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ASSESSMENT OF ASPHALTENE STABILITY AT DIFFERENT TEMPERATURES USING SALICYLIC AND ISO- PHTHALIC ACIDS AS INHIBITORS

MSc (50/50) RESEARCH REPORT

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Submitted to

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Johannesburg, February 7th, 2019

DECLARATION

I declare that this Research Report is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

_____

Luísa Tuaira Agostinho

06 day of February 2019 in Johannesburg

ABSTRACT

During crude oil production, processing, transportation and storage, the change in temperature, pressure and fluid composition can lead to the instability of asphaltene in the system. The posterior deposition of asphaltene can clog or completely close the production, processing, and transportation facilities, thus decreasing production and increasing maintenance costs. A cost-saving manner to prevent this problem is the use of processes such as addition of chemicals inhibitors, which prevent asphaltene precipitation. In this project, several experiments were performed to assess the stability of asphaltene in crude oil varying parameters as temperature, precipitant amount, inhibitors concentrations and time.

The asphaltene behaviour and the reduction of the precipitated particles size in crude oil samples were controlled using an optical microscope. In order to propose a preventive method for the asphaltene deposition, different amount of Salicylic and Iso-Phthalic acids as asphaltene inhibitors and n-heptane as asphaltene precipitant agent were added at 35 ºC, 65 ºC, and 80 ºC. The results showed that the sizes of the asphaltene particles were reduced with increase in temperature.

At almost room temperature such as 35 ºC, the inhibition of Salicylic acid was better for lower concentration (15%). While at higher temperature such as 65 ºC and 80 ºC, the best inhibition concentration for Salicylic acid was 25%. For Iso-Phathalic acid, at 35 ºC it was found that 25% was the best concentration, at 65 ºC, 20% was the best concentration, and at 80 ºC, small concentration of 2.5 % was sufficient to inhibite asphaltene in the crude oil. The precipitant agent n-heptane had an effect on the size of asphaltene aggregates. A minimum of 2 ml n-heptane was able to initiate the precipitation process at various temperatures (35 ºC, 65 ºC and 80 ºC). An increase in precipitant agent amount such as 3.5 ml increased the aggregates particle sizes.

It was concluded that asphaltene is more stable at 80 ºC for Salicylic acid, showing the best inhibition capacity at this temperature, when compared to Iso-Phthalic acid which showed the best inhibition capacity at 65 ºC, for both inibitors asphaltene showed to be more instable at 35 ºC. The inhibition profile of Salicylic acid showed less variation with temperature than the inhibition of Iso-Phathalic acid.

DEDICATION

To my beloved parents for their unconditional love:

In memory of my father Agostinho Fernando (1949-2011).

My mother Açucena Inácio Furvela.

ACKNOWLEDGEMENTS

I would like to thank the Almighty God for all blessings and strengths throughout my life.

I sincerely express my deepest gratitude to my supervisor Doctor Diakanua Bavon Nkazi, for all the valuable advice and all the support since my first day at the Richard Ward Building as well as the encouragement and technical discussions throughout my research project.

I would like to acknowledge Mom Graça Machel and the Graça Machel Trust for their financial support especially to Tebello Ralebitso for all the Support and encouragement. This project would not have been possible without their funding.

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Table of Contents

DECLARATION ii
ABSTRACT iii
DEDICATION iv
ACKNOWLEDGEMENTS v
List of Figures ix
List of Tables xi
Nomenclature xii
CHAPTER 1. INTRODUCTION 1
1.1 Background 1
1.2 Problem statement 3
1.3 Research questions 4
1.4 Justification for the study 4
1.5 Research aim and specific objectives 6
1.5 Outline of the research report 6
CHAPTER 2. LITERATURE REVIEW 7
2.1 Crude oil 7
2.2 Asphaltenes 7
2.2.1 Asphaltene molecular structure 8
2.3 Asphaltene stability 9
2.3.1 Colloidal theory 10
2.3.2. Solubility theory 10
2.4 Asphaltene precipitation 10
2.4.1 Asphaltene precipitation envelope 10
2.4.2 Asphaltene precipitation mechanism 11
2.4.3 The Yen-Mullins model 13
2.5. Effect of the factors affecting asphaltene precipitation 13
2.5.1 Effect of temperature 14
2.5.2 Effect of n-alkanes precipitants 15
2.5.3 Effect of carbon dioxide as asphaltene precipitant 15
2.5.4 Effect of pressure 15
2.6 Previous studies on asphaltene precipitation 16

2.7 Asphaltene inhibitors....17
2.7.1 Chemical and physical properties of salicylic and iso-phthalic acids....17
2.8 Methods used for asphaltene deposits removal....18
2.8.1 Chemical methods....19
2.8.2 Mechanical methods....20
2.8.3 Thermal methods....20
2.8.4 Other methods....20
CHAPTER 3. EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES....22
3.1 Materials and experimental procedures....22
3.1.1 Materials....22
3.1.2 Experimental procedures....22
3.2 Crude oil and n-heptane mixture preparation....27
3.3 Inhibitors preparation....28
CHAPTER 4. RESULTS AND DISCUSSION....29
4.1 Pre-treatment of crude oil sample....29
4.2 Comparison of different inhibitors concentrations effect on the size of the precipitated particles at 35 ºC, 65 ºC, and 80 ºC....30
4.3 Effect of temperature on the precipitated particles size using Salicylic and Iso-Phthalic acids....34
4.4 Effect of the addition of n-heptane on the particles size at 80 ºC using inhibitors....35
4.4.1 Effect of the addition of n-heptane on the particles size at 80 ºC using Salicylic acid....35
4.4.2 Effect of the addition of n-heptane on the particles size at 80 ºC using Iso-Phthalic acid....37
4.5 Effect of time on the average precipitated particles size using inhibitors at 80 ºC....38
4.5.1 Effect of time on the average precipitated particles size using Salicylic acid....38
4.5.2 Effect of time on the average precipitated particles size using Iso-Phthalic acid....39
4.6 Comparison of the effect of n-heptane on salicylic and Iso-phthalic acids samples at 80 ºC....40
4.7 Comparison of the effect of time on salicylic and Iso-Phthalic acids samples at 80 ºC.42
4.8 Asphaltene aggregates formation by addition of n-heptane in crude oil samples....44
4.8.1 Asphaltene aggregates formation with the addition of n-heptane at 35 ºC....44
4.8.2 Asphaltene aggregates formation with the addition of n-heptane at 65 ºC....45

4.8.3 Asphaltene aggregates formation with the addition of n-heptane at 80 ºC 46
CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS 48
5.1 Conclusions 48
5.2 Recommendations 49
REFERENCES 50
APPENDICES 55
APPENDIX A: Asphaltene deposition mitigation and removal techniques.....55
APPENDIX B: Crude Oil - n-heptane - Salicylic acid mixture at 35 ^{o}C.....56
APPENDIX C: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 35 ^{o}C 72
APPENDIX D: Crude Oil - n-heptane - Salicylic acid mixture at 65 ^{o}C 89
APPENDIX E: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 65 ^{o}C.....105
APPENDIX F: Crude Oil - n-heptane - Salicylic acid mixture at 80 ^{o}C 122
APPENDIX G: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 80 ^{o}C 138
APPENDIX H: Crude Oil - n-heptane mixture at 35 ºC 155
APPENDIX I: Crude Oil - n-heptane mixture at 65 ºC 158
APPENDIX J: Crude Oil - n-heptane mixture at 80 ºC.....161

List of Figures

Figure 2. 1: Separation of crude oil into Saturates, Aromatic, Resin, and Asphaltene (SARA) fractions....8
Figure 2. 2: Asphaltene deposition issues....9
Figure 2. 3: Continental model. 10
Figure 2. 4: Archipelago model. 10
Figure 2. 5: Asphaltene precipitation envelope. 12
Figure 2. 6: Stabilizing effect of asphaltenes and other solids on water droplet. 13
Figure 2. 7: The Yen-Mullins model. 14
Figure 2. 8: Schematic diagram of asphaltene in oil....15
Figure 2. 9: Factors that influence asphaltene precipitation. 17
Figure 3. 1: Crude oil + inhibitors and crude oil + n-heptane samples. 24
Figure 3. 2: Picture of the Olympus GX41 optical microscope....27
Figure 3. 3: Dissolution of Iso-Phthalic acid 29
Figure 4. 1: Crude oil sample before pre-treatment....30
Figure 4. 2: Crude oil sample after pre-treatment....31
Figure 4. 3: Effect of inhibitors concentrations on the size of precipitated particles at 35 ºC. 32
Figure 4. 4: Effect of inhibitors concentrations on the size of precipitated particles at 65 ºC. 33
Figure 4. 5: Effect of inhibitors concentrations on the size of precipitated particles at 80 ºC. 34
Figure 4. 6: Effect of temperature on precipitated particles size. 35
Figure 4. 7: Effect of addition of n-heptane on the particles size at 80 ºC using Salicylic acid 37
Figure 4. 8: Effect of addition of n-heptane on the particles size at 80 ºC using Iso-Phthalic acid....38
Figure 4. 9: Effect of time on the average precipitated particles size using Salicylic acid ...39
Figure 4. 10: Effect of time on the average precipitated particles size using Iso-Phthalic acid 40
Figure 4. 11: Comparison of the effect of n-heptane on Salicylic and Iso-Phthalic acids samples 42

Figure 4. 12: Comparison of the effect of time on Salicylic and Iso-Phthalic acid samples..44
Figure 4. 13: Asphaltene aggregates formation with n-heptane at 35 ºC 45
Figure 4. 14: Asphaltene aggregates formation with n-heptane at 65 ºC 46
Figure 4. 15: Asphaltene aggregates formation with n-heptane at 80 ºC 47
Figure A: Asphaltene deposition mitigation and removal techniques. 57
Figure B: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 35 ºC. 58
Figure C: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 35 ºC. 74
Figure D: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 65 ºC 90
Figure E: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 65 ºC 106
Figure F: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 80 ºC. 122
Figure G: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 80 ºC. 138
Figure H: Asphaltene aggregation stages with the presence of n-heptane at 35 ºC 154
Figure I: Asphaltene aggregation stages with the presence of n-heptane at 65 ºC. 157
Figure J: Asphaltene aggregation stages with the presence of n-heptane at 80 ºC. 160

List of Tables

Table 2. 1: Chemical and physical proprieties of Salicylic and Iso-Phthalic acids. 19
Table 3. 1: Materials and equipment.....23
Table 3. 2: Inhibitors samples.....23
Table 3. 3: Samples composition.....25
Table 3. 4: Microscope properties.....27
Table 4. 1: Average deposited asphaltene particles using both inhibitors. 36

Nomenclature

APE: Asphaltene Precipitation Envelope

C_7: Heptane

HPM: High-Pressure Microscope

NIR: Near-Infrared Spectroscopy

PAH: Polycyclic Aromatic Hydrocarbon

rpm: Revolutions per minute

SARA: Saturates, Aromatics, Resins, and Asphaltene

SEM: Scanning Electron Microscopy

CHAPTER 1. INTRODUCTION

1.1 Background

Crude oil is a complex multicomponent mixture which consists of hydrocarbons, organic compounds and traces of metals. The hydrocarbons include saturates, aromatics, resins and asphaltenes. The organic compounds include sulphur, nitrogen and oxygen, and the traces of metals include vanadium, nickel and iron (Tharanivasan, 2012). Asphaltenes are the heaviest components of crude oil that are soluble in aromatics such as benzene, toluene and xylene, and insoluble in light alkanes such as n-pentane, n-hexane and n-heptane (Maqbool *et al.*, 2011).

Asphaltenes differ from other crude oil components due to their wide tendency of self-aggregation when there is a variation in temperature, reduction of pressure or a change in the mixture composition (Ting, 2003). Due to their instability, asphaltene molecules can deposit in upstream and downstream processes (Hoepfner *et al.*, 2013). The stability of crude oil depends on the molecular interaction of asphaltenes and resins and the equilibrium that they have with the remaining constituents of crude oil. Thereby the stability of petroleum can be represented by a three-phase system, where asphaltene constituents, aromatic fractions, resin constituents and saturates are balanced accordingly (Speight, 2004). Several factors, such as changes in pressure, temperature, and composition affect the deposition of asphaltenes in the reservoir during crude oil production and oil pipeline transportation.

Goharzadeh *et al.*(2014) studied the asphaltene deposition in a transparent mini-channel using a mixture of n-heptane as a precipitant and crude oil. It was observed that with an addition of n-heptane the dissolved asphaltene in crude oil precipitates. The precipitated asphaltene particles thrived towards the wall of the transparent mini-channel at ambient temperature.

Maqbool *et al.* (2011) investigated the effect of temperature on the kinetics of asphaltene precipitation on crude oil samples. It was observed that by adding n-heptane as a precipitant, the asphaltene precipitation onset time was shorter at higher temperatures, and the asphaltene particles decreased in size due to their higher degree of solubility. Asphaltene precipitation in the transportation tubing, production facilities and near wellbore regions, reduce oil production, permeability and storage space. thus affecting the productivity and final oil

recovery. As an economical measure to prevent or delay the asphaltene precipitation process, the use of inhibitors is required (Madhi *et al.*, 2017).

In recent years, researchers focussed on the inhibition process of asphaltene precipitation and deposition using different inhibitors. The assessment for the right inhibitor temperature for asphaltene precipitation inhibition and the ideal concentration for inhibitors for better performance is a subject of extreme importance (Shadman *et al.*, 2012; Karambeigi and Kharrat, 2014; Salimi *et al.*, 2016; Madhi *et al.*, 2017).

Asphaltenes can be characterised according to the n-alkane used to precipitate them, and called C_n asphaltene, depending on the number of n. In this report, the stability of n-heptane asphaltene, also referred to as C_7 asphaltene, is investigated. This study gives continuity to the work which was previously conducted on the same subject and helps providing a better understanding in terms of the effects of temperature, the addition of n-heptane, the inhibitors type and the concentrations on the average precipitated asphaltene particles size.

1.2 Problem statement

In the oil and gas industry, asphaltenes are known as the problematic crude oil constituents because they clog wells, flow lines, surface facilities and subsurface formations (Zhang *et al.*, 2007). The asphaltene precipitation phenomena can affect the oil productivity by resulting in flow line blockages and a reduction of storage capacity. Due to the depletion of conventional resources, there is a need for unlocking unconventional resources such as heavy oil reservoirs, as well as deep and ultra-deep water reservoirs. To improve the recovery factor in these reservoirs, enhanced oil recovery techniques have to be used. These techniques involve chemicals or/and steam injection, which will lead to changes in parameters such as the crude oil temperature, composition and pressure, starting from the reservoir to the production and processing facilities. Variation of these parameters can initiate the asphaltene precipitation process.

Temperature, pressure and composition of crude oil plays a huge role in asphaltene stability (Clegg and Lake, 2007). For stabilising asphaltene in oil and mitigating its precipitation, inhibitors are used. Despite several studies on the mitigation of asphaltene precipitation, the problem is still under investigation. Therefore, it is of great importance to understand the effects of the changes in temperature on asphaltene precipitation, as well as to select the best inhibitors to delay or mitigate the precipitated asphaltene particles. The determination of the particle size of asphaltene have been an area of uncertainty, whereas, the use of microscopes to visualise and measure the asphaltene particles size, has been one of the most used techniques by researchers (Ashoori *et al.*, 2012).

According to Mohammadi *et al.* (2011) there are two well-known methods to minimise asphaltene precipitation issues. The first method is the removal of precipitated asphaltene and the second method is asphaltene inhibition. For removal of precipitated asphaltene particles, solvents have to be used to dissolve it, or clean-up techniques, such as a mechanical treatment, are used.

Kokal and Sayegh (1995) concluded that wellbore and well tubing are the locations where asphaltene is most problematics. This research will contribute to the asphaltene stability and precipitation in crude oil and will elucidate on the use of Salicylic acid and Iso-Phthalic acid as inhibitors to prevent asphaltene precipitation problems, as well as the effect of inhibitors and n-heptane precipitant contact time on the size of the precipitated asphaltene particles.

1.3 Research questions

- Which temperature and inhibitor concentration are efficient in the prevention of asphaltene precipitation with the presence of n-heptane and its amount as a precipitant?
- What is the effect of inhibitors and precipitant contact times on the precipitated particles size?
- What is the effect of the presence of n-heptane and its amount on the asphaltene aggregates size?
- What is the effect of Salicylic acid when compared to Iso-Phthalic acid as inhibitors agents?

1.4 Justification for the study

Due to the economic problems associated with asphaltenes, numerous investigations on asphaltene have been carried out. These investigations were done in order to determine the conditions which may lead to the precipitation of asphaltenes from different crude oils, and to understand their definition and structures (Verdier *et al.*, 2006; Maqbool, 2011).

For the past decades, researchers have been concerned about the understanding of the effect of temperature on asphaltene stability and have used several experimental tools, such as the Near-Infrared Spectroscopy (NIR) technique and the High Pressure Microscopy (HPM) technique. The NIR technique is used to study the onset of asphaltene destabilisation pressure at various temperatures, and the HPM technique is used to study the asphaltene precipitation problem (Verdier *et al.*, 2006; Maqbool, 2011; Hassanvand *et al.*, 2012).

The determination and measurement of asphaltene particles size have also been a subject of extreme importance for researchers. Ashoori *et al.* (2012) analysed several mixtures of crude oil and n-heptane with various dilution ratios, using an OLYMPUS BX60 polarising microscope, a high-resolution scanning electron microscopy (SEM) and X-ray diffraction techniques. It was concluded that the quantity of deposited asphaltene was increased due to the increase of the concentration of n-heptane in mixture and the particle size of asphaltene was independent of the n-heptane concentration.

Pressure effect is studied in many literatures but the temperature effect remains obscure. In order for this project to add value to the already existing literature on the effect of temperature on asphaltene precipitation, a crude oil from Sasolburg is analysed to study the

effect of three temperatures (35 °C, 65 °C and 80 °C) on asphaltene stability using an optical microscope.

1.5 Research aim and specific objectives

The aim of this project is to evaluate the asphaltene stability in crude oil at various temperatures. To achieve the aim, the following specific objectives will be carried out:

- Compare the effect of Salicylic acid and Iso-Phthalic acid as inhibition agents on the size of precipitated asphaltene particles at 35 ºC, 65 ºC and 80 ºC.
- Evaluate the effect of inhibitors and precipitant contact time on size of the precipitated asphaltene particles.
- Determine the best temperature and inhibitors concentrations for reduction of precipitated asphaltene particles size.
- Assess the effect of the addition of n-heptane on inhibitors efficiency.

1.6 Outline of the research report

The following is a brief description of each chapter in this research report:

Chapter 1: Contains the introduction, the problem being investigated, the project objectives and the research report outline.

Chapter 2: Comprehends the review of the relevant literature on the crude oil compounds, asphaltene molecular structure, stability, precipitation, asphaltene deposits removal, inhibitors and the previous studies on the thermodynamic stability, phase behaviour, destabilisation and deposition of asphaltene.

Chapter 3: Describes in detail the experimental procedures and analytical techniques, from the crude oil samples preparation to the precipitant and inhibitors mixtures preparation.

Chapter 4: Presents the results of the experimentations.

Chapter 5: Contains the conclusions and provides the recommendations for future work.

CHAPTER 2. LITERATURE REVIEW

2.1 Crude oil

Crude oil is a complex blend of hydrocarbons and other compounds, widely divided into several fractions with different solubilities such as Saturates, Aromatics, Resins and Asphaltenes (SARA) as shown in Figure 2.1 (Wang and Buckley, 2003).

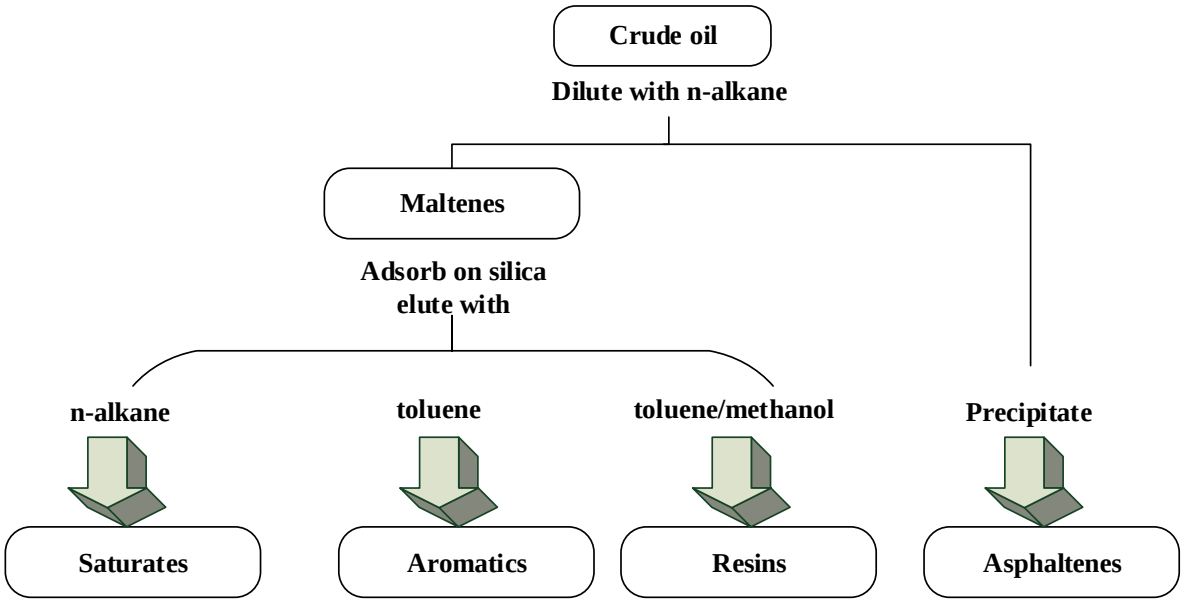


Figure 2.1 : Separation of crude oil into Saturates, Aromatic, Resin, and Asphaltene (SARA) fractions (Adapted from Auflem, 2002)

2.2 Asphaltenes

In 1837, Boussingault invented the word asphaltene after describing the constituents of some bitumen (asphalts) encountered in eastern France and Peru. He defined asphaltenes as a residue of the distillation of crude oil, which is not soluble in alcohol, and behaved like asphalt (Al-Qasim and Bubshait, 2017).

Asphaltenes are the most aromatic organic solids consisting of various polyaromatic structures with aliphatic chains. They also consist of heteroatoms such as sulphur, nitrogen,

and oxygen, as well as metals such as nickel, vanadium, and iron. The electrical charge that the metal forms can have an impact on asphaltene deposition (Kelland, 2009). Asphaltene deposition can damage production and processing facilities as shown in Figure 2.2.

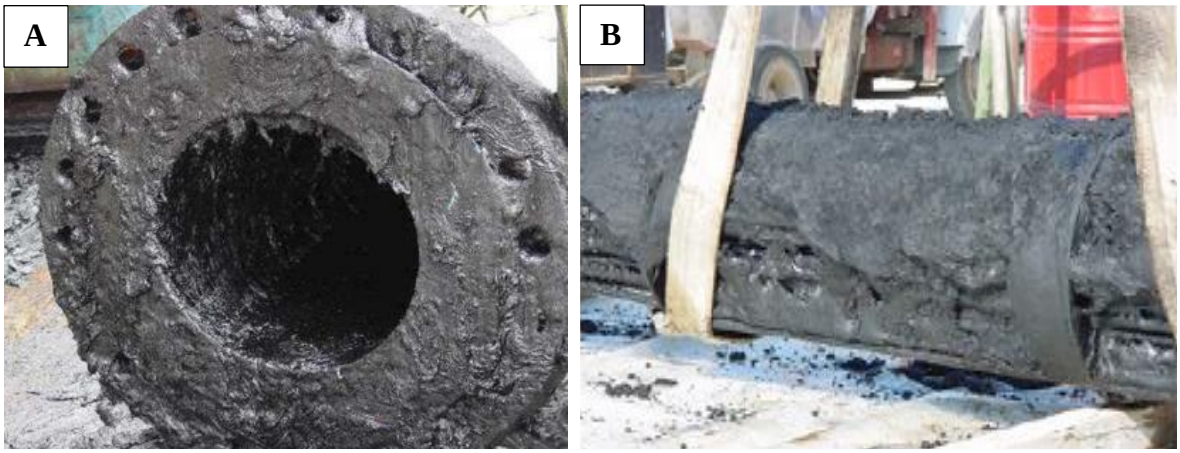


Figure 2. 2: Asphaltene deposition issues

A: Partially destroyed pipeline due to asphaltene deposits (Marioli, 2011);

B: Completely destroyed heat exchanger due to asphaltene deposits (Garner, 2015).

2.2.1 Asphaltene molecular structure

Asphaltene elemental composition is well defined and advances in understanding asphaltene characteristics are constantly registered, but the molecular structures dominating asphaltenes are still poorly understood. Several asphaltene models have been proposed over the years and only two of them are representative. The first model, which is illustrated in Figure 2.3, is the continental model, which is also known as the island model. It suggests a monomer molecular asphaltene structure. This model has a core of approximately six or seven fused aromatic rings, with some aliphatic groups containing heteroatoms which are connected to the edges of the aromatic ring system (Kelland, 2009; Sabbah *et al.,* 2011). The second model, which is illustrated in Figure 2.4, is the archipelago model, which is also known as the rosary-type model. The individual asphaltene monomers are made of clusters of polycondensed groups containing five to seven aromatic rings bounded with short aliphatic side chains that may contain polar heteroatom bridges (Kelland, 2009).

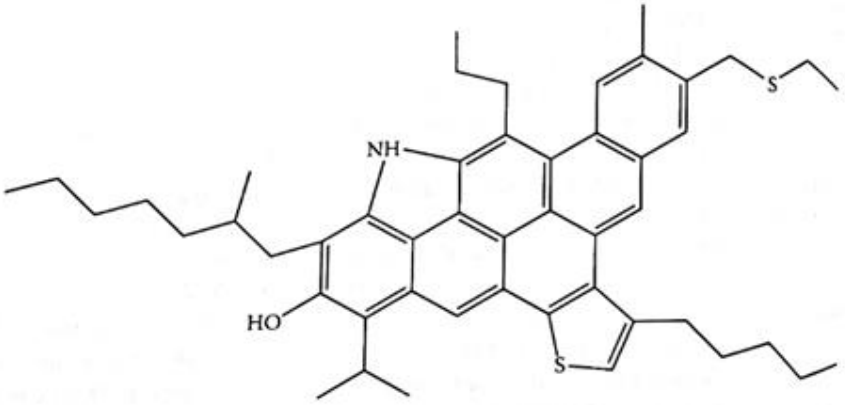


Figure 2. 3: Continental model (Kelland, 2009)

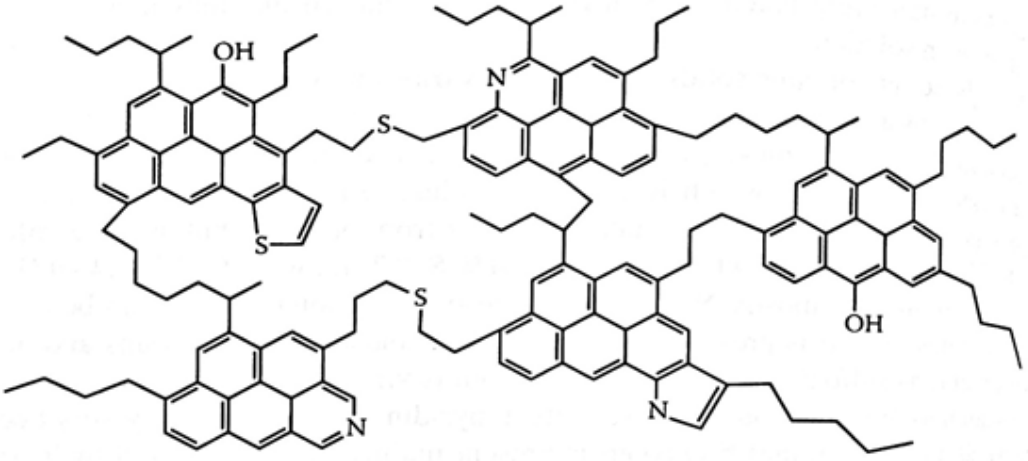


Figure 2. 4: Archipelago model (Kelland, 2009)

2.3 Asphaltene stability

The incompatibility of crude oil and its blends, with other chemicals and its instability due to the changes in temperature, pressure and fluid composition are the main reasons for asphaltene precipitation. Therefore, understanding the stability of asphaltene is a subject of extreme importance in the petroleum industry. Two theories, known as the colloidal and solubility approaches, have been proposed to better understand asphaltene stabilisation (Hammadi, 2016).

2.3.1 Colloidal theory

The colloidal models for the asphaltene precipitation assume that asphaltene occurs in suspension, also known as colloidal form, and it is stabilised by resin molecules that are absorbed in the asphaltene surface. This theory also suggests that the precipitation of asphaltene is an irreversible phenomenon, but with a determinate amount of resins, asphaltene can be fully peptised in crude oil (Subramanian *et al.*, 2016). In general, to maintain asphaltene, both dispersed and in solution, sufficient resin molecules must be present in the crude oil.

2.3.2. Solubility theory

Solubility models are widely used for forecasting asphaltene precipitation, based on the concept of solubility parameters which take into account that petroleum crude comprises of two phases namely, asphaltenes and de-asphalted oil. According to the solubility theory, any change in the solubility parameter in one of the two phases leads to a change in their phase equilibria (Subramanian *et al.*, 2016). In other words, the solubility theory believes that asphaltene dissolves in crude oil thus forming a solution.

2.4 Asphaltene precipitation

In order to avoid the asphaltene precipitation, it is crucial to review and identify the mechanism of asphaltene formation. The following mechanism of the precipitation of asphaltenes assists in the understanding of the deposition behaviour of asphaltenes during crude oil production and transportation.

2.4.1 Asphaltene precipitation envelope

Under virgin (not yet produced) reservoir conditions, asphaltenes are usually stable in the crude oil. To understand the asphaltenes stability boundaries in pressure-temperature diagram, a model called Asphaltenes Precipitation Envelope (APE) has been proposed and it is illustrated in Figure 2.5. The red curve (upper asphaltene envelope) demarcates the stability

zones when asphaltenes are in solution. At reservoir conditions the red dot curve illustrates the primary depletion within the reservoir that causes a reduction in pressure. When the asphaltene-precipitation onset pressure (upper asphaltene-precipitation envelope) is reached, the least-soluble asphaltene will precipitate, the precipitation will continue until the gas is released from the solution, which is also known as the bubble point pressure (black curve). At the lower asphaltene envelope, the crude oil begins to redissolve asphaltene due to the continuous decrease in pressure and a deficit of gas within the system (Zhang *et al.*, 2007).

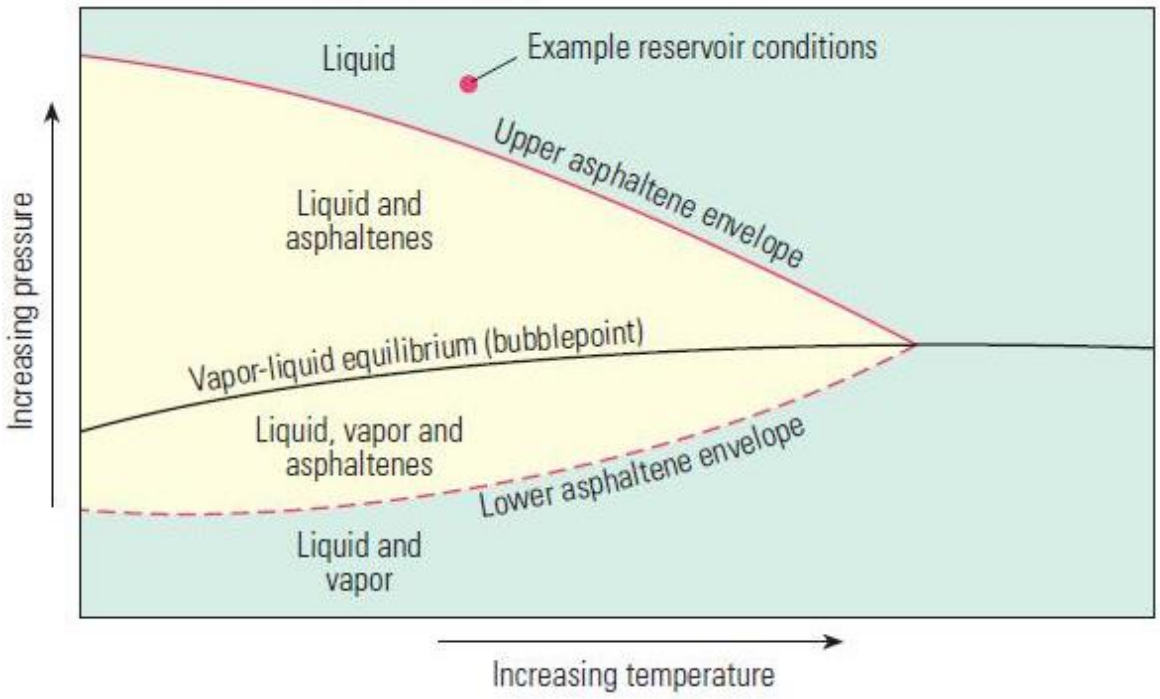


Figure 2. 5: Asphaltene precipitation envelope (Zhang *et al.*, 2007)

2.4.2 Asphaltene precipitation mechanism

Asphaltene precipitation can be defined as a process of destabilising asphaltene nanoaggregates from crude oil owing to the addition of a precipitant. The destabilisation is followed by asphaltene aggregation and particle growth in size (Maqbool, 2011). The mechanism of asphaltene precipitation has been widely investigated normally through titration of the crude oil with an n-alkane precipitant, usually n-pentane or n-heptane (Haji-Akbari, 2014).

Asphaltene precipitation occurs frequently in light crude oils even though light crude oils contain very low asphaltene content. The explanation behind this is that light crudes are rich in n-alkanes and asphaltene has limited solubility on n-alkanes (Goual, 2012). When great amounts of alkanes are added or when resin molecules are removed from the crude oil, the solubility of the asphaltene molecules may be lost. This is because asphaltene molecules can easily associate to each other thus resulting in aggregates and then precipitate out. These aggregates can increase in size up to microscale and become visible under an optical microscope as dark particles (Clegg and Lake, 2007).

In petroleum production, the onset of water production can be accompanied with asphaltene precipitation and deposition problems. When in production, the fluid consists of water, other solids such as minerals, and wax as shown in Figure 2.6. The asphaltene instability problem can aggravate and start creating a large mass of solids or stable emulsions. Asphaltene or resin adsorb with minerals and wax onto water droplets, generating a stable and very strong emulsion that can plug production (Clegg and Lake, 2007).

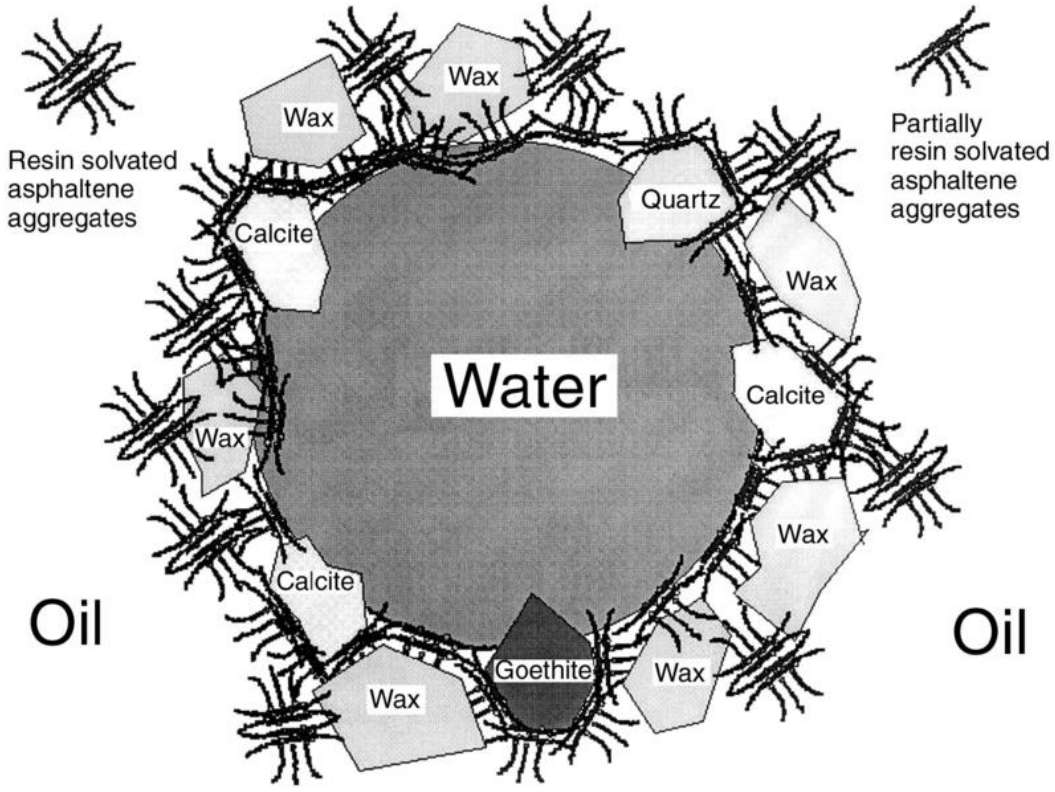


Figure 2. 6: Stabilising effect of asphaltenes and other solids on a water droplet (Clegg and Lake, 2007)

2.4.3 The Yen-Mullins model

The modified Yen model or simply Yen-Mullins model is one of the most used models for asphaltene aggregation studies. It has been proven triumphant for comprehension of the interfacial phenomena involving asphaltenes. This model suggests that the most likely asphaltene molecular weight is approximately 750 g/mol and has the island molecular architecture dominant. Asphaltene nanoaggregates with an agglomeration number less than 10 can be formed by asphaltene molecules at sufficient concentrations in crude oil, while clusters with small aggregation numbers can result from nanoaggregates at higher concentrations (Mullins, 2010; Mullins *et al.*, 2012; Pradilla, 2016). The asphaltene nanoaggregates and clusters formation stages can be seen in the Figure 2.7. The image on the left shows the asphaltene molecular architecture with moderately large polycyclic aromatic hydrocarbons (PAH) with surrounding alkanes. The image in the middle shows the process of formation of nanoaggregates by asphaltene molecules with an aggregation number of six, and the image on the right shows the formation of clusters by asphaltene nanoaggregates, with an aggregation number of eight.

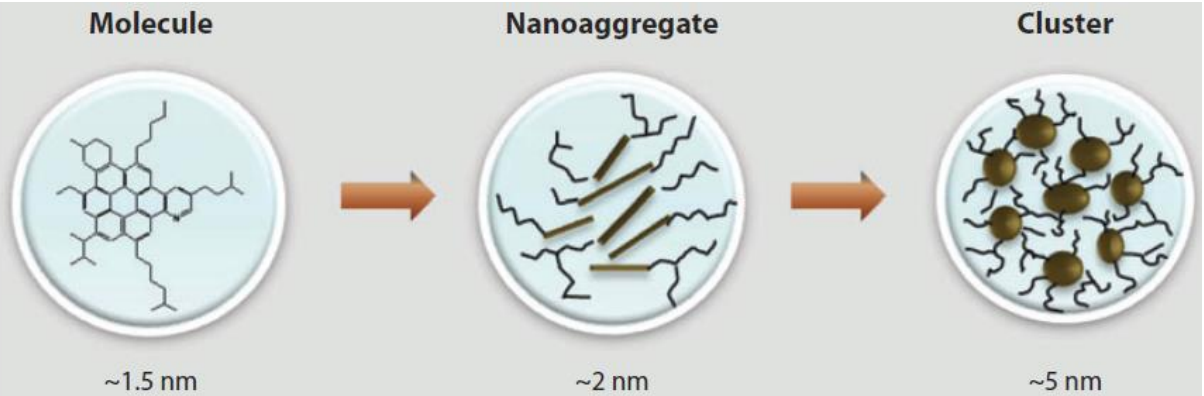


Figure 2. 7: The Yen-Mullins model (Mullins, 2011)

2.5. Effect of the factors affecting asphaltene precipitation

Various factors such as temperature, pressure and oil composition affect the precipitation behaviour of asphaltenes. Those factors are reviewed in the following sub-sections.

2.5.1 Effect of temperature

Asphaltene precipitation can be induced by changes in temperature during crude oil production and processing. Primary oil recovery has no significant effect on the temperature variation within the reservoir. This variation is perceptible during secondary and tertiary recovery. Literature suggests that there is no evident trend for temperature effect on asphaltene as a result of crude oil composition (Al-Qasim and Bubshait, 2017).

According to Leontaritis (1996), there is a positive linear relationship between solubility and temperature. As the temperature increases up to the reservoir temperature, there is also an increase in solutbility. Once the reservoir temperature has been reached, there is an inversely proportional relationship between solubility and temperature. As the temperature continues to increase, the solubility decreases. Chandio *et al.* (2015) based on the Hildebrand solubility parameters of oil, observed that asphaltene dissolves in oil at high temperatures. This shows that the overall stability of oil increases as the temperature increases as illustrated in Figure 2.8.

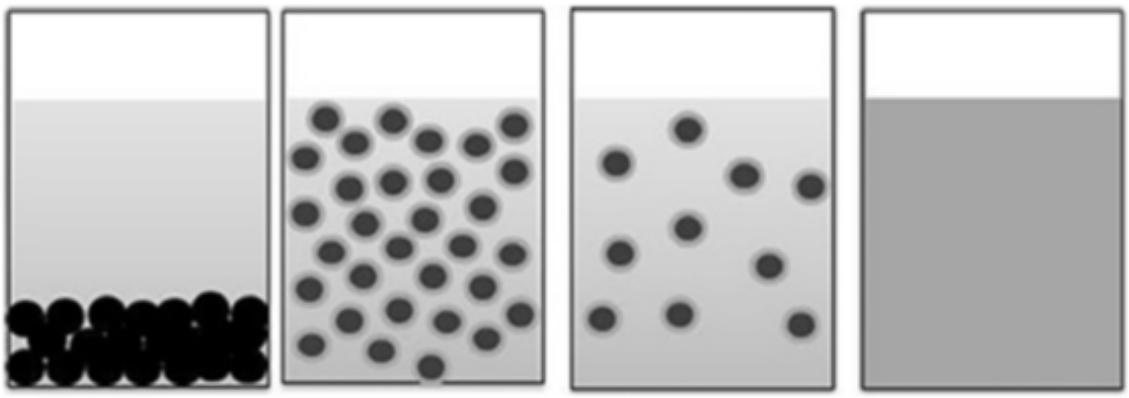


Figure 2. 8: Schematic diagram of asphaltene in oil (Adapted from Chandio *et al.*, 2015)

2.5.2 Effect of n-alkanes as asphaltene precipitants

The type of precipitant used to destabilise asphaltene molecules, plays a huge role in the properties of the precipitated asphaltene, therefore knowing which precipitant to use is also equally important. Various factors influence the asphaltene kinetics behaviour in distinct n-alkanes precipitants (Haji-Akbari, 2014).The first factor is the increase of viscosity along with the increase in chain length of the n-alkane precipitant. This leads to the decrease in aggregate rate due to the higher viscosity and consequently, an increase in the time needed for detecting asphaltene instability. The second factor is related to the increase in the solubility parameter of the mixture, which leads to a slower aggregation rate as a result of smaller coagulation efficiency among aggregating asphaltenes (Haji-Akbari, 2014).

2.5.3 Effect of carbon dioxide as asphaltene precipitant

During enhanced oil recovery (EOR) operations, carbon dioxide can be a source of asphaltene precipitation problems due to the interaction between the injected gas and heavy components in oil. Asphaltene precipitation is initiated by CO_2 as soon as the critical content of CO_2 is exceeded. The critical content point of CO_2 depends on the reservoir oil composition, temperature and pressure, and has to be evaluated at an early stage of the EOR screening (Al-qasim, 2011). Gonzalez *et al.* (2008) concluded that in the presence of CO_2, asphaltene becomes more stable with a decrease in temperature.

2.5.4 Effect of pressure

A change in pressure is one of the main factors which contribute to asphaltene flocculation and deposition, as shown in Figure 2.9. Changes in pressure and temperature have an important role in the number of precipitated asphaltenes. When the fluid pressure decreases and reaches the bubble point pressure (temperature and pressure conditions at which the first bubble of gas can be seen out of solution in oil), asphaltene precipitation increases. On the other hand, when the pressure decreases to below the bubble point pressure, there is a noticeable decrease in asphaltene precipitation. It is evident that reduction in pressure leads to

more expansion in the relative volume fraction of the light components of crude oil in relation to heavy components. This behaviour can be compared to the process of adding a light hydrocarbon fraction, such as an n-alkanes, in the crude oil (Rastgoo and Kharrat, 2017).

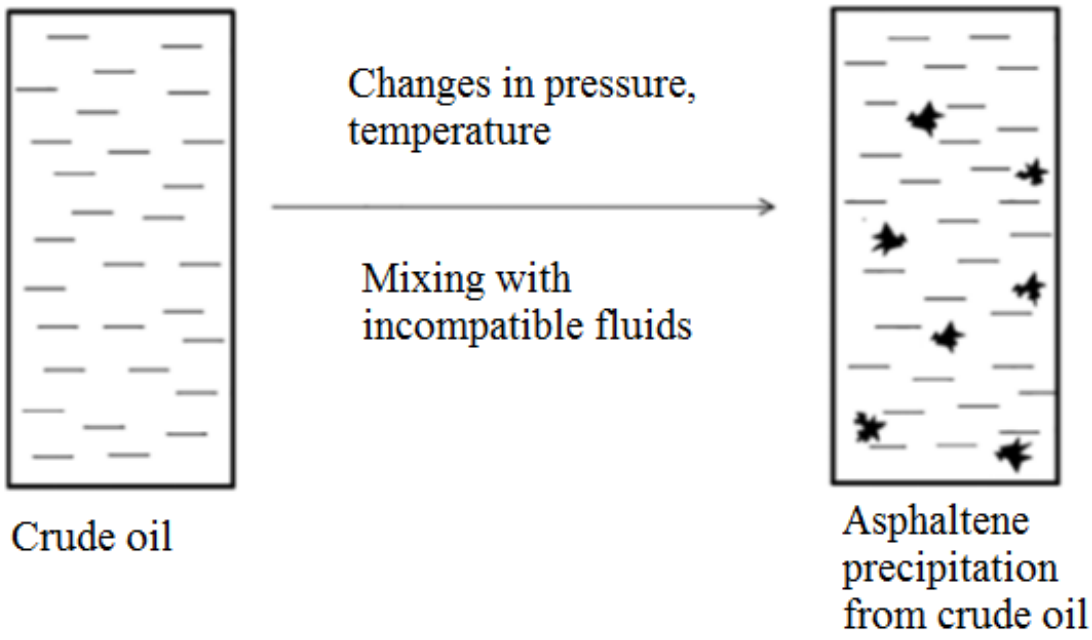


Figure 2. 9: Factors that influence asphaltene precipitation (Subramanian *et al.*, 2016)

2.6 Previous studies on asphaltene precipitation

Ting (2003) studied the thermodynamic stability and phase behaviour of asphaltene in oil, measuring asphaltene stability boundaries under reservoir conditions as functions of pressure, temperature and dissolved gas concentration using n-alkanes precipitants. It was concluded that some asphaltene molecules will stay in the solution even at high precipitant volume fractions, and much more asphaltene molecules can be precipitated by lower molecular weight n-alkanes. Furthermore, Ting (2003), concluded that the contribution of pressure to asphaltene phase separation is more noticed for light oil near its bubble point. Asphaltene is frequently stable in highly under-saturated oils. At pressures below the bubble point, asphaltene tends to be stable as a result of the scape from the liquid of most of the precipitants. Some of these precipitants include methane, ethane and nitrogen.

Hassanvand *et al.* (2012) studied the effect of temperature on asphaltene precipitation by quantitative methods, using NIR and HPM, and concluded that asphaltene nucleation is more likely to occur in low pressure when an increase in temperature is observed. In his study about the kinetics of asphaltene precipitation from crude oils, Maqbool (2011) used n-alkanes as asphaltene precipitants. By using an optical microscopy, it was concluded that the precipitant concentration plays a huge role in the asphaltene precipitation onset time and can vary from a few minutes to several months. In addition, Maqbool (2011) mentioned that the precipitation onset time at higher temperatures is shorter and the solubility is higher.

