This result indicates that the crude samples with lower IFT are more capable of forming water micro dispersion at the oil phase which resulted in higher oil recovery.
Figure 5-15 Total oil recovery versus IFT of Crude A-F (without crude G) and MO I in 0.164M NaCl brine.

R² = 0.7807
Moreover, to ensure that the IFT data at low salinity brine (0.164M) is not affected by any contamination in the oil sample such as having any surfactant, the IFT of oils are measured
in 0.164M NaCl brine which is not equilibrated with calcium carbonate powder (pH=7.1). Interfacial tension of the oil samples is often between 18-32 mN/m with the error ±15%. Figure 5-18 shows the IFT of crude A-H as a function of time. Also, Figure 5-19 compares the IFT at 0.164M NaCl brine before and after equilibration with calcium carbonate powder. As it was expected the IFT of the oil samples before equilibration is between 15-30 mN/m and the IFT in non-equilibrated brine is higher than IFT in equilibrated brine. The surface activity of the ionized species such as naphthenates will increase if the pH increases from 7 to 9.4. As a result, there is more affinity for the surface active components to adsorb at the oil /brine interface.
Figure 5-18 IFT versus time in 0.164M NaCl brine (not equilibrated with calcium carbonate powder).

Figure 5-19 Comparison IFT in 0.164M before and after equilibration with calcium carbonate powder. $pH_{Eq}=9.5$ and $pH_{Neq}=7.1$

Among crude oil fractions, asphaltene and resin have polar groups which are responsible for changing the IFT. The relationship between the asphaltene plus resin and only asphaltene content versus IFT are illustrated in Figure 5-20 and Figure 5-21. No clear trend
has been observed between IFT in 0.164M NaCl brine and asphaltene plus resin contents or asphaltene content. The results indicate that the whole asphaltene and resin are not interfacially active. Therefore, fractionating the asphaltene and resin based on their surface activity properties can be an interesting future work which is described more in detail in chapter 6.

![Figure 5-20 IFT in 0.164M NaCl brine versus asphaltene + resin content.](image)
Figure 5-21 IFT in 0.164M NaCl brine versus asphaltene content.

5.4. Chapter summary

In this chapter, SARA analysis of crude oil was performed, and several parameters including, micro dispersed water content in oil after it mixed with brine (0.164M and 5M), asphaltene onset point of precipitation and oil-brine interfacial tension were measured to study their potential correlation with oil recovery. We showed that there are correlations between some of the crude oil properties and its oil recovery from spontaneous imbibition test.

According to test results, this study is in the right direction to elucidate some of the main parameters affecting oil recovery by low-salinity water flooding.

- Micro dispersion formation is one of the important effective parameters in improving the oil recovery by low salinity brine. Formation of micro dispersion water is related to the interaction between the polar component of crude oil and low salinity brine. Crude oil with highest micro-dispersion ratio and most stable
asphaltene in solution (highest asphaltene detection point) has the highest oil recovery from spontaneous imbibition test (Crude oil A).

- Except for oil D, which has no asphaltene, additional oil recovery increased by increasing the micro dispersion ratio. Our hypothesis is that the water micro dispersion formed in oil with no asphaltene is not stable.

- Asphaltene precipitation and deposition affects the wettability properties of the substrate. AOP was chosen previously to study the stability of asphaltene in the oil media. However, it is found that no direct correlation exists between AOP and total oil recovery.

- Interfacial tension has been found to decrease by increasing the NaCl brine concentration from 0.164M to 5M.

- The best correlation between oil recovery and crude oil properties is the relationship between IFT and oil recovery. The crude samples with higher IFT have lower oil recovery. By comparing the IFT of the samples at low salinity brine, crude with lower IFT has higher surface active components at oil/brine interface. It is concluded that in this condition the surface active components prefer to stay at the oil/brine interface rather than absorption by the substrate.

In conclusion, all the evidence in this study indicates that water-micro dispersion formation and interfacial tension play a dominant role in the mechanism of improving oil recovery by low salinity brine. Also, the correlation between micro dispersion formations with additional oil recovery appears to be not universal since the outlier is the crude oil that is free of asphaltene.
Chapter 6

Conclusions and recommendations

6.1. Conclusion

In this thesis, two novel fast and reliable chromatography methods are introduced for crude oil fractionation. Both approaches are based on column chromatography separation. Both techniques are faster, easier and use less solvent and sample in comparison with the available chromatography methods. The amount of solvent needed for desorption step is independent of the polar fractions content. In the “improved chromatographic technique” which is for maltene analysis, the solvent is recovered since there is a distillation column for washing the aromatic and resin fractions. In the “clay/alumina chromatography method” which is for SARA analysis the washing step is in soxhlet which only needs a specific amount of solvent (150 ml). These two methods are easy to perform, and they do not need any expert operator for analyzing the data. Although the time of process in the “improved chromatographic technique” is longer (5days) than clay/alumina
chromatography method (2 days) in this method, it is possible to collect the separated fractions for further analysis.