Gonzalez *et al.* (2012) predicted the asphaltene stability based on dead crude oil proprieties and concluded that asphaltene precipitation has a huge kinetic effect and with respect to asphaltene stability in crude oil, it decreases at lower temperatures. Hoepfner (2013) studied the destabilisation and deposition of asphaltene using a capillary flow apparatus. In order to destabilise asphaltene, a precipitant was added in a crude oil sample, and the results indicate that the asphaltene deposition rate decreases with decreasing precipitant concentration.

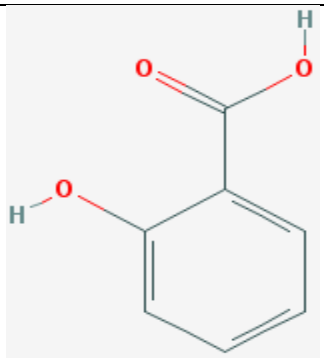
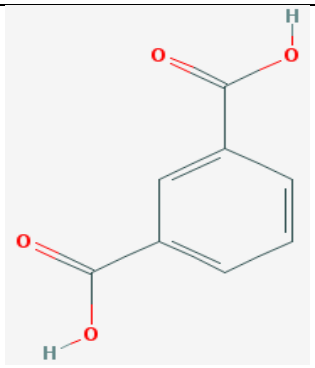
2.7 Asphaltene inhibitors

Aggregation inhibitors are designed to prevent or delay asphaltene precipitation and it is necessary to identify the mechanisms that are responsible for aggregation between the asphaltene monomers, in order to design efficient inhibitor molecular structures (Subramanian *et al.*, 2016). Asphaltene inhibitors are substances that mitigate asphaltene precipitation by moving the aggregation of asphaltene molecules out of the well path to a point in the production system where it could be dealt with much more easily (Kelland, 2009). The oil has to be mixed with the inhibitors before the asphaltene precipitation onset. These inhibitors are oil soluble which means they have short functional time (Clegg and Lake, 2007). Asphaltene inhibitors need various molecular points of interaction for good inhibition. This is one of the reasons why asphaltene inhibitors are usually polymers or resins. Moreover, if the asphaltene inhibitor contains alkyl long chains, any formed asphaltene aggregate can easily be dispersed (kelland, 2009).

2.7.1 Chemical and physical properties of Salicylic acid and Iso-Phthalic acid

To understand the behaviour, in terms of efficiency, of asphaltene inhibitors, it is important to know their chemical and physical proprieties, which are tabulated in Table 2.1.

Table 2. 1: Chemical and physical proprieties of Salicylic and Iso-Phthalic acids (U.S. National Library of Medicine, 2018)

	Salicylic acid	**Iso-Phthalic acid**
Chemical structure		
Molecular formula	$C_7H_6O_3$	$C_8H_6O_4$
Molecular weight	138.122 g/mol	166.132 g/mol
Boiling point	211°C	Sublimes
Melting point	157 °C	345 °C
Density	1.44 kg/m^3 at 20 °C	1.54 kg/m^3 at 25 °C

2.8 Methods used for asphaltene deposits removal

Asphaltene can be deposited in all of the petroleum production systems. To remove these plugs from a production system, several techniques are used according to the deposition location. In less accessible equipment, such as flow lines, techniques such as solvents soak with or without dispersants are used. The use of solvents and heating at the same time can also be efficacious, and according to the hardness of the deposit, the pipelines might be cut for asphaltene deposits removal (Clegg and Lake, 2007).

There are several techniques used for cleaning up pipelines and other production and transportation facilities, such as, chemical, mechanical and thermal methods depending on the type of solid deposited on the wall of the facilities.

2.8.1 Chemical methods

Chemical methods are the most common methods for asphaltene deposition treatment. In chemical treatment, several techniques can be applied, such as the addition of dispersants, antifoulants, and aromatic solvents in order to control asphaltene deposition. Dispersants surround the asphaltene molecules in the same way as the natural resin materials. Aromatic solvents for asphaltene deposits must have a high aromaticity to be effective, and antifoulants have proven to be efficient in condensate stabilisation units in gas plants. Chemicals have wide areas of application. They can be used to treat the asphaltene deposits in tubing, flowlines, wellbore, formation and other production, processing and transportation facilities (Bimuratkyzy and Sagindykov, 2016).

In most cases, a chemical solvent injection, to soften the asphaltene deposit is followed by a mechanical removal. As the cleaning of asphaltene deposits is expensive and comes up with several problems, to undertake these clean-up operations regularly to prevent complete plug-ups should be a very efficient method to prevent blockages by asphaltene deposits. A pre-treatment of the well using solvent or hot water and surfactant is another manner to mitigate asphaltene deposition, this can be done a day before any well stimulation project (Kokal and Sayegh, 1995; Bimuratkyzy and Sagindykov, 2016). Solvents such as xylene, toluene, benzene, pyridine and carbon disulphide are widely used to dissolve asphaltene deposits, but there are some limitations on using them such as cost, environmental safety and personal exposure considerations. Moreover, they have low flash points, making them fire and explosion hazard prone and they can also create corrosion issues.

The other group of substances widely used on asphaltene deposits treatment are dispersants, they accelerate the rupture and dissolution of asphaltene deposits, and are also used to avoid the formation of sludge and rigid film emulsions.

Asphaltene inhibitors are also very popular on asphaltene deposits treatment. Some inhibitors such as alkyl phenol, natural resin, non-ionic surfactant as ethoxylated alcohols and phenols, vegetable oils such as sweet almond, coconut essential oil and dodecyl benzene sulfonic acid are some of the inhibitors that were evaluated and showed a good result in asphaltene inhibition in many reservoirs (Bimuratkyzy and Sagindykov, 2016). The deposit location and

amount must be well understood and the direct contact between the deposits and solvent is needed as well as sufficient soaking time and circulation of the solvent are required, to get optimum results (Gatekeeper, 2017).

2.8.2 Mechanical methods

Mechanical and chemical methods are usually used together. Techniques such as coiled tubing are often used to take the inhibitor or solvent to the blockage location, as well as to run tools to help with grinding of solids through drilling of the plug by hydro-blasting using a coiled tubing unit. However, the pressure required for the coiled tubing is a limitation as higher external pressure can favour a tubing collapse process.(Kokal and Sayegh, 1995; Gatekeeper, 2017).

When flow lines are not fully blocked, a very common technique known as pigging is used to sweep out asphaltene deposits inside the flow lines. Pigging operations can be executed through dissolving or melting of the solids (Gatekeeper, 2017). Another widely used method for cleaning asphaltene deposits inside the wells is by wireline, however, this method is slow and costly, especially when the asphaltene plug is long and hard (Kokal and Sayegh, 1995).

2.8.3 Thermal methods

These methods use downhole heaters and hot oil that is pumped down the well tubing or casing to minimise asphaltene deposition. Heat-liberating chemicals are also used, for example, a mixture of equi-molar concentrations of ammonium chloride and sodium nitrate can be pumped down the well using a buffer to delay the exothermic reaction until the fluid reaches the bottom-hole with a large quantity of nitrogen gas (Bimuratkyzy and Sagindykov, 2016).

2.8.4 Other methods

Different methods are used to reduce the precipitation process of asphaltenes. The following focusses on the two main methods, microorganisms and laser energy treatments.

2.8.4.1 Bacterial treatment

Some naturally occurring marine microorganisms have the ability to absorb paraffin and asphaltenes, they are also able to reduce paraffin and asphaltene deposition over a certain period or even remove them effectively. There are some microorganism based products used for asphaltene deposits treatment. For example, PARAGONE is a bacterial product made of naturally occurring microorganisms, created by Strata International and is used to remove asphaltene and paraffin deposits, inhibit corrosion or scale formation as well as emulsion breakers for production and injection wells (Bimuratkyzy and Sagindykov, 2016).

2.8.4.2 Laser technology

Cleaning-up of asphaltenes deposits using laser energy is a novel technique as proposed by Zekri*et al.,* (2001), in their experiments using bitumen, powdered limestone cores and brine. They have proved that laser energy in different laser intensities and different laser exposure times modifies the thermodynamics of the system resulting in a reversible process, some of the redissolved asphaltene goes back into the liquid phase. In petroleum reservoirs, higher laser intensity provides better improvement of the rock-damaged permeability. In addition, the exposure time has an effect on the improvement of the damaged core permeability, however, there is an optimum exposure time beyond which no additional improvement is registered. The summary of the asphaltene deposition mitigation and removal methods is presented in the Appendix A.

CHAPTER 3. EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES

3.1 Materials and experimental procedures

Below materials and methods were used in order to meet the set objectives of this investigation.

3.1.1 Materials

Table 3.1 presents the materials and equipment used in this project.

Table 3. 1: Materials and equipment

Materials or equipment	Source or model
Crude oil	Sasolburg (South Africa)
Salicylic and Iso-Phthalic acids	Sigma Aldrich (South Africa)
n-heptane	Sigma Aldrich (South Africa)
Temperature controlled water bath	Labcon
Microscope	Olympus – GX41

3.1.2 Experimental procedures

A detailed procedures involved in samples preparation and characterization are discussed below. Tables in this section provide details of each sample used in this investigation.

3.1.2.1 Samples preparation

In this project, 12 volumetric flasks were prepared and stored at room temperature. 50 ml of ethanol was used as the solvent in the 12 samples. 6 of the samples had Salicylic acid as the inhibitor and the other 6 samples had Iso-Phthalic acid as the inhibitor. This is illustrated in Table 3.2.

Table 3.2: Inhibitors samples

Samples	Ethanol (ml)	Inhibitors (type)	Inhibitors (%)
1	50	Salicylic acid	2.5
2	50	Salicylic acid	5
3	50	Salicylic acid	10
4	50	Salicylic acid	15
5	50	Salicylic acid	20
6	50	Salicylic acid	25
7	50	Iso-Phthalic acid	2.5
8	50	Iso-Phthalic acid	5
9	50	Iso-Phthalic acid	10
10	50	Iso-Phthalic acid	15
11	50	Iso-Phthalic acid	20
12	50	Iso-Phthalic acid	25

Three temperatures were used in order to determine the effect of temperature on the inhibition process and precipitated particle size. These temperatures are 35 ℃, 65 ℃ and 80 ℃. Each temperature was allocated 12 samples thus giving a total of 36 samples which were prepared. Of the 12 samples for each temperature, 6 samples contained crude oil and Salicylic acid, with the percentages of the inhibitor of each sample being 2.5%, 5%, 10%, 15%, 20% and 25%, respectively. The other 6 samples contained crude oil and Iso-Phthalic acid, with the percentages of the inhibitor of each sample being 2.5%, 5%, 10%, 15%, 20% and 25%, respectively. Some of the samples are shown in Figure 3.1. Salicylic acid samples have green labels and Iso-Phthalic acid have orange labels.

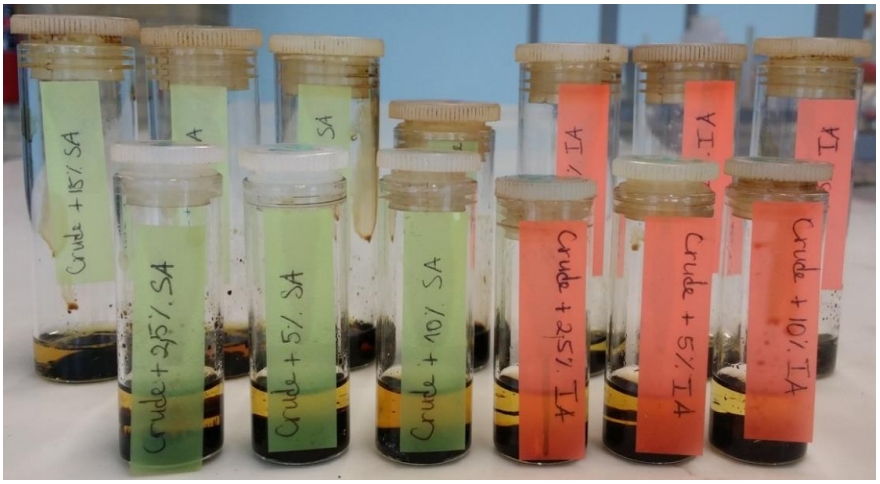


Figure 3. 1: Crude oil + inhibitors and crude oil + precipitant samples

The prepared samples which contain crude oil and inhibitors (Salicylic or Iso-Phthalic acids) were prepared, heated up to 35 °C, 65 °C and 80 °C and immediately observed under the microscope for particles size analysis. Posteriorly, 34 samples for each temperature were prepared to investigate the effect of a precipitant agent, such as n-heptane, on the aggregates size. The results are shown in Table 3.3. Samples of crude oil and heptane with and without inhibitors were prepared, heated up to 35 °C, 65 °C and 80 °C, left for 30 minutes, 60 minutes, 90 minutes and 120 minutes, and observed under the microscope.

Table 3.3: Samples composition

Samples (inhibitors : n-heptane)	Crude oil (g)	Salicylic acid (%)	Iso-Phthalic acid (%)	n-heptane (ml)
0.0:2	0.5	0	0	2
0.0:2.5	0.5	0	0	2.5
0.0:3.5	0.5	0	0	3.5
0.0:5	0.5	0	0	5
2.5:0	0.5	2.5	2.5	0
2.5:2	0.5	2.5	2.5	2
2.5:2.5	0.5	2.5	2.5	2.5

2.5:3.5	0.5	2.5	2.5	3.5
2.5:5	0.5	2.5	2.5	5
5.0:0	0.5	5	5	0
5.0:2	0.5	5	5	2
5.0:2.5	0.5	5	5	2.5
5.0:3.5	0.5	5	5	3.5
5.0:5	0.5	5	5	5
10.0:0	0.5	10	10	0
10.0:2	0.5	10	10	2
10.0:2.5	0.5	10	10	2.5
10.0:3.5	0.5	10	10	3.5
10.0:5	0.5	10	10	5
15.0:0	0.5	15	15	0
15.0:2	0.5	15	15	2
15.0:2.5	0.5	15	15	2.5
15.0:3.5	0.5	15	15	3.5
15.0:5	0.5	15	15	5
20.0:0	0.5	20	20	0
20.0:2	0.5	20	20	2
20.0:2.5	0.5	20	20	2.5
20.0:3.5	0.5	20	20	3.5

20.0:5	0.5	20	20	5
25.0:0	0.5	25	25	0
25.0:2	0.5	25	25	2
25.0:2.5	0.5	25	25	2.5
25.0:3.5	0.5	25	25	3.5
25.0:5	0.5	25	25	5

3.1.2.2 Determination of asphaltene particle sizes

The oil sample used in this study is depressurised crude oil, therefore, there was higher probability of having precipitated asphaltenes particles from the crude oil sample. In order to see if there is any particle in the crude oil sample a drop of crude oil was placed in a glass slice and observed under an optical microscope, as shown in Figure 3.2. Table 3.4 provides the properties of the optical microscope used for the characterisation of the samples prepared in this investigation.

Table 3.4: Microscope properties

Model	Magnification	Microscope objective lens	Microscope ocular	Microscope camera
Olympus GX41	6.3 x	MPlan 10X/ 0.25 ∞/-	WHB10X/20	SC50



Figure 3. 2: The Olympus GX41 optical microscope

3.1.2.3 Crude oil preparation

To remove water, sand or any other precipitated particle commonly present in the crude oil samples, the crude oil sample was centrifuged for 3 hours at a speed of 1000 rpm. After that, the sample was reanalysed to make sure that it is clean enough to start the experimentations.

3.2 Crude oil and n-heptane mixture preparation

0.5 g of crude oil was placed in a vial and 2 ml of n-heptane was added. The mixture was shaken manually for 5 minutes to homogenise it. The sample was heated up on a water bath at 35 ºC, 65 ºC and 80 ºC for 30 minutes, and then, using a dropper, a drop of the mixture was placed on a glass slice and observed under the microscope to analyse the growth of asphaltene particles and measure the size of the particles. The samples were analysed using an Olympus GX41 optical microscope and the measurements were made by using the linear ruler on the Olympus ST software. Thereafter, 0.5 ml of n-heptane was added and the sample was placed in the water bath for 60 minutes, and observed under the microscope. 1 ml of n-

heptane was then added to the mixture, placed in a water bath for 90 minutes and then observed. Lastly, 1.5 ml of n-heptane was added, placed in a water bath for 120 minutes and then observed.

3.3 Inhibitors preparation

2.5%, 5%, 10%, 15%, 20% and 25% of inhibitors concentrations that are equivalent to 0.985g, 1.97g, 3.94g, 5.91g, 7.88g and 9.85g, respectively, of each solvent were used during the experimentations. After weighing the solvent powders, they were mixed with 50 ml of ethanol. Each concentration was in a separate volumetric flask.

Figure 3.4 provides the preparation of Iso-Phthalic acid. The mixtures with 15%, 20% and 25% of Iso-Phthalic acid took longer to dissolve, therefore, a magnetic stirrer was used to accelerate the dissolution process. The 15% of Iso-Phthalic acid mixture was placed on a magnetic stirrer for 55 minutes at a speed of 7 rpm. The 20% mixture was placed on a magnetic stirrer for 79 minutes at a speed of 7 rpm, and the 25% mixture was placed on a magnetic stirrer for 198 minutes at a speed of 7 rpm.



Figure 3. 3: Dissolution of Iso-Phthalic acid

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Pre-treatment of crude oil sample

The crude oil sample was pre-treated for solid and suspension removal. This step was required to avoid contamination of the precipitated asphaltene produced in this investigation. Figure 4.1 shows that the crude oil sample from Sasolburg had some solid impurities. Figure 4.2 shows a crude oil sample without any solid impurities. The pre-treatment process removed the solid impurities through centrifuge.

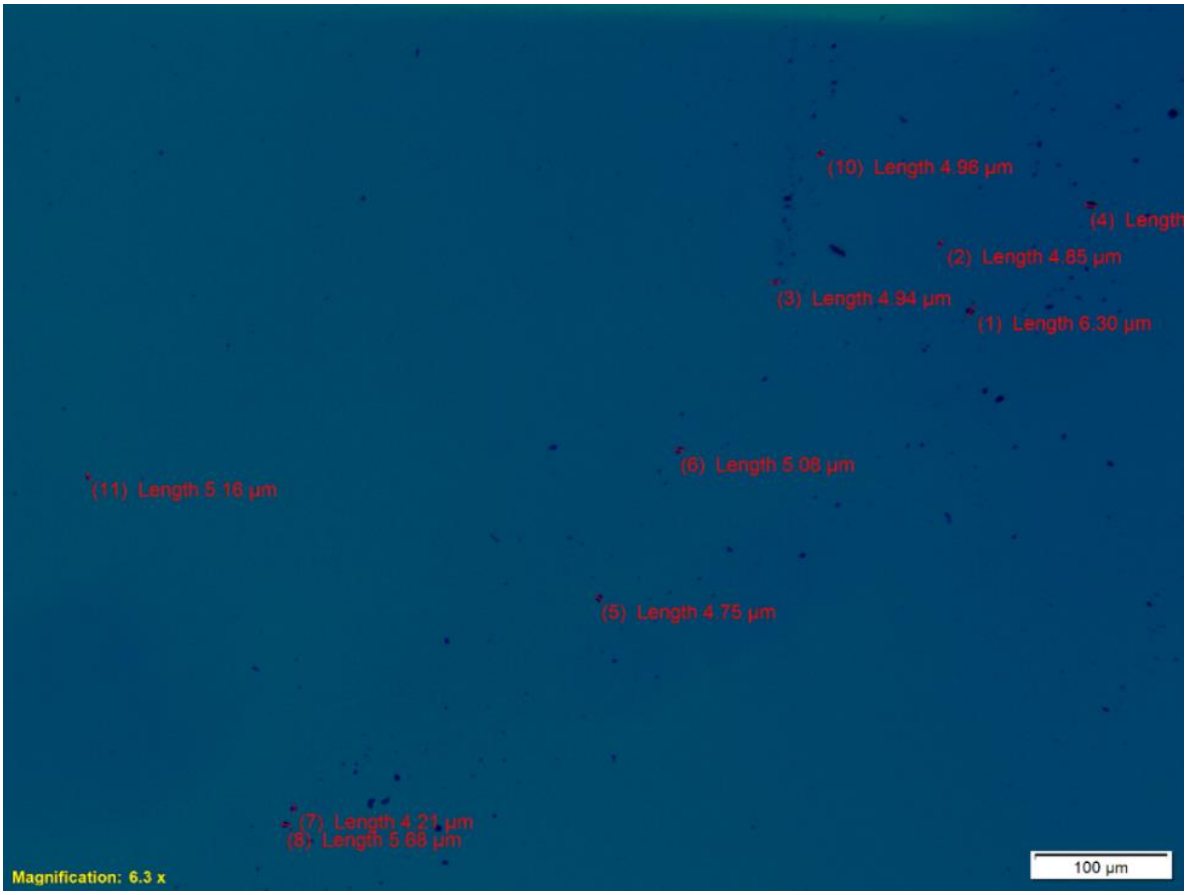


Figure 4. 1: Crude oil sample before pre-treatment



Figure 4. 2: Crude oil sample after pre-treatment

4.2 Inhibitors concentrations effect on the size of the precipitated particles at 35 ºC, 65 ºC and 80 ºC

Based on the microscope photographs, presented in Appendices B to G, and using a linear ruler to measure the asphaltene particles, the average length of the precipitated particles was calculated on each sample using the various measurements taken in each microscope photograph.

For each temperature, 60 samples of similar composition (crude oil, inhibitor and precipitant), differing only on the inhibitors type and temperature. The results gathered were used to plot graphs in order to make the analysis of the results relatively easy.

Figure 4.3 shows the results of the samples at 35 ºC. For each sample, the mean and standard deviation were calculated and the error bars to quantify the scatter among the values were plotted.

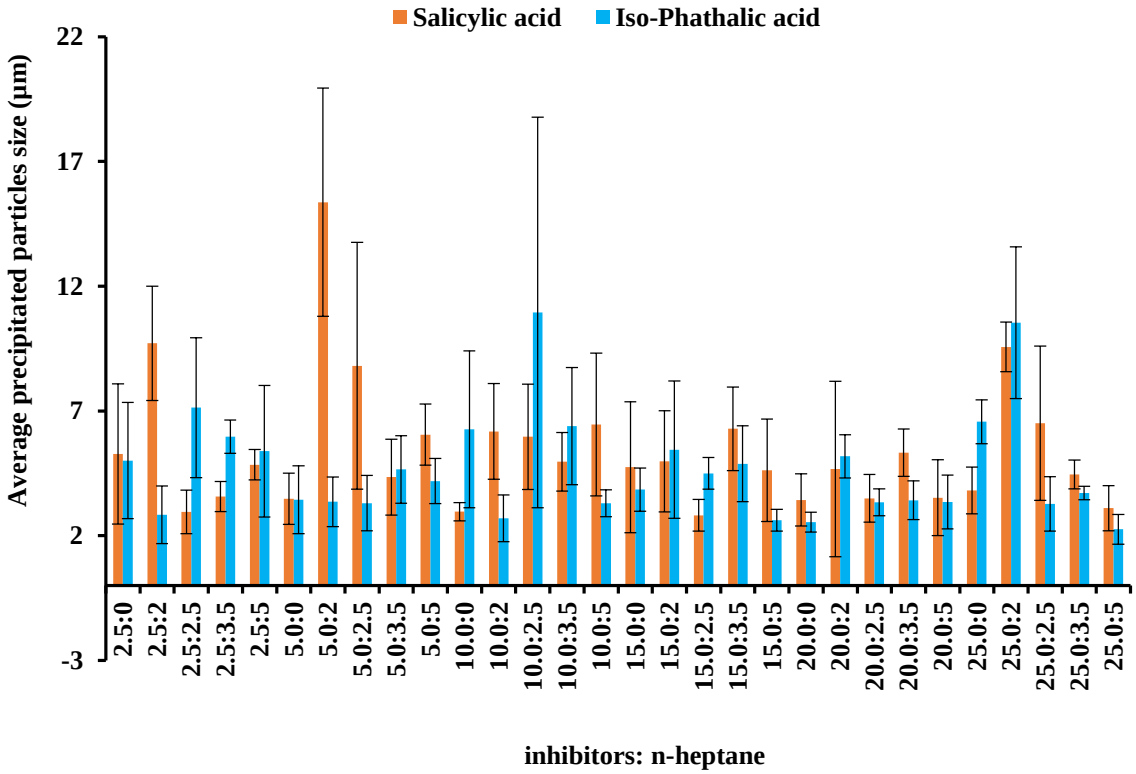


Figure 4. 3: Effect of the inhibitors concentrations on the size of the precipitated particles at 35 ºC

At 35 ºC the best concentration for Salicylic acid on the asphaltene precipitation inhibition was 15% Salicylic acid and 2.5 ml of n-heptane, in which the average deposited particles size is 2.82 µm. However, Salicylic acid showed the lowest inhibition effect (highest precipitated asphaltene particle in terms of size) at 5% Salicylic acid and 2 ml of n-heptane, with an average precipitated particle size of 15.36 µm.

For the Iso- Phthalic acid, the results showed that the best inhibitor was 25% Iso-Phthalic acid and 5 ml of n-heptane, with an average particle size of 2.26 µm. The highest precipitated particle size for Iso-Phthalic acid was identified on the sample containing 10% Iso-Phthalic acid and 2.5 ml of n-heptane with an average precipitated particle of 10.94 µm. At 35 ºC Iso-Phthalic acid showed better inhibition efficiency.

Figure 4.4 shows the results of the samples at 65 ºC.

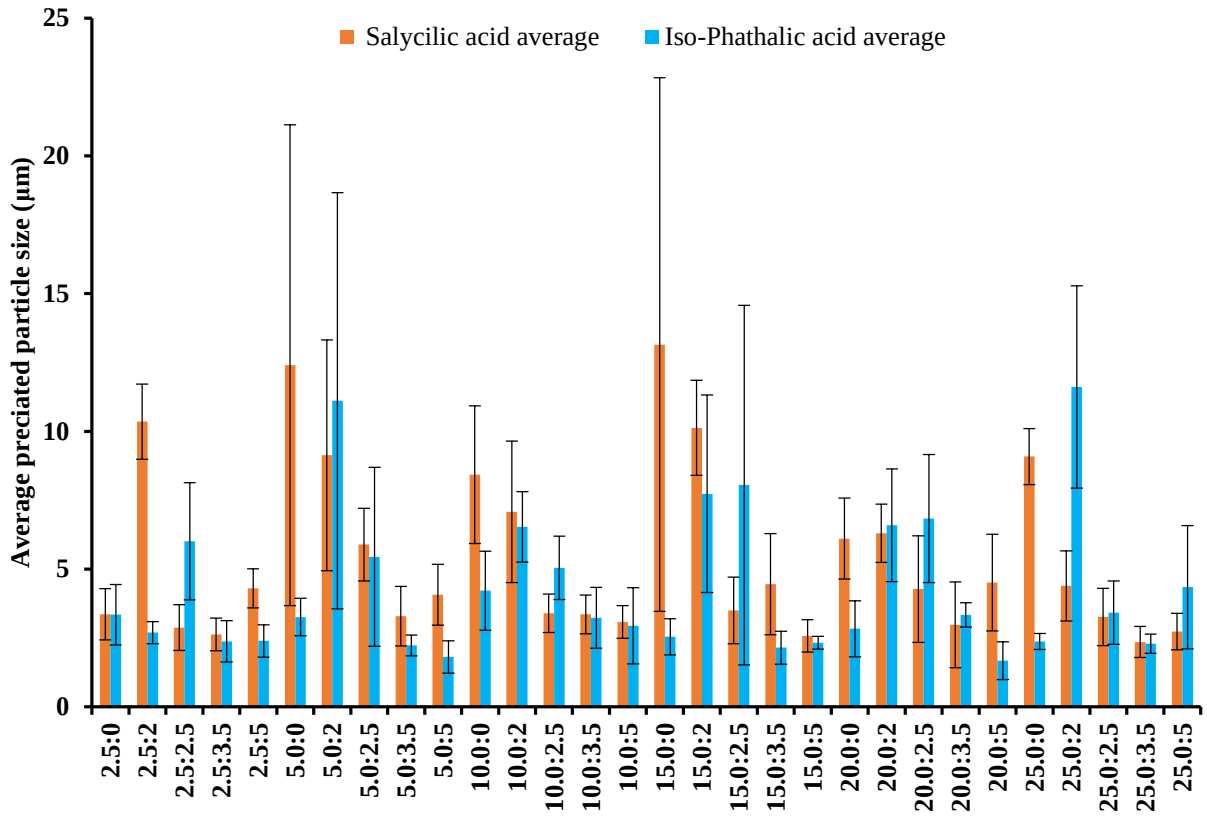


Figure 4. 4: Effect of the inhibitors concentrations on the size of the precipitated particles at 65 ºC

The best concentration for Salicylic acid on asphaltene precipitation inhibition was 25% Salicylic acid and 3.5 ml of n-heptane, where the average precipitated particles size was 2.35 µm. An increase in the average particle size was observed on the sample containing 15% Salicylic acid and 0 ml of n-heptane, reaching the highest value in terms of average precipitated particle of 13.14 µm, at 65 ℃.

For the Iso- Phthalic acid, the results showed that the best concentration for better inhibition was 20% Iso-Phthalic acid and 5 ml of n-heptane, with an average particles size of 1.68 µm. The highest average precipitated particle size was identified on the sample containing 25% Iso-Phthalic acid and 2 ml of n-heptane, where the average precipitated particles size was 11.61 µm. At 65 ºC, the best inhibition was observed with Iso-Phthalic acid.

Figure 4.5 shows the results of the samples at 80 ºC.

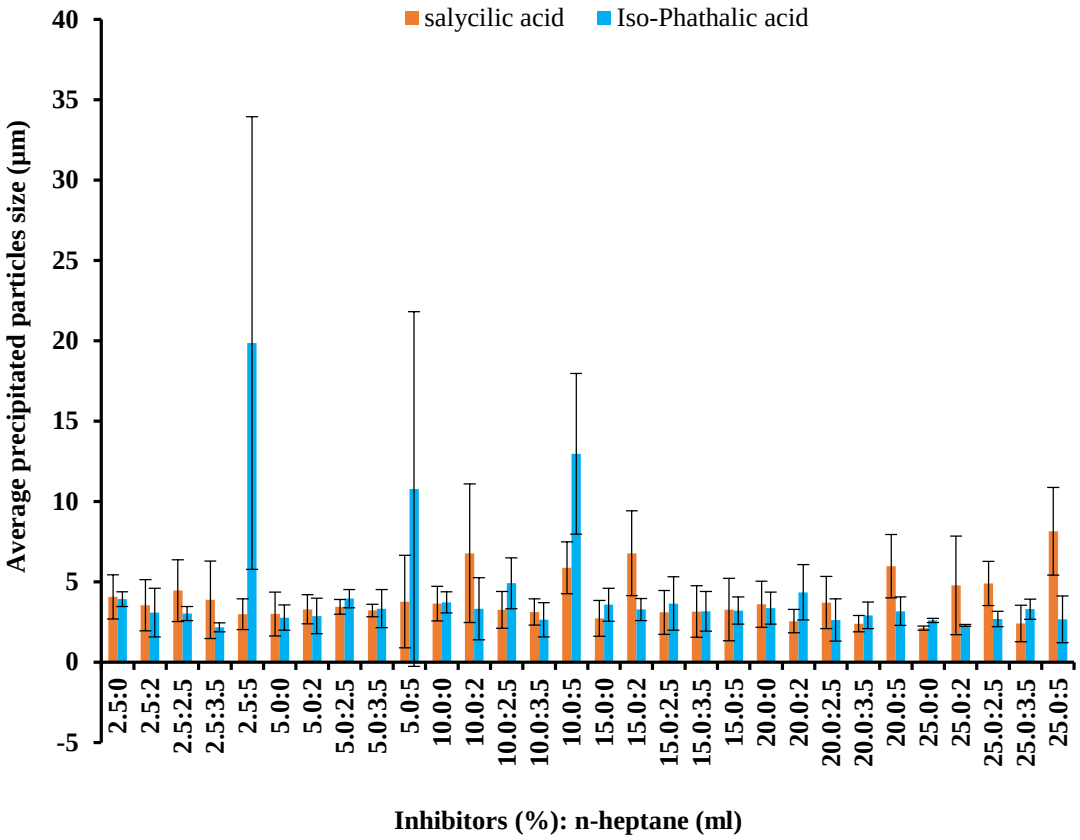


Figure 4. 5: Effect of the inhibitors concentrations on the size of the precipitated particles at 80 ºC

The best concentration for Salicylic acid on the asphaltene precipitation inhibition was 25% Salicylic acid and 3.5 ml of n-heptane where the average deposited particles size was 2.4 µm. The highest average particle size was observed on the sample containing 25% Salicylic acid and 5 ml of n-heptane and the average precipitated particle size was 8.14 µm. For the Iso-Phthalic acid the results of the experiments showed that the best concentration for better inhibition was 2.5 % Iso-Phthalic acid and 3.5 ml of n-heptane and the average precipitated particles size was 2.16 µm.

The highest average precipitated particle size was registered on the sample containing 2.5% Iso-Phthalic acid and 5 ml of n-heptane, where the average precipitated particles size was 19.86 µm. At 80 ºC the best inhibitor for asphaltene inhibition was Salicylic acid.

For all the temperatures, there is no linearity trend of increasing of inhibitor efficiency with increase or decrease of inhibitor and precipitant concentration. However, at high temperatures (80 ºC) Salicylic acid in higher concentrations (25%) has shown to be the best and worse

inhibitor for 3.5 ml and 5 ml of n-heptane, respectively. Iso-Phthalic acid with a concentration of 2.5% showed the same behaviour for 3.5 ml and 5 ml of n-heptane, respectively. As agreed by Mansur *et al*. (2012) investigation, a large amount n-heptane (5 ml) has negative effects on the inhibition efficiency of asphaltene at higher temperatures (80 ºC).

4.3 Effect of temperature on the precipitated particles size using Salicylic and Iso-Phthalic acids

The effect of temperature on asphaltenes precipitation can be seen in Figure 4.6, where salicylic and iso-phthalic acids were compared.

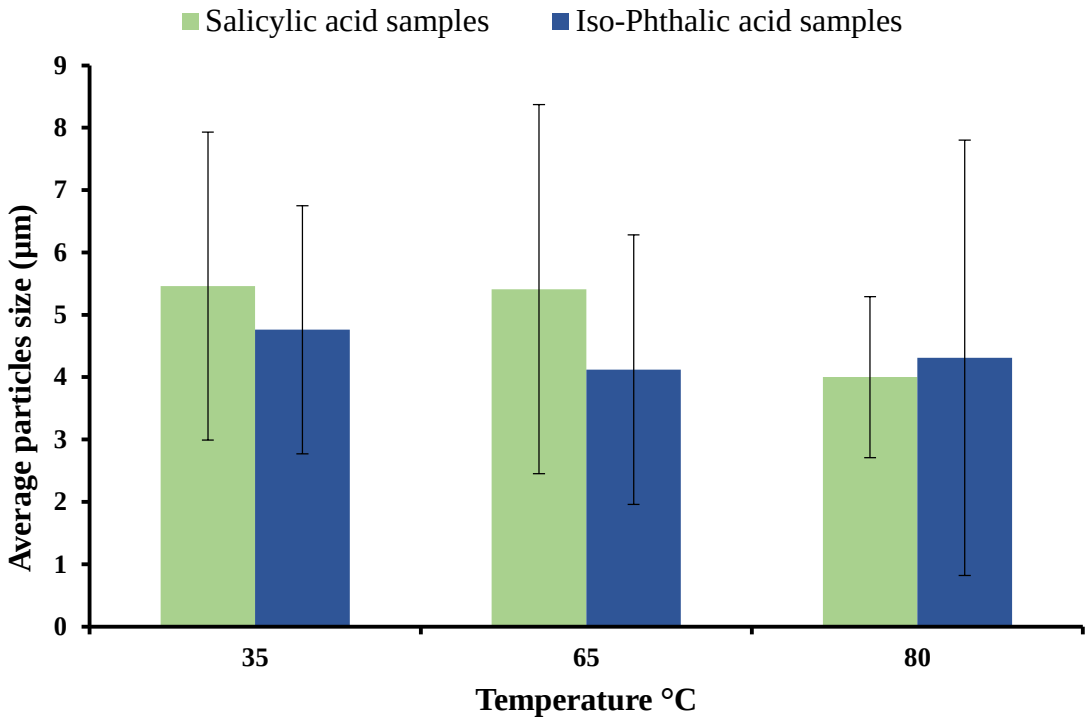


Figure 4. 6: Effect of temperature on the precipitated particles size

Table 4. 1: Average deposited asphaltene particles using both inhibitors

Temperature (°C)	35	65	80

Average precipitated particles size for both inhibitors (µm)	10.22	9.53	8.31

From the results presented in Table 4.1 it is clear that by using the two inhibitors the precipitated particles size reduces as the temperature increases. As discussed and concluded by Andersen and Stenby (1996), there is an increase in the solubility of asphaltenes in hydrocarbon solvents with an increase in temperature.

Rassamdana and Sahimi (1996) mentioned that one of the consequences of the increase in temperature in the system is the dissolution of more resins and the electrical charge imbalance between the asphaltene particles or clusters is much lower, thus maintaining more asphaltene in the solution rather than their precipitation. This can be seen in the results presented in Table 4.1. However, in this research, there are particularities when it comes to the analysis of each inhibitor, as shown in Figure 4.6. The size of the precipitated particles was higher for Salicylic acid at 35 °C and 65 °C, and lower at 80 °C. While for Iso-phthalic acid, the size of the precipitated particles was lower at 35 °C and 65 °C and higher at 80 ° C. This behaviour shows that the inhibition capacity for Salicylic acid was greater in high temperatures (80 °C) while for Iso-phthalic acid was greater in lower temperatures (35 ° C and 65 °C).

4.4 Effect of the addition of n-heptane on the particles size at 80 ºC using inhibitors

The behaviour of n-heptane as precipitant in the presence of Salicylic or Iso- phthalic acids (as inhibitors) are given in the following.

4.4.1 Effect of the addition of n-heptane on the particles size at 80 ºC using Salicylic acid

Figure 4.7 showed the variations on the precipitated particles size with addition of the following amounts of n-heptane: 2 ml, 0.5 ml, 1 ml and 1.5 ml.

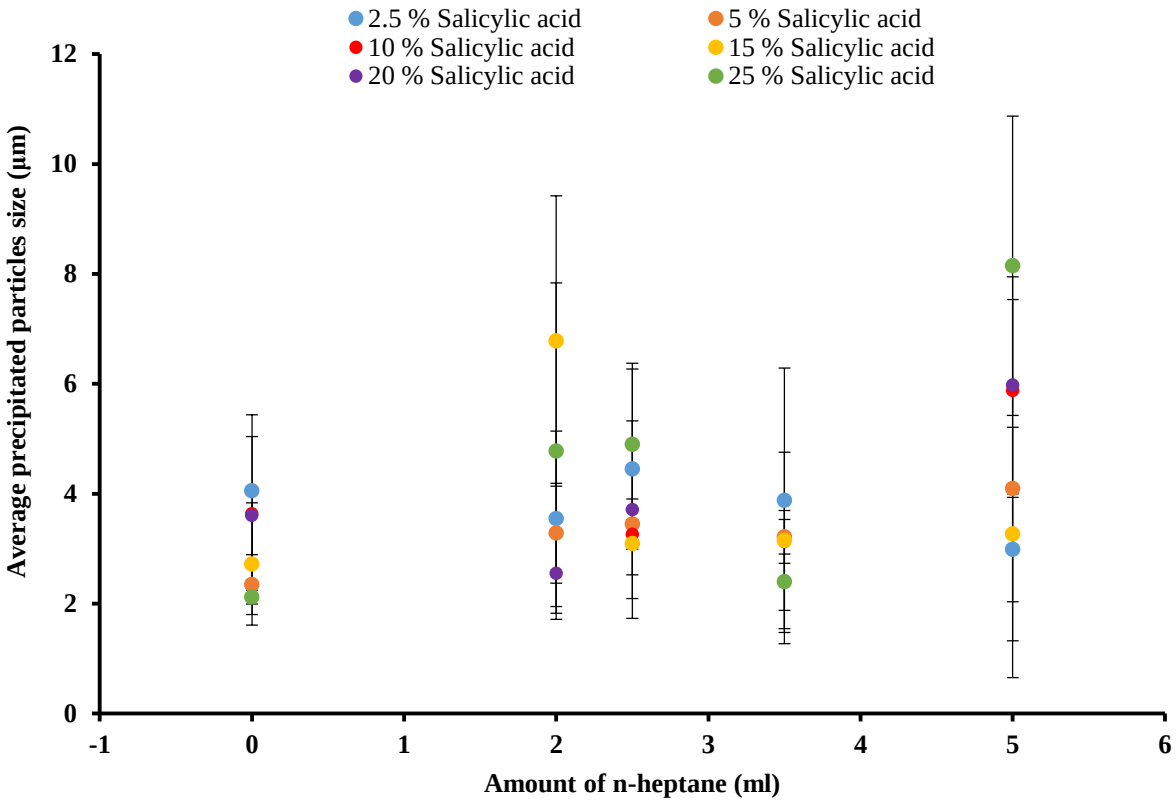


Figure 4. 7: Effect of the addition of n-heptane on the particles size at 80 ºC using Salicylic acid

These amounts were added to the mixture of crude oil and Salicylic acid, at different times. According to the results, it was concluded that the more stable samples (without many variations in the particles size) were the samples containing 5% Salicylic acid. This means that 5% Salicylic acid was the best concentration for asphaltene inhibition in this particular crude oil sample. The samples that showed more instability in terms of inhibitor concentration were the ones containing 25% Salicylic acid.

When it comes to the amount of n-heptane the most unstable samples (where there was a significant amount of variations in terms of the average precipitated particles size as well as the highest value in terms of particles size), were the ones containing 5 ml of n-heptane. The samples with the lowest values in terms of the average precipitated particles size were the ones contain 3.5 ml of n-heptane.

4.4.2 Effect of the addition of n-heptane on the particles size at 80 ºC using Iso-Phthalic acid

From the results presented on Figure 4.8, the samples containing 25% of Iso-Phthalic acid were more stable in terms of the average precipitated particles size and at this concentration the size of the particles were smaller than in the samples with less inhibitor concentration (2.5%).

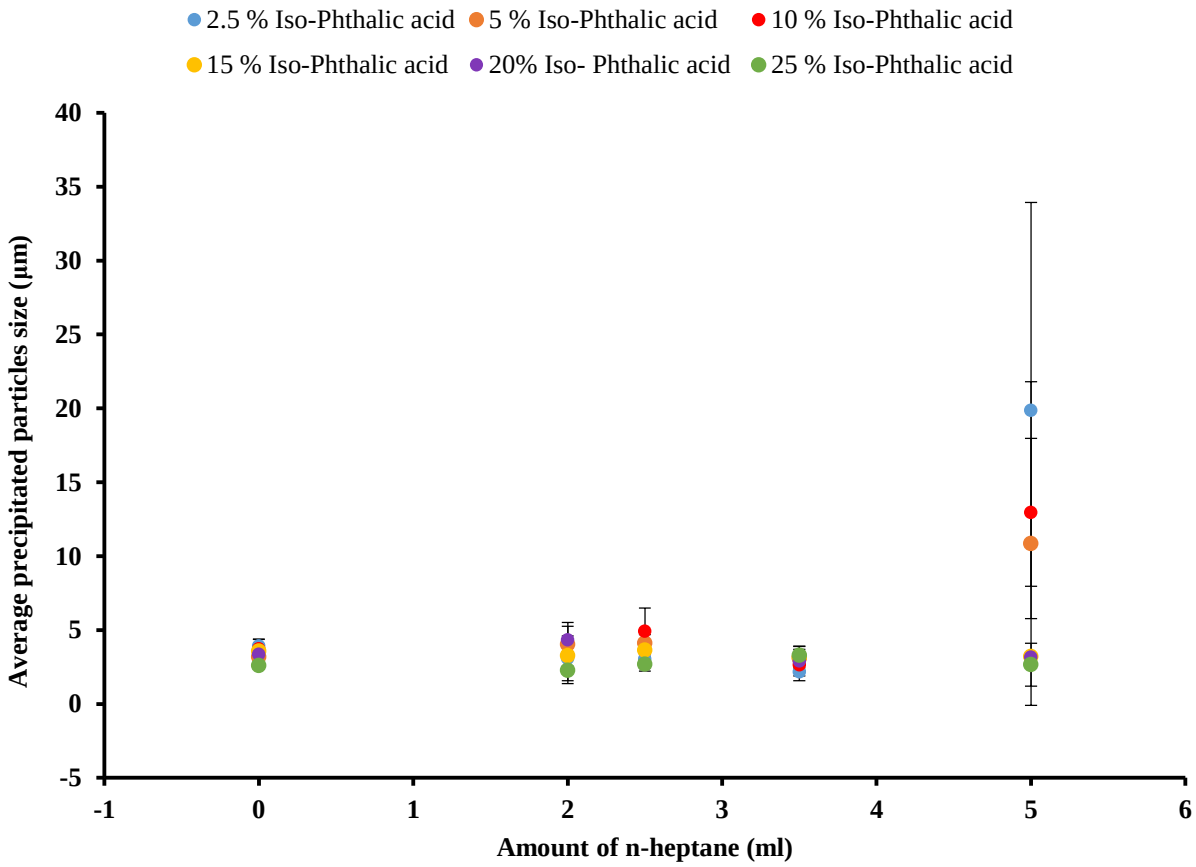


Figure 4. 8: Effect of the addition of n-heptane on the particles size at 80 ºC using Iso-Phthalic acid

The samples containing higher amount of n-heptane (5 ml) showed more instability in term of the average precipitated particles size. There were significantly large variations in the size as well as the highest value in terms of the size of the particles. As suggested by Ashoori *et al.* (2012) the size of the precipitated asphaltenes is not dependent on the n-heptane amount in

each mixture, however, the highest precipitated particle size was registered on the sample with a much higher amount of n-heptane.

4.5 Effect of time on the average precipitated particles size using inhibitors at 80 ºC

The results of sizes of precipitated particles at various times are given below. These results provide a better kinetic behaviour of asphaltenes in the presence of salicylic and Iso-phthalic acids.

4.5.1 Effect of time on the average precipitated particles size using Salicylic acid

Figure 4.9 confirmed that the highest average precipitated particles size was observed when the samples rested for 120 minutes. The lowest average particle size was observed when the samples rested for 90 minutes.

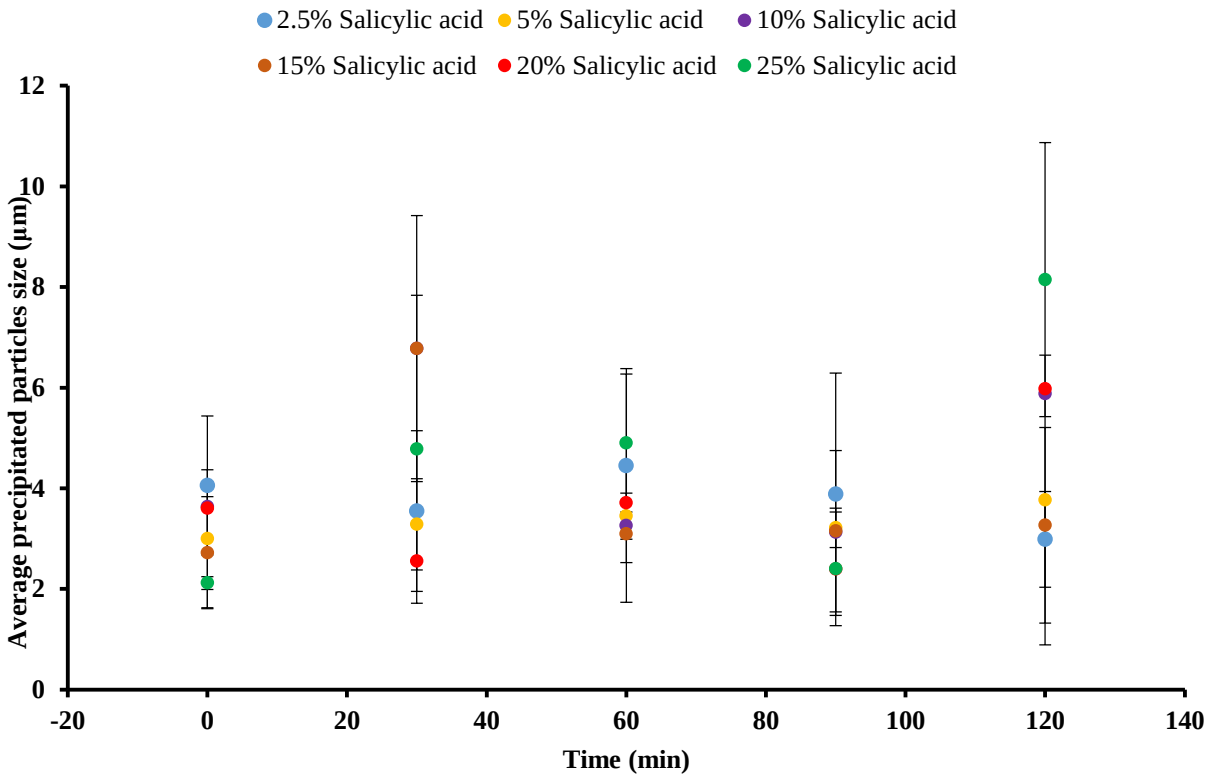


Figure 4. 9: Effect of time on the average precipitated particles size using Salicylic acid

4.5.2 Effect of time on the average precipitated particles size using Iso-Phthalic acid

The results presented in Figure 4.10 show that on the Iso-Phthalic acid samples, with a concentration of 2.5%, the highest average particle size was observed on the sample left resting for 120 minutes in the water bath, and the lowest average precipitated particle size was observed on the same Iso- Phthalic acid concentration at 90 minutes.

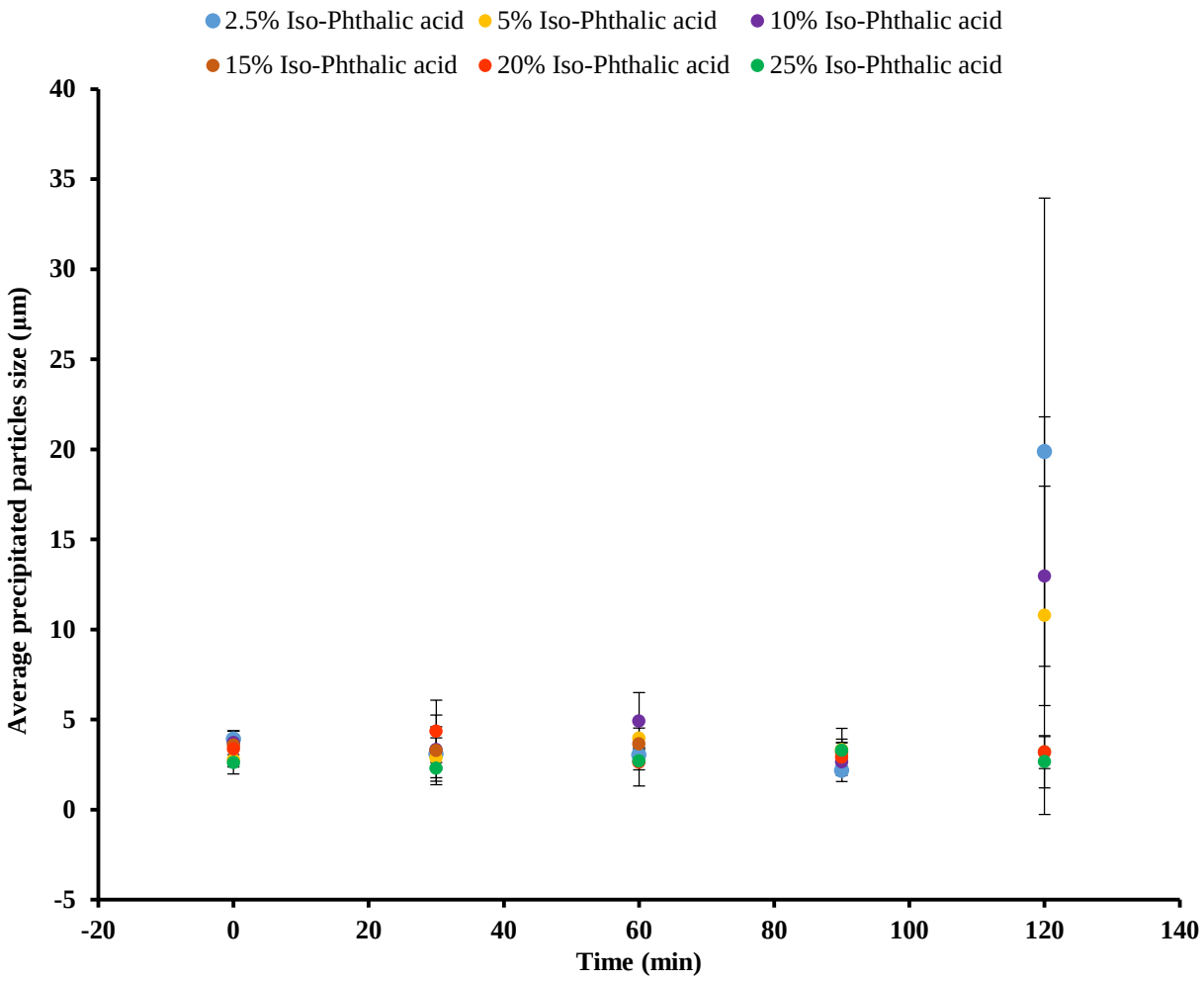


Figure 4. 10: Effect of time on the average precipitated particles size using Iso-Phthalic acid

It was clear that the mixtures interaction time plays an important role in the precipitated particles size. Mansur *et al.* (2012) analysed the size of the precipitated asphaltenes in crude

oil, solvent (toluene) and precipitant (n-heptane) mixtures, and also concluded that there is a tendency to increase the particles size with time. On that particular project, the particles growth was observed after 18 hours of mixture interaction. Similar behaviour was observed in the results using both inhibitors where the largest average precipitated particle size was observed at 120 minutes.

4.6 Comparison of the effect of n-heptane on Salicylic and Iso-Phthalic acids samples at 80 ºC

According to the Figure 4.11, for both inhibitors, the highest average particle size was achieved with 5 ml of n-heptane and the lower average precipitated particle size was achieved with 3.5 ml of n-heptane.

For Salicylic acid, the highest average precipitated particle size was observed at a higher concentration of this inhibitor (25%) with the addition of 5 ml of n-heptane, and the lowest average precipitated particle size was observed on the sample containing the same concentration of Salicylic acid with an addition of 3.5 ml of n-heptane. The lowest Iso-Phthalic concentration (2.5%) precipitated a larger average particle size with the addition of 5 ml of n-heptane, and the same concentration of Iso-Phthalic acid showed the smallest particles size with the addition of 3.5 ml of n-heptane.

From these results, Iso-Phthalic acid at lower concentrations, precipitated larger and smaller average precipitated particle sizes with the addition of 5 ml and 3.5 ml of n-heptane, respectively, while Salicylic acid at higher concentrations, precipitated larger and smaller average precipitated particle size with the addition of 5 ml and 3.5 ml of n-heptane, respectively.

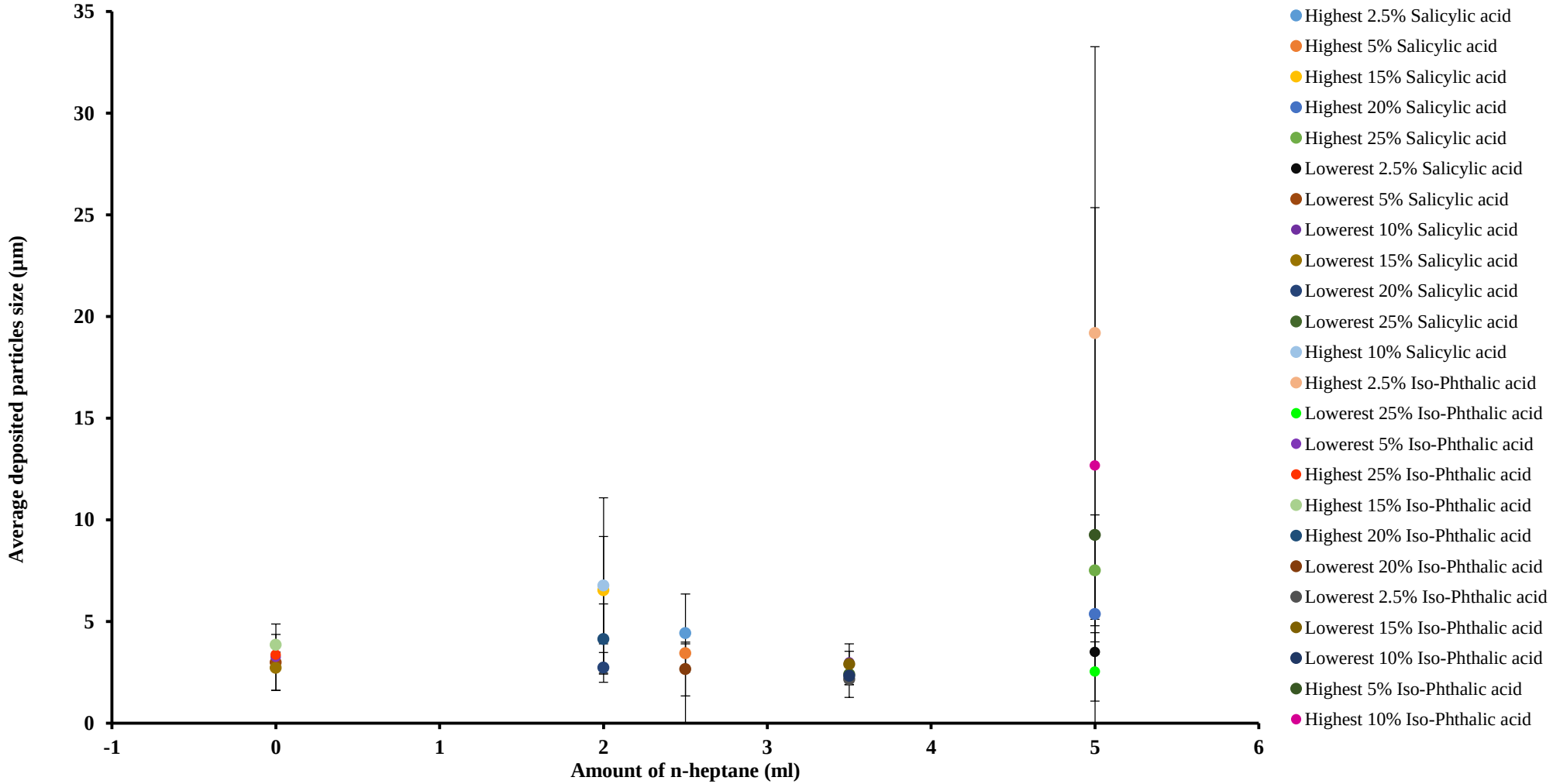


Figure 4. 11: Comparison of the effect of n-heptane on Salicylic and Iso-Phthalic acid samples

4.7 Comparison of the effect of time on Salicylic and Iso-Phthalic acids samples at 80 ºC

Figure 4.12 shows that for Salicylic and Iso-Phthalic acids the highest average particle size was achieved at 120 minutes and the lower average precipitated particle size was achieved at 90 min. For Salicylic acid the highest average precipitated particle size was observed at a higher concentration of this inhibitor (25%) at 120 minutes, and the lowest average precipitated particle size was observed on the sample containing the same concentration of Salicylic acid at 90 minutes. The lowest Iso-Phthalic concentration (2.5%) precipitated a larger average particle size at 120 minutes, and the same concentration of Iso-Phthalic acid shows the smallest particles size at 90 minutes.

From these results, Iso-Phthalic acid at lower concentrations, precipitated larger and smaller average precipitated particle sizes at 120 minutes and 90 minutes, respectively, while Salicylic acid at higher concentrations, precipitated larger and smaller average precipitated particle size at 120 minutes and 90 minutes, respectively.

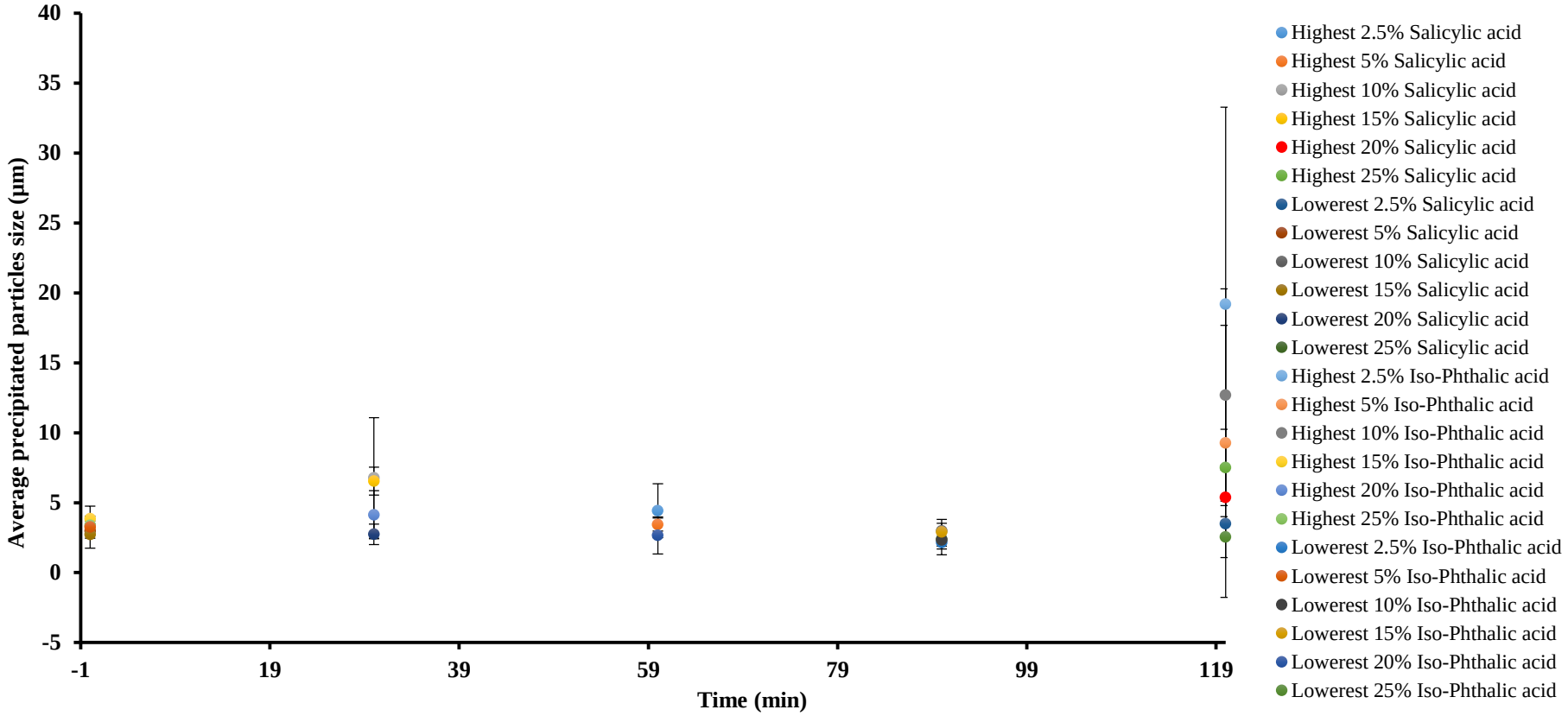


Figure 4. 12: Comparison of the effect of time on Salicylic and Iso-Phthalic acid samples

4.8 Asphaltene aggregates formation by addition of n-heptane in crude oil samples

The effect of n-heptane on the asphaltenes aggregates formation was observed, and below are the results observed at various temperatures.

4.8.1 Asphaltene aggregates formation with the addition of n-heptane at 35 ºC

Figure 4.13 showed the behaviour of crude oil and n-heptane samples on the asphaltene aggregates formation at 35 ºC. The average of the individual precipitated particles size was measured as showed in Appendices H, I and J at 35 ºC, 65 ºC and 80 ºC, respectively, and the shape and stages of asphaltene aggregation are discussed.

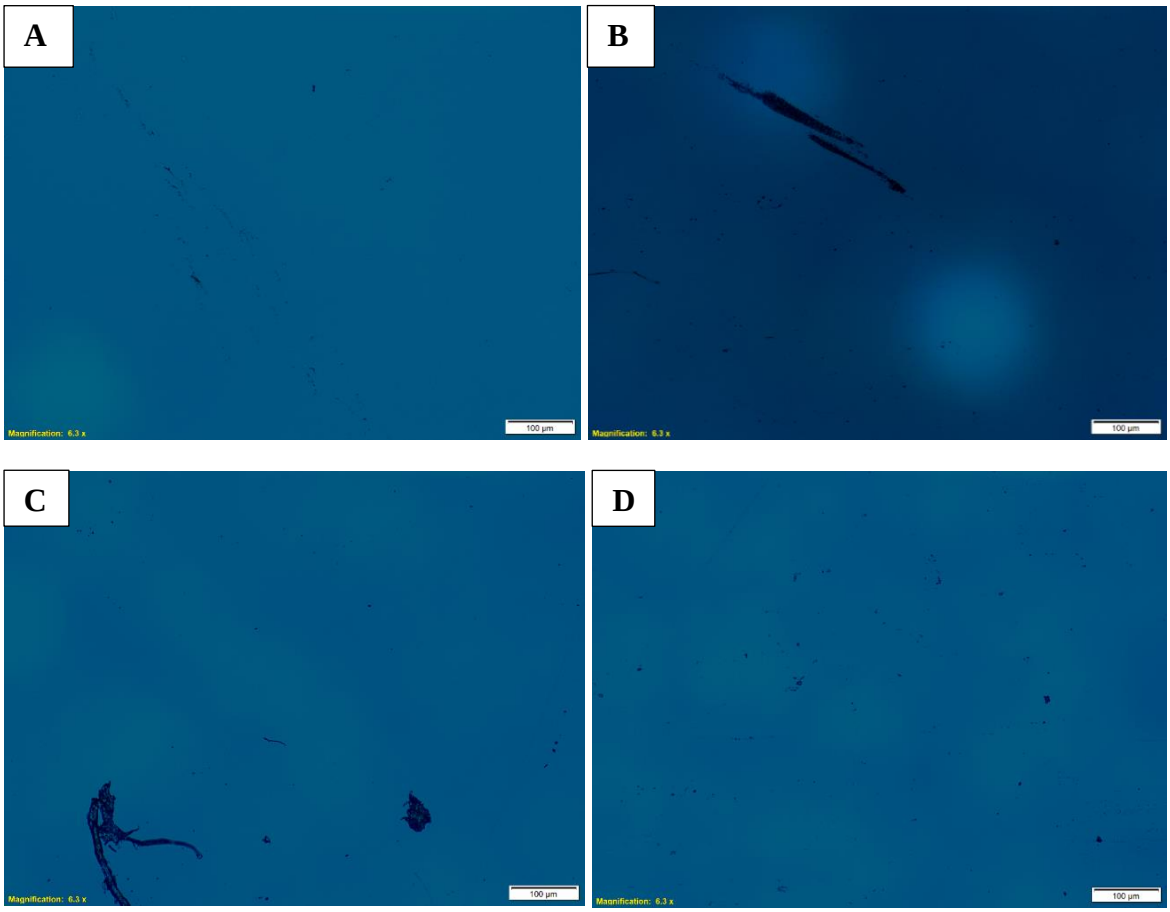


Figure 4. 13: Asphaltene aggregates formation with n-heptane at 35 ºC

A: 0.5g of Crude Oil + 2 ml of n-heptane (30 min); **B:** 0.5g of Crude Oil + 2.5 ml of n-heptane (60 min); **C:** 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min); **D:** 0.5g of Crude Oil + 5 ml of n-heptane (120 min).

The aggregation process started after adding 2 ml of n-heptane, where the formation of very small and linear aggregates as presented on Image A was observed, and the average precipitated particles size was 3.1 µm.

With the addition of 2.5 ml of n-heptane at 60 minutes (Image B), the linear aggregates showed an increase in size, with an average size of 4.22 µm in terms of precipitated particles size.

Thereafter, continued growth was observed in the aggregates in the presence of 3.5 ml of n-heptane (Image C), but a decrease in the average precipitated particles (3.8 µm) was also observed. With continued addition of n-heptane (5 ml), no more aggregation was registered (Image D), and the size of the individual precipitated particles size was 2.7 µm.

4.8.2 Asphaltene aggregates formation with the addition of n-heptane at 65 ºC

Figure 4.14 shows asphaltene aggregation stages at 65 ºC at different times. Image A showed small tendencies of asphaltene aggregation upon the addition of 2 ml of n-heptane, where the average precipitated particles size was 3.9 µm. With continued addition of n-heptane (2.5 ml) an increase in size of the aggregates was observed but there was a reduction in terms of the amount. At this stage the average precipitated particles size was 2.28 µm (Image B). Adding 3.5 ml of n-heptane (Image C) the aggregates become longer and the average precipitated particles size was 6.6 µm. Lastly with 5 ml of n-heptane (Image D) the tendency of much longer aggregates formation increased, but there was a decrease in the precipitated asphaltene particles.

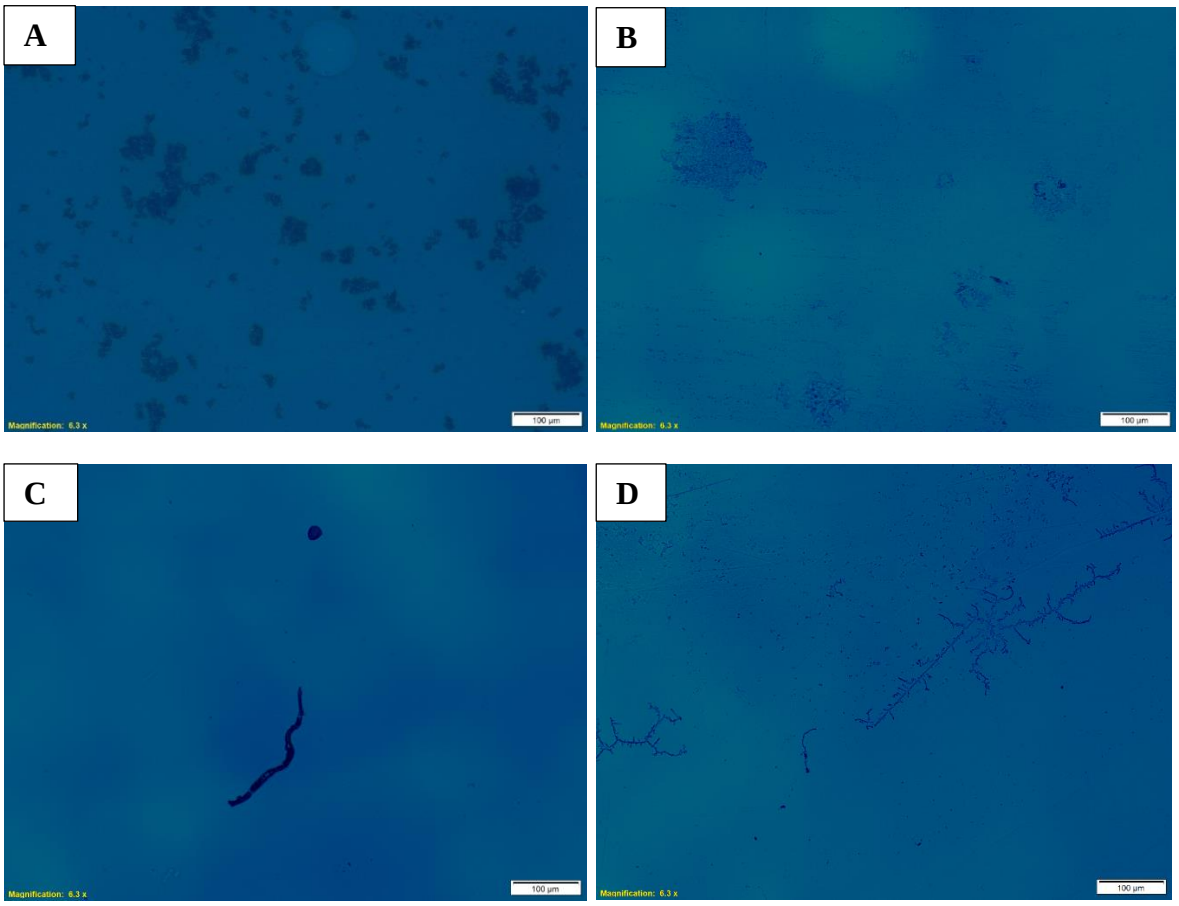


Figure 4. 14: Asphaltene aggregates formation with n-heptane at 65 ºC

A: 0.5g of Crude Oil + 2 ml of n-heptane (30 min); **B:** 0.5g of Crude Oil + 2.5 ml of n-heptane (60 min); **C:** 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min); **D:** 0.5g of Crude Oil + 5 ml of n-heptane (120 min).

4.8.3 Asphaltene aggregates formation with the addition of n-heptane at 80 ºC

From Figure 4.15, it was observed that there is a tendency of aggregation (dispersed clusters) in the first stage of n-heptane addition (2 ml). At this stage the average precipitated particles size was 2.8 µm (Image A). In the second stage (2.5 ml of n-heptane) it was observed that there is a linear trend in terms of aggregation. It showed a tendency of growth in aggregate size and a decrease of the average precipitated particle size to 2.6 µm (Image B). With continued addition of n-heptane (3.5 ml), the particles increased in size and it was observed that there is an increase in a number of aggregates. At this stage the precipitated particles size

was 3.09 µm (Image C). Image D (5 ml of n-heptane) showed more compact asphaltene aggregates formation, with a slight variation in terms of precipitated particles size (3.06 µm) when compared to the particles size on Image C.

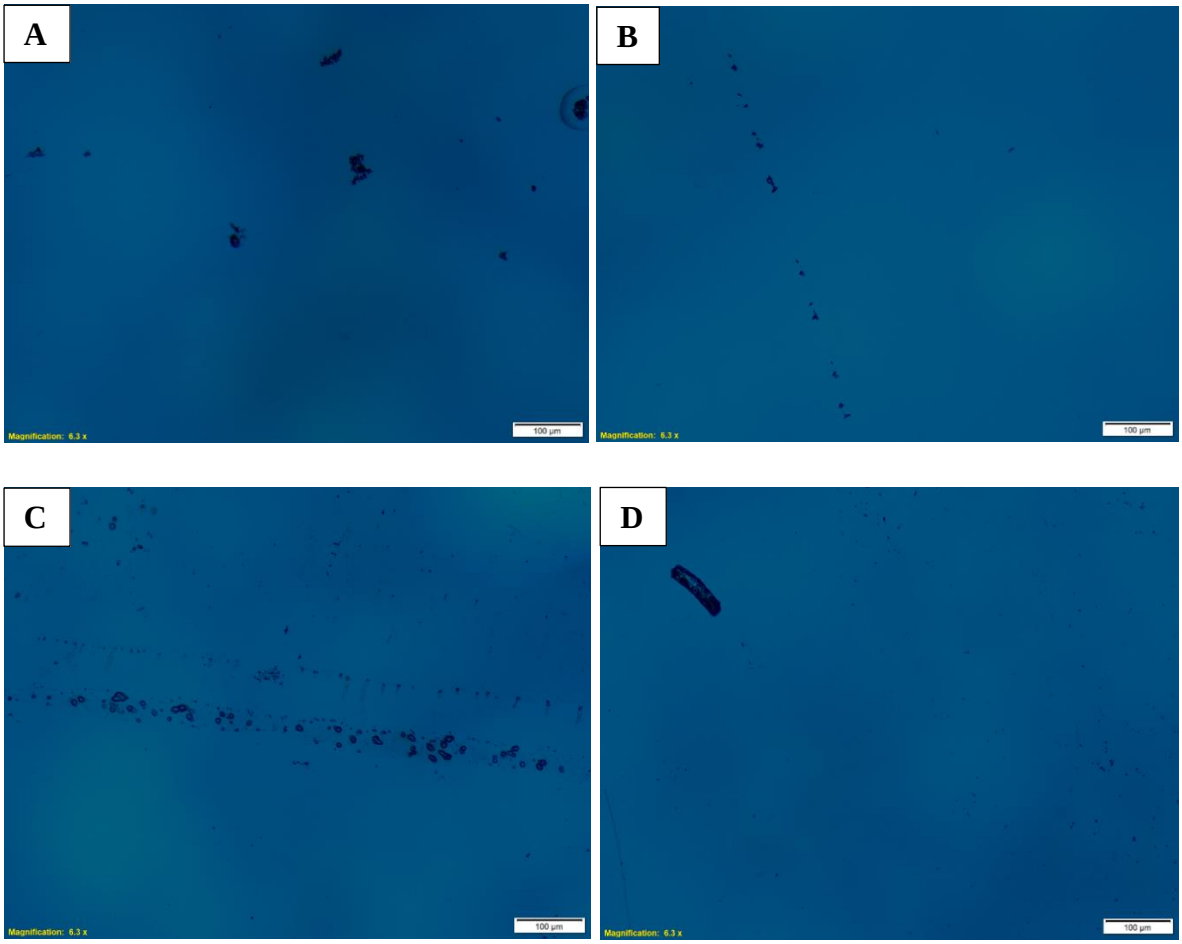


Figure 4. 15: Asphaltene aggregates formation with n-heptane at 80 ºC

A: 0.5g of Crude Oil + 2 ml of n-heptane (30 min); **B:** 0.5g of Crude Oil + 2.5ml of n-heptane (60 min); **C:** 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min); **D:** 0.5g of Crude Oil + 5 ml of n-heptane (120 min).

Maqbool (2011), proved that without the presence of inhibitors the solubility of asphaltene decreases with the increase of n-heptane content, this could be observed on 65 ºC and 80 ºC samples, but on 35 ºC samples, no aggregates were registered with the addition of the highest amount of n-heptane used in this project (5 ml).

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Temperature plays an important role in the asphaltene inhibitors efficiency, and for both inhibitors (Salicylic and Iso-Phthalic acids), it was observed that the solubility of asphaltene increases with an increase in temperature. In general, the experiments showed that the smaller average particles size was observed at higher temperatures such as at 80 ºC.

Analysis of each inhibitor showed that for Salicylic acid, asphaltene solubility increases linearly with increase in temperature (35 ºC, 65 ºC, and 80 ºC) but for Iso-Phthalic acid, the solubility of asphaltene is higher at 65 ºC followed by 80 ºC and lastly 35 ºC.

It was observed that in the presence of 2.5 ml of n-heptane, 15% of Salicylic acid was the best concentration for asphaltene inhibition at 35 ºC, where the average deposited particles size was 2.82 µm. At 65 ºC, in the presence of 3.5 ml of n-heptane, the best concentration of Salicylic acid was 25%, with the average precipitated particles size of 2.35 µm, and at 80 ºC, in the presence of 3.5 ml of n-heptane, 25% Salicylic acid was the best inhibitor concentration for asphaltene inhibition where the average deposited particles size was 2.4 µm.

For Iso-Phthalic acid, it was concluded that, in the presence of 5 ml of n-heptane, the best concentration for asphaltene inhibition at 35 ºC was 25%, with an average precipitated particle size of 2.26 µm. At 65 ºC, the best concentration for better inhibition was 20%, with an average particles size of 1.68 µm. This was achieved in a sample which contained crude oil and inhibitor, and did not contain n-heptane. At 80 ºC, in the presence of 3.5 ml of n-heptane the best concentration for asphaltene inhibition was 2.5%, with an average particles size of 2.16 µm.

Bigger particles sizes were observed at very high amounts of n-heptane (5 ml), but at lower amounts of heptane, there was no linear behaviour between the precipitated particles size and the amount of n-heptane.

The highest inhibition stability was observed at 90 minutes. At a contact time of 120 minutes, there were more variations in terms of the precipitated particles size for both inhibitors as well as the highest value in terms of average precipitated particle size. This was the contact time for the most unstable mixtures.

5.2 Recommendations

Below are the recommendations for future investigations:

- The effect of n-heptane on the average precipitated particles size was investigated through the addition of n-heptane on the samples in an interval of 0.5 ml. It is recommended to reduce this interval to better understand the trend of the particles size growth as a function of n-heptane addition.

- The effect of increasing the mixture's (crude oil, inhibitors and precipitant) interactions contact time for better behaviour profile of the precipitated particle size.

- The effect of asphaltene content by using different crude oil samples on the inhibition efficiency of the two inhibitors used in this investigation.

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APPENDICES

APPENDIX A: Asphaltene deposition mitigation and removal techniques

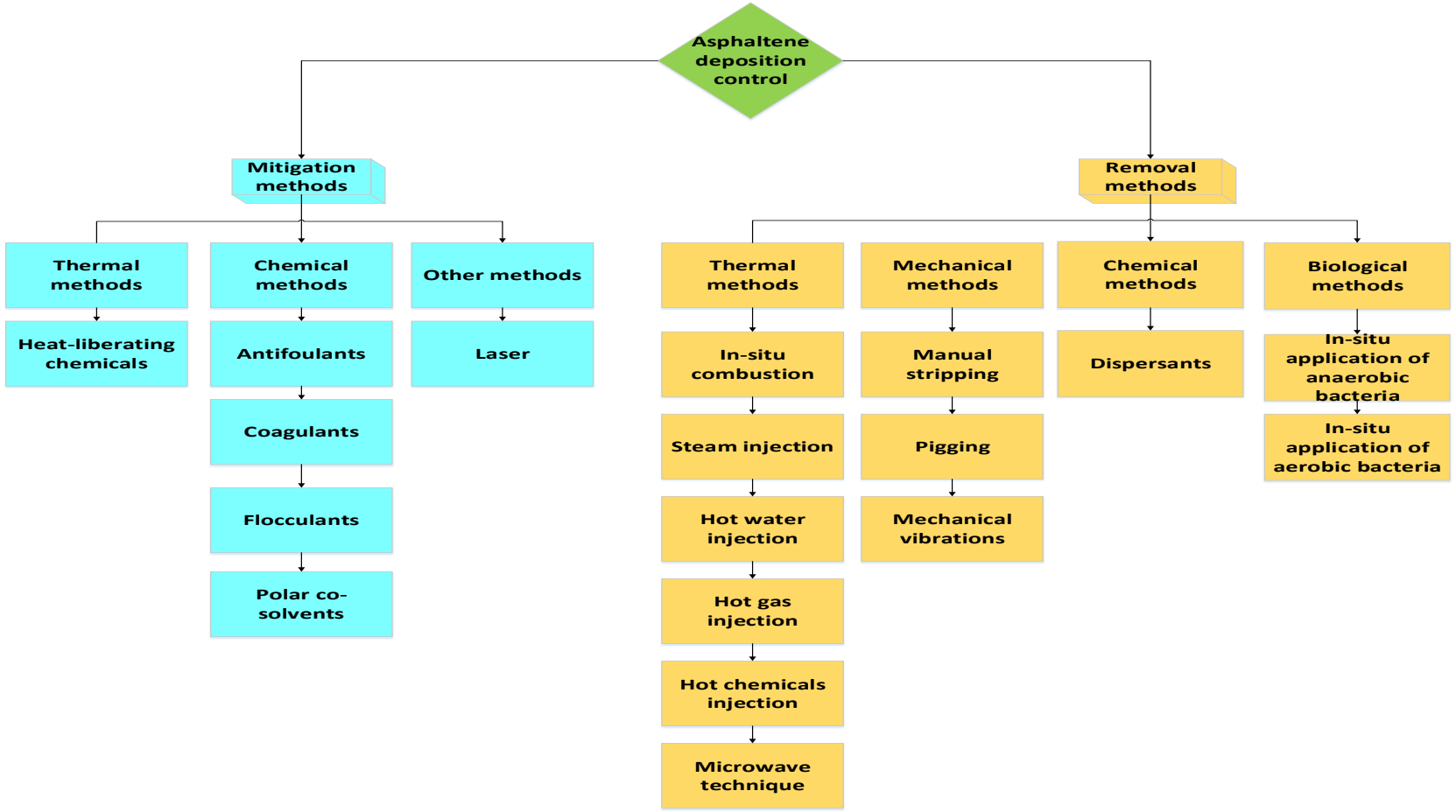


Figure A: Asphaltene deposition mitigation and removal techniques (adapted from Bimuratkyzy and Sagindykov, 2016)

APPENDIX B: Crude Oil - n-heptane - Salicylic acid mixture at 35 ^{o}C

Figure B: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 35 ºC

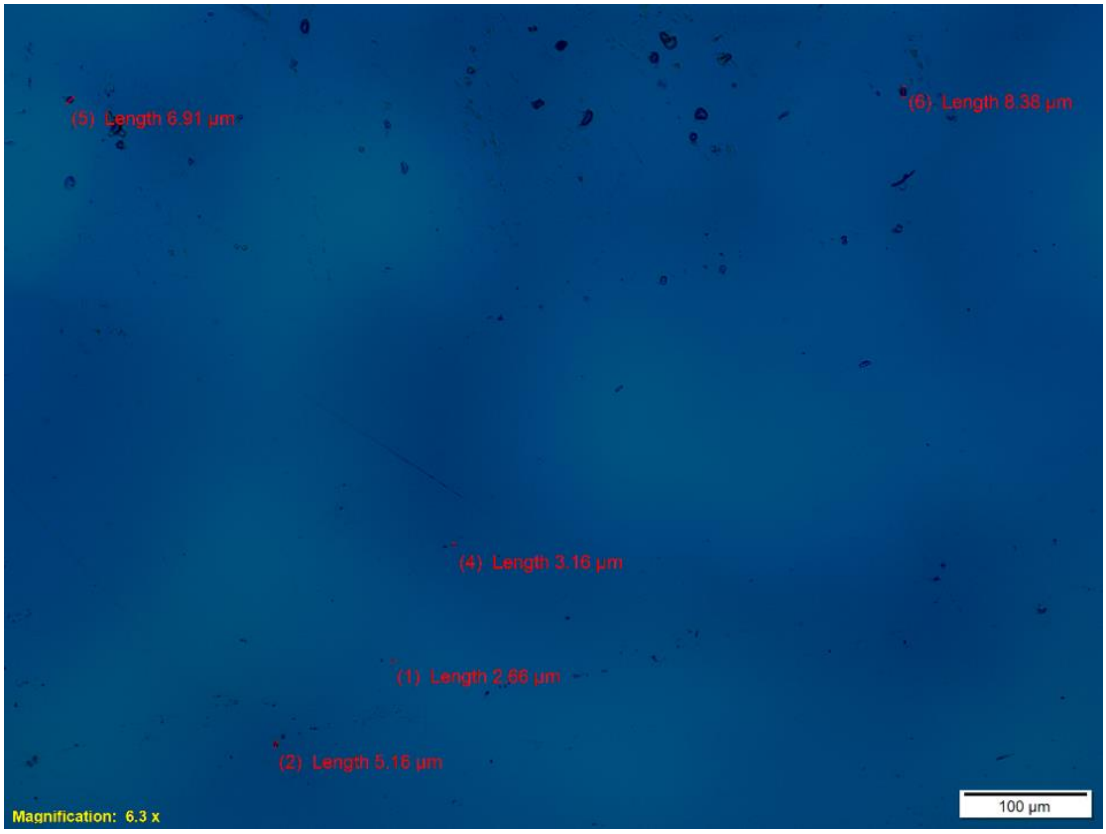


Figure B.1: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid (Time zero)

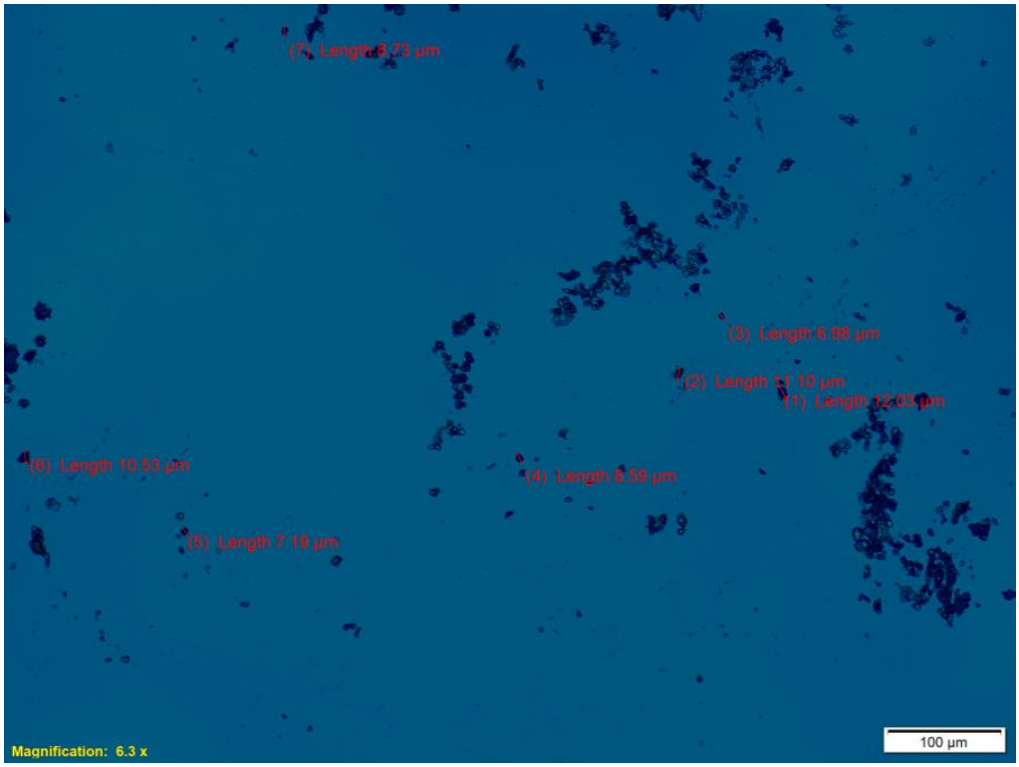


Figure B.2: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2 ml n-heptane (30 min)

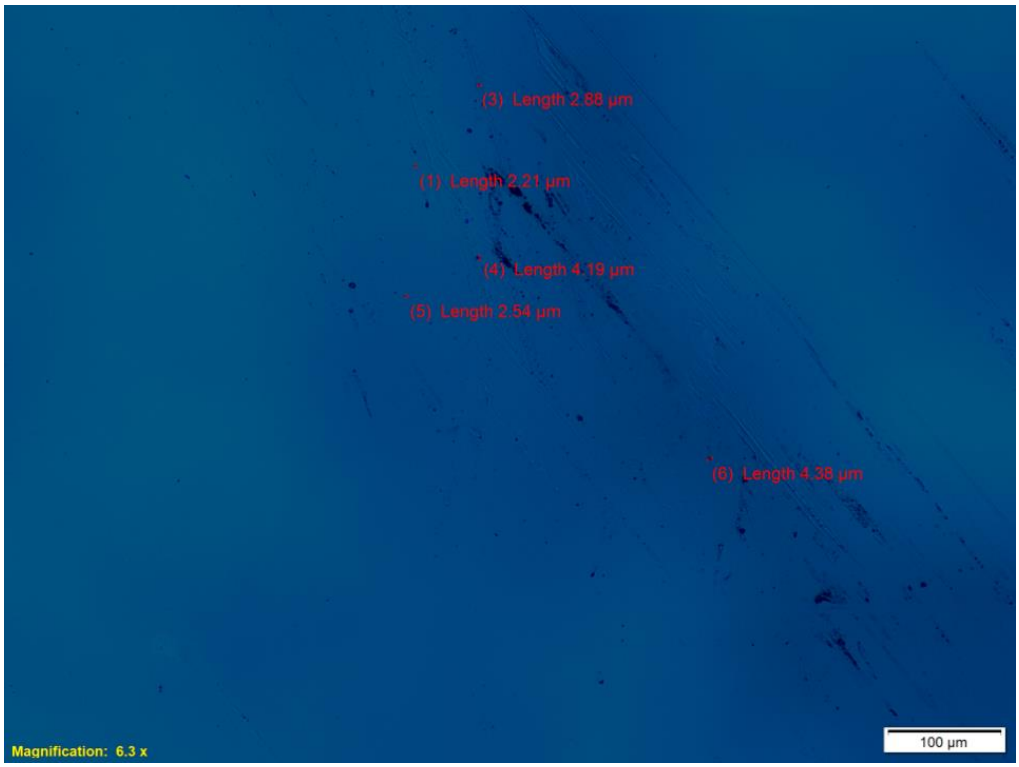


Figure B.3: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2.5ml n-heptane (60 min)



Figure B.4: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 3.5 ml n-heptane (90 min)

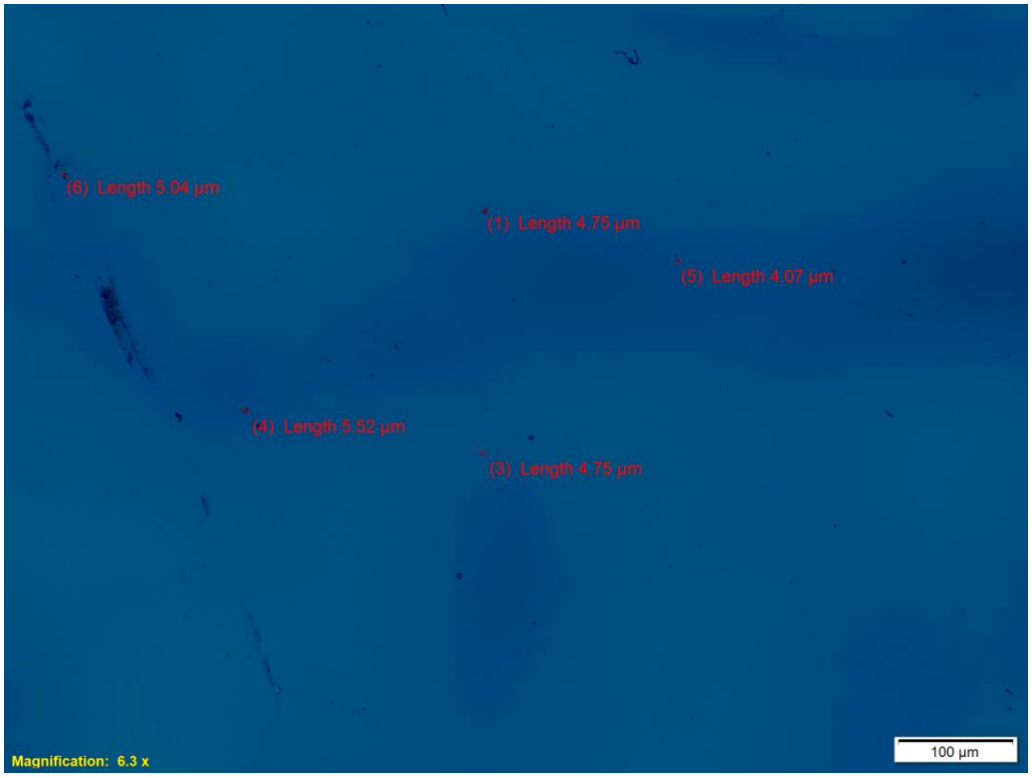


Figure B.5: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 5 ml n-heptane (120 min)

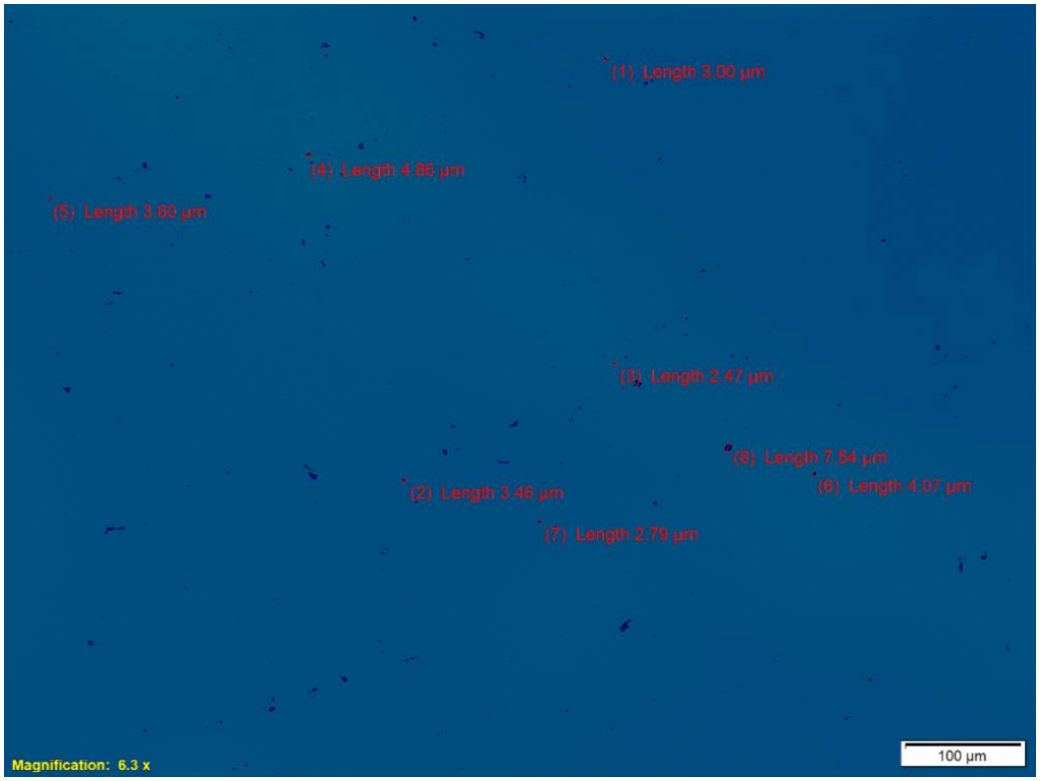


Figure B.6: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid (Time zero)