Asphaltene is one of the most problematic fractions of the crude oil due to its deposition in reservoirs that causes one of the most important flow assurance challenges. To mitigate this challenge, we fractionated it based on its solubility in n-alkane and characterized by its aromaticity and molecular weight distribution. A new approach is proposed for aromaticity calculation based on the elemental analysis, and the data was verified by comparing the result to the aromaticity based on FTIR method. Among asphaltene fractions, C₅₋₆ asphaltene as the most soluble fraction of asphaltene has the lowest aromaticity and narrowest molecular weight distribution. The importance of determining the aromaticity and molecular weight is for predicting asphaltene behavior by modeling.

The wettability property of the rock surfaces is important on the production flow and oil recovery efficiency. Contact angle measurement was used to study the effect of crude oil fractions on wetting properties of calcium carbonate reservoir. Tilting plate is chosen as an appropriate method for CA measurement. In this method there is not a problem of rigid film formation since the volume of the drop is constant and it is not changing by the time for RCA and ACA measurements. Because of the irreproducibility in CA data shown by our result and other research studies, the CA measurement method is modified by controlling the water layer thickness on the surface of the substrate. The standard deviation of the contact angle measurements for MO in 5M NaCl brine has been improved from 30° (Vertical gravity drainage) to 15° (Spin coater, V=50 rpm for 20 s). Calcite tends to be more oil wet when the water layer thickness became thinner. The effect of brine concentration, crude oil fractions and oil aging time are investigated. By increasing the oil
aging time from one week to three weeks and brine concentration from 0.164M to 5M the calcite plate wettability changes toward more oil wet condition. Among crude oil fractions, asphaltene and resin, asphaltene affect more on changing wettability properties of the substrate.

A hypothesis has been proposed to describe the enhancing oil recovery by low salinity brine injection. A consistent correlation is found between interfacial tension of the oil samples in 0.164M NaCl brine and their total/additional oil recovery. Oil sample with lower interfacial tension has more surface active components at the oil/brine interface which leads to less attraction between substrate surfaces and active components. As a result, an oil sample with lower IFT shows higher additional oil recovery. Furthermore, micro dispersion formation experiment reveals that the additional oil recovery is higher in samples which form water micro dispersion in contact with low salinity brine. A good correlation is found for micro dispersion ratio and additional oil recovery with one outlier (oil sample with no asphaltene). This inconsistency may be caused by the fact that in samples with no asphaltene the water micro dispersion is not stable.

### 6.2. Recommendation

**6.2.1. Effect of crude oil and low salinity brine aging on wettability properties of calcite by CA measurement at high temperature**

In this study, the CA measurement was done at room temperature. Since the temperature affects the activity of surface active components and their interaction to the rock surfaces. It is crucial to investigate the wettability properties of calcite at elevated temperature.
Therefore, we mimic similar conditions for CA measurement as those in spontaneous imbibition test and measuring the CA at reservoir temperature (120 °C). The following is the procedure that can be used for future work.

**Procedure**

RCA and ACA were measured after calcite plates were aged at 120°C with test oil in the presence of 5M NaCl brine. The process of aging is as follow:

**Oil aging**

**Preparation of previously tested calcite plate:**

- Rinse calcite plate with toluene and acetone.
- Polish calcite plate in the presence of DI water with 600 (3 min.) and 1200 (3 min.) paper grit.
- Rinse plate with DI water and thereafter with test brine.

**Aging calcite plate at 120°C:**

- Leave calcite in brine overnight at room temperature.
- Equilibrate oil and brine overnight at 120°C.
- Take calcite out of the brine, control the water layer thickness by a spin coater (V=50 rpm for 20 s) and insert it into an aging vessel containing oil and some test brine.
- Age calcite in oil in the presence of test brine for 2 weeks at 120°C.
Removing the bulk oil from calcite plate:

- Remove calcite from the vessel and soak it in Cyclohexane for 10 minutes.
- Take calcite out of Cyclohexane and insert in a humidity control chamber until solvent completely evaporates.
- Immerse calcite in test brine (5M) and after 5 min start the CA measurement.