Figure B.7: 0.5g of Crude Oil + 2 ml of 5% salicylic acid + 2 ml of n-heptane (30 min)

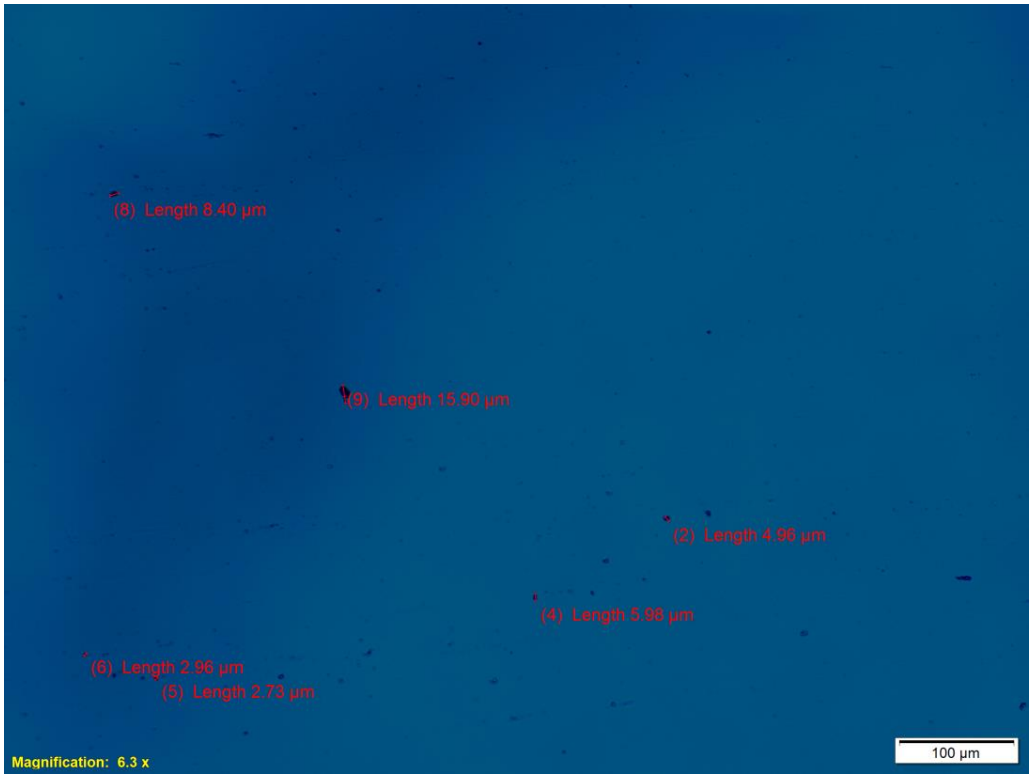


Figure B.8: 0.5g of Crude Oil + 2 ml of 5% salicylic acid + 2.5 ml of n-heptane (60 min)

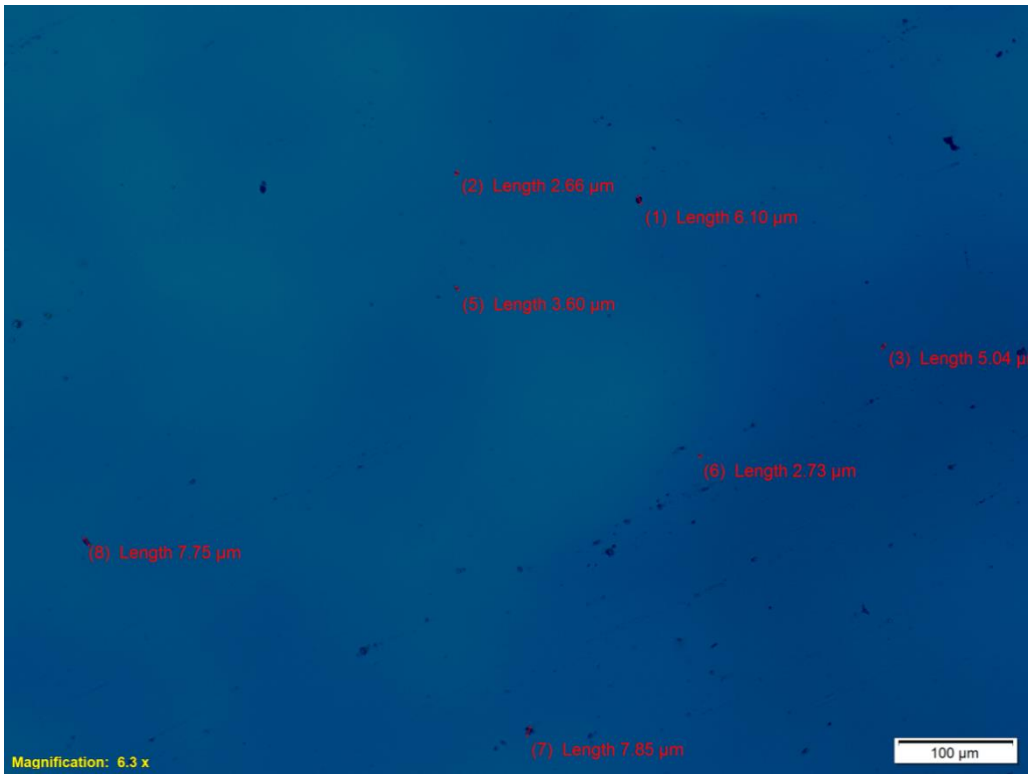


Figure B.9: 0.5g of Crude Oil + 2 ml of 5% salicylic acid + 3.5 ml of n-heptane (90 min)

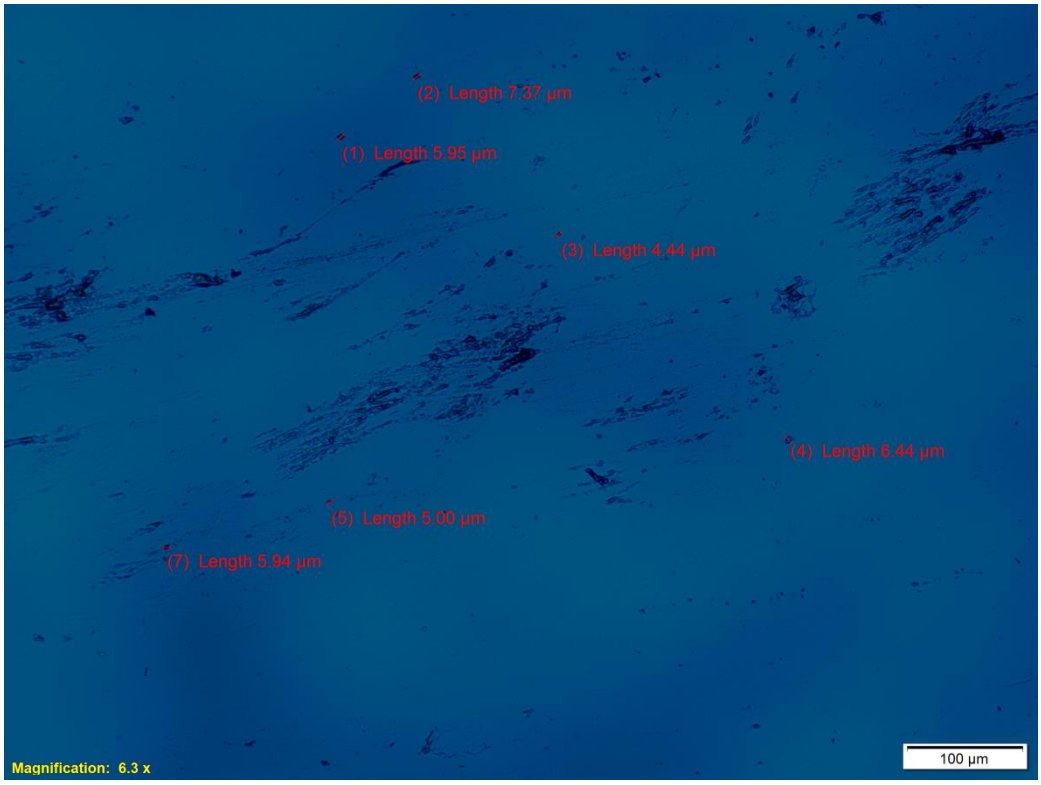


Figure B.10: 0.5g of Crude Oil + 2 ml of 5% salicylic acid + 5 ml of n-heptane (120 min)

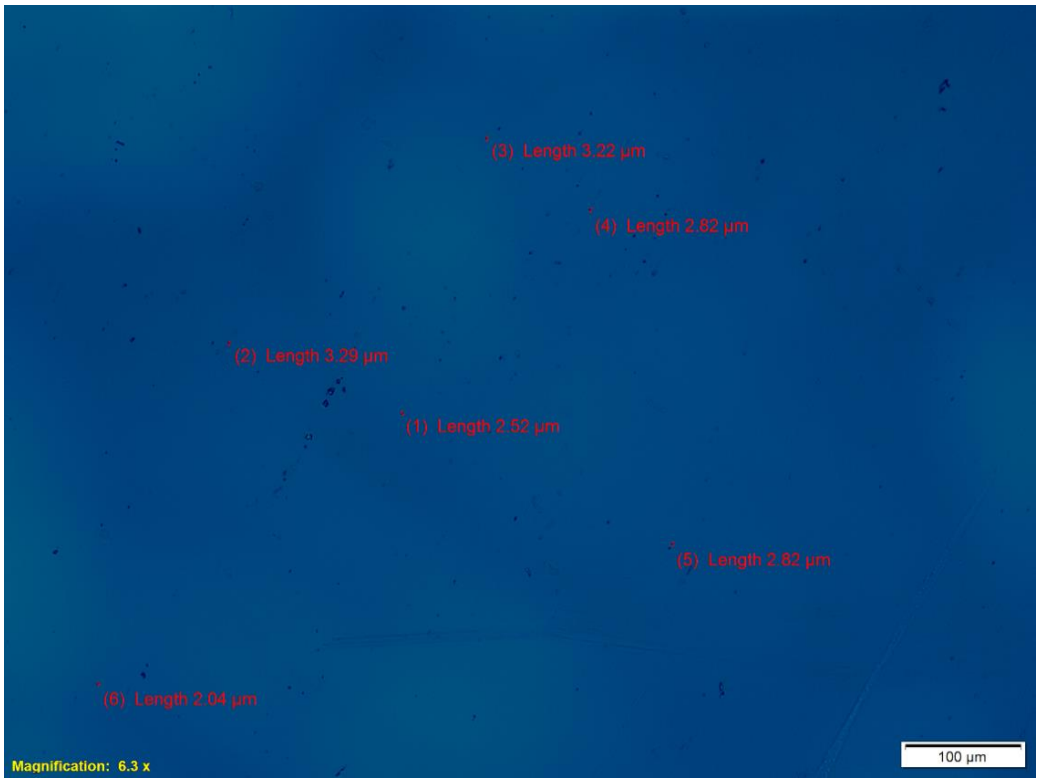


Figure B.11: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid (Time zero)

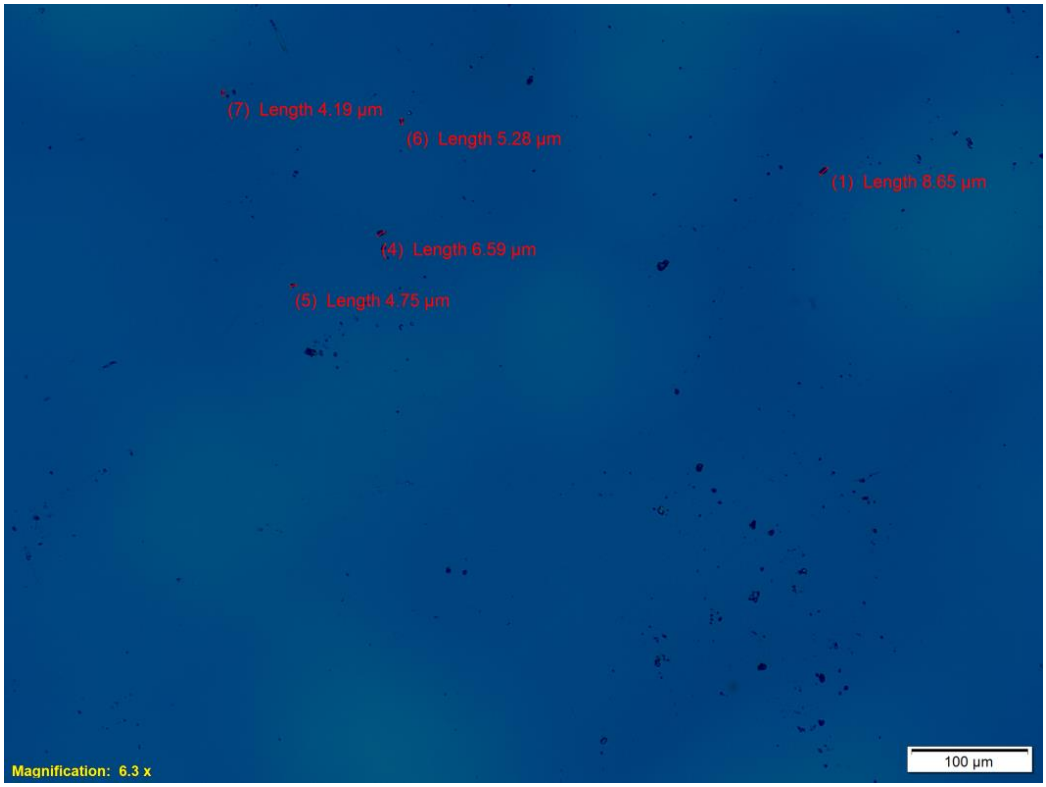


Figure B.12: 0.5g of Crude Oil + 2 ml of 10% salicylic acid + 2 ml of n-heptane (30 min)

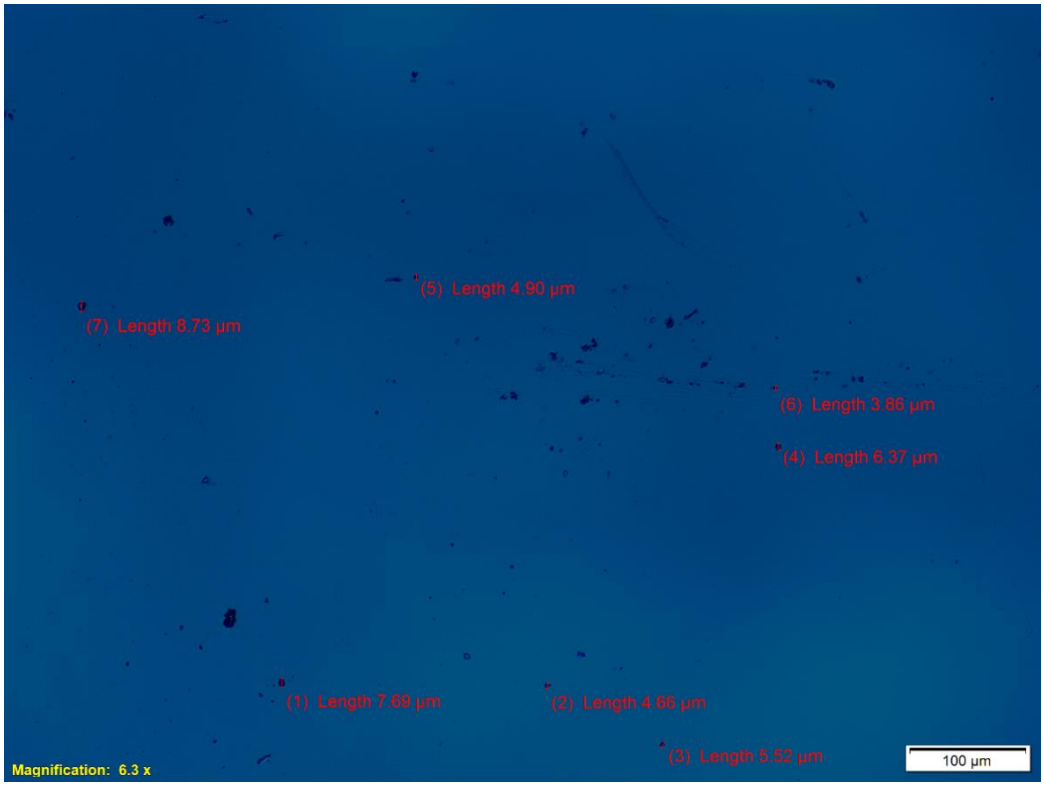


Figure B.13: 0.5g of Crude Oil + 2 ml of 10% salicylic acid + 2.5 ml of n-heptane (60 min)

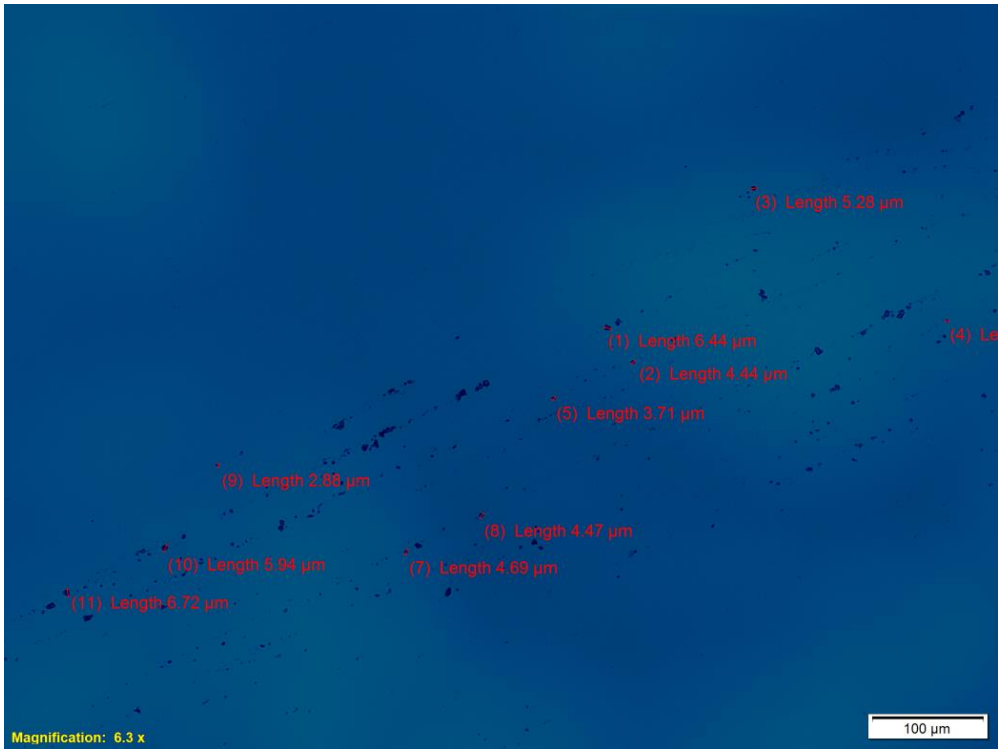


Figure B.14: 0.5g of Crude Oil + 2 ml of 10% salicylic acid + 3.5 ml of n-heptane (90 min)

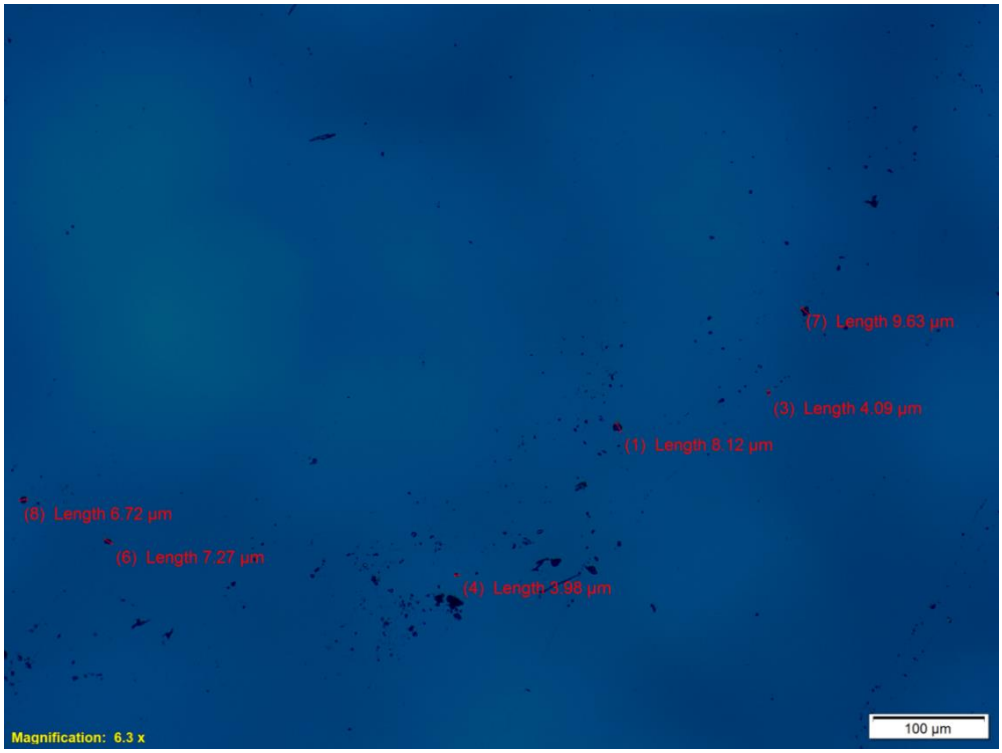


Figure B.15: 0.5g of Crude Oil + 2 ml of 10% salicylic acid + 5 ml of n-heptane (120 min)

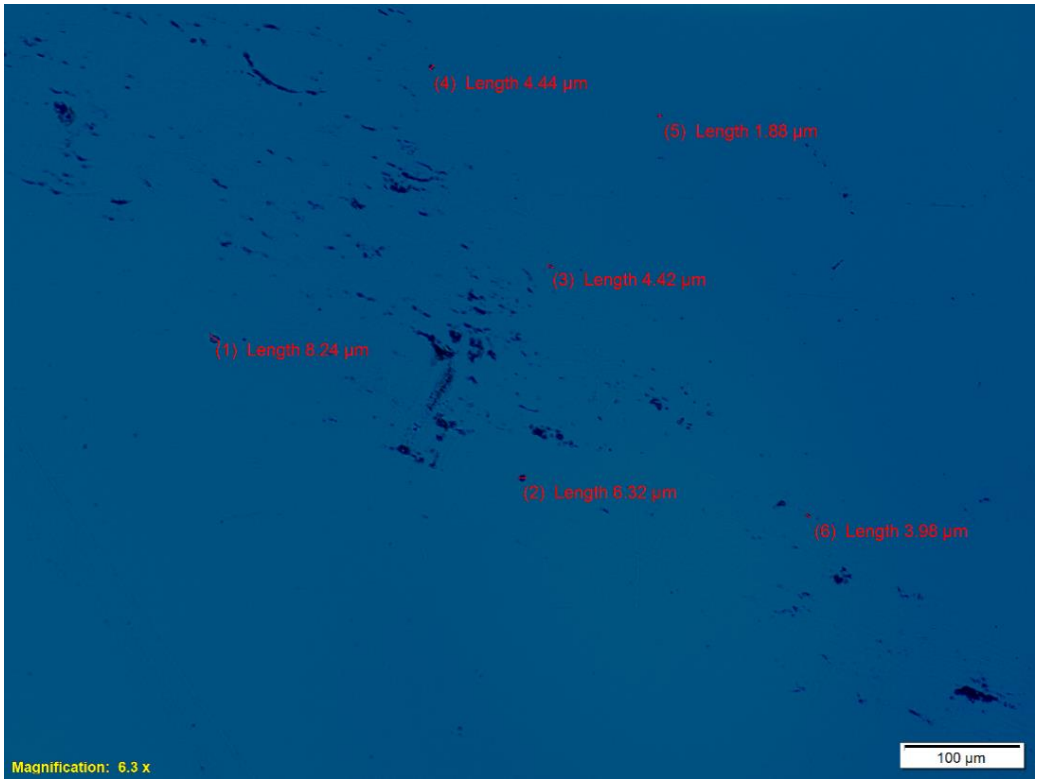


Figure B.16: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid (Time zero)

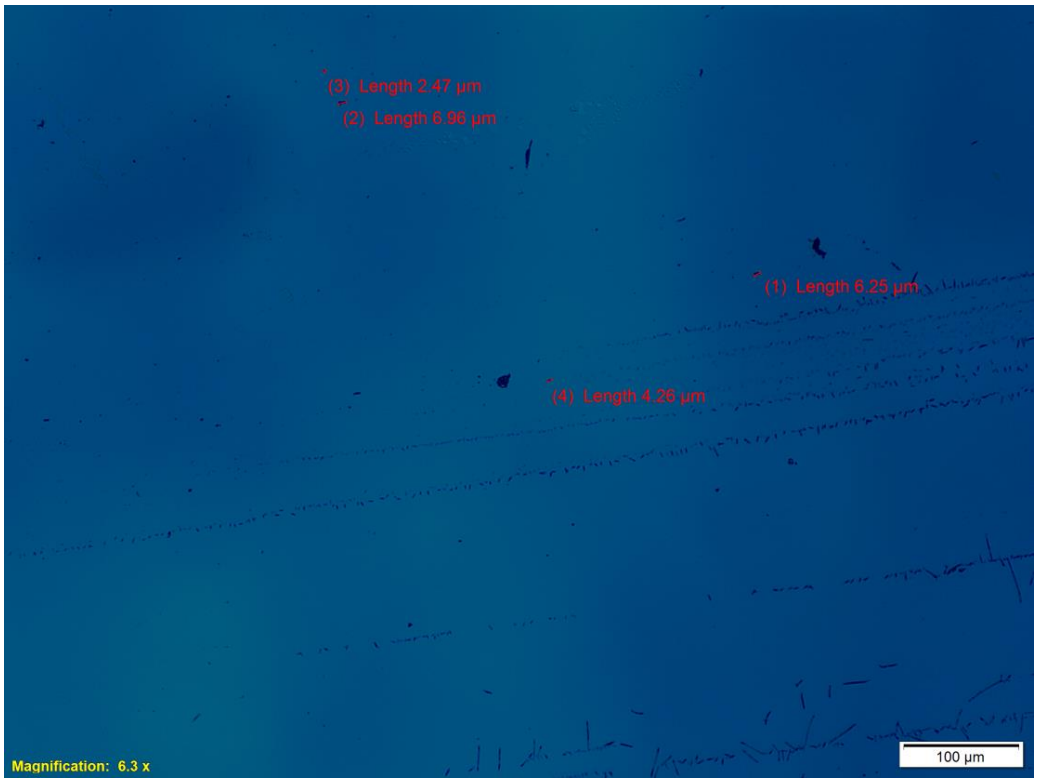


Figure B.17: 0.5g of Crude Oil + 2 ml of 15% salicylic acid + 2 ml of n-heptane (30 min)

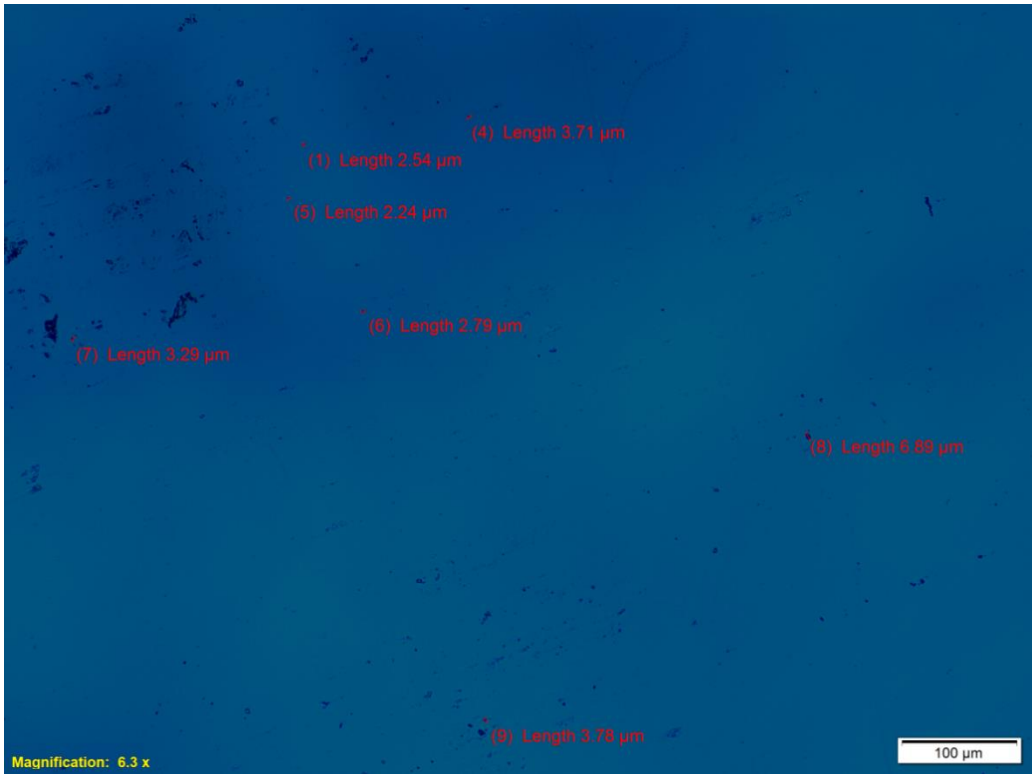


Figure B.18: 0.5g of Crude Oil + 2 ml of 15% salicylic acid + 2.5 ml of n-heptane (60 min)

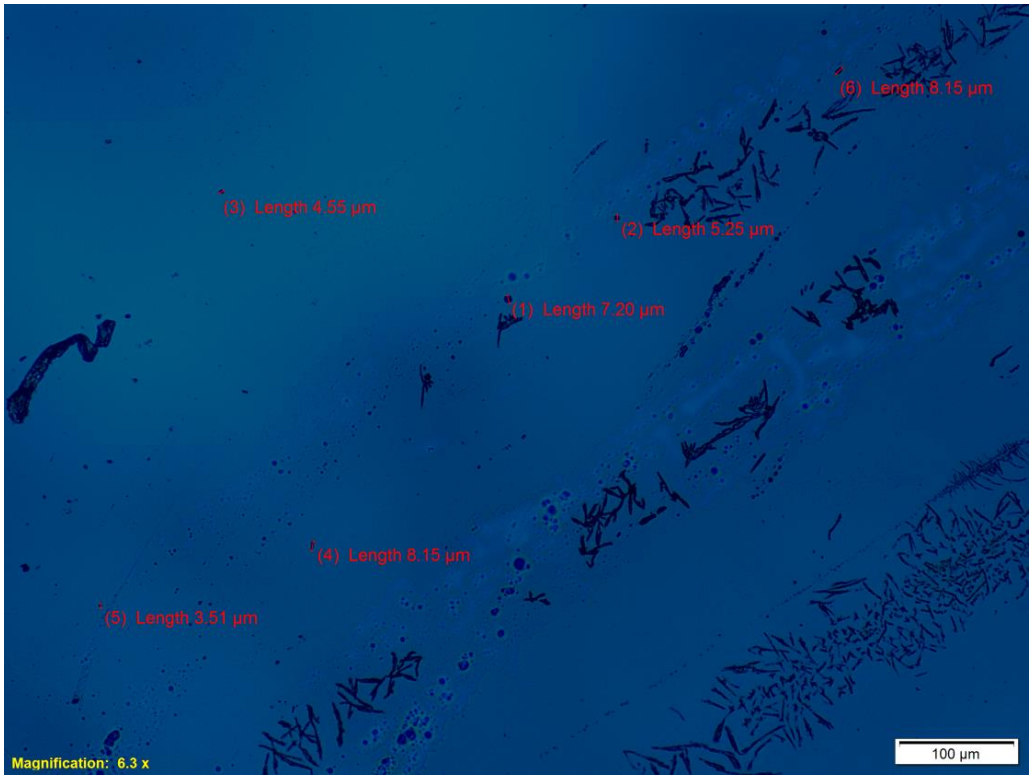


Figure B.19: 0.5g of Crude Oil + 2 ml of 15% salicylic acid + 3.5 ml of n-heptane (90 min)

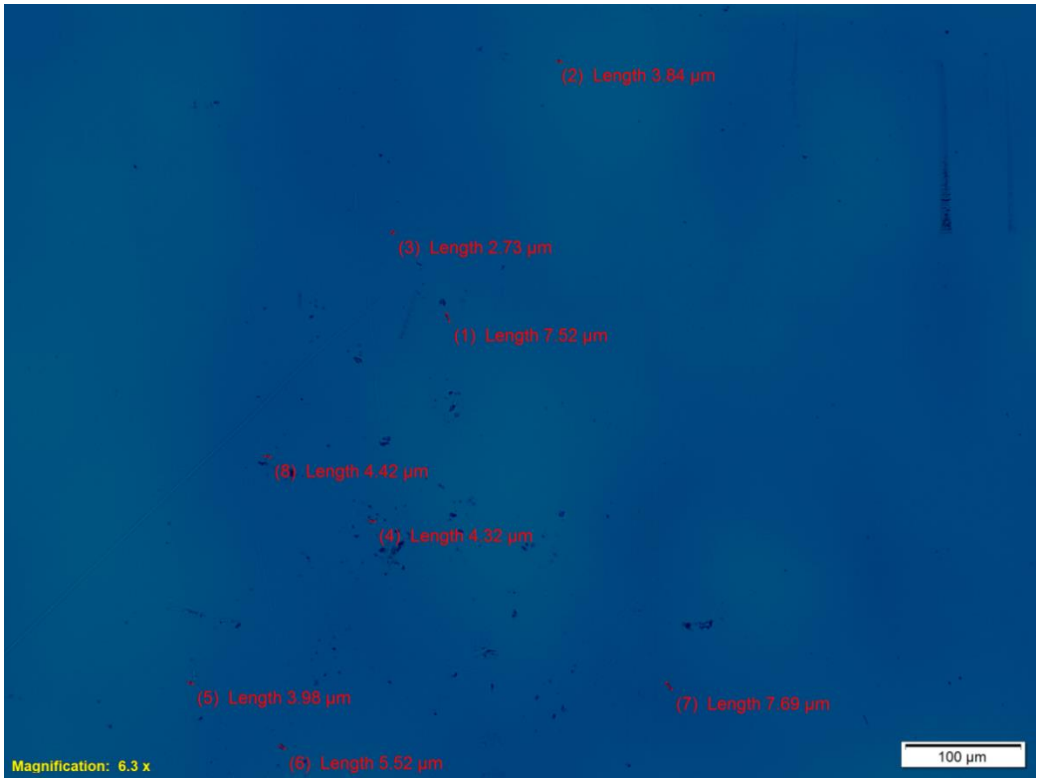


Figure B.20: 0.5g of Crude Oil + 2 ml of 15% salicylic acid + 5 ml of n-heptane (120 min)



Figure B.21: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid (Time zero)



Figure B.22: 0.5g of Crude Oil + 2 ml of 20% salicylic acid + 2 ml of n-heptane (30 min)



Figure B.23: 0.5g of Crude Oil + 2 ml of 20% salicylic acid + 2.5 ml of n-heptane (60 min)

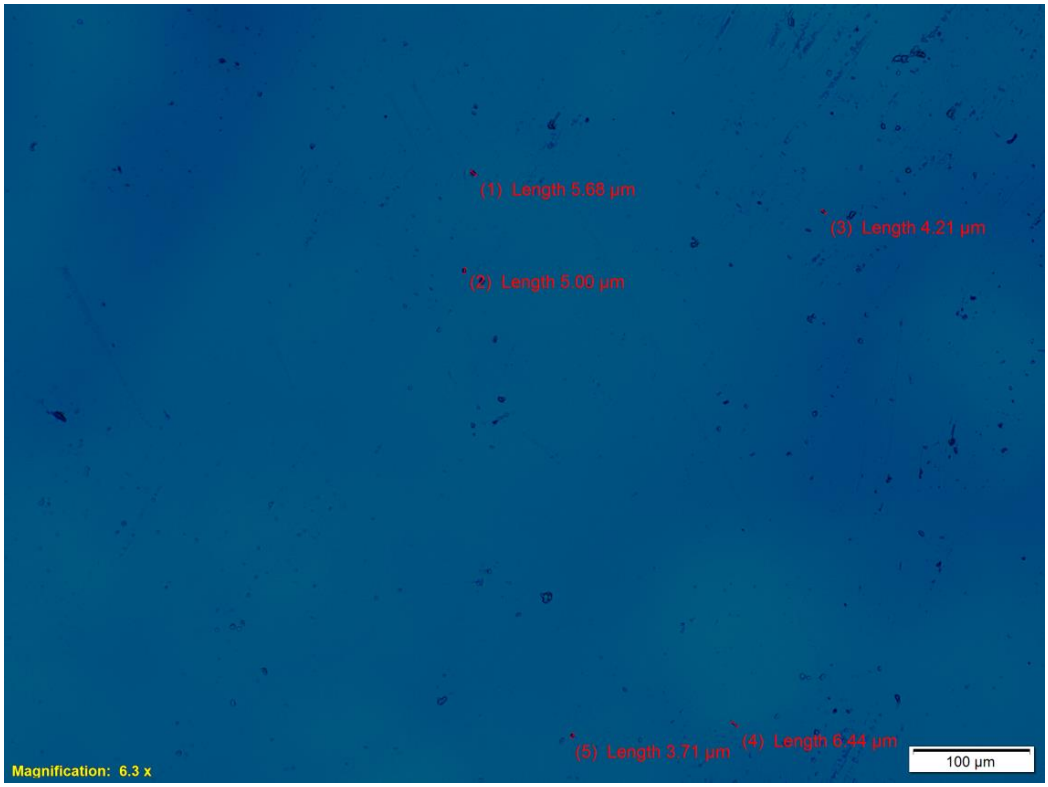


Figure B.24: 0.5g of Crude Oil + 2 ml of 20% salicylic acid + 3.5 ml of n-heptane (90 min)

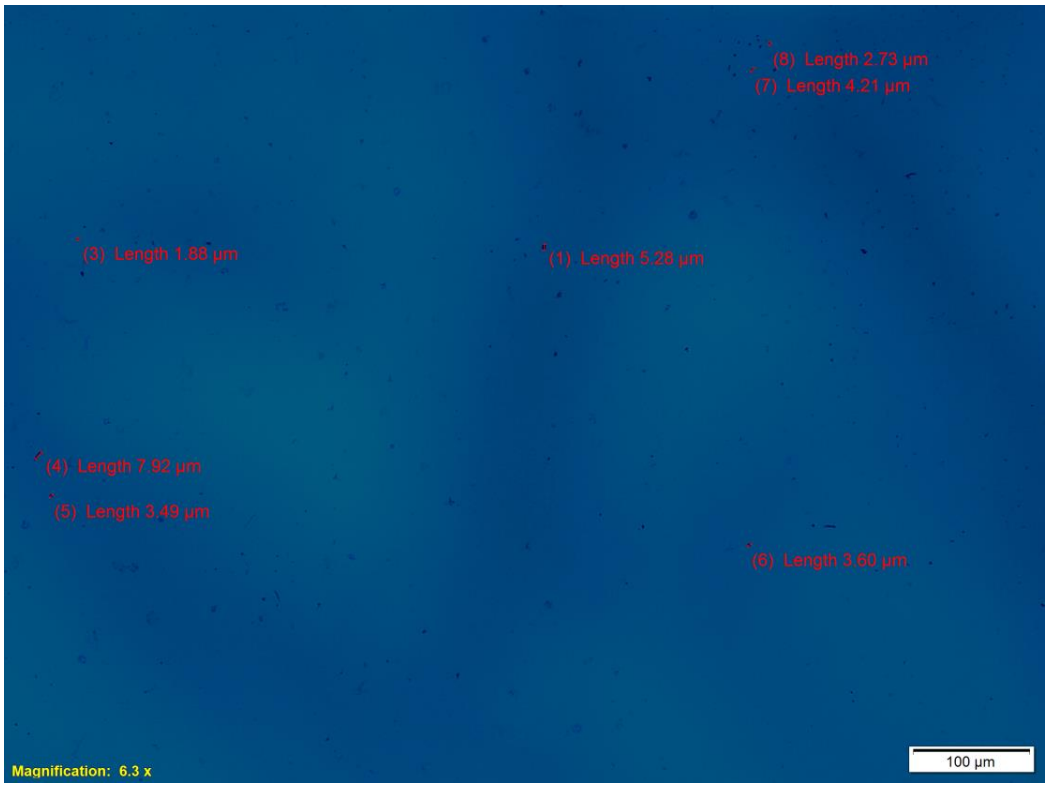


Figure B.25: 0.5g of Crude Oil + 2 ml of 20% salicylic acid + 5 ml of n-heptane (120 min)



Figure B.26: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid (Time zero)

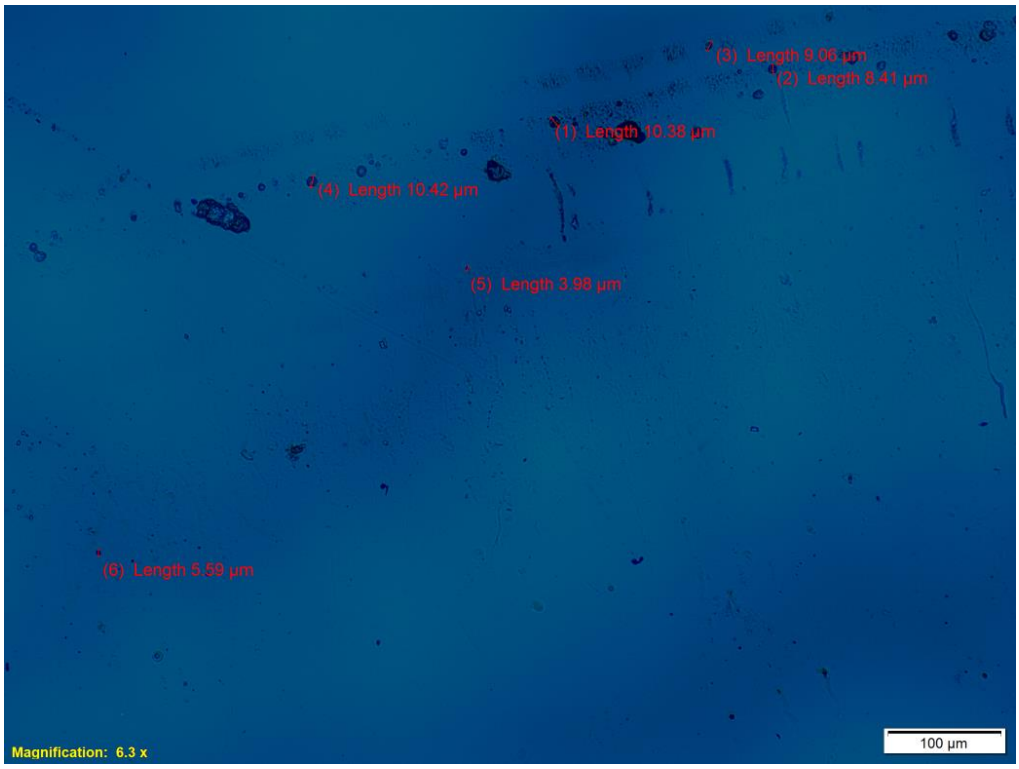


Figure B.27: 0.5g of Crude Oil + 2 ml of 25% salicylic acid + 2 ml of n-heptane (30 min)

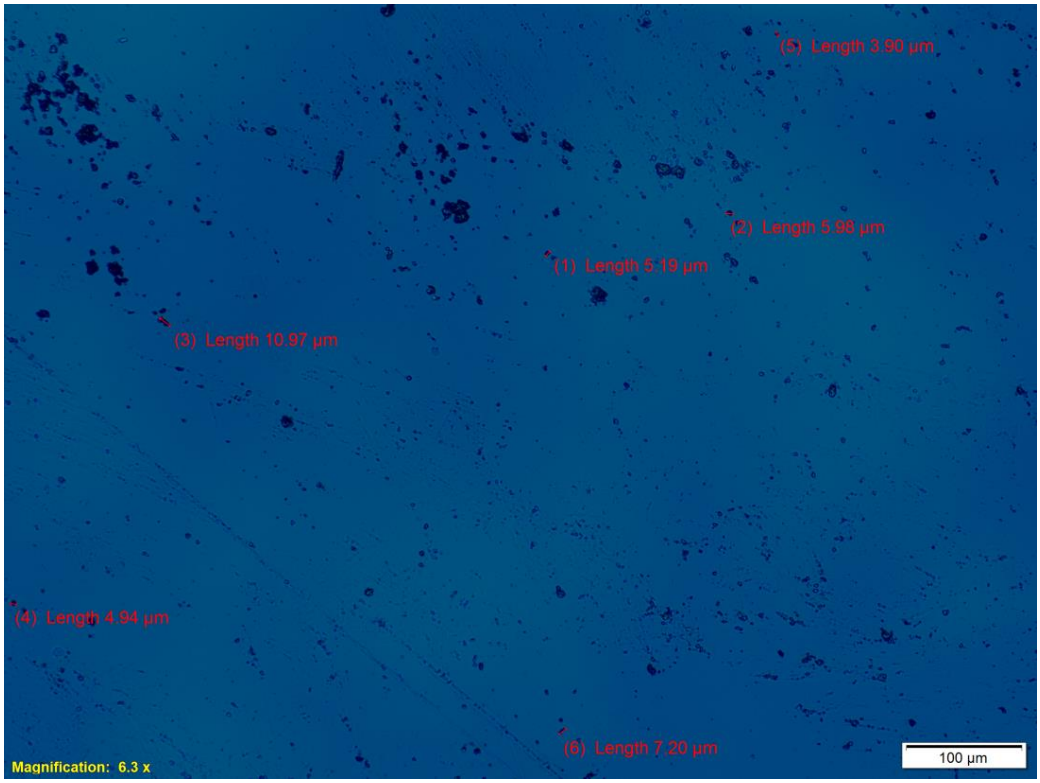


Figure B.28: 0.5g of Crude Oil + 2 ml of 25% salicylic acid + 2.5 ml of n-heptane (60 min)

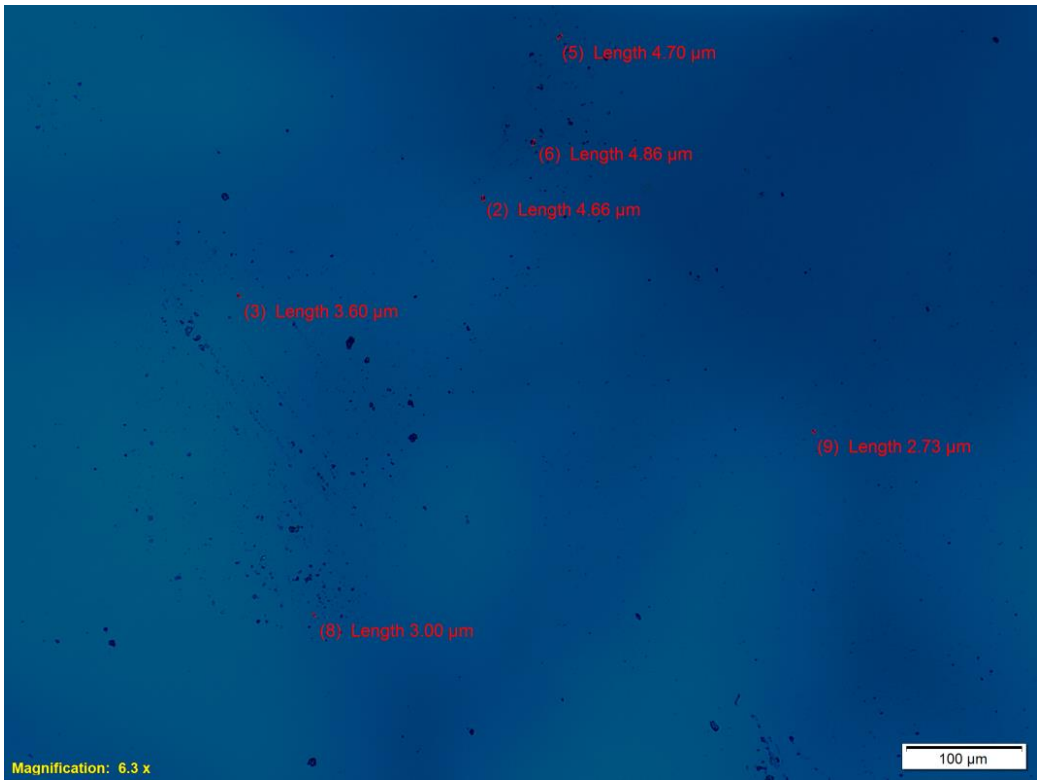


Figure B.29: 0.5g of Crude Oil + 2 ml of 25% salicylic acid + 3.5 ml of n-heptane (90 min)



Figure B.30: 0.5g of Crude Oil + 2 ml of 25% salicylic acid + 5 ml of n-heptane (120 min)

APPENDIX C: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 35 ^{o}C

Figure C: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 35 ºC

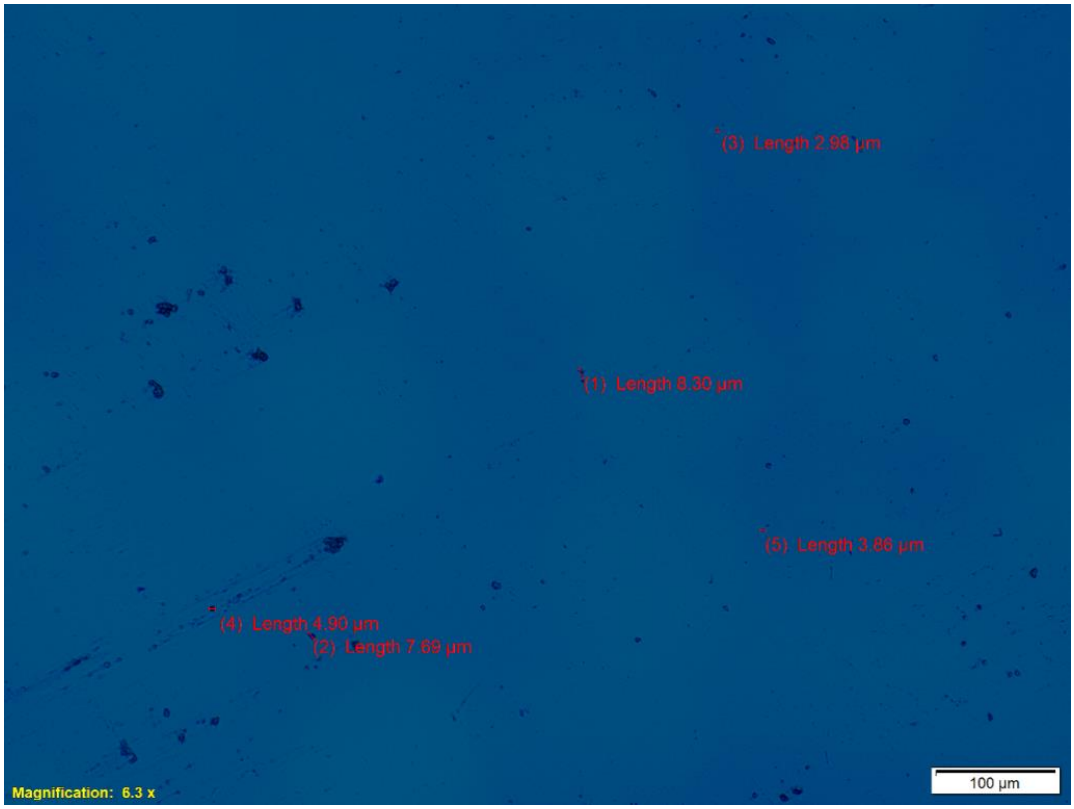


Figure C.1: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic Acid (Time zero)

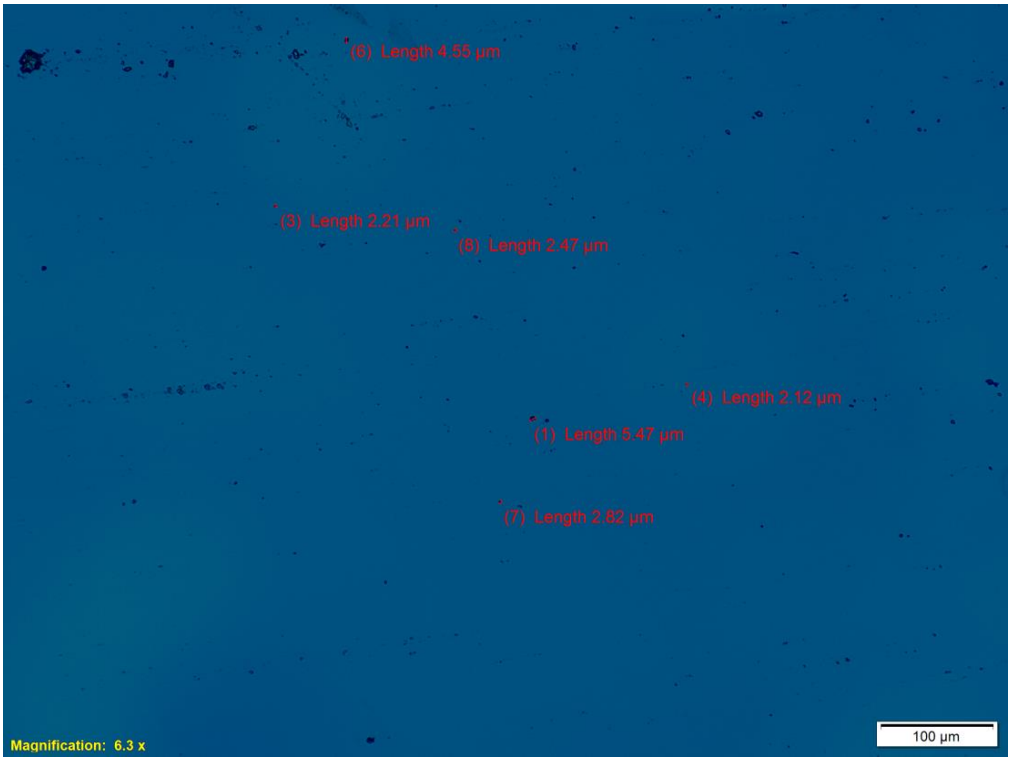


Figure C.2: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic Acid + 2 ml of n-heptane (30 min)

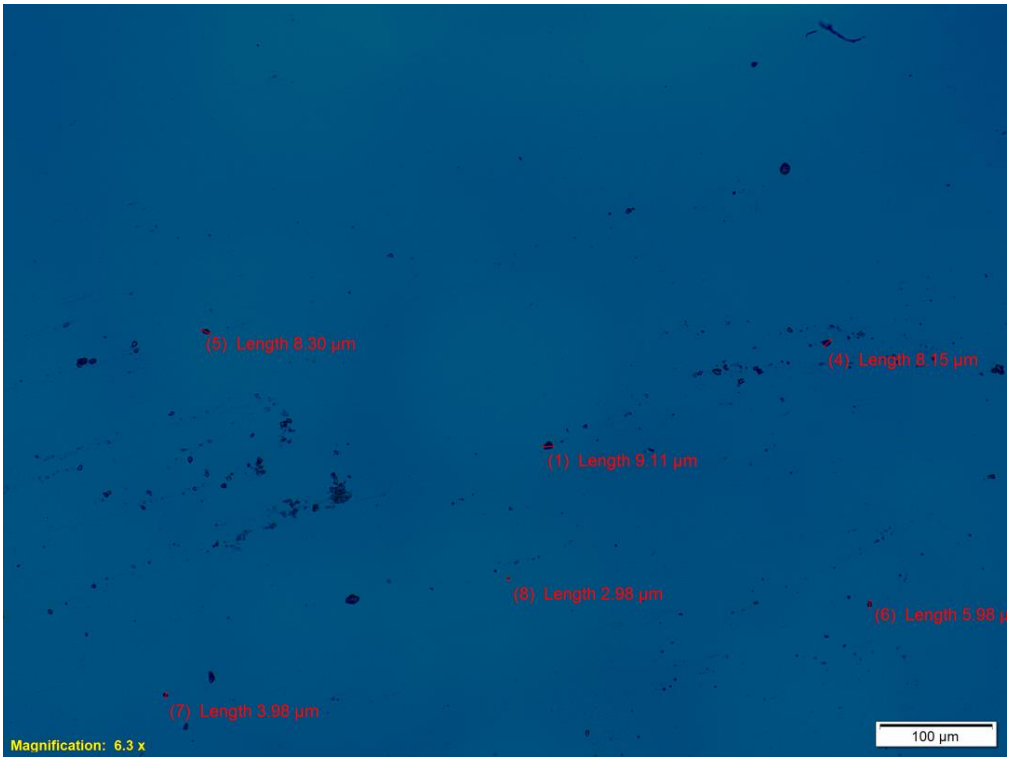


Figure C.3: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic Acid + 2.5 ml of n-heptane (60 min)

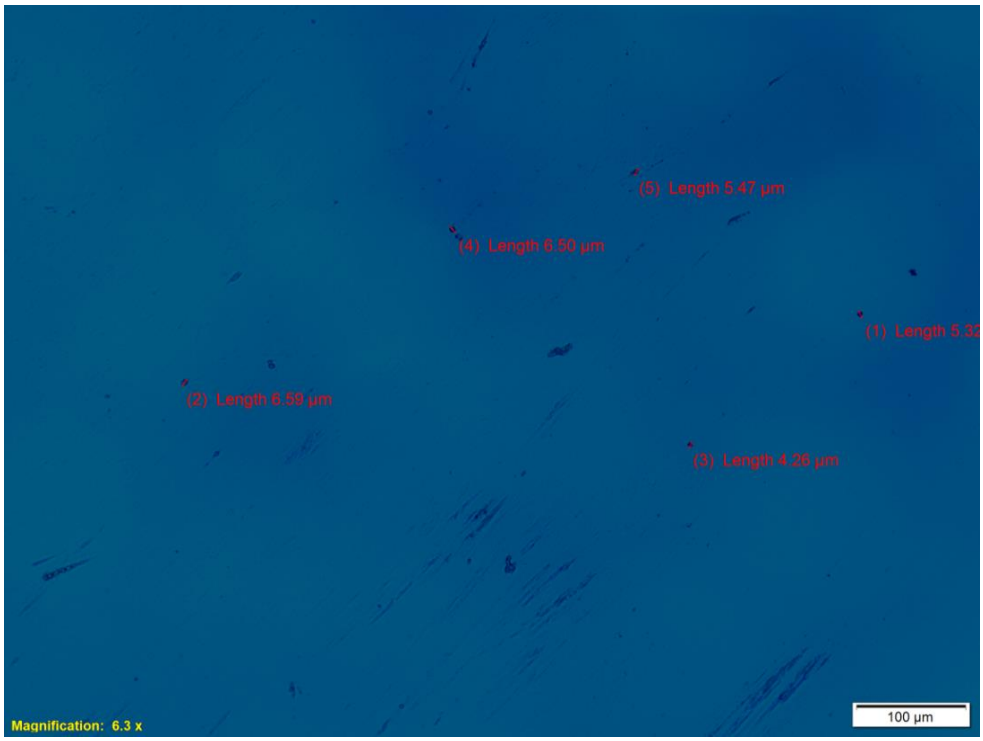


Figure C.4: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic Acid + 3.5 ml of n-heptane (90 min)

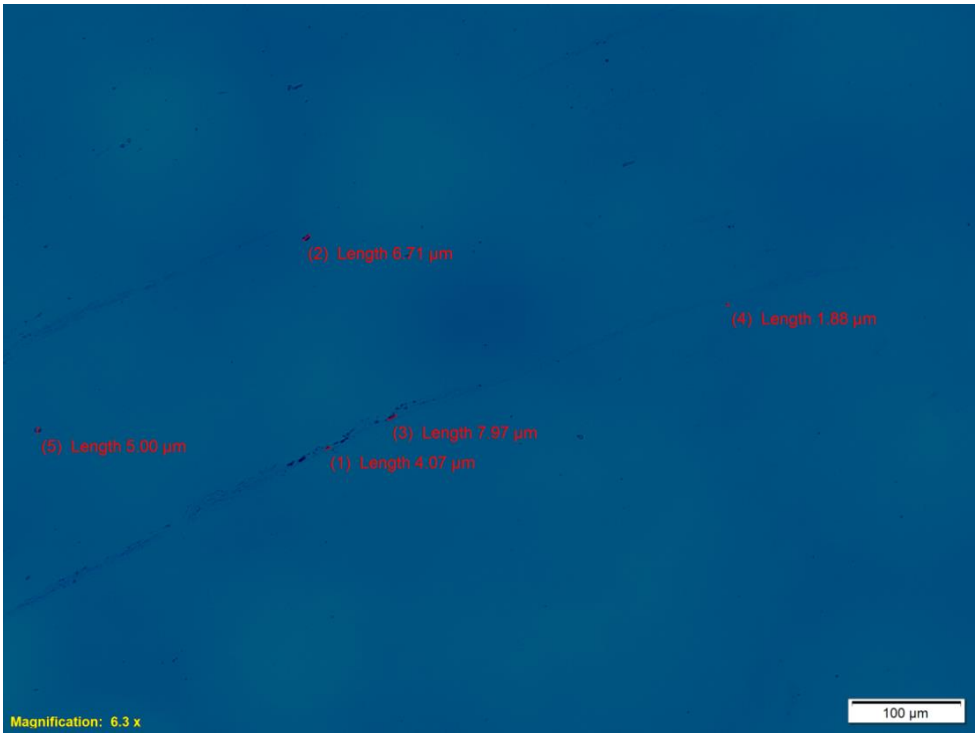


Figure C.5: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic Acid + 5 ml of n-heptane (120 min)



Figure C.6: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic Acid (Time zero)

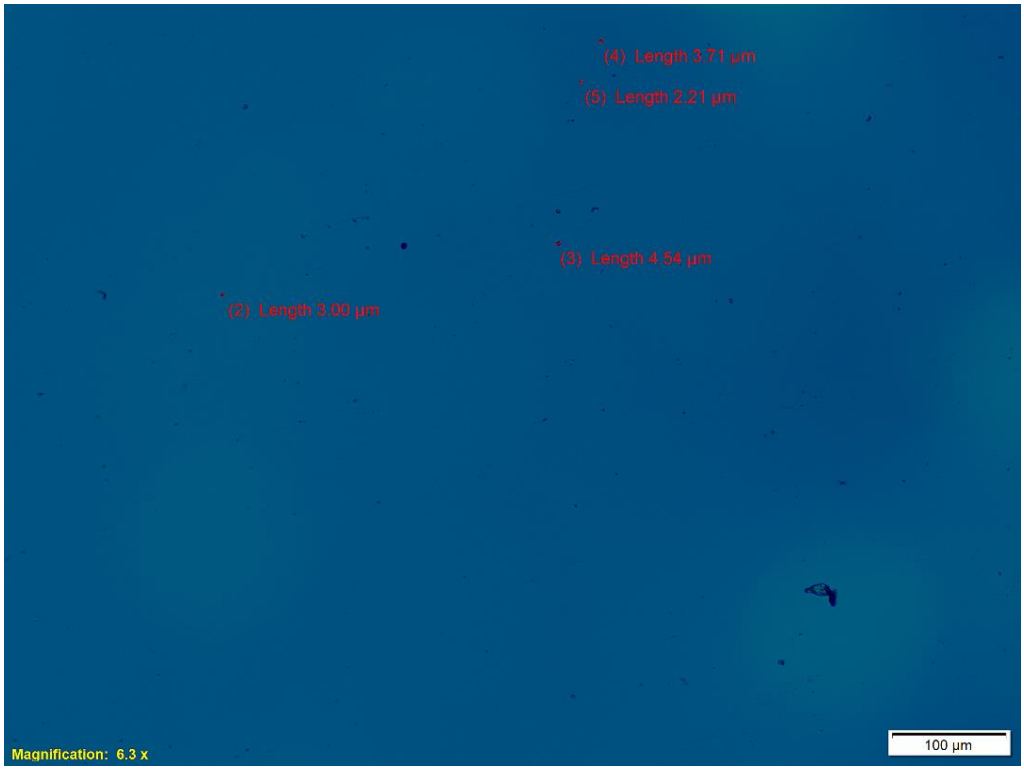


Figure C.7: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic Acid + 2.5 ml n-heptane (30 min)

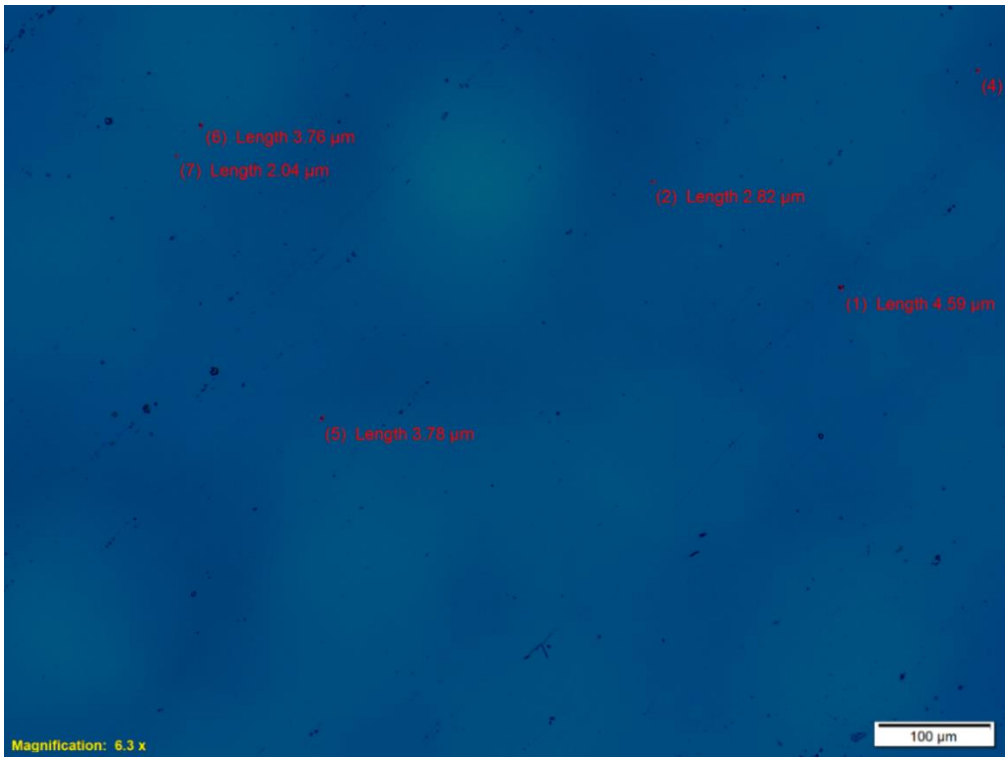


Figure C.8: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic Acid + 2.5 ml of n-heptane (60 min)

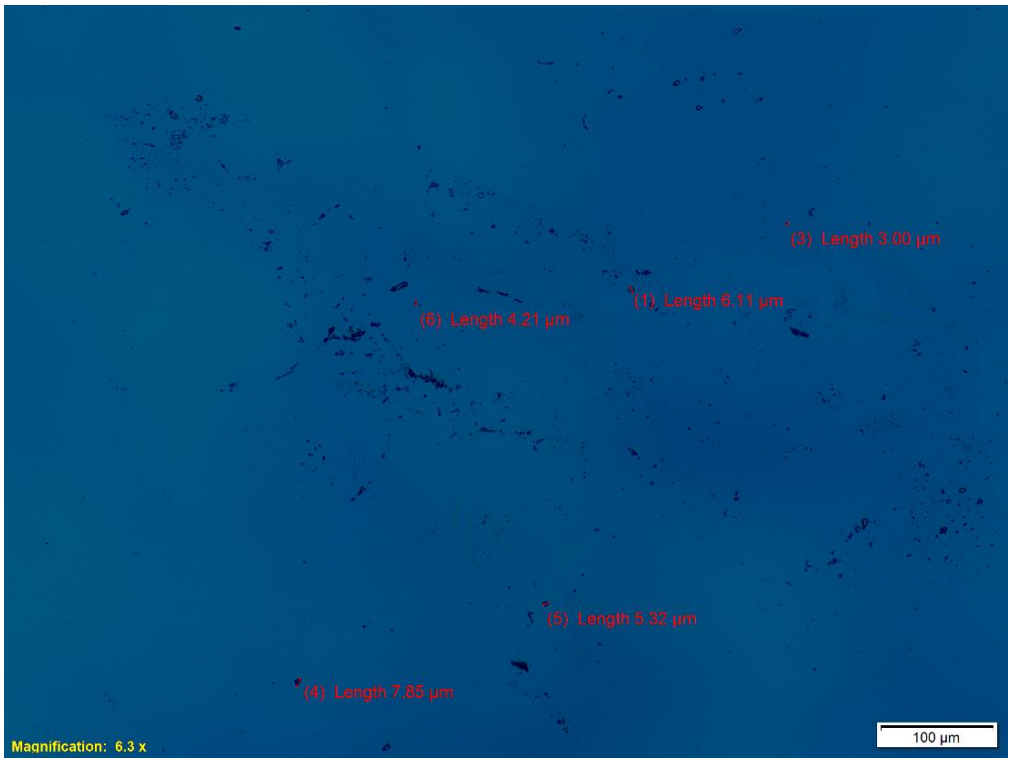


Figure C.9: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic Acid + 3.5 ml of n-heptane (90 min)

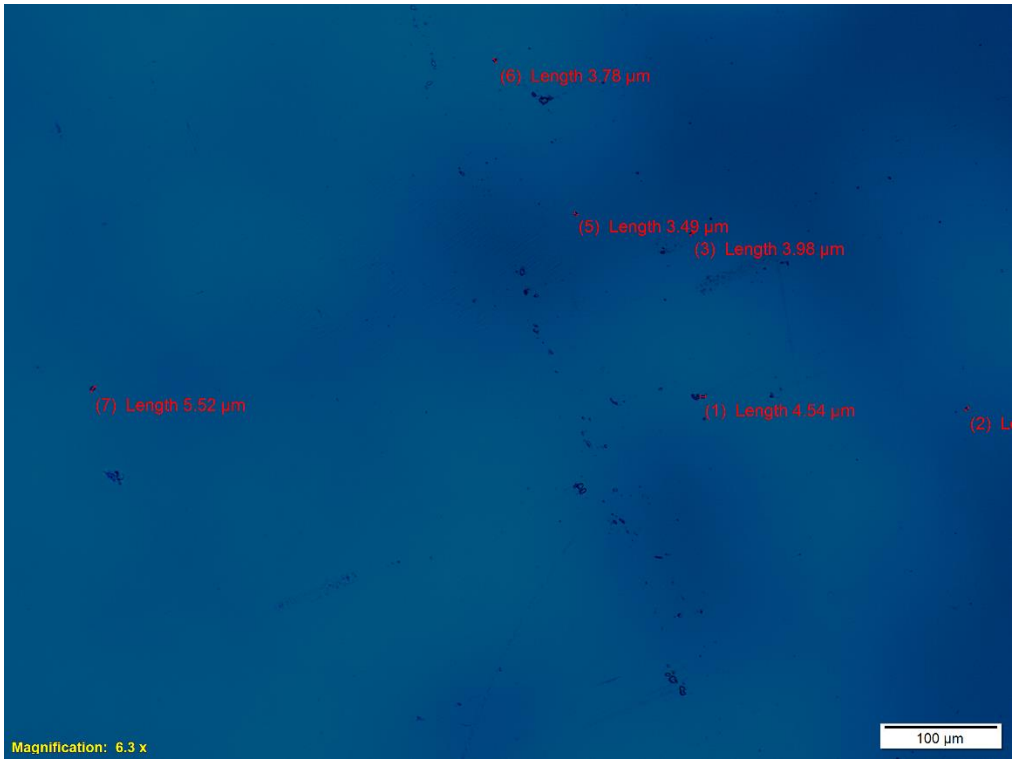


Figure C.10: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic Acid + 5 ml of n-heptane (120 min)

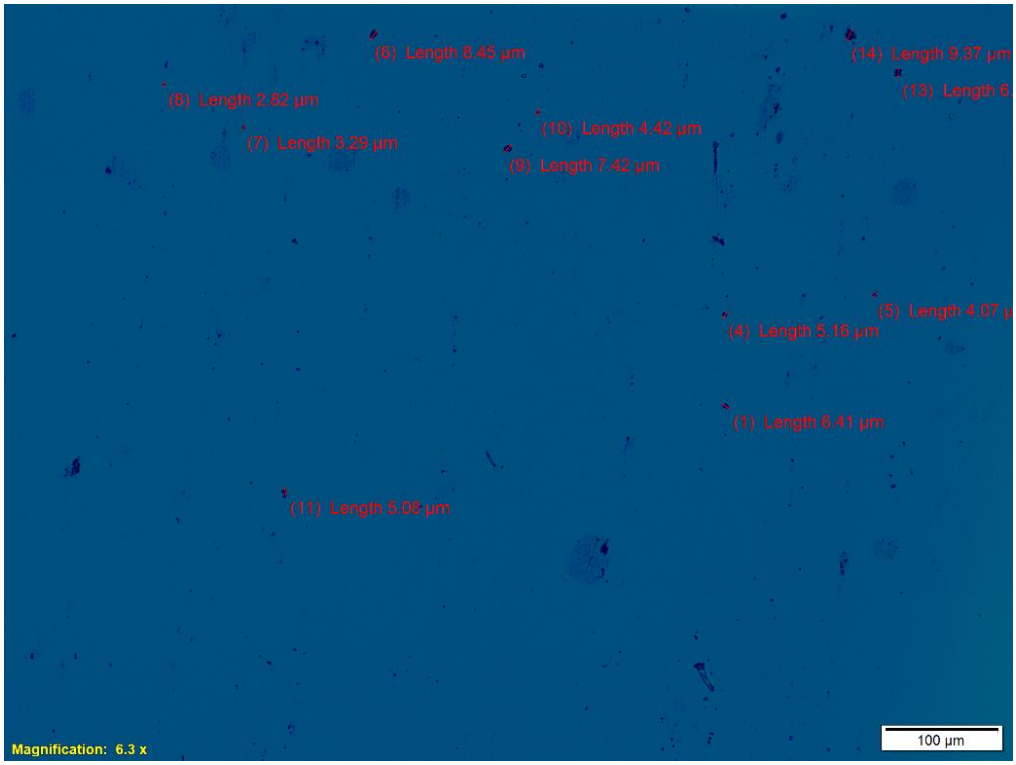


Figure C.11: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic Acid (Time zero)



Figure C.12: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic Acid + 2 ml of n-heptane (30 min)

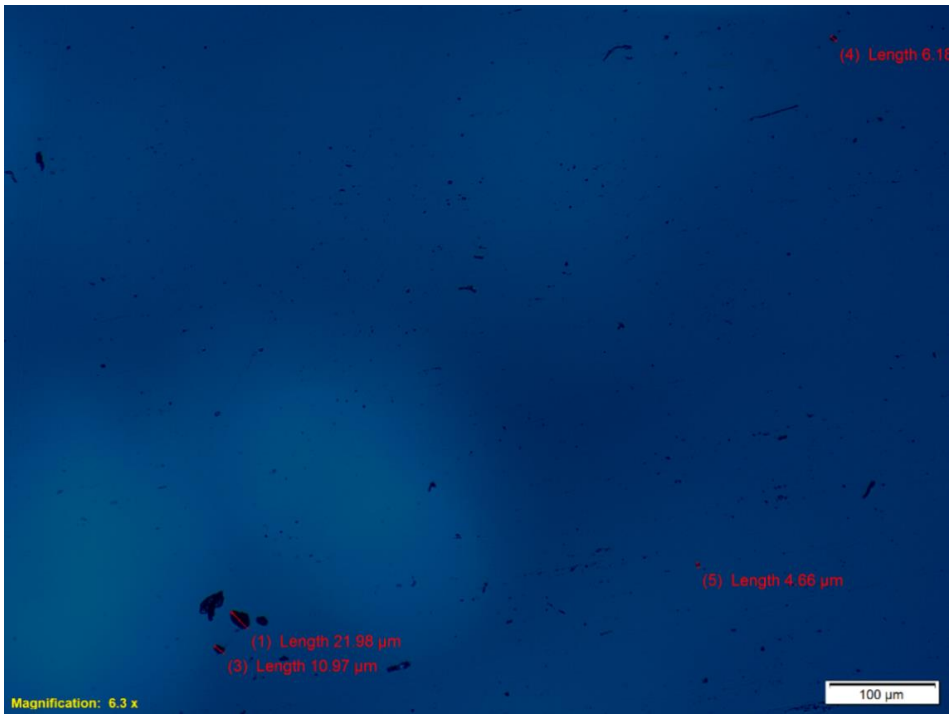


Figure C.13: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic Acid + 2.5 ml of n-heptane (60 min)

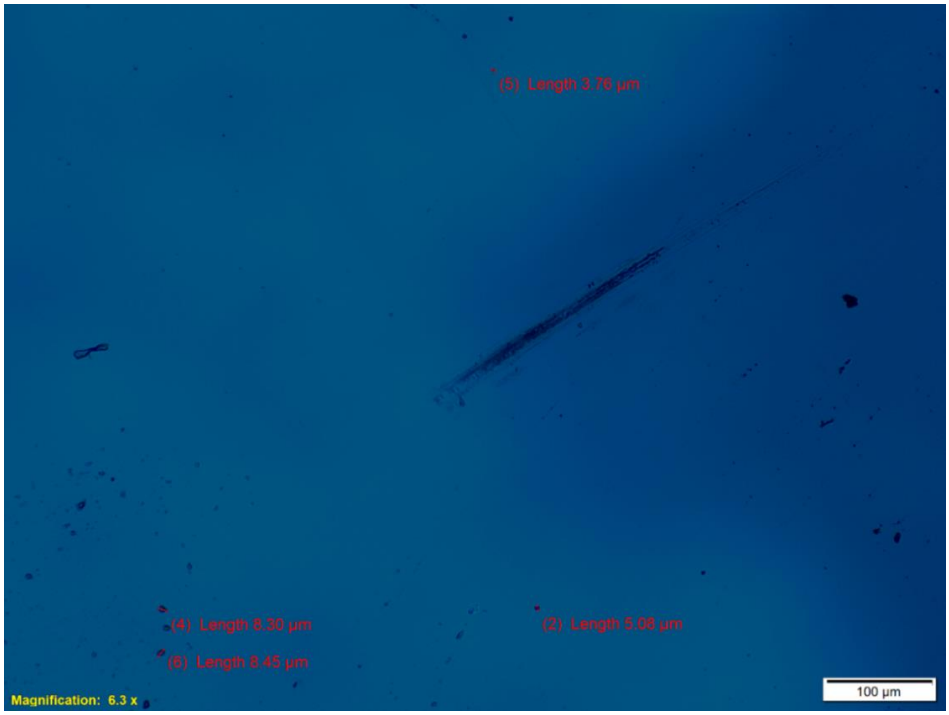


Figure C.14: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic Acid + 3.5 ml of n-heptane (90 min)

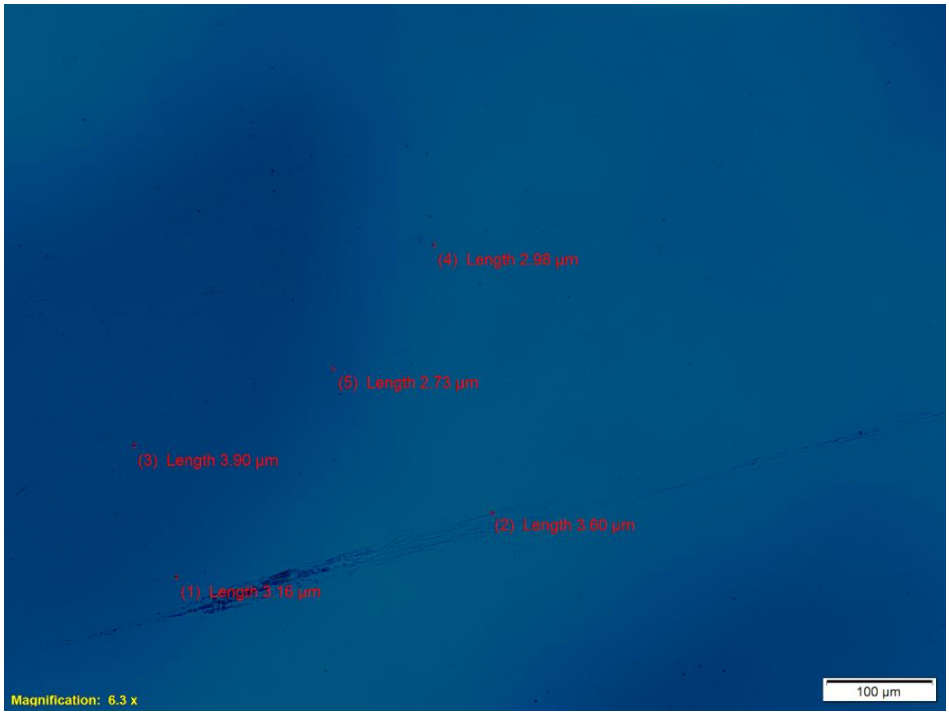


Figure C.15: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic Acid + 5 ml of n-heptane (120 min)

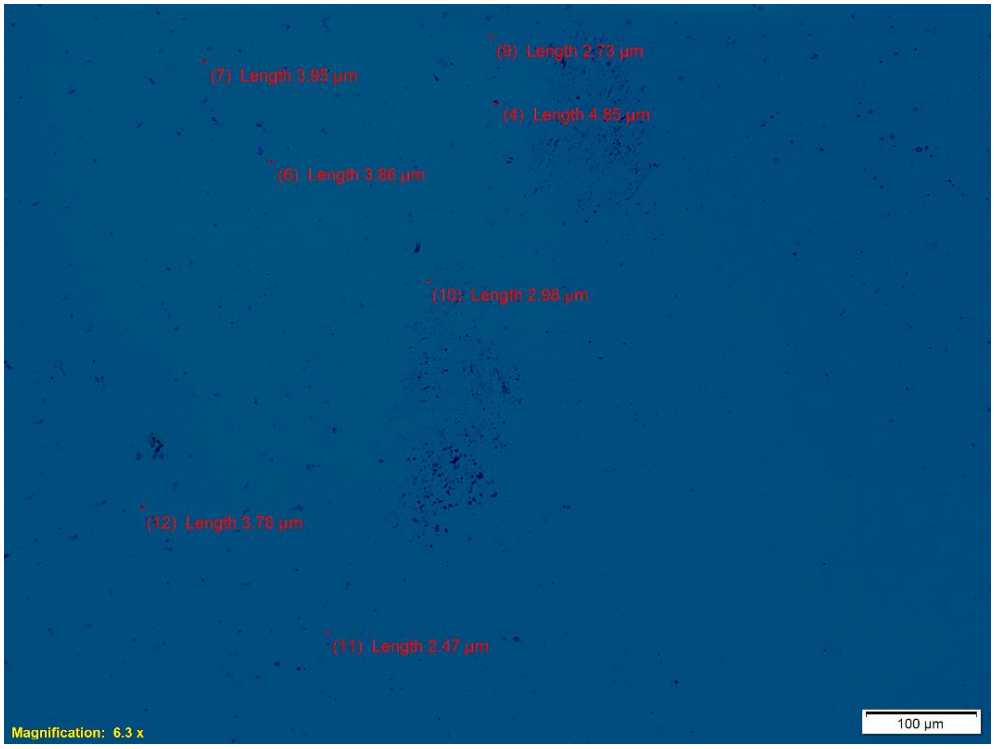


Figure C.16: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic Acid (Time zero)



Figure C.17: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

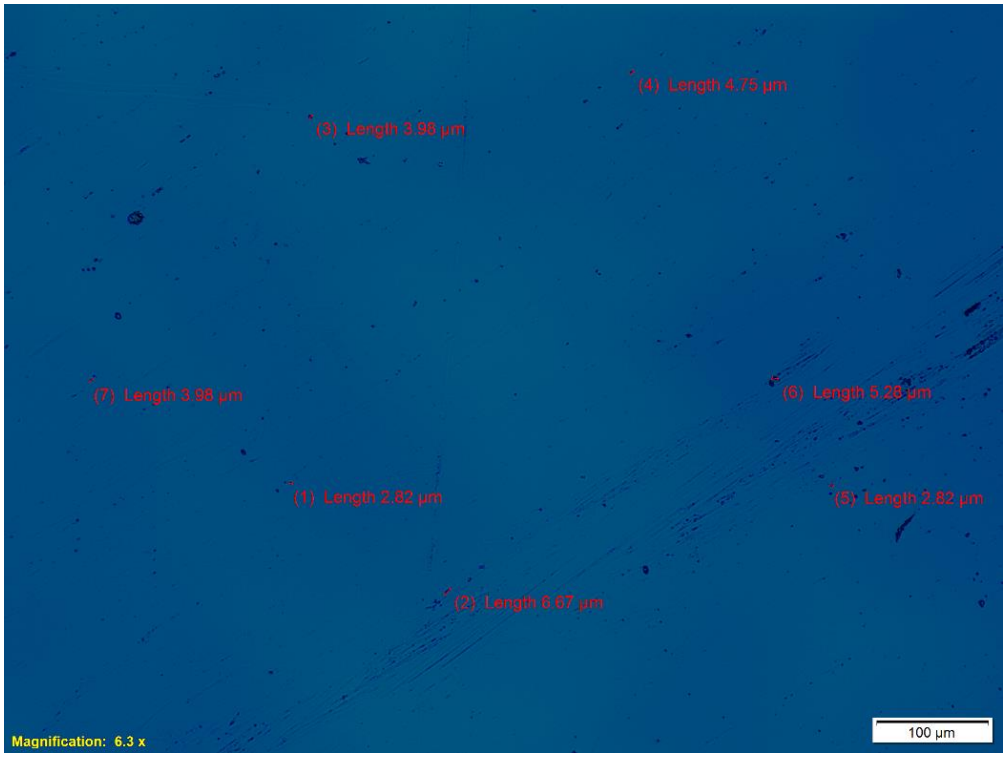


Figure C.18: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

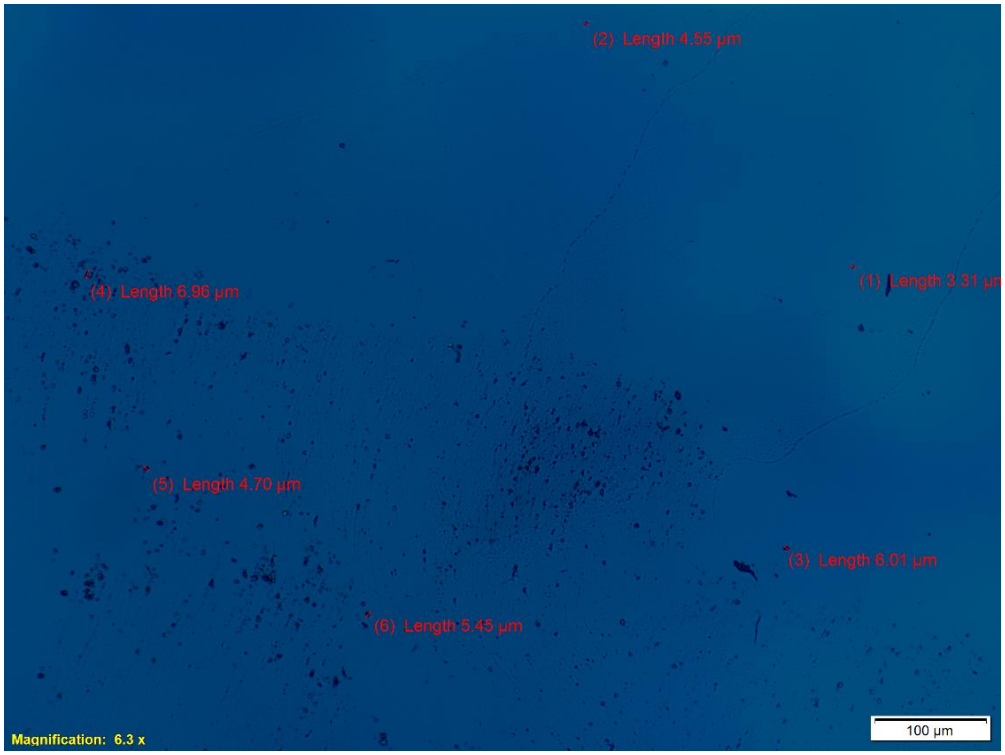


Figure C.19: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

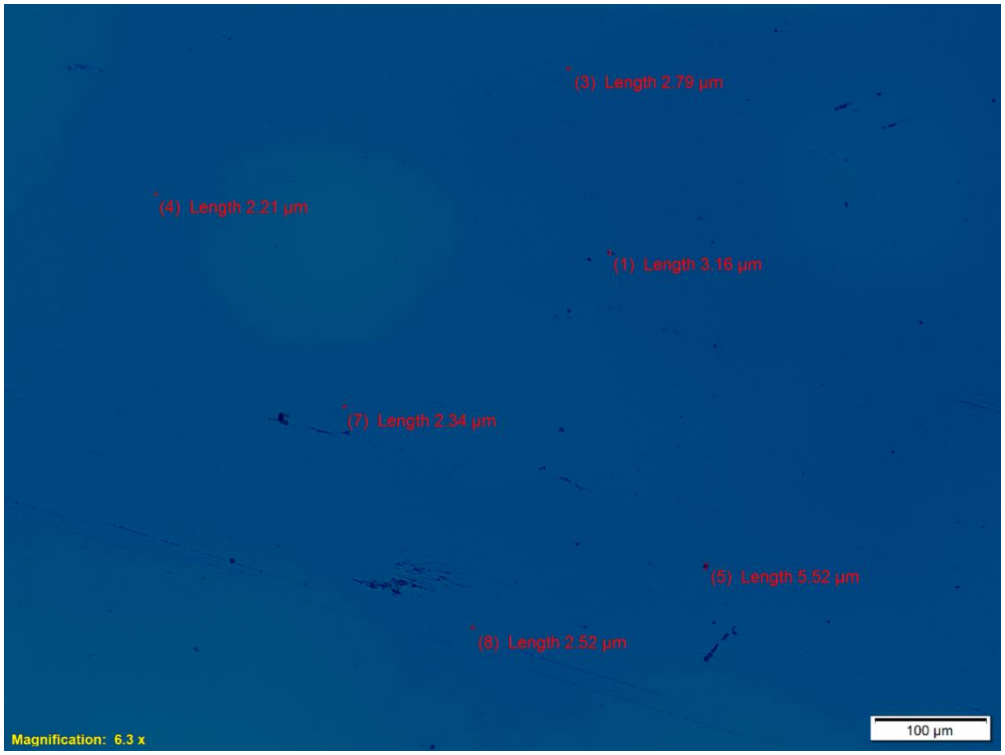


Figure C.20: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

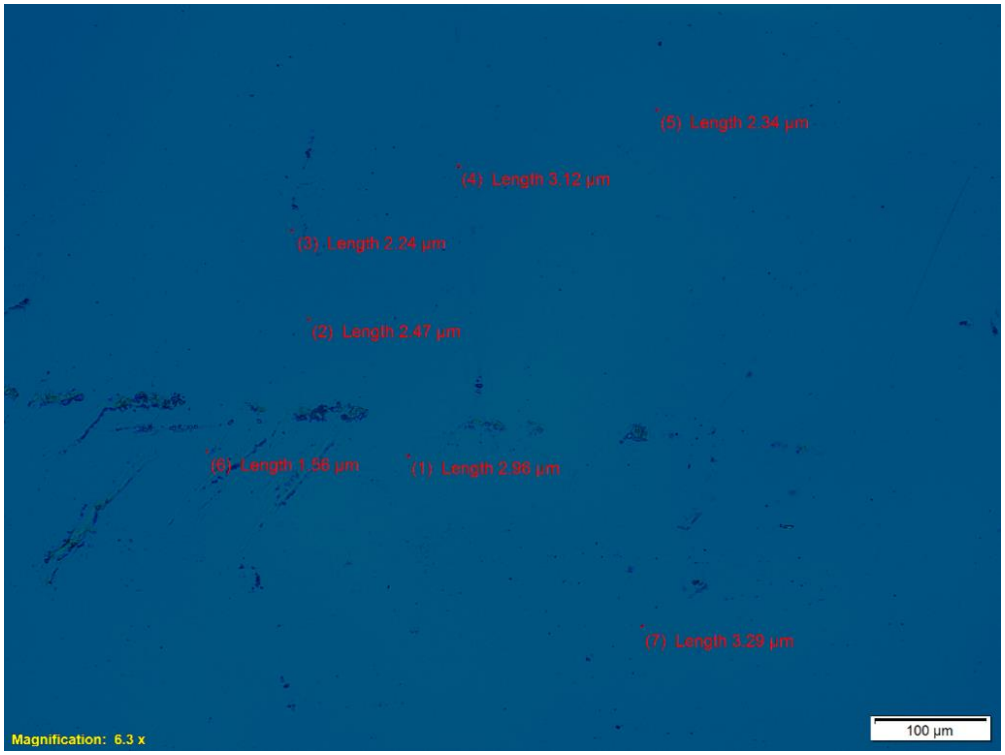


Figure C.21: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid (Time zero)



Figure C.22: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2 ml n-heptane (30 min)

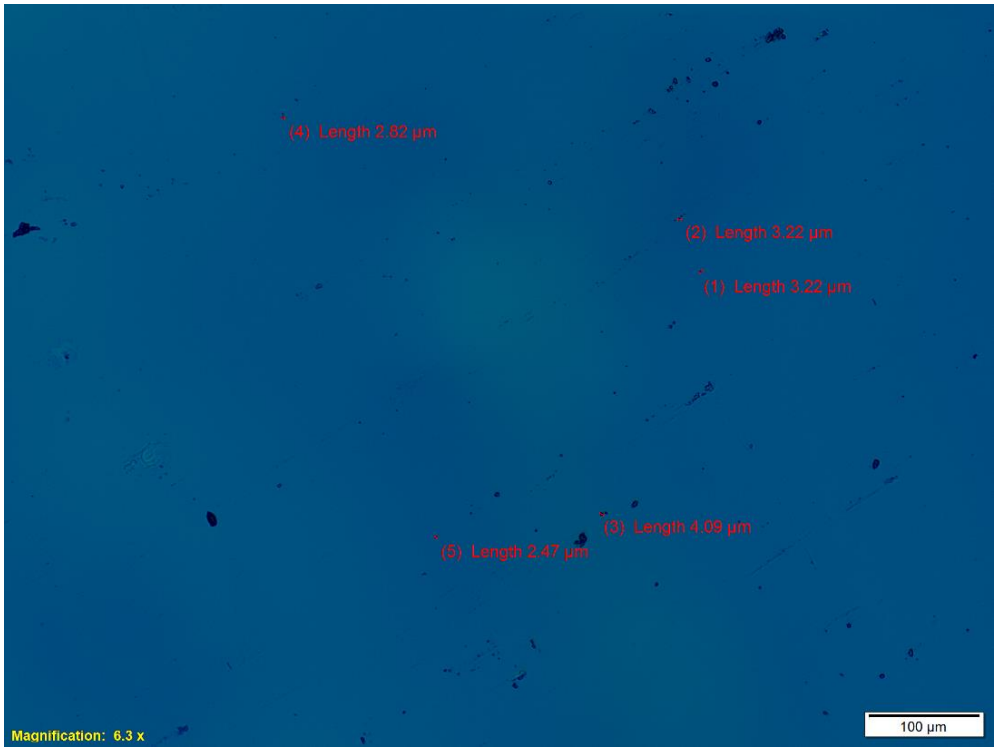


Figure C.23: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2.5 ml n-heptane (60 min)

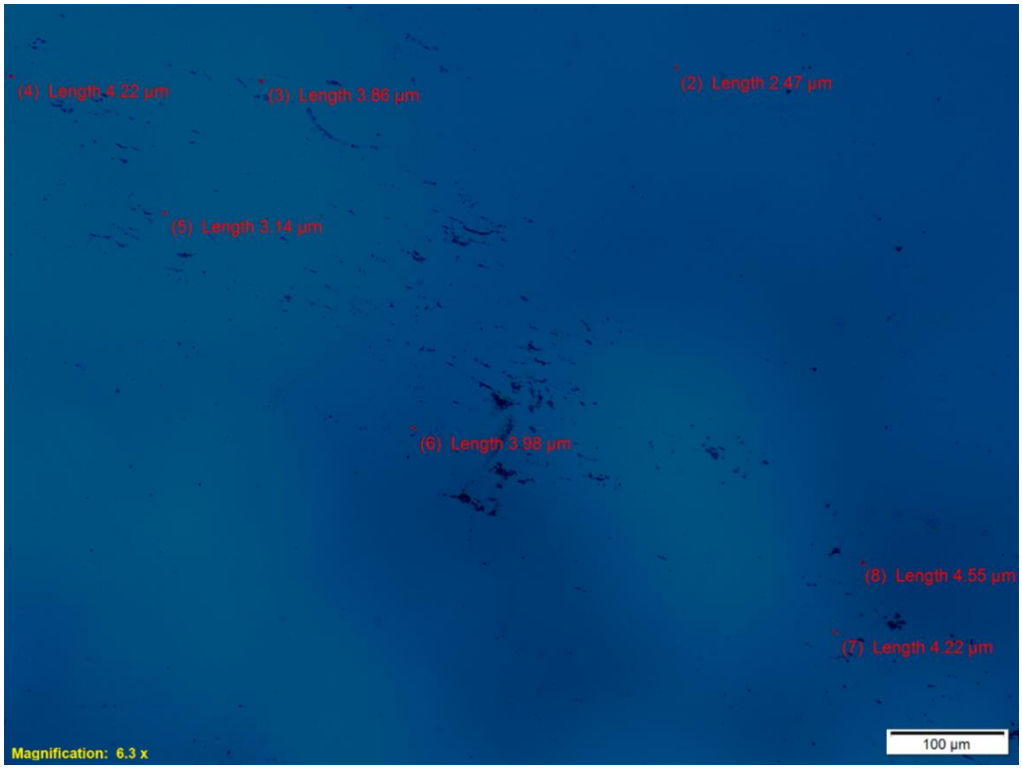


Figure C.24: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 3.5 ml n-heptane (90 min)



Figure C.25: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 5 ml n-heptane (120 min)



Figure C.26: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid (Time zero)



Figure C.27: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2 ml of n-heptane (30 min)



Figure C.28: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)



Figure C.29: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

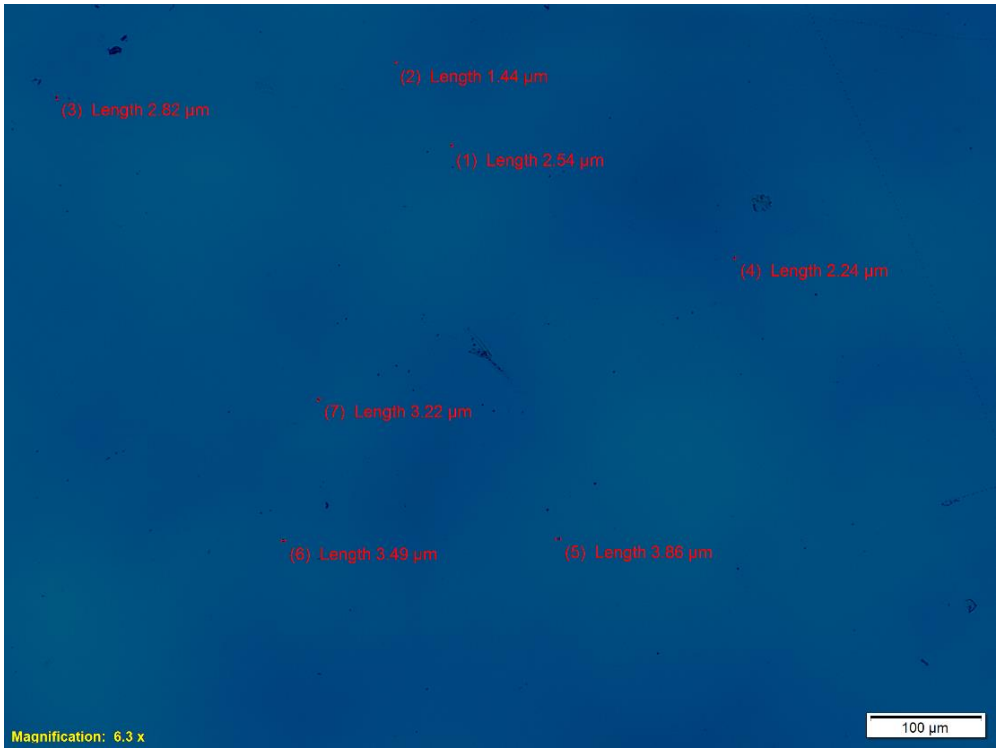


Figure C.30: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

APPENDIX D: Crude Oil - n-heptane - Salicylic acid mixture at 65 ^{o}C

Figure D: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 65 ºC.