Low salinity water aging (0.164M NaCl)

- Deposit oil drop under calcite in 5M NaCl brine at room temperature.
- Increase the temperature to 120 °C.
- After reaching equilibrated RCA, pump 0.164M NaCl slowly (0.05ml/min) to replace 5M NaCl brine from the cell.
- Record CA changes versus time till equilibration.
- Tilt the cell.
- Measure the RCA/ACA.

Brine preparation

- Purge brine with N2 bubbling.
- Add 100 ppm Carbohydrazole which dissolved easily while purging.
- For transferring brine into piston vessel, N2 atmosphere was kept over brine while pouring it into vessel.
• Close the vessel rapidly.

Discussion of test results

The first test was a control experiment in a clean calcite plate after aging it in 5M NaCl brine at 120 °C for 1 day, RCA/ACA of MO was measured. Images of the results are in Figure 6-1. It was challenging to deposit the MO drop on the surface of calcite which indicates that calcite surface is completely water wet--- drop was left contacting the calcite for about 15 minutes---.

![Image](image1.png)

**Figure 6-1 Measuring RCA/ACA of MO in 5M NaCl at 120 °C.**

The second test was done with C₅₊ asphaltene in MO. Calcite aged in 0.05 wt. % in MO was found oil wet (CA=165°) in 5M NaCl brine. By changing the brine salinity from high (5M) to low salinity (0.164M) brine, the calcite wettability properties did not change, as it is shown in Figure 6-2. The contact angle was 165° at 120 °C in 5M NaCl brine while by changing brine to 0.164M there were insignificant changes observed. Thus, this CA result is consistent with the imbibition test result. There was only ~4% oil recovery of 0.05% C₅₊ asphaltene in MO by spontaneous imbibition test when changing 5M with 0.164M NaCl brine.
Test results, from Receding and Advancing Contact Angle at high temperature (120 °C) made by mixing asphaltene fractions with a Model Oil, indicates that calcites are intermediate-to-oil wet after oil aging in the presence of 5M NaCl brine at 120°C. For case of only MO, free of surface-active components, calcite is water wet. While in the other case, 0.05 C₅⁺ asphaltene in MO the calcite after the oil aging become oil wet. For the low salinity brine injection, contact angle remains unchanged for 0.05 wt. % C₅⁺ asphaltene in MO when switching 5M brine by 0.164M NaCl, this finding is consistent with the poor oil recovered of ~4% by imbibition. Future efforts are needed to investigate the effect of low salinity water injection for different oil sample at elevated temperature and compare the result to oil recovery by spontaneous imbibition test.

6.2.2. Asphaltene deposition tendency on surfaces with different wettability properties

Another idea is evaluating asphaltene deposition tendency to different pure solid surfaces (defined based on reservoir rock) that can be characterized by their Hamaker constant. The Hamaker constant represents the difference between the adhesive interaction with a
substrate and the cohesive interaction with the bulk liquid. This work was proposed by Gonzalez\textsuperscript{171} which is based on the Lifshitz-Hamaker theory to predict the adhesion energy between liquid and solid and compares that with the cohesion energy of the liquid molecules. On the other side, contact angle measurement is helpful to study the wettability properties of reservoir surfaces. In principle, the value of contact angle indicates the competing tendencies between the cohesion energy of the liquid molecules and the adhesion energy between liquid and solid. Based on the above definition, we believe that evaluation of asphaltene-deposition tendency by Hamaker constant can be extended to predict wettability alteration by crude oil.

In order to study the asphaltene deposition tendency, it is assumed that the system has three phases; the asphaltene lean phase (solvent or crude oil phase), the precipitated asphaltene rich phase and the solid substrate. The asphaltene deposition tendency can be predicted by combining two Hamaker constants, $A_{SLR}$ and $A_{SRL}$, to compare the interactions between asphaltene lean phase ($L$), asphaltene rich phase ($R$) and solid substrate ($S$). Figure 6-3 is a cartoon for showing the approach of prediction of wettability alteration by measuring Hamaker constant ($A_{SLR}$ and $A_{SRL}$).
$A_{SLR}$ is the solid interaction with the rich phase in the media of lean phase. If it is positive, it means that the interaction between solid and rich phase is favorable and the rich phase sticks to the substrate. If it is negative, it means the rich phase does not like the substrate and, it is repelled from the substrate. Therefore, there would be any deposition problem in this case.

$A_{SRL}$ is the interaction between the solid and lean phase in the rich phase as the media. If it is positive, lean phase likes the solid and sticks to the solid. But if $A_{SRL}$ is negative only the rich phase likes the solid and spreads on the solid phase which causes severe problem of asphaltene deposition.