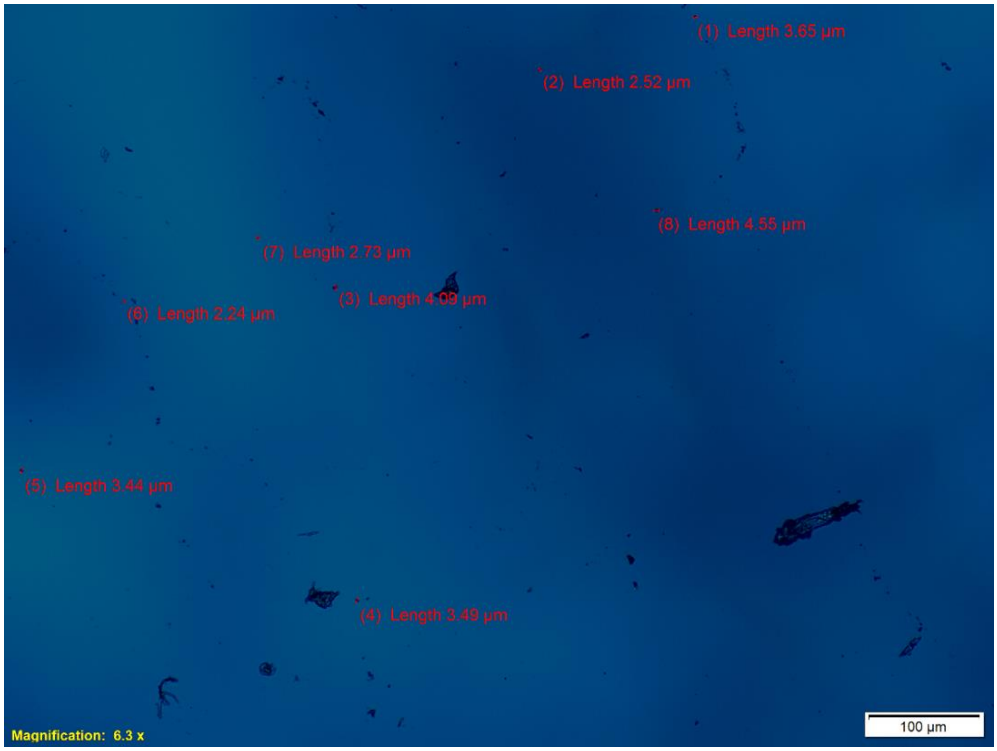


Figure D.1: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid (Time zero)

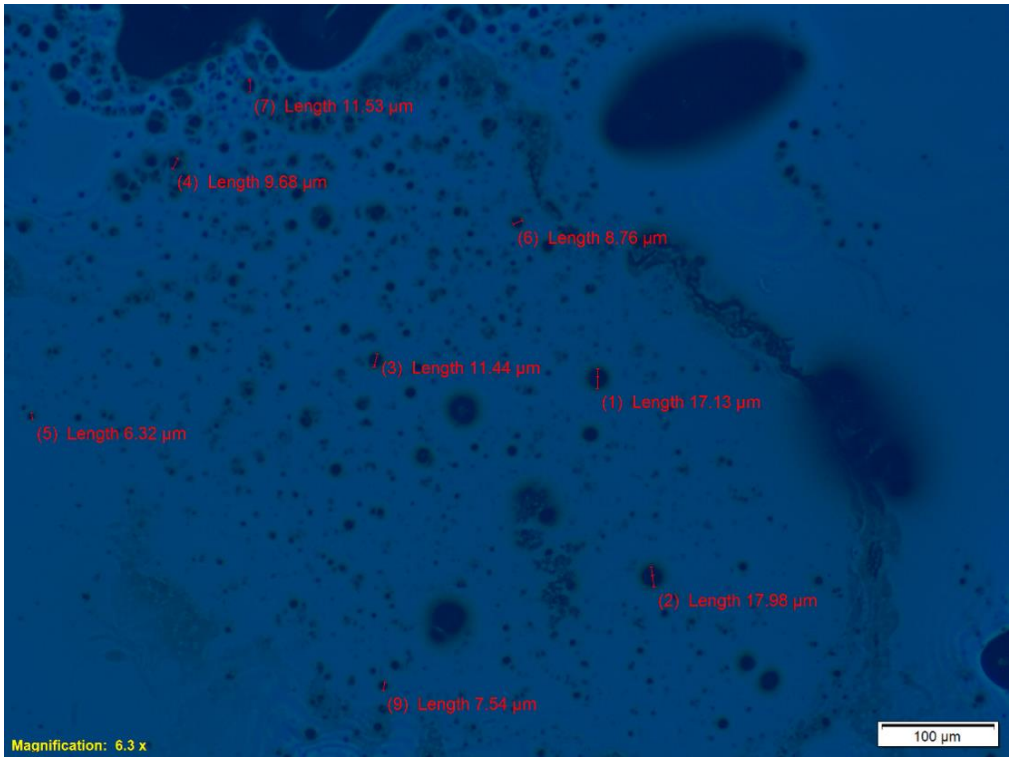


Figure D.2: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2 ml of n-heptane (30 min)

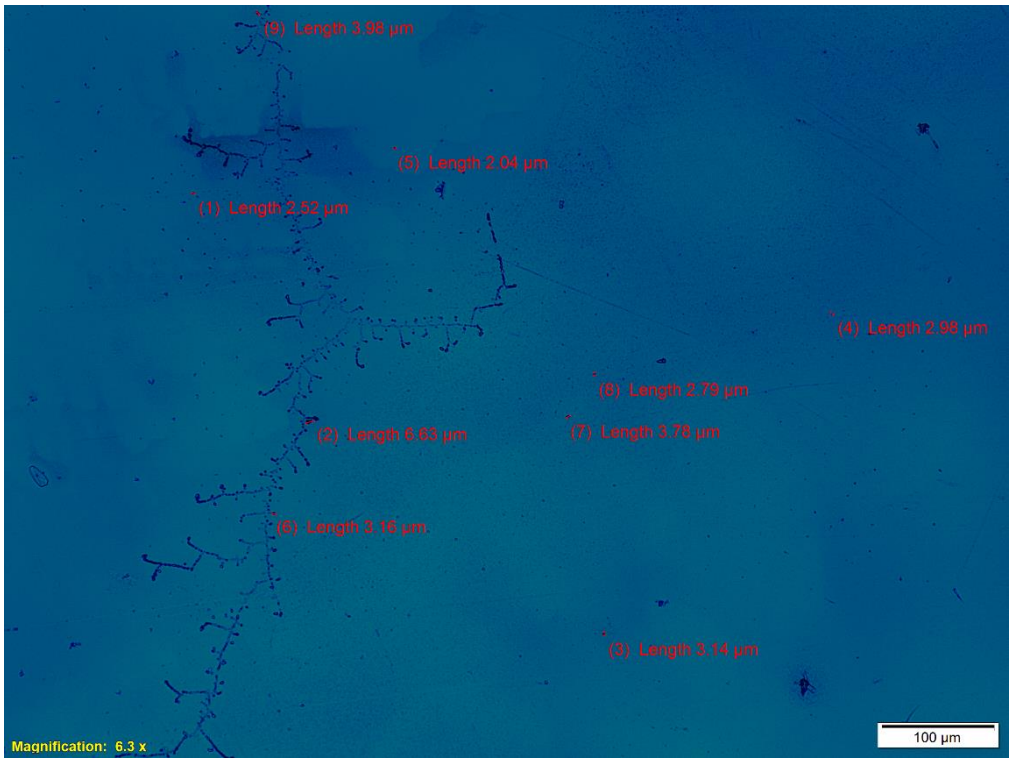


Figure D.3: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2.5 ml of n-heptane (60 min)

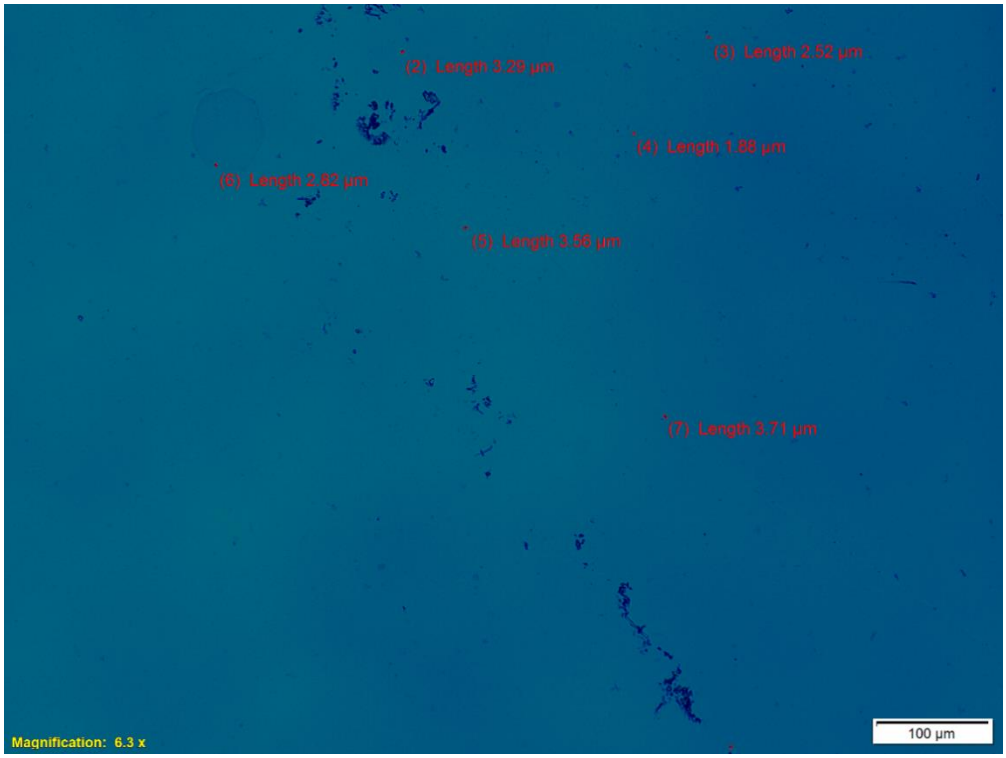


Figure D.4: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 3.5 ml of n-heptane (90 min)

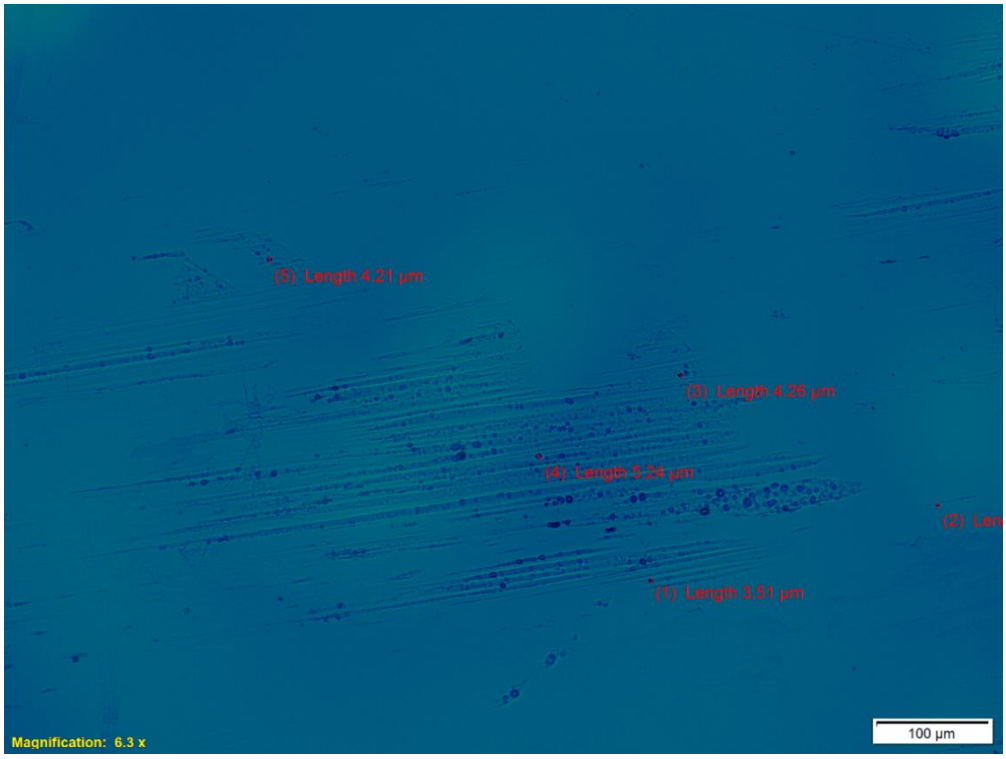


Figure D.5: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 5 ml of n-heptane (120 min)

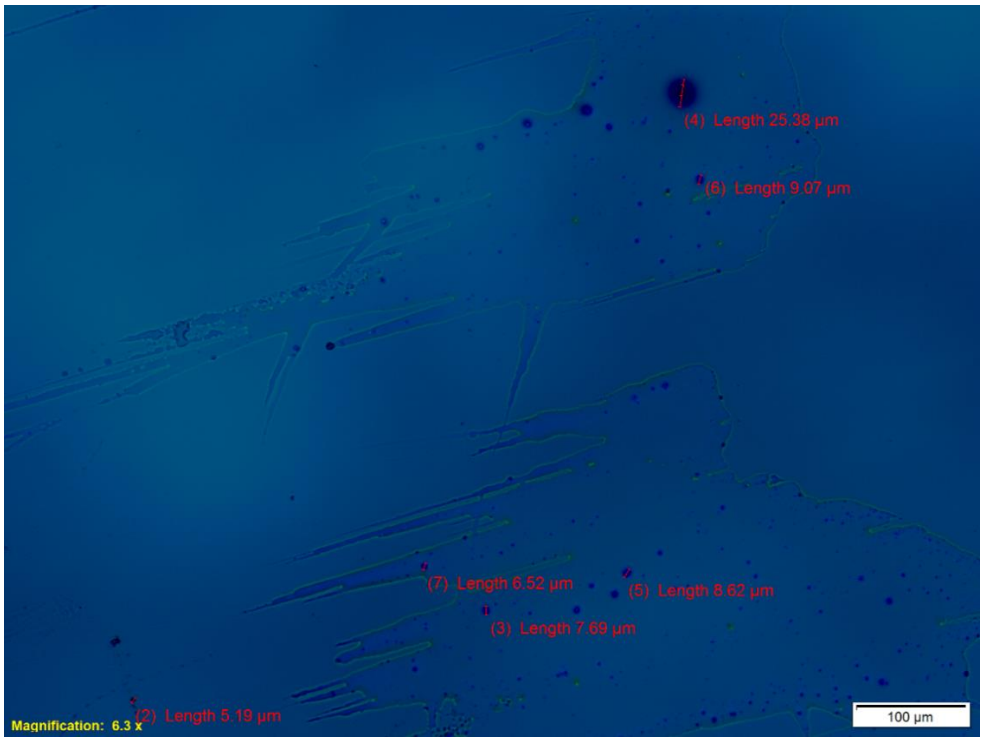


Figure D.6: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid (Time zero)

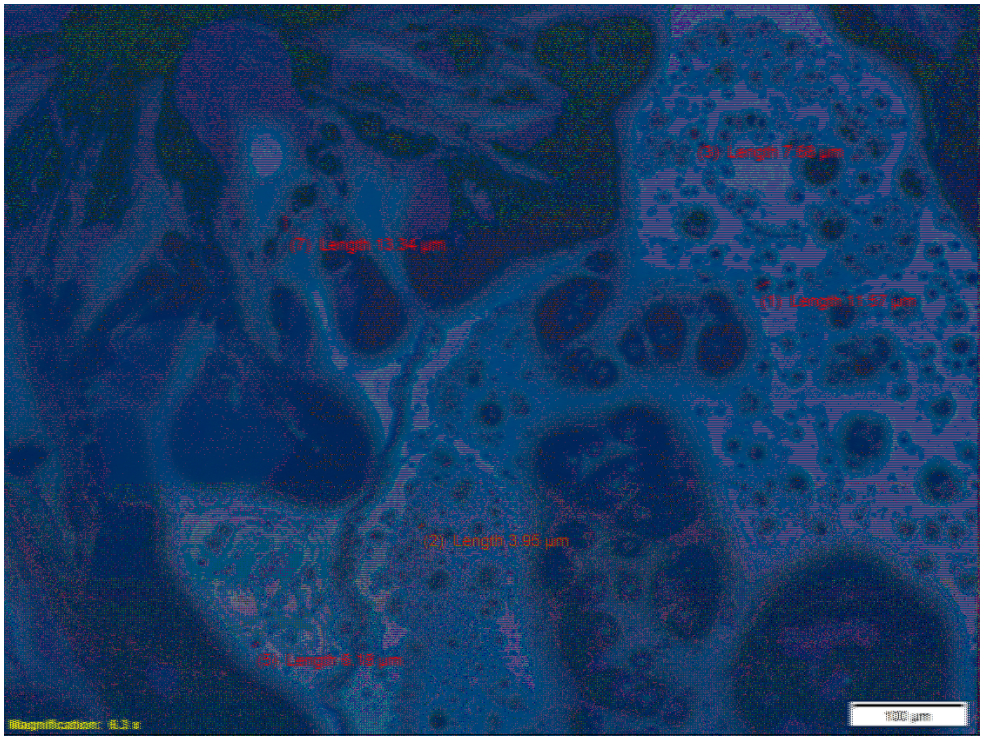


Figure D.7: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 2 ml of n-heptane (30 min)

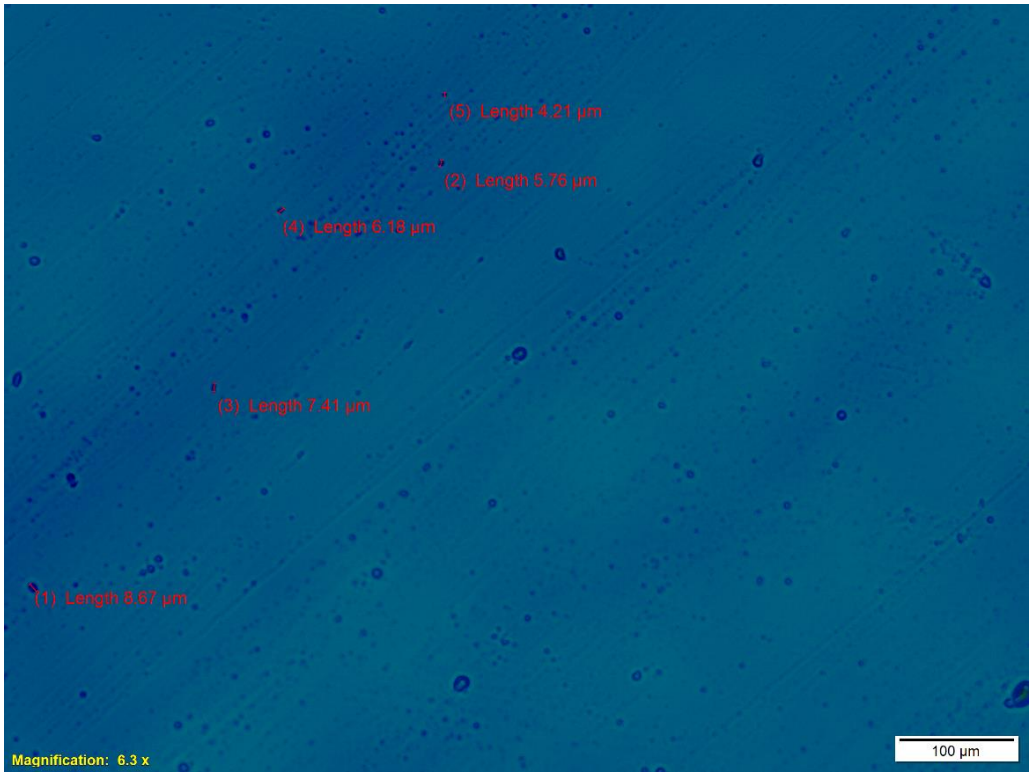


Figure D.8: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 2.5 ml of n-heptane (60 min)

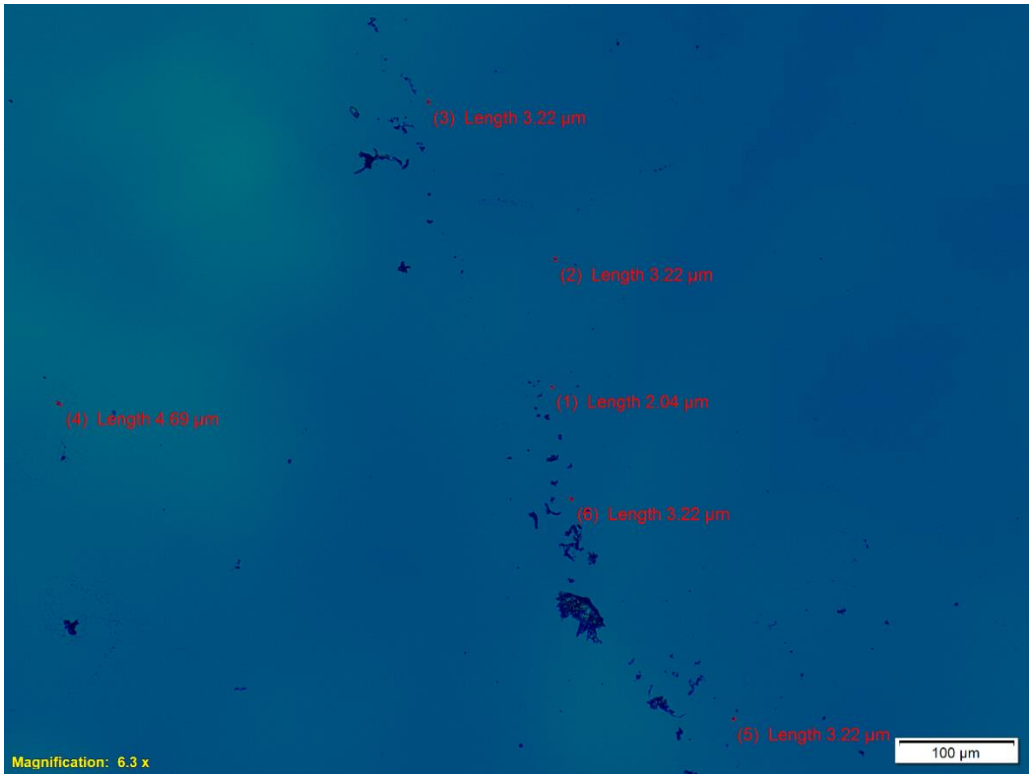


Figure D.9: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 3.5 ml of n-heptane (90 min)

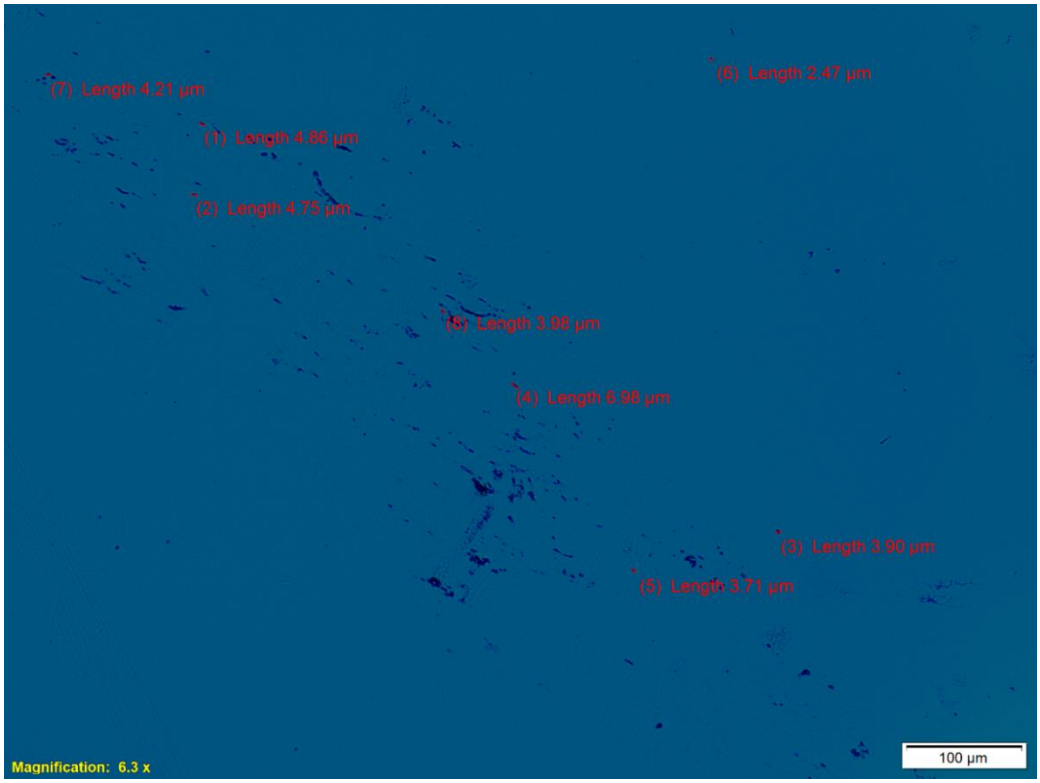


Figure D.10: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 5 ml of n-heptane (120 min)

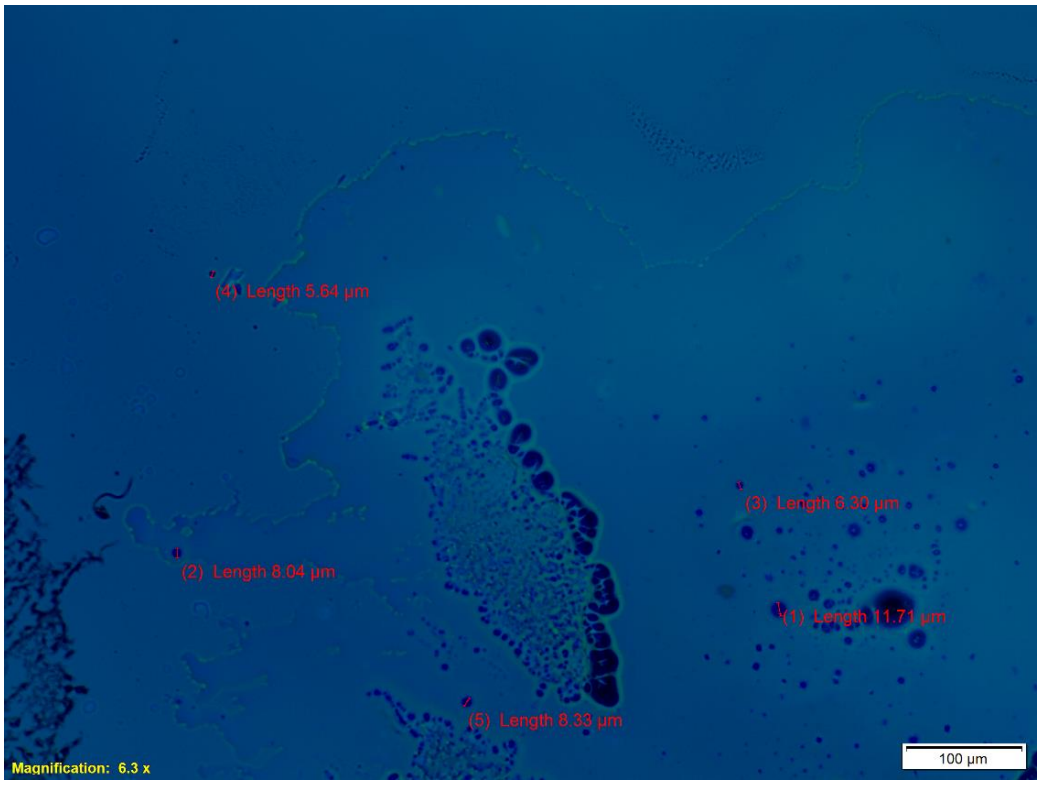


Figure D.11: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid (Time zero)

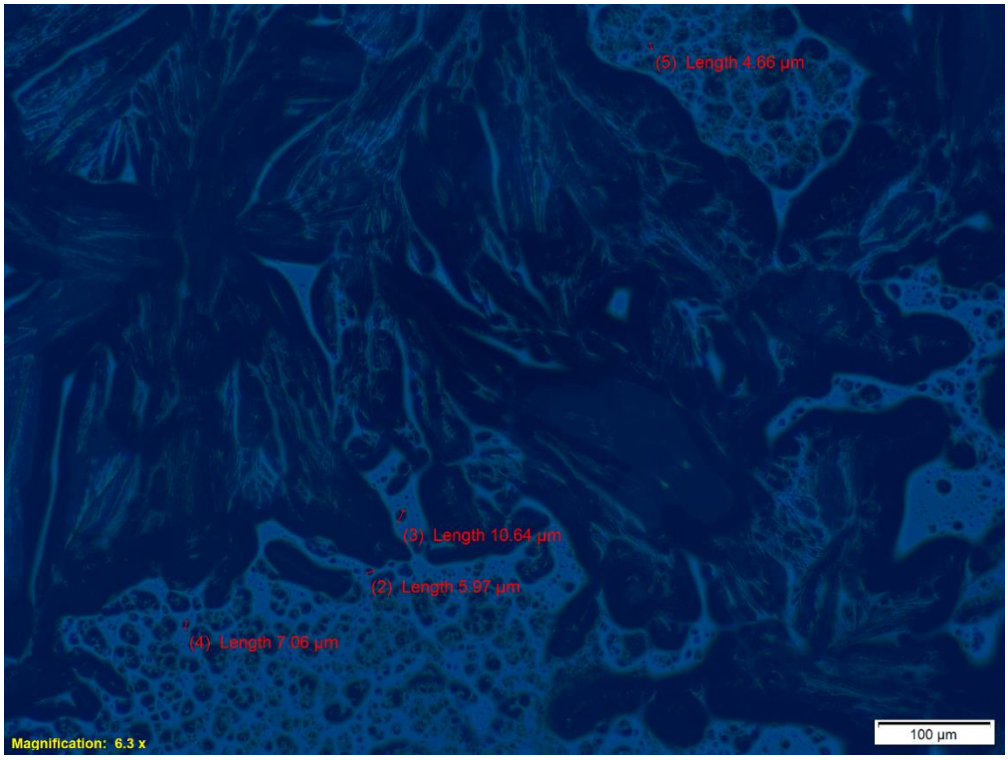


Figure D.12: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 2 ml of n-heptane (30 min)

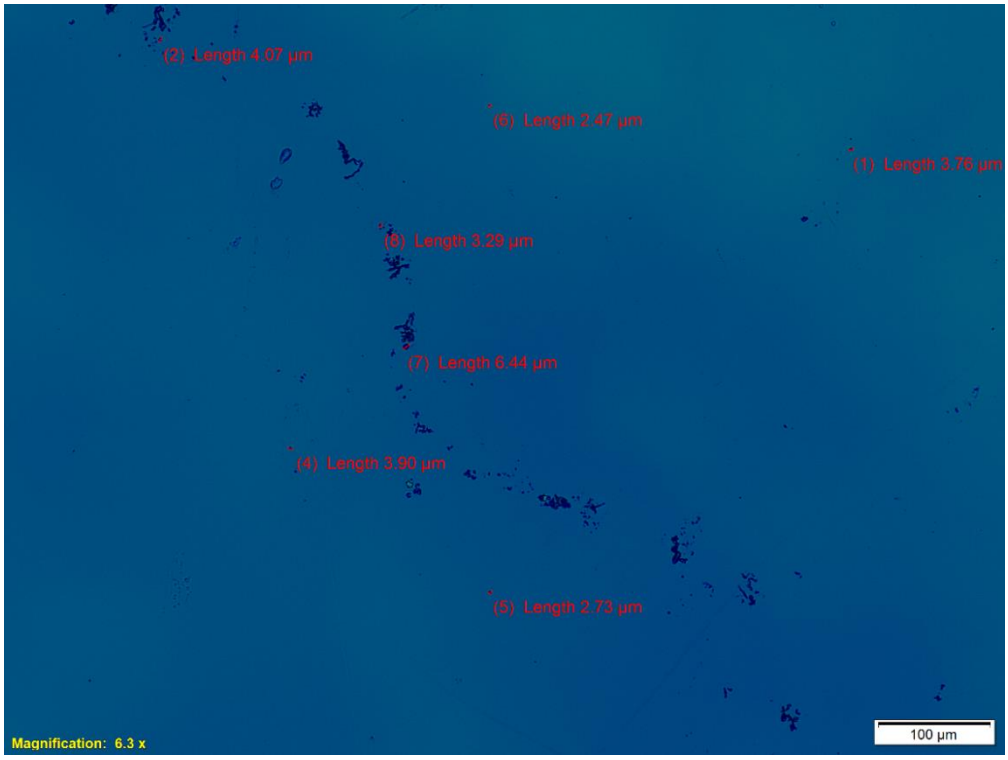


Figure D.13: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 2.5 ml of n-heptane (60 min)

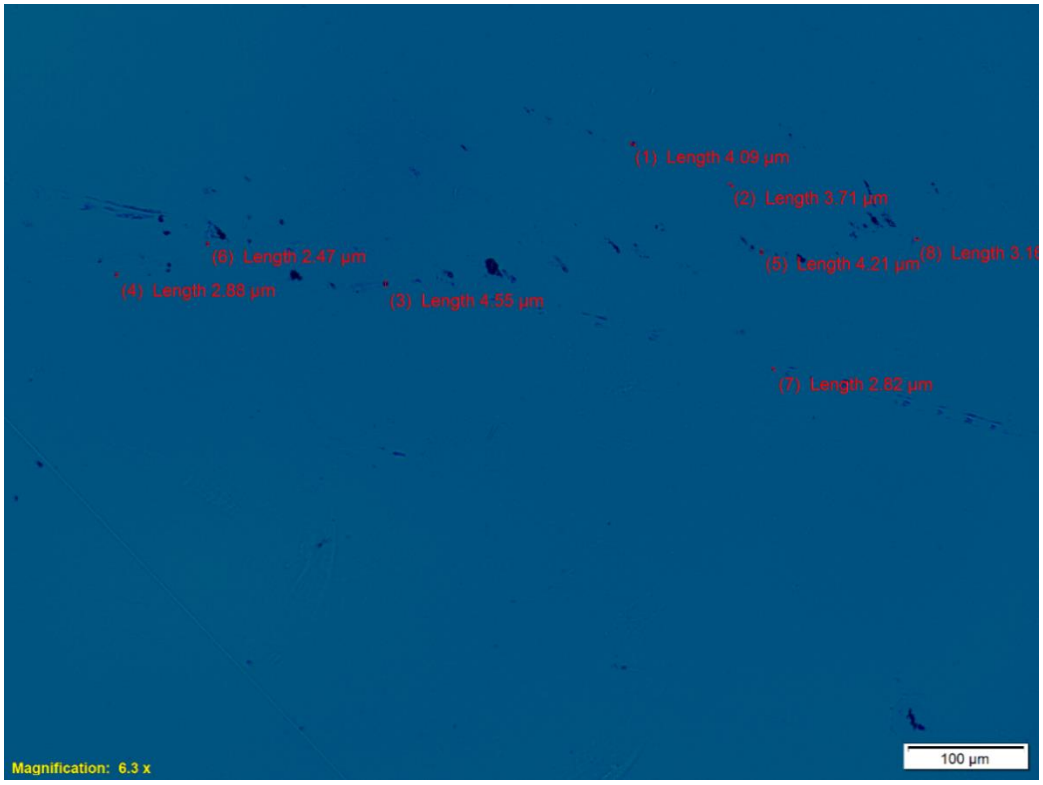


Figure D.14: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 3.5 ml of n-heptane (90 min)

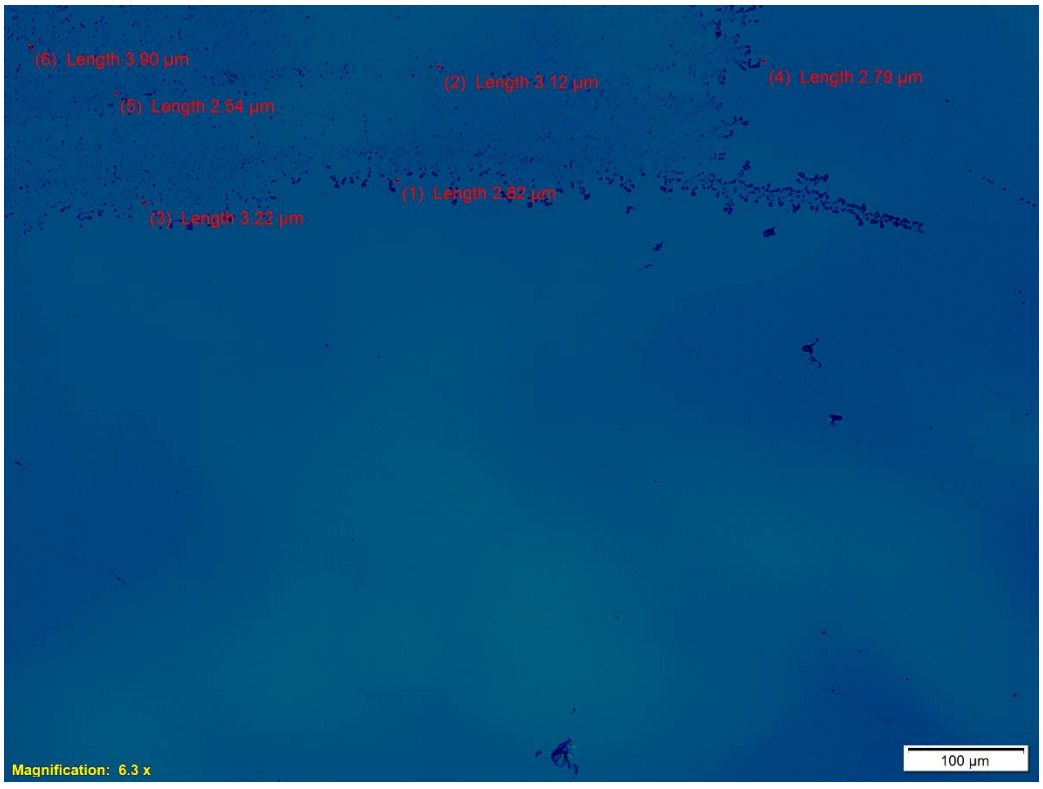


Figure D.15: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 5 ml of n-heptane (120 min)

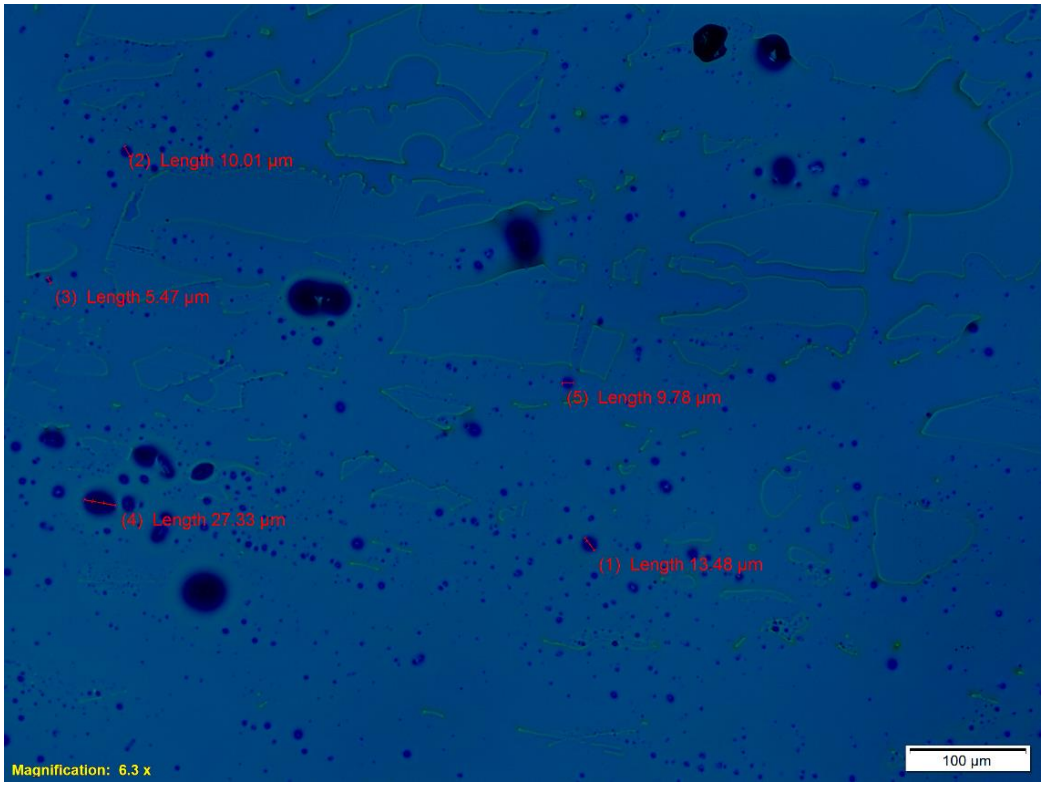


Figure D.16: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid (Time zero)

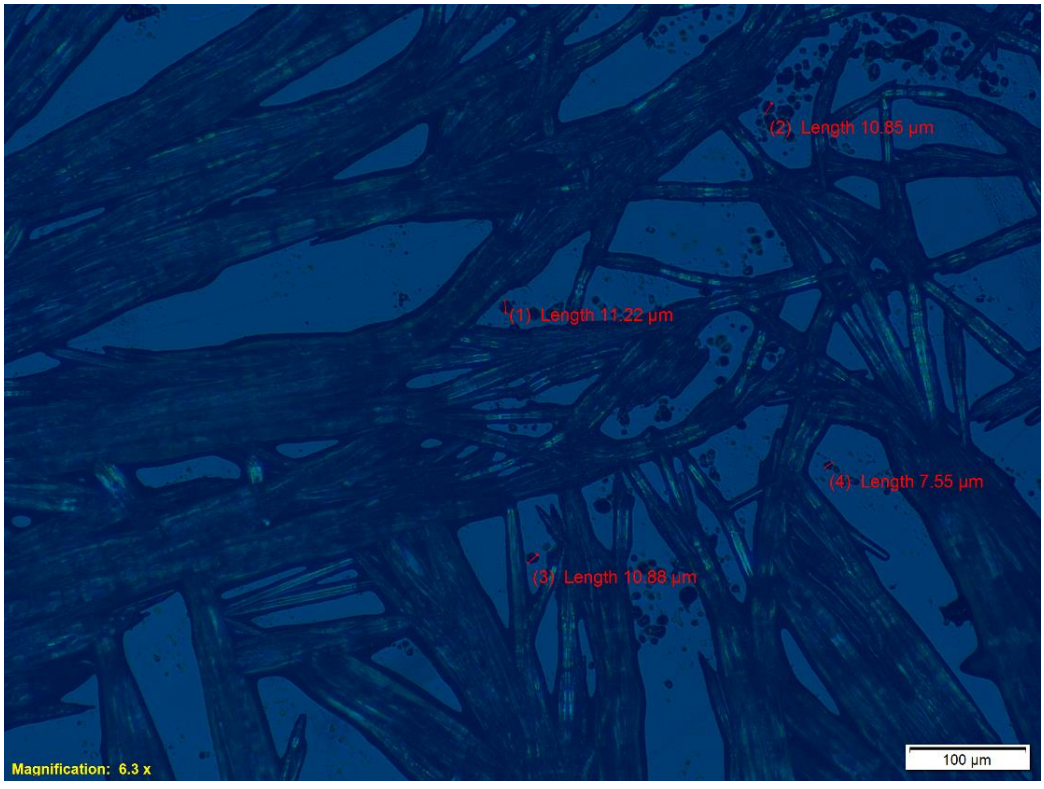


Figure D.17: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 2 ml of n-heptane (30 min)



Figure D.18: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 2.5 ml of n-heptane (60 min)

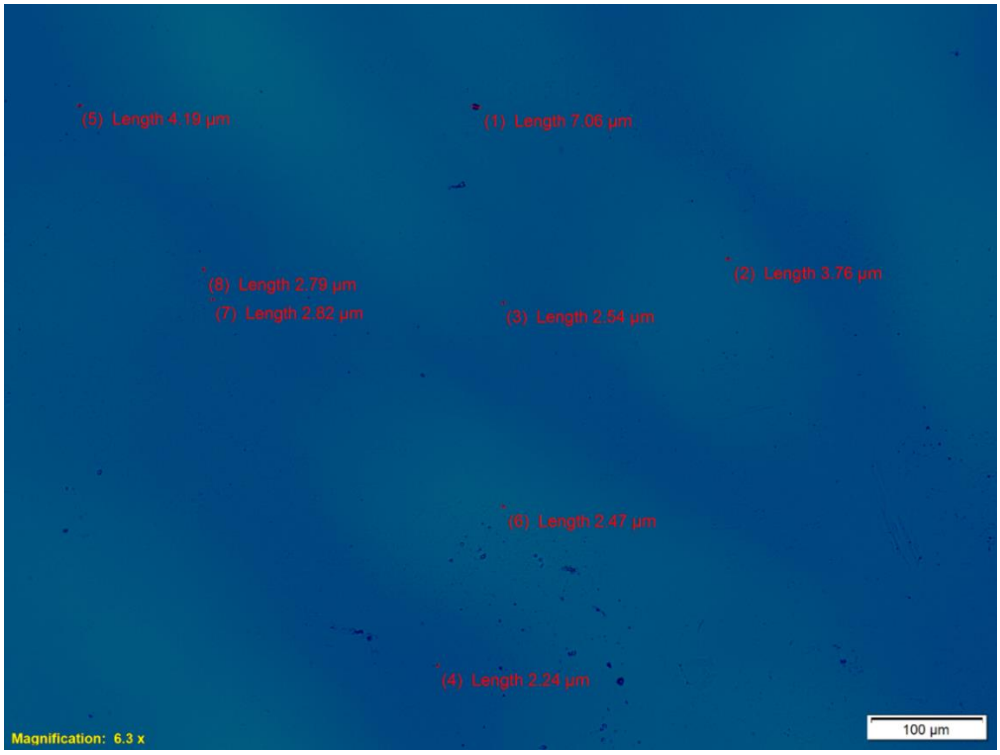


Figure D.19: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 3.5 ml of n-heptane (90 min)



Figure D.20: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 5 ml of n-heptane (120 min)

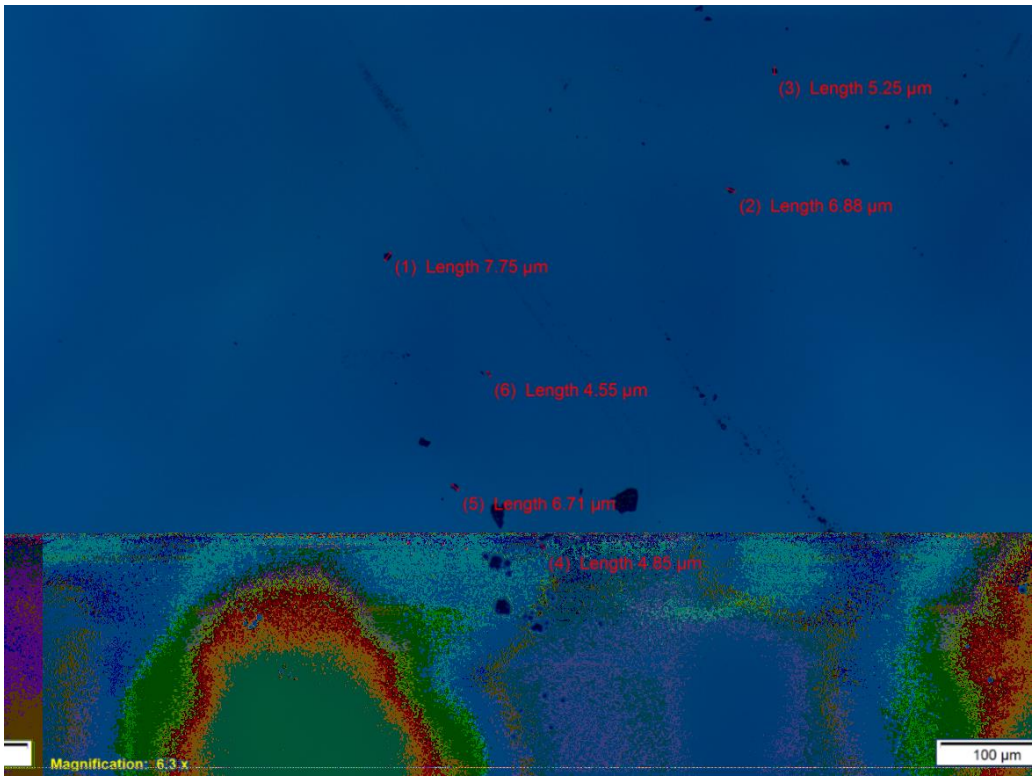


Figure D.21: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid (Time zero)

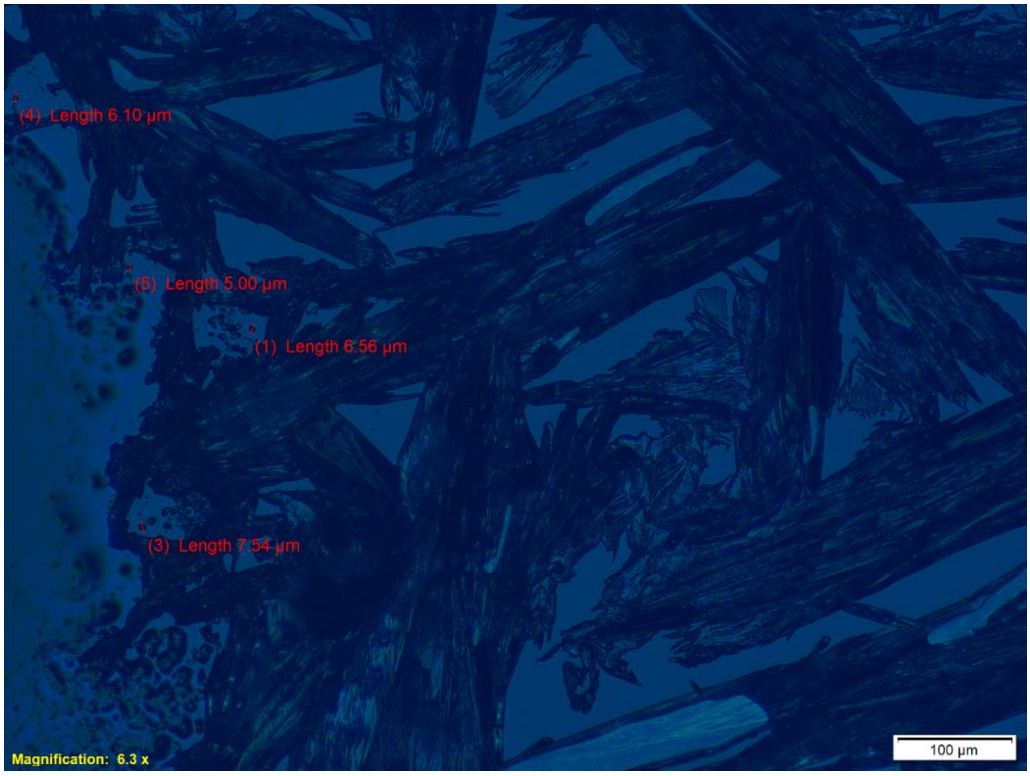


Figure D.22: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 2 ml of n-heptane (30 min)

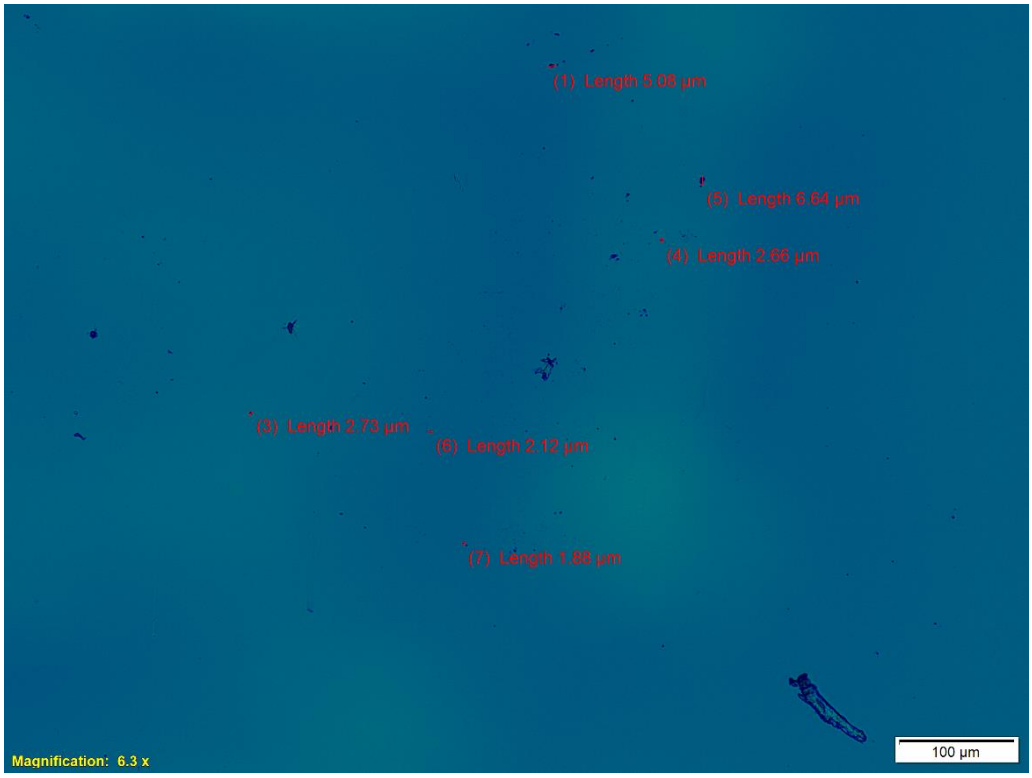


Figure D.23: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 2.5 ml of n-heptane (60 min)

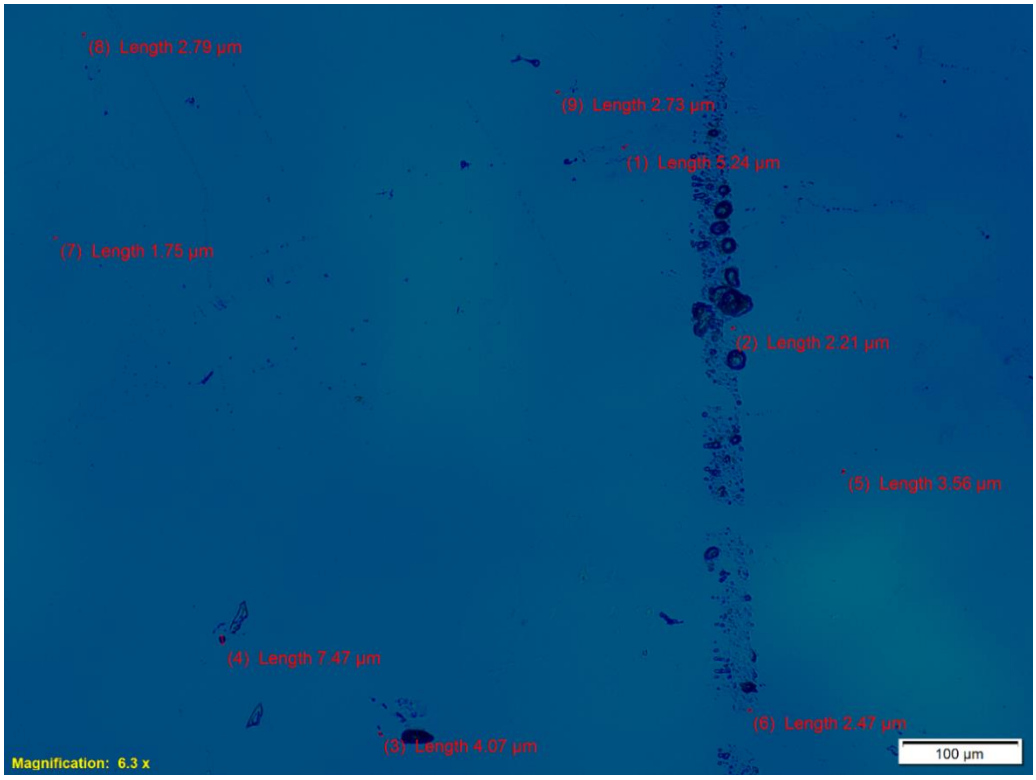


Figure D.24: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 3.5 ml of n-heptane (90 min)

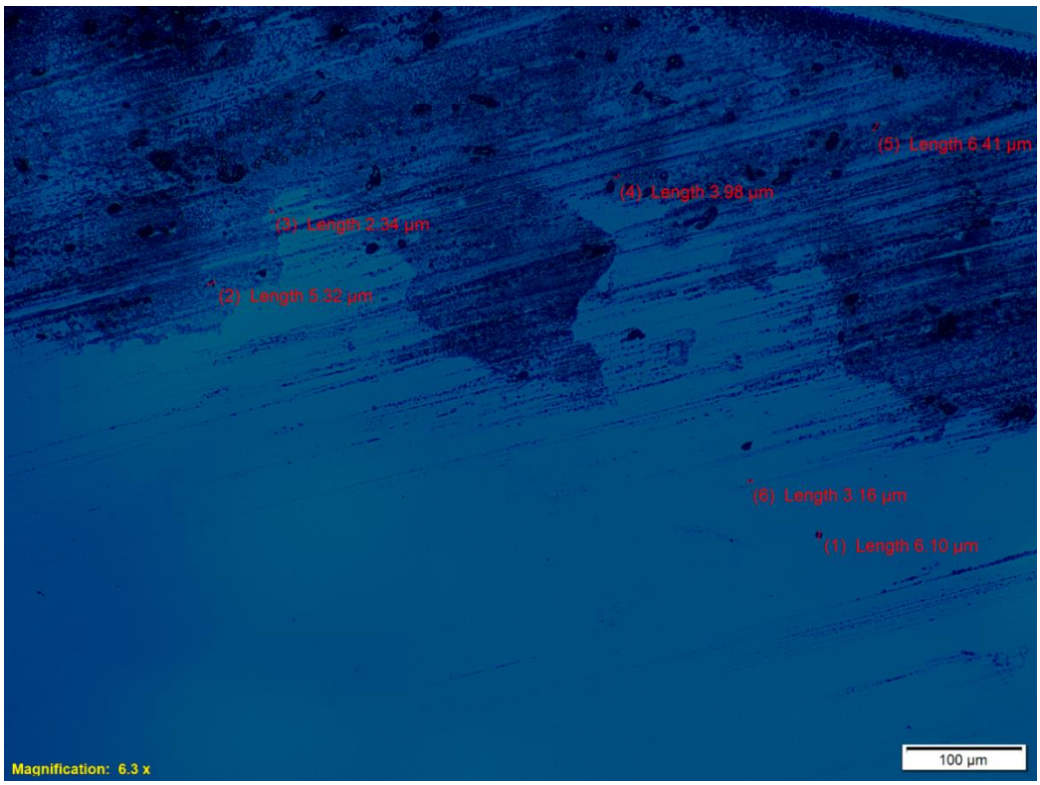


Figure D.25: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 3.5 ml of n-heptane (120 min)

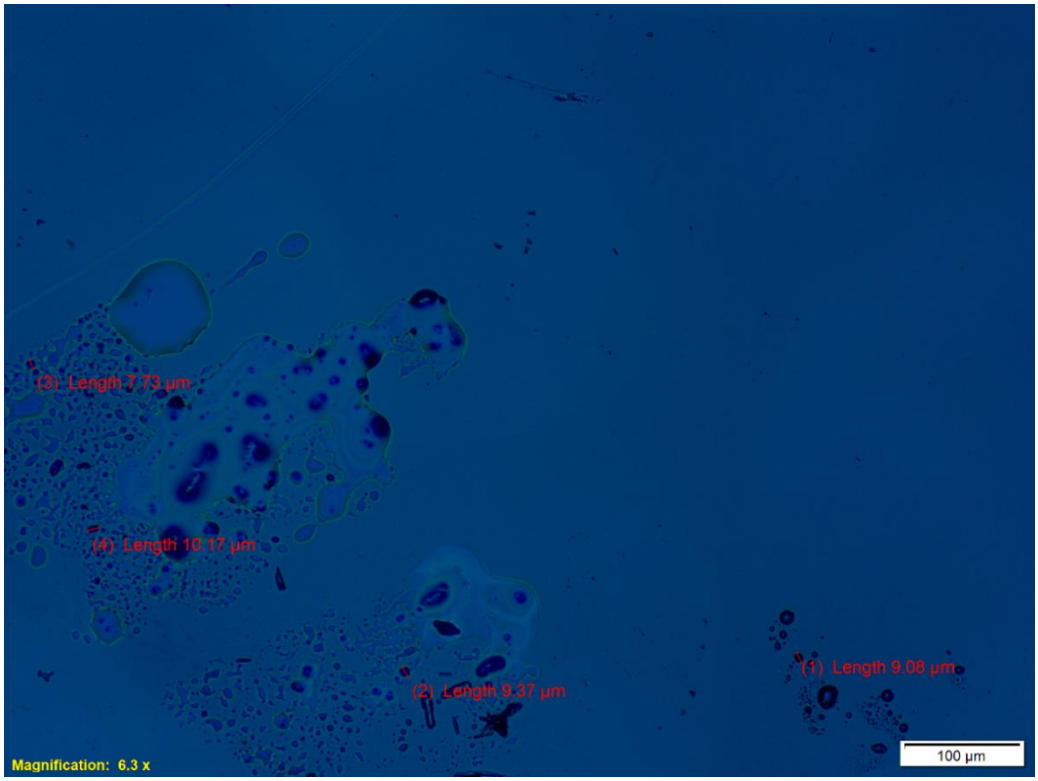


Figure D.26: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid (Time zero)

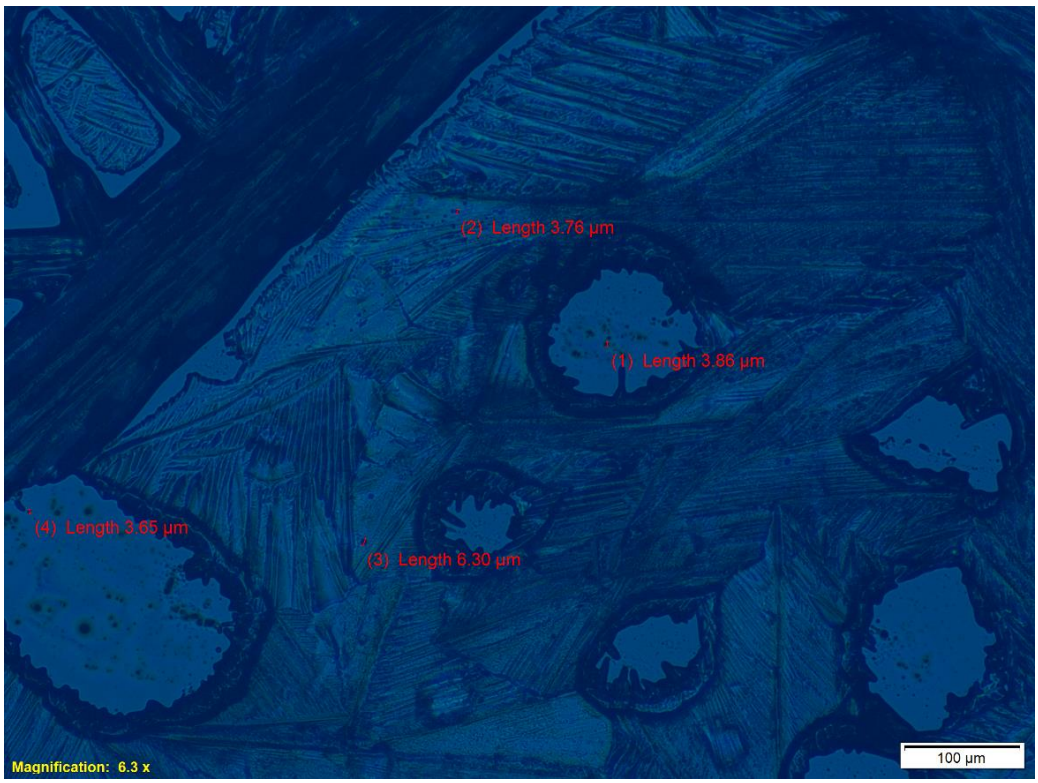


Figure D.27: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 2 ml of n-heptane (30 min)



Figure D.28: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 2.5 ml of n-heptane (60 min)

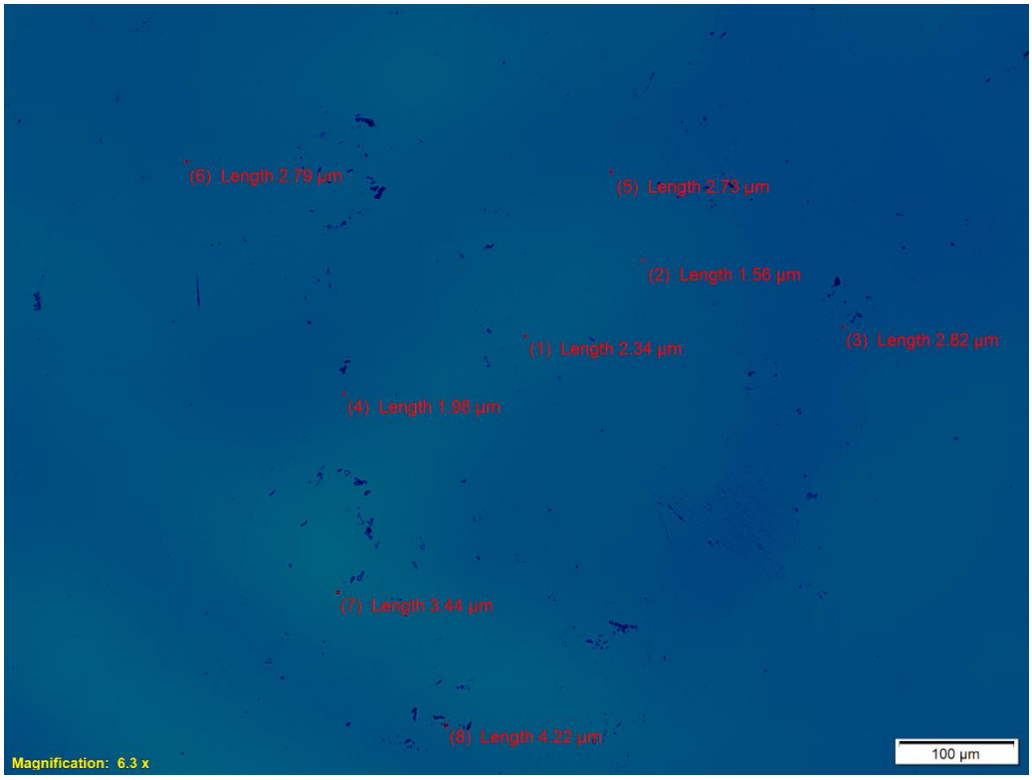


Figure D.29: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 3.5 ml of n-heptane (90 min)

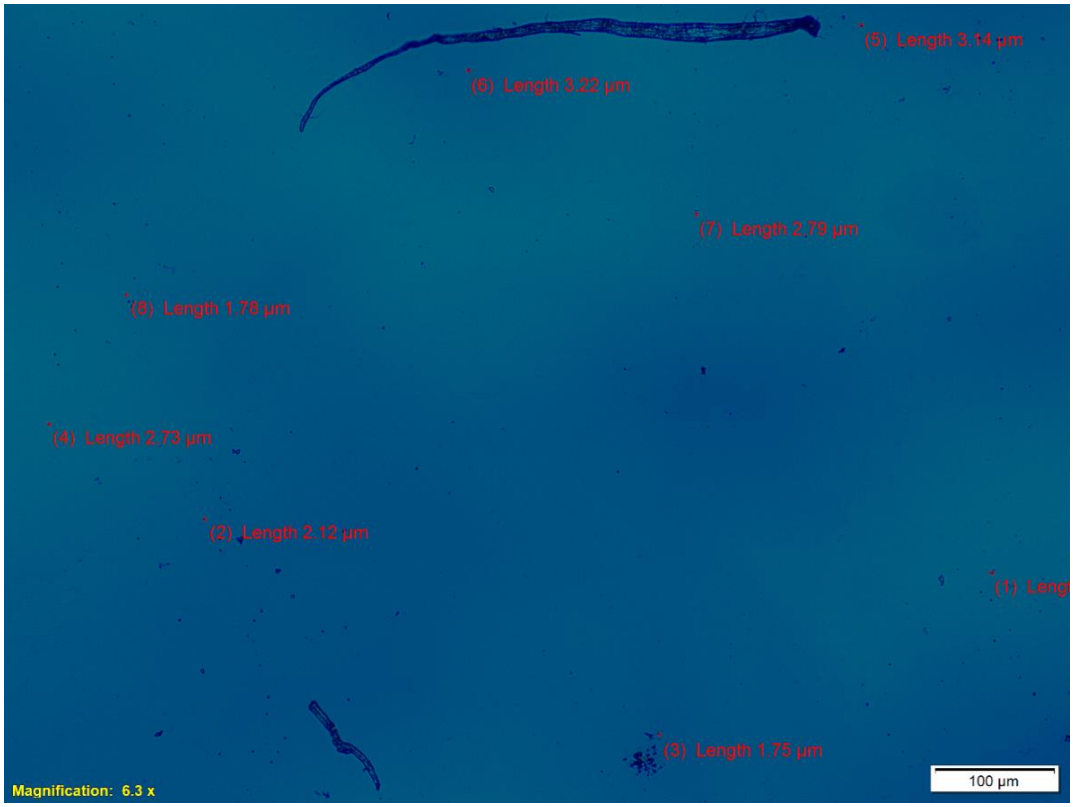


Figure D.30: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 5 ml of n-heptane (120 min)

APPENDIX E: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 65 ^{o}C

Figure E: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 65 ºC

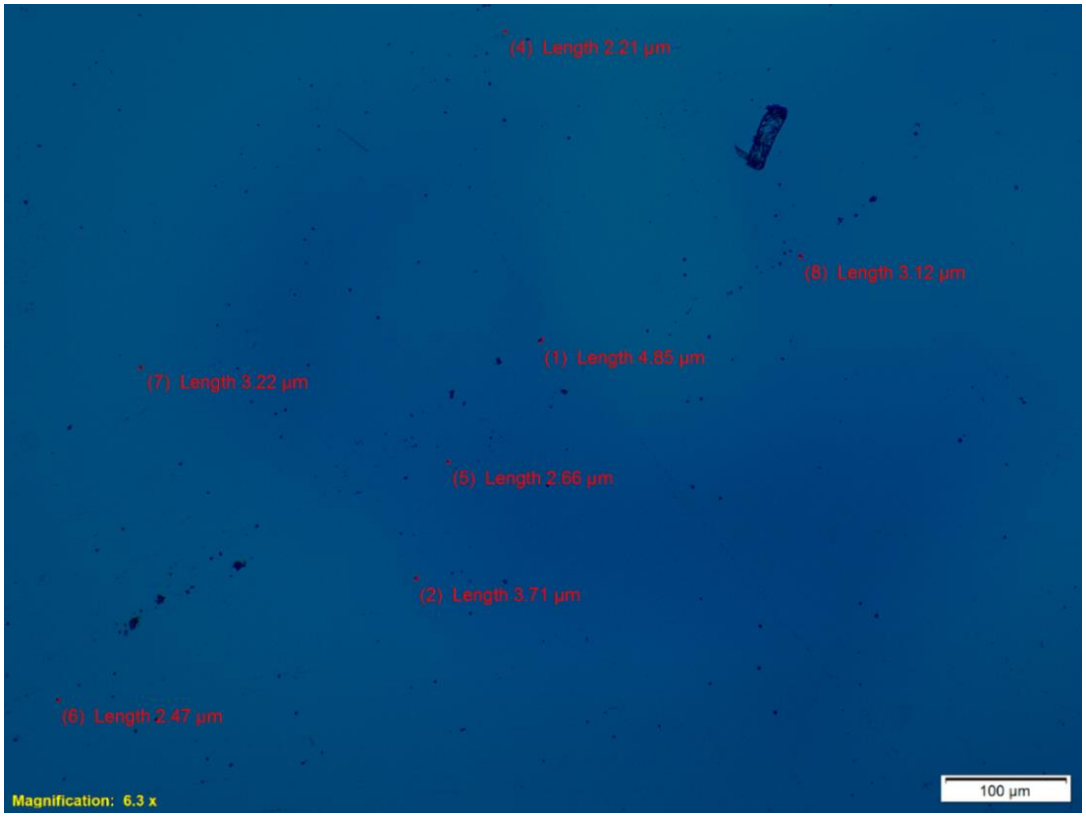


Figure E.1: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid (Time zero)

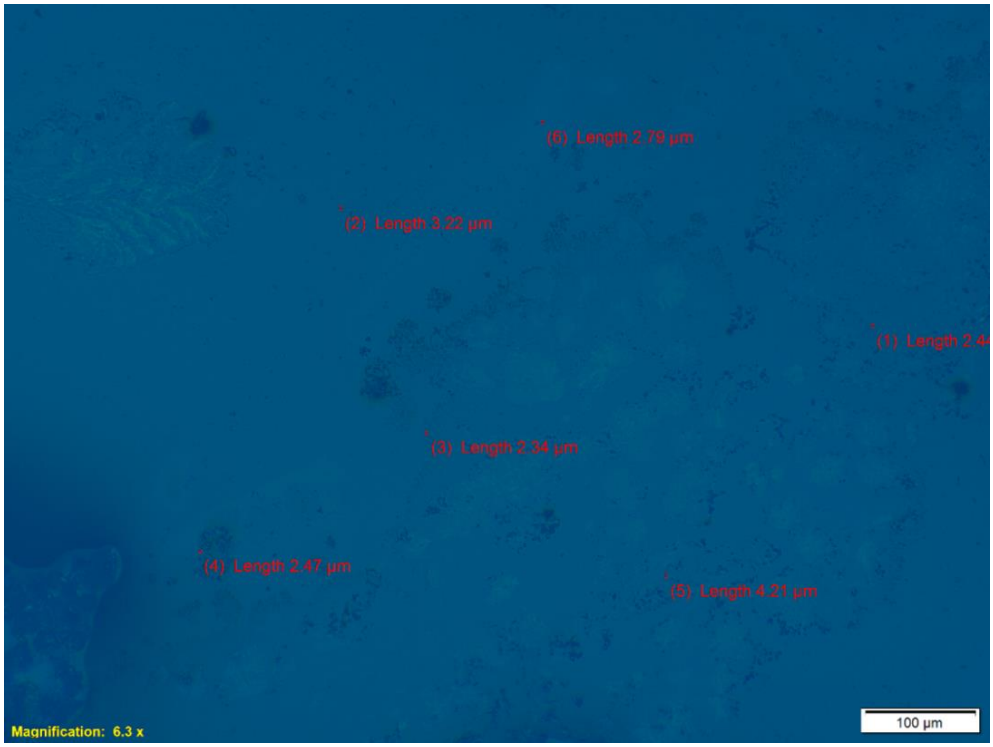


Figure E.2: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

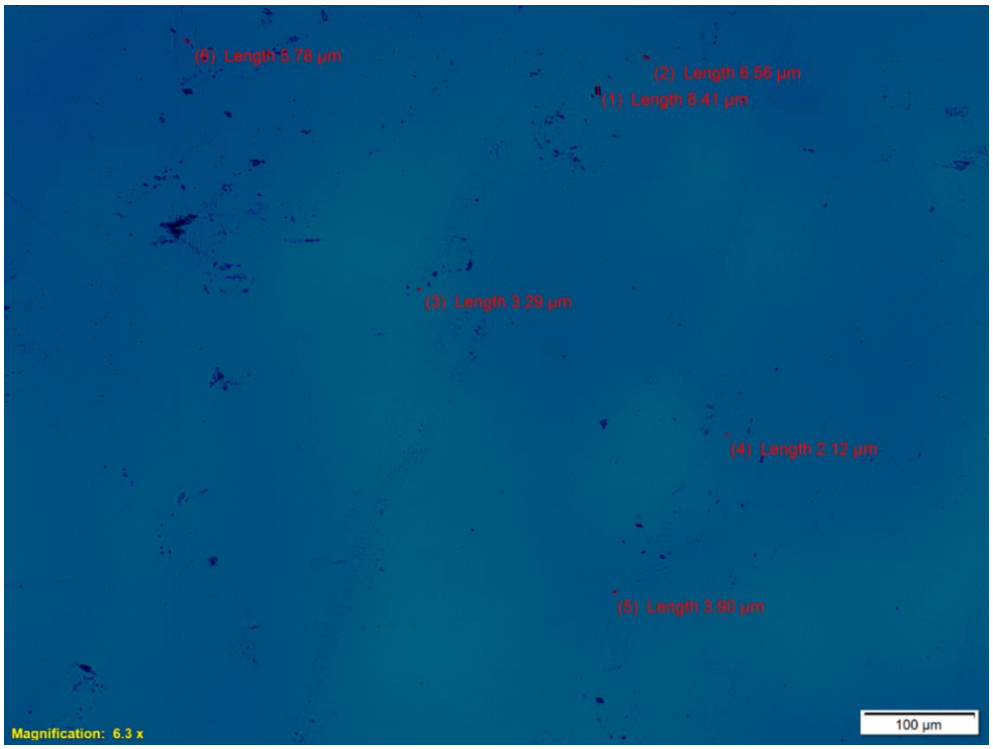


Figure E.3: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

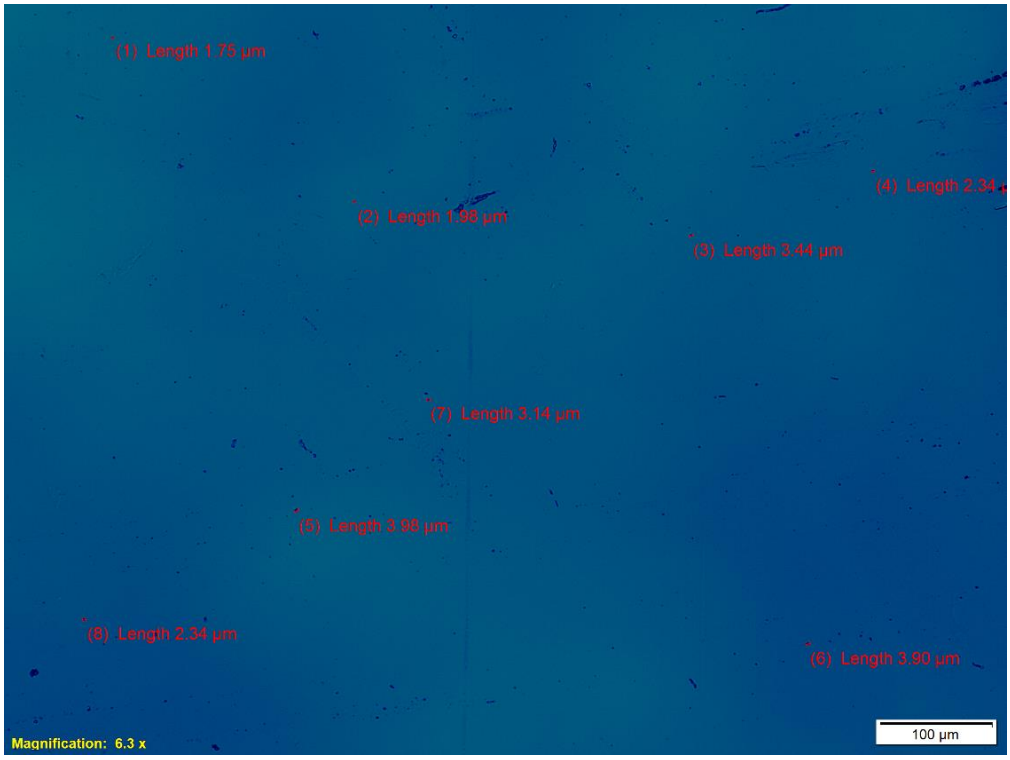


Figure E.4: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

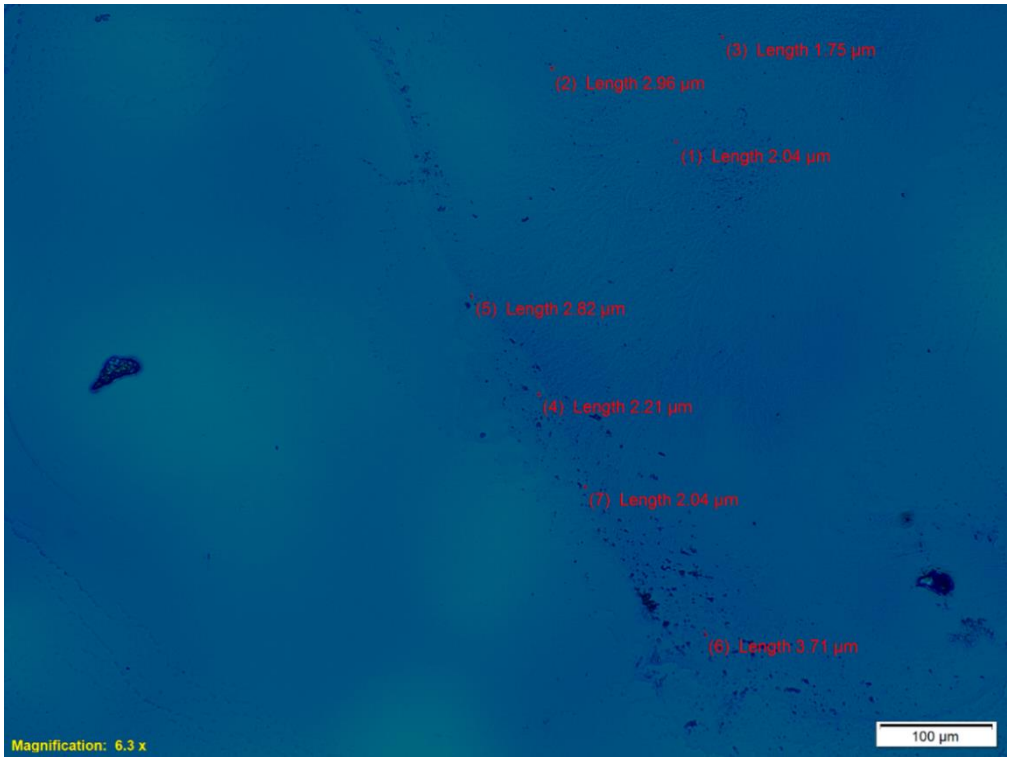


Figure E.5: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 5 ml of n-heptane (120 min)



Figure E.6: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid (Time zero)

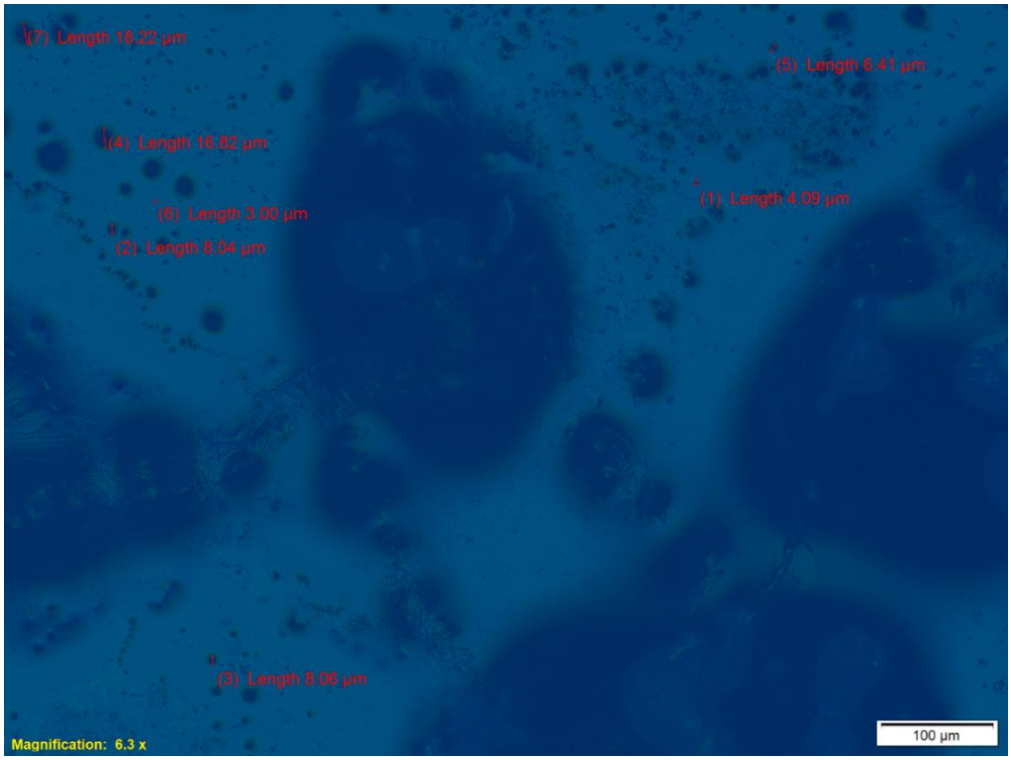


Figure E.7: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

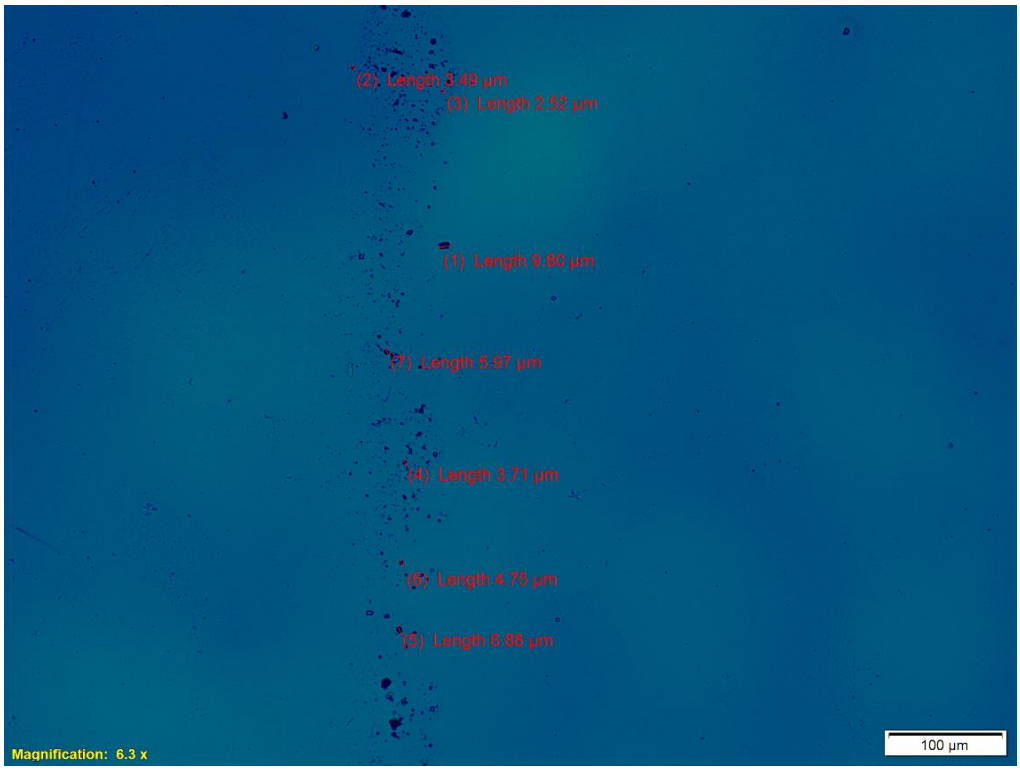


Figure E.8: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

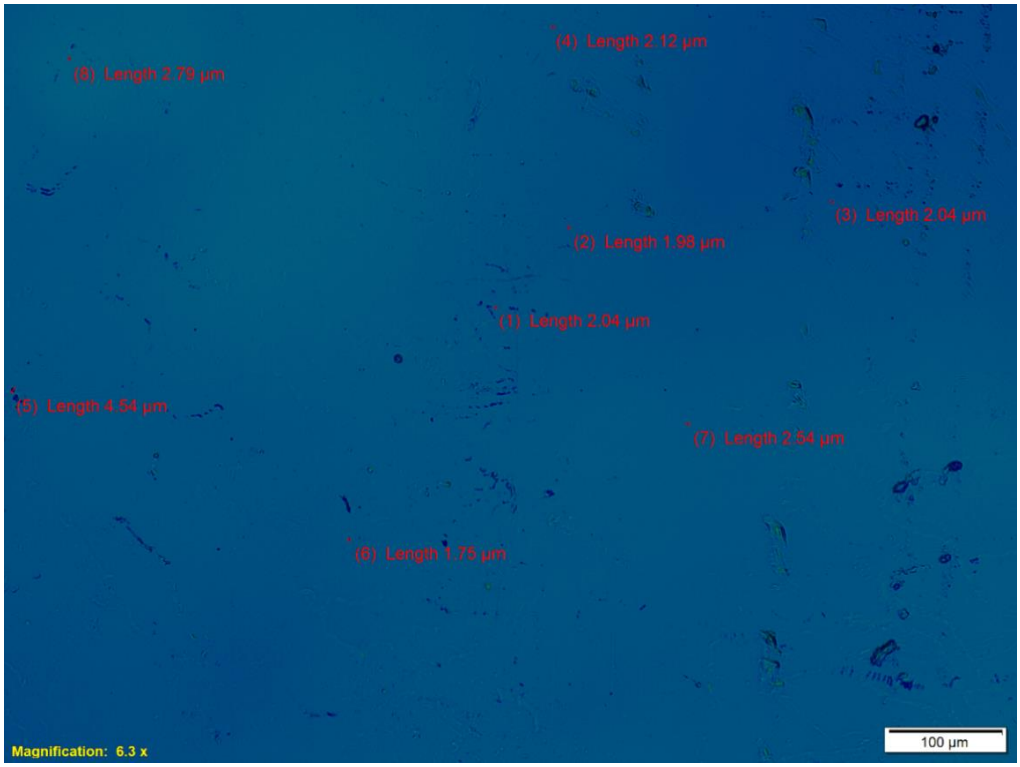


Figure E.9: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)



Figure E.10: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

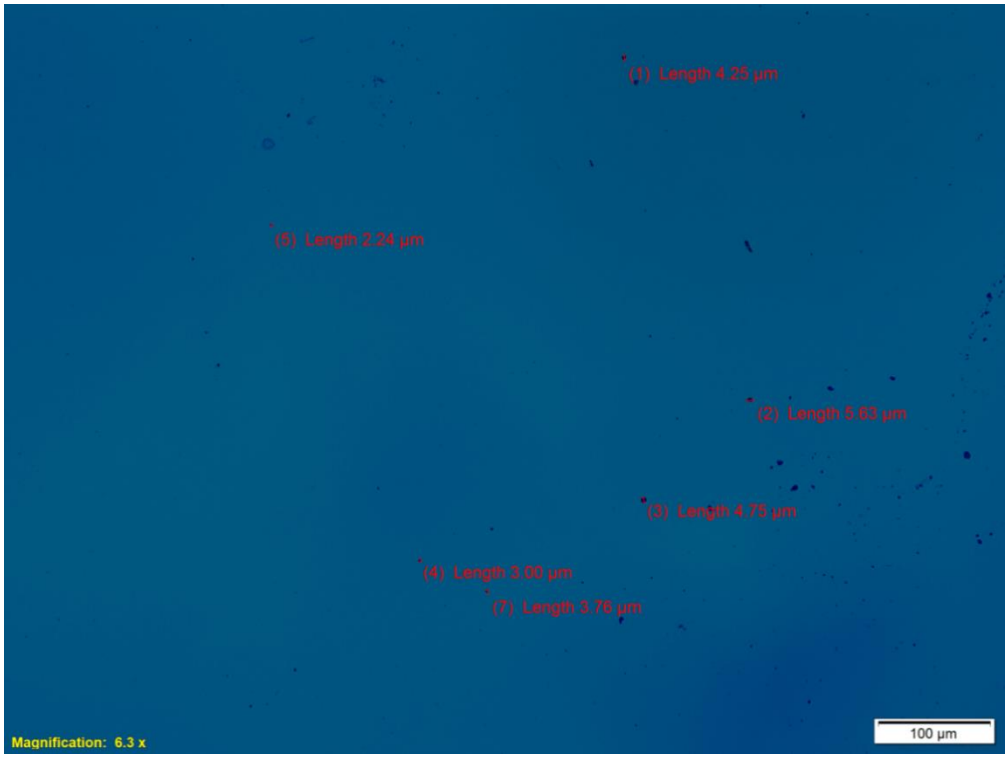


Figure E.11: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid (Time zero)