These two parameters, $A_{SLR}$ and $A_{SRL}$ help to predict the deposition tendency and wettability alteration of reservoir rock surfaces. The Hamaker constant of a pure substance can be calculated as a function of refractive index based on below Equation 6-1.
\[ A_{11} \approx \frac{3}{4} kT \left( \frac{n_1^2 - 1}{n_1^2 + 1} \right)^2 + \frac{3h\nu_e (n_1^2 - 1)^2}{16\sqrt{2} (n_1^2 + 1)^3} \]  

Equation 6-1

Where:

\( k \) is a Boltzmann’s constant.

\( h \) is a Plank constant \((6.63 \times 10^{-34} \text{ Js})\).

\( \nu_e \) is the main adsorption frequency in the UV region \((3.0 \times 10^{15} \text{s}^{-1})\).

\( n \) is the refractive index.

Also, it is possible to relate the refractive index to density by using one-third rule\(^{172}\) (Equation 6-2). Density can be evaluated by the equation of state, such as PC-SAFT. Therefore, by knowing the density of the phases, it will be possible to estimate the sticking-spreading tendency of the asphaltene. An Equation of State is often applied for predicting asphaltene precipitation and deposition amount. However, by correlating density to Hamaker constant and applying Lifshitz-Hamaker theory, it will be possible to predict phase equilibrium of asphaltenes, partitioning between bulk phase(s), and their sticking-spreading tendency by a unified EOS model.
Also, the combined Hamaker constant can be evaluated by using Hamaker constant of pure substances\(^{173}\) (Equation 6-3).

\[
A_{132} = \left( \sqrt{A_{11}} - \sqrt{A_{33}} \right) \left( \sqrt{A_{22}} - \sqrt{A_{33}} \right)
\]

Equation 6-3

Therefore, the combined Hamaker constant is calculated from the Hamaker constant of pure substances which can be characterized by their refractive indexes. In this case, it is needed to calculate the Hamaker constant of rich phase, lean phase and solid. The Hamaker constant of some of the solids is reported in the literature. But if there is solid with an unknown Hamaker constant, it is possible to calculate its constant based on surface energy and contact angle measurement\(^{171}\). Some preliminary experiments had been done in Vargas’ lab\(^{174}\) to predict the asphaltene spreading tendency on different solid surfaces by calculating \(A_{SRL}\) and compared with the reported result by Gonzalez\(^{171}\). Figure 6-4 is to indicate the results of asphaltene stickiness tendency on various substances. The sample is 0.25 wt. % C\(_{7+}\) asphaltene (extracted from Bitumen) in toluene. The asphaltenes demonstrate low sticking tendency on the studied polymer surfaces, indicated by the left square in the Figure 6-4. Polymer materials are ideal to prevent the asphaltene deposition problems while they are not suitable for oil production and transportation. The asphaltenes exhibit higher sticking tendency on metal surfaces with larger \(A_{SLR}\). The last five materials in the right square are commercial coating materials developed to mitigate asphaltene
deposition problems. Asphaltenes have very low sticking tendency on those coated surfaces.

![Asphaltene sticking tendency on 32 different solid surfaces.](image)

**Figure 6-4** Asphaltene sticking tendency on 32 different solid surfaces.

6.2.3. Asphaltene fractionation based on their surface activity

Asphaltenes and resin also contain acidic and basic compounds, heteroelements and polar functional groups contain oxygen, nitrogen, and sulfur. Acidic and basic sites of the asphaltene and resin make them interfacially active. Therefore, it is worth to fractionate these natural surfactants of the oil based on their surface activity properties. In this way, we will have a better understanding of how the asphaltene and resin contribute to changing wettability properties.
References

1. Aske, N. Characterisation of crude oil components, asphaltene aggregation and emulsion stability by means of near infrared spectroscopy and multivariate analysis. (Norwegian University of Science and Technology Trondheim, 2002).


115. Yang, S.-Y. Mechanisms of wettability for crude oil/brine/Mica system. (Rice University, 2000).


   doi:10.2118/174371-MS

   doi:10.2118/165974-MS


   doi:10.2118/119835-MS
doi:10.2118/129722-MS


166. Kumar, B. Effect of salinity on the interfacial tension of model and crude oil systems. (University of Calgary, 2012).


171. Gonzalez Rodriguez, D. L. Modeling of asphaltene precipitation and deposition tendency using the PC-SAFT equation of state. (Rice University, 2008).