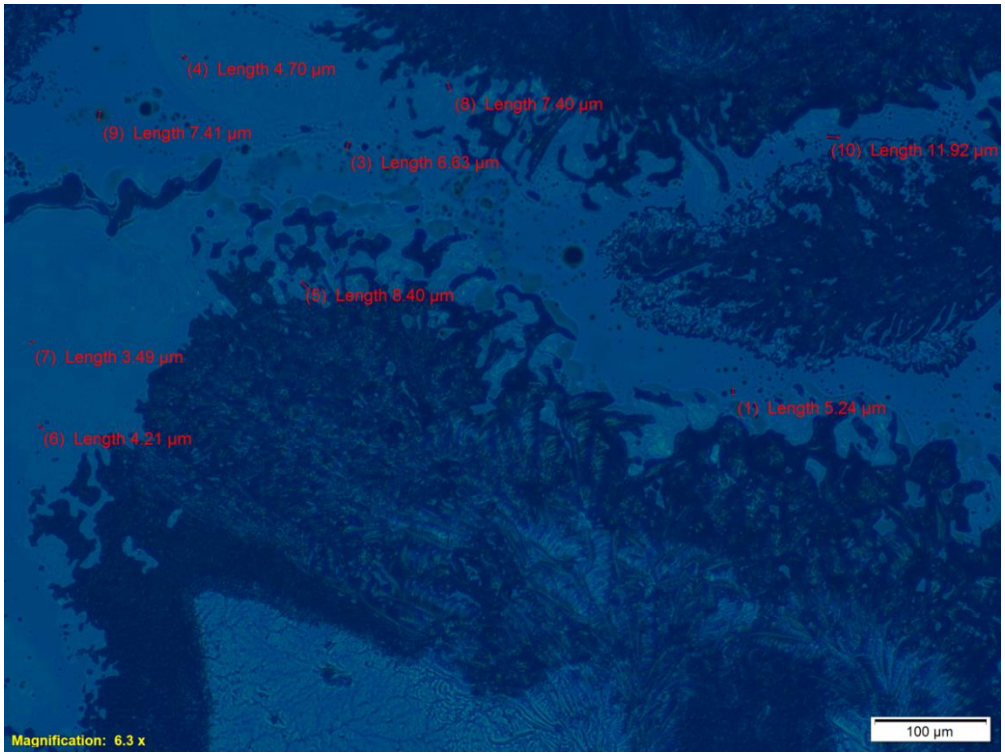


Figure E.12: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 2 ml n-heptane (30 min)

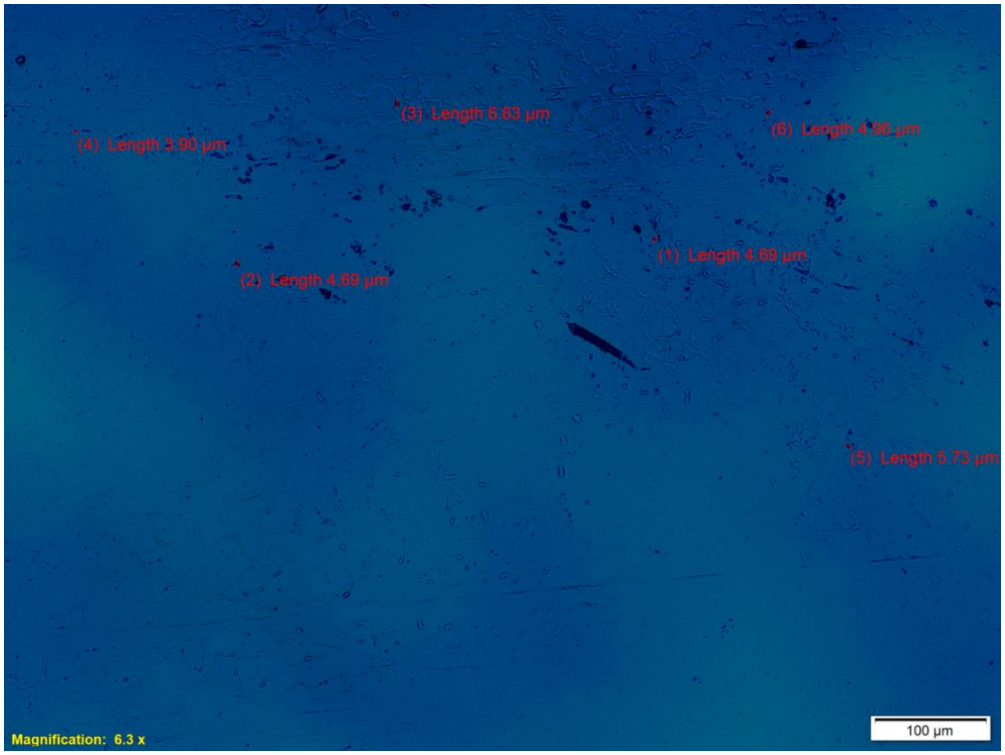


Figure E.13: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 2.5 ml n-heptane (60 min)

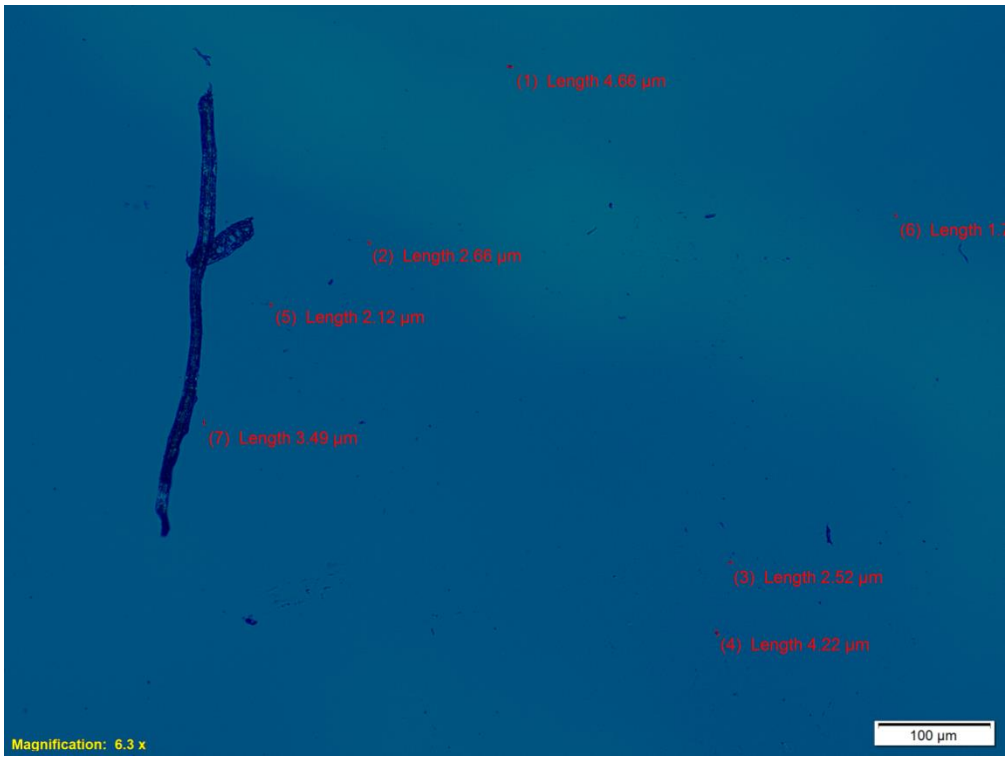


Figure E.14: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 3.5 ml n-heptane (90 min)

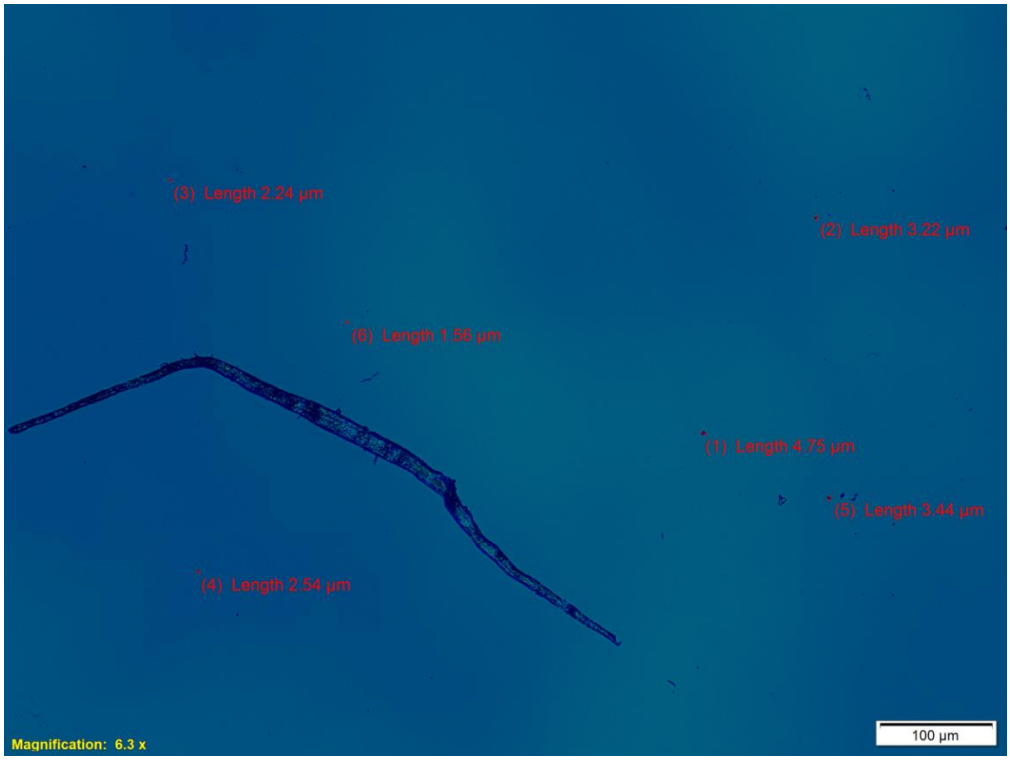


Figure E.15: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 5 ml n-heptane (120 min)



Figure E.16: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid (Time zero)

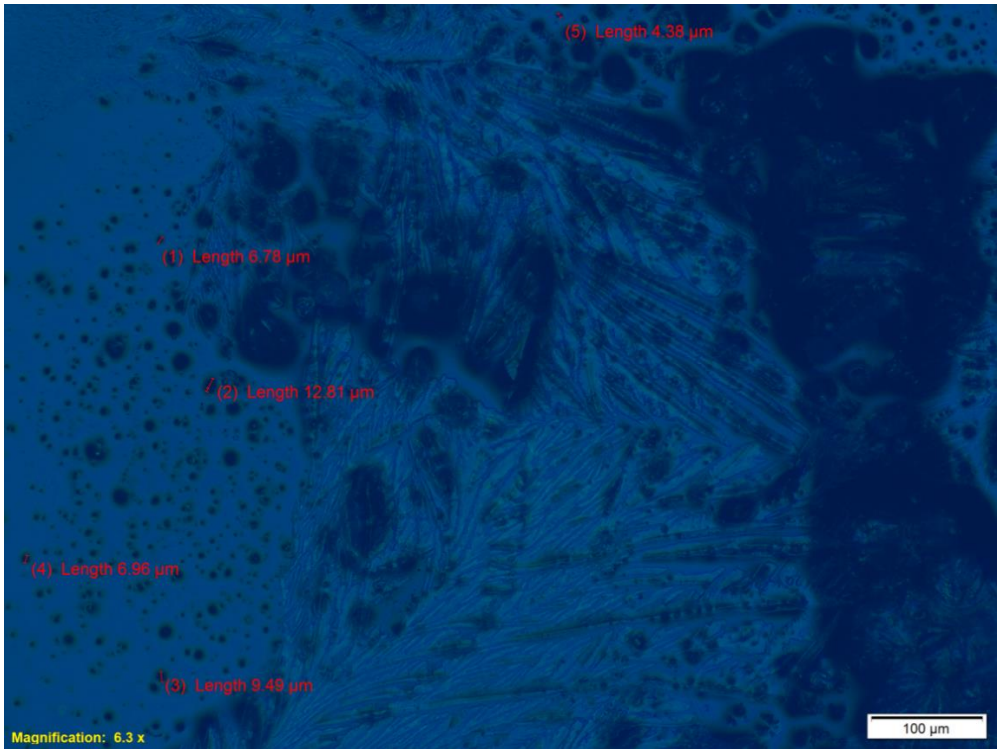


Figure E.17: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

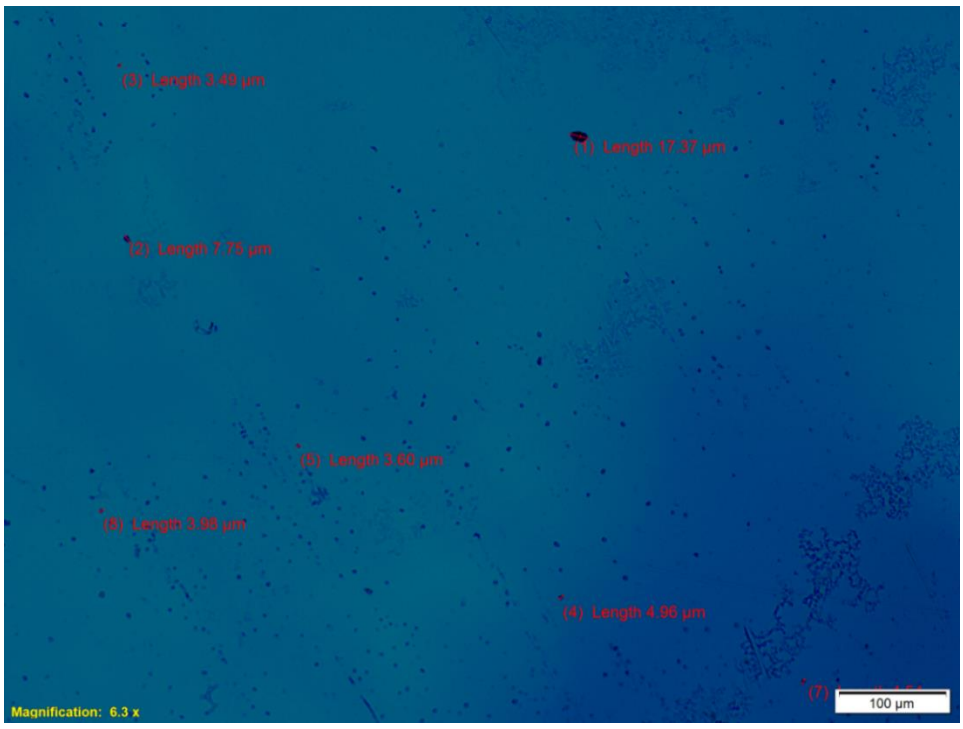


Figure E.18: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

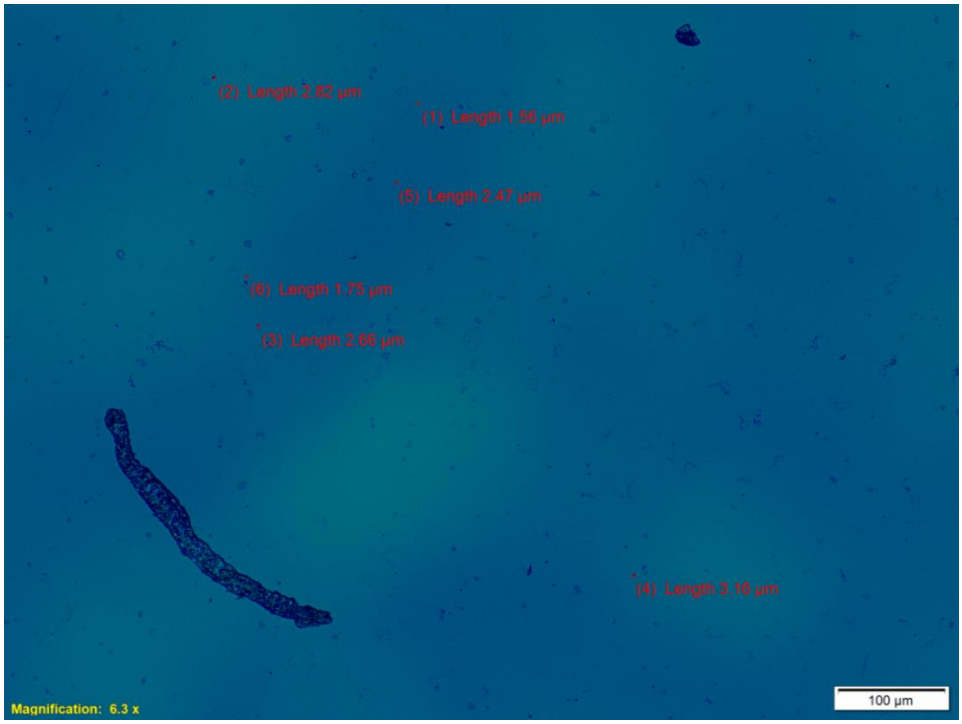


Figure E.19: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

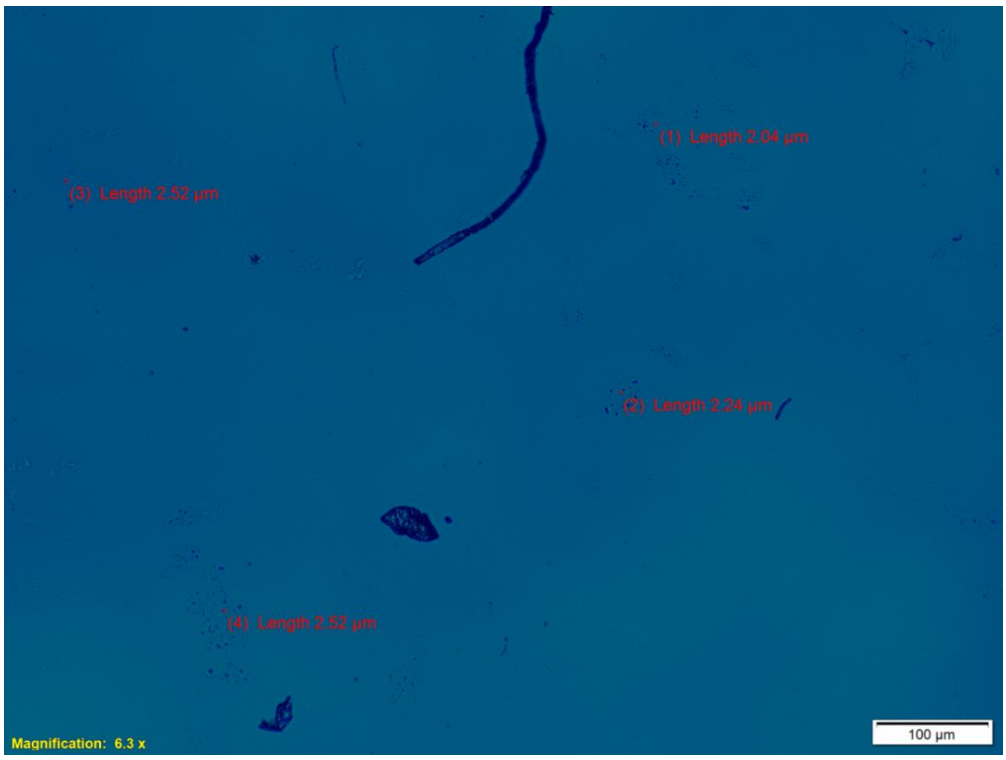


Figure E.20: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

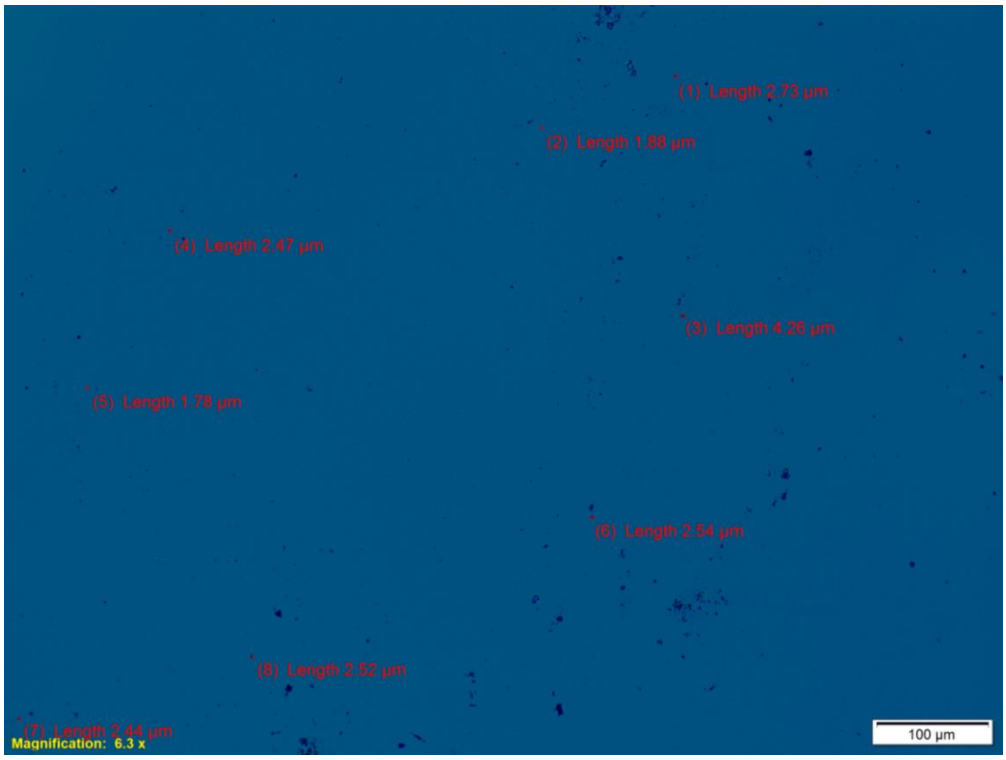


Figure E.21: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid (Time zero)

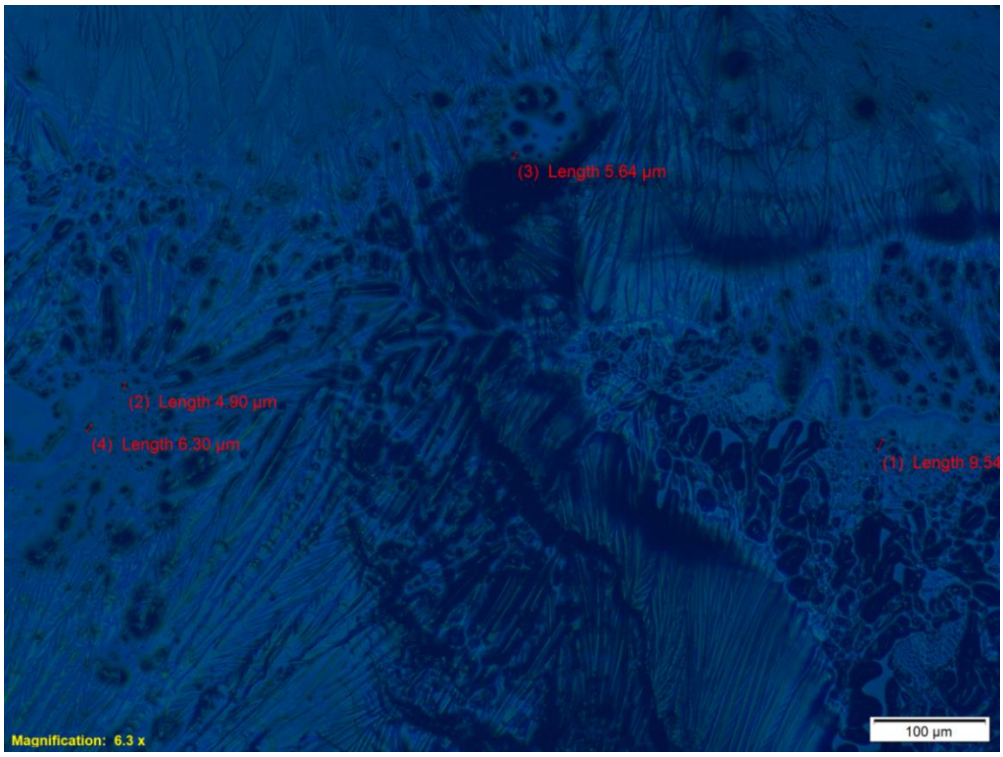


Figure E.22: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

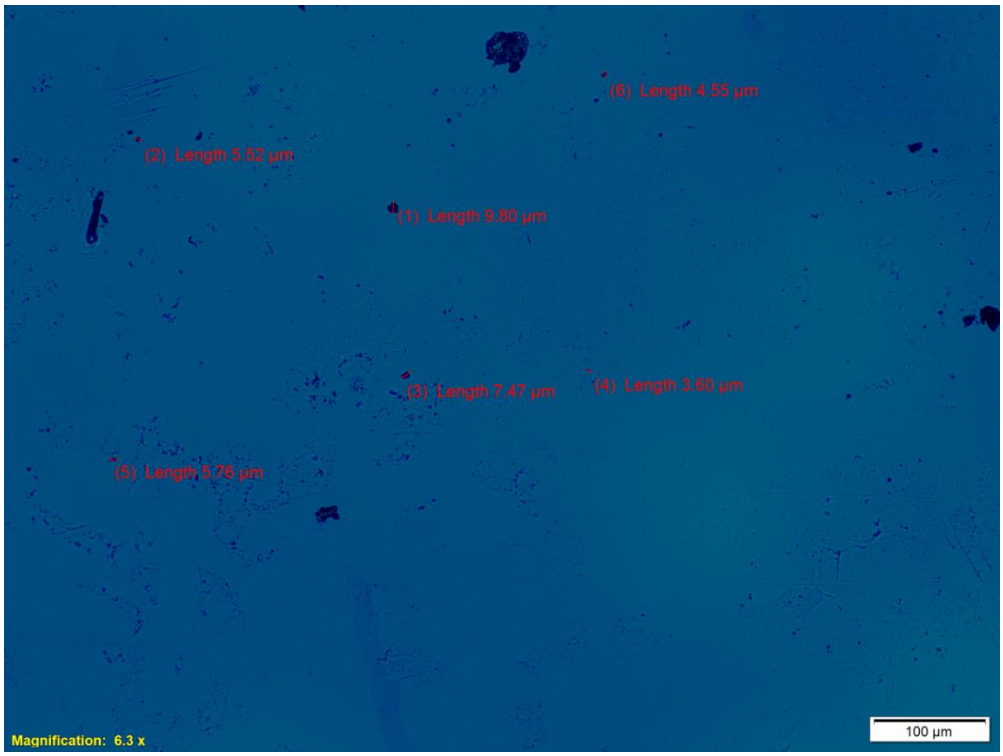


Figure E.23: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

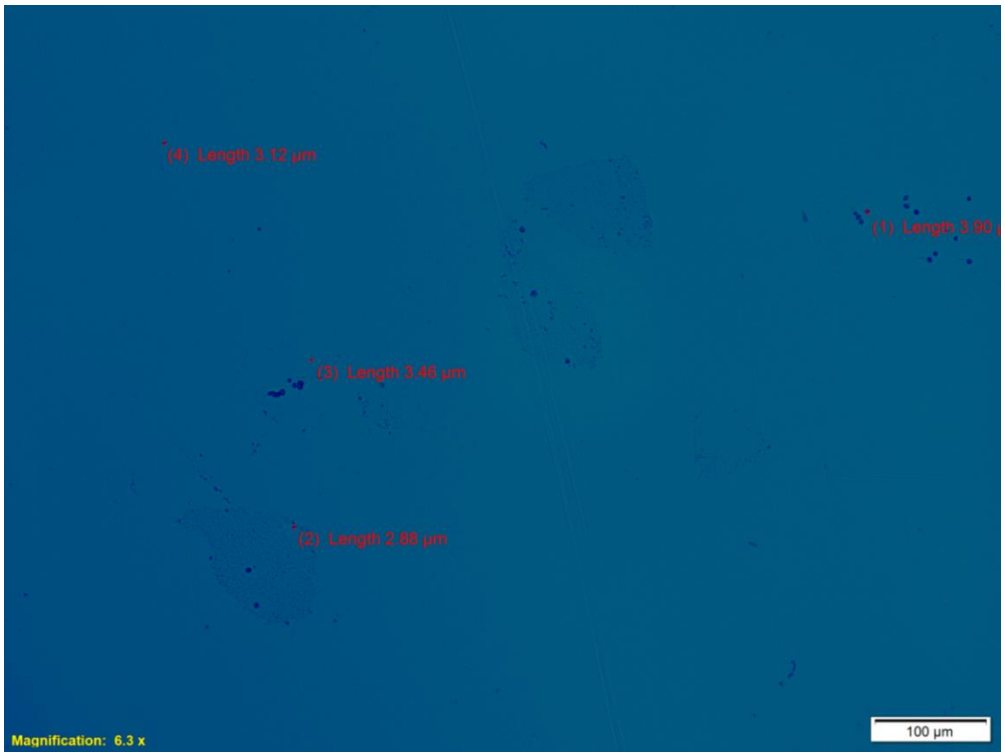


Figure E.24: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

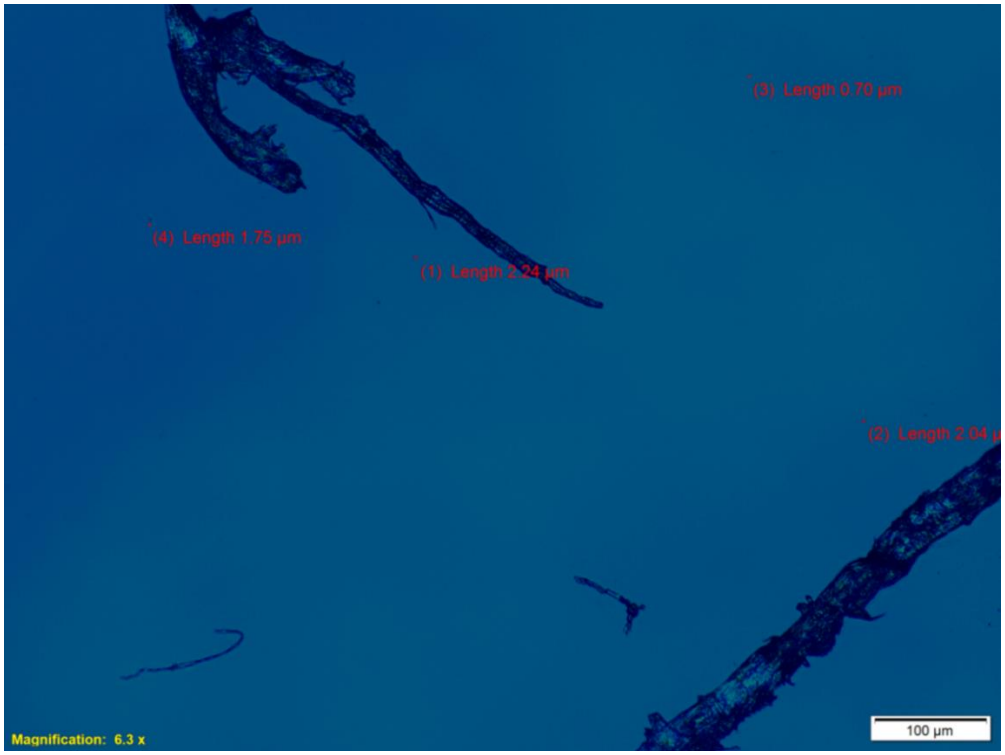


Figure E.25: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

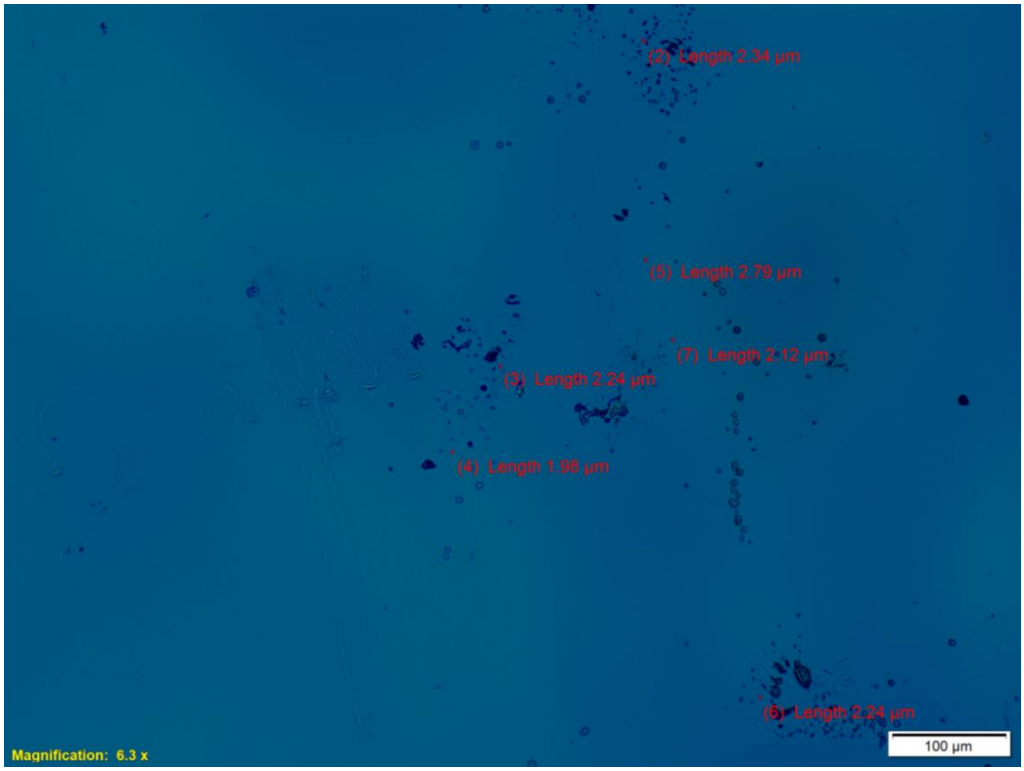


Figure E.26: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid (Time zero)

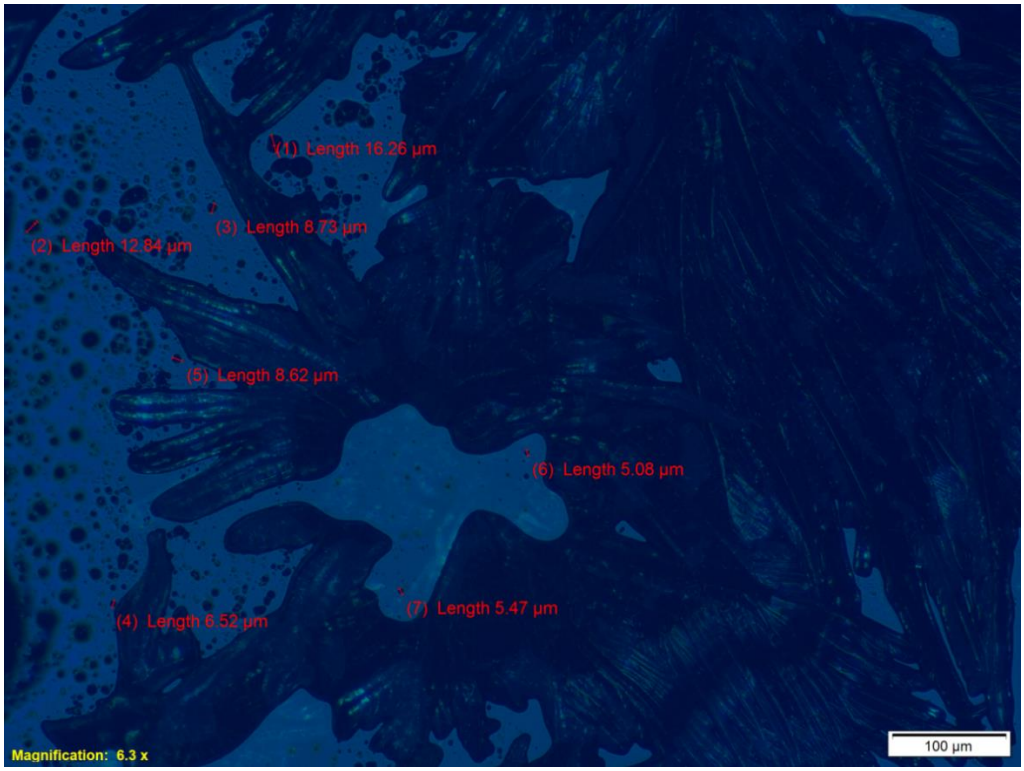


Figure E.27: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2 ml n-heptane (30 min)

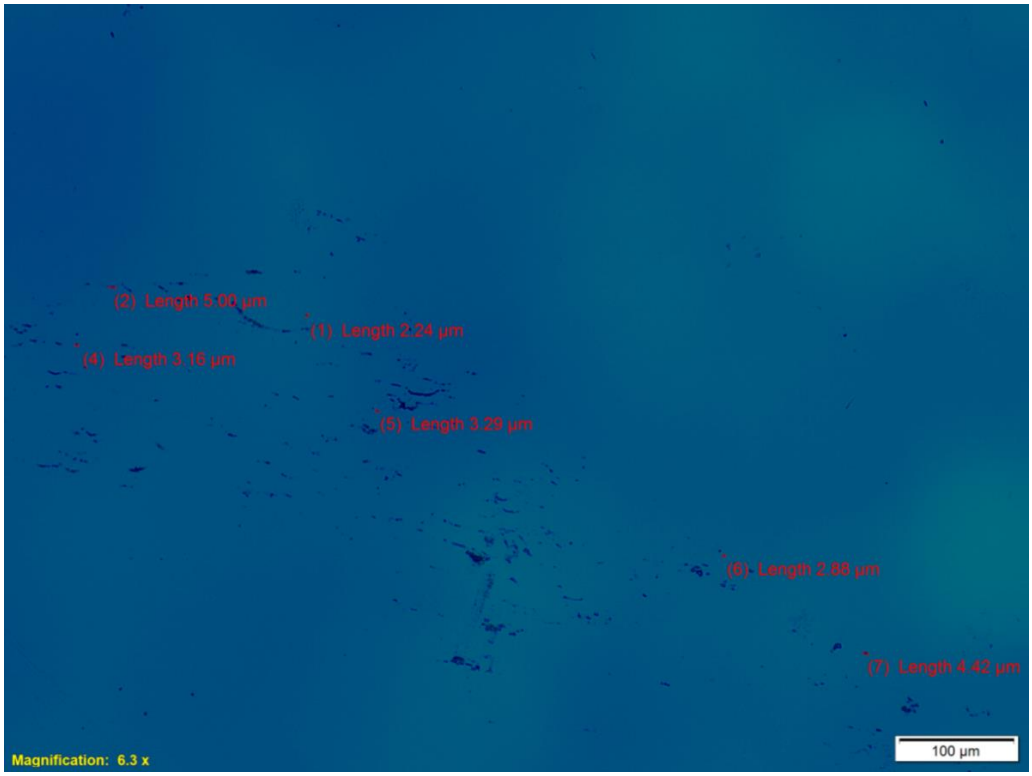


Figure E.28: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2.5 ml n-heptane (60 min)

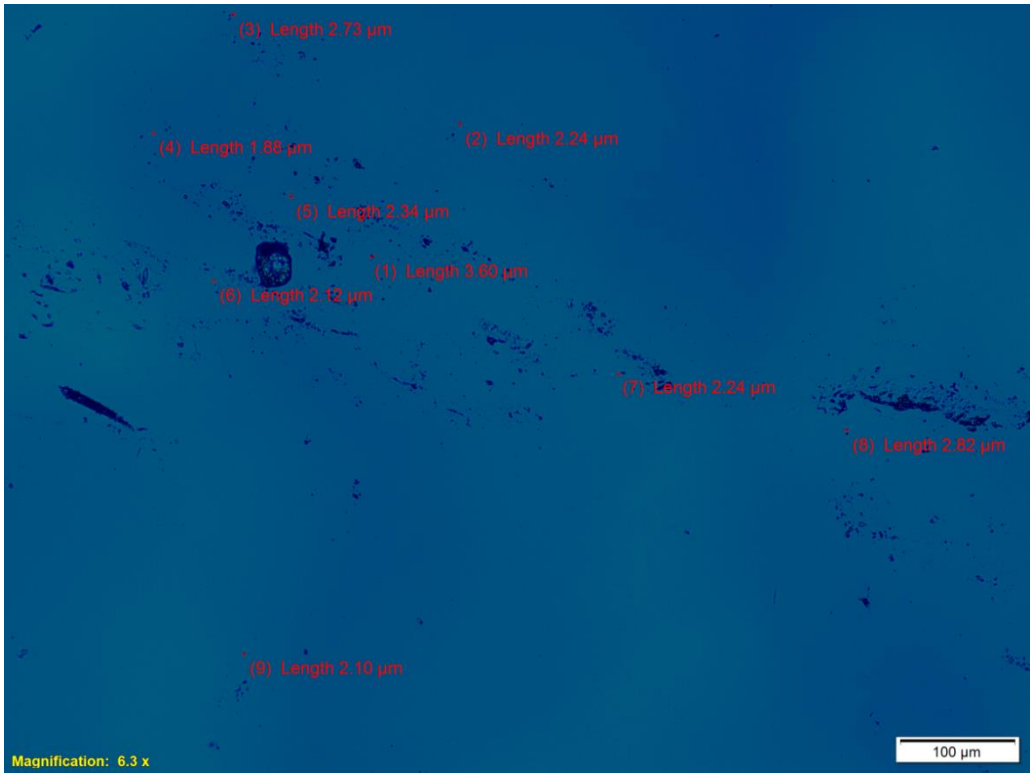


Figure E.29: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 3.5 ml n-heptane (90 min)

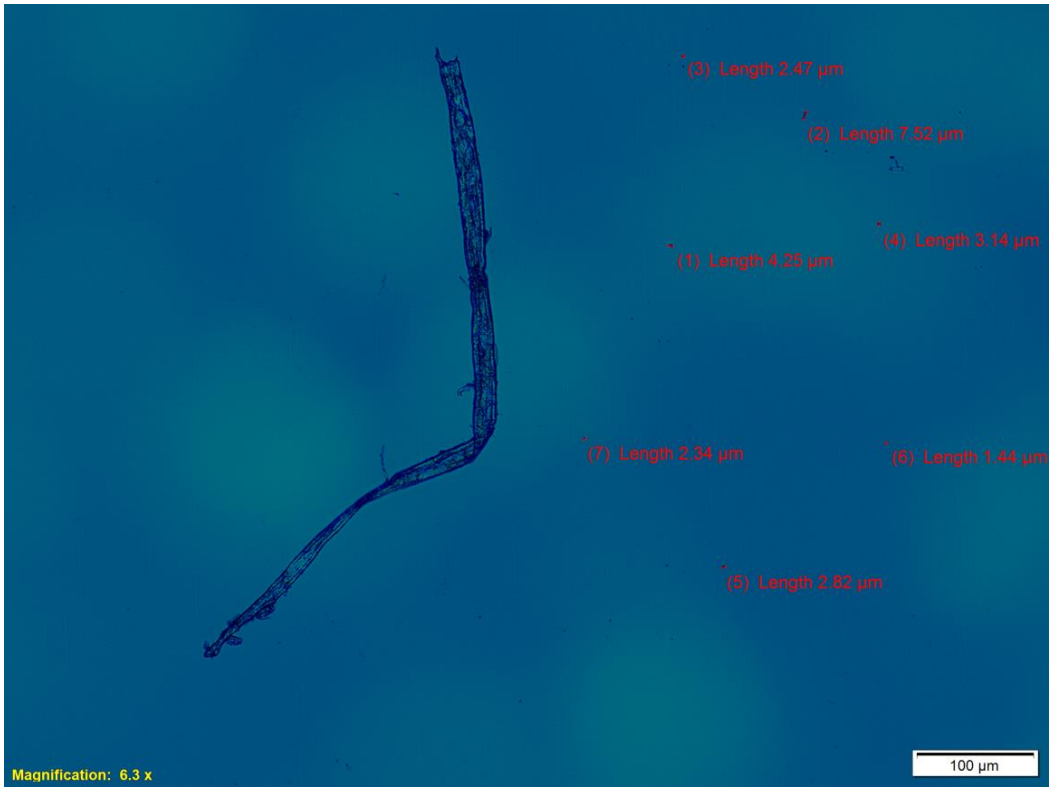


Figure E.30: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 5 ml n-heptane (120 min)

APPENDIX F: Crude Oil - n-heptane - Salicylic acid mixture at 80 ^{o}C

Figure F: Effect of addition of n-heptane on the mixture (Crude Oil + Salicylic acid) on asphaltene aggregation at 80 ºC

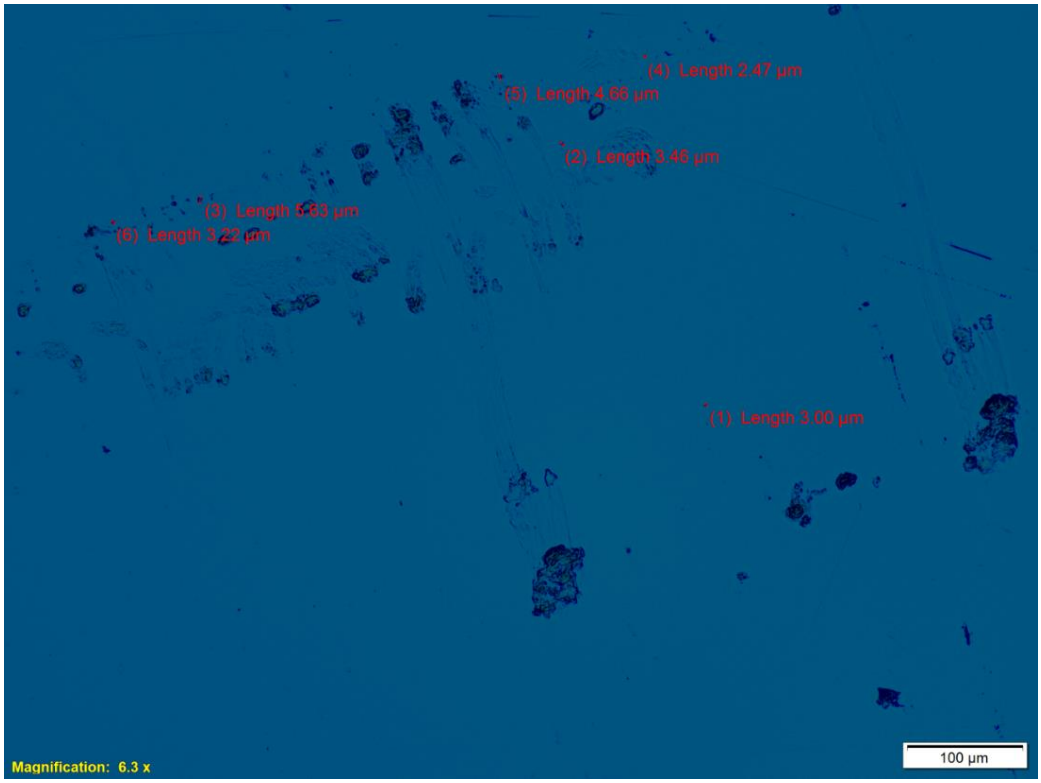


Figure F.1: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid (Time zero)

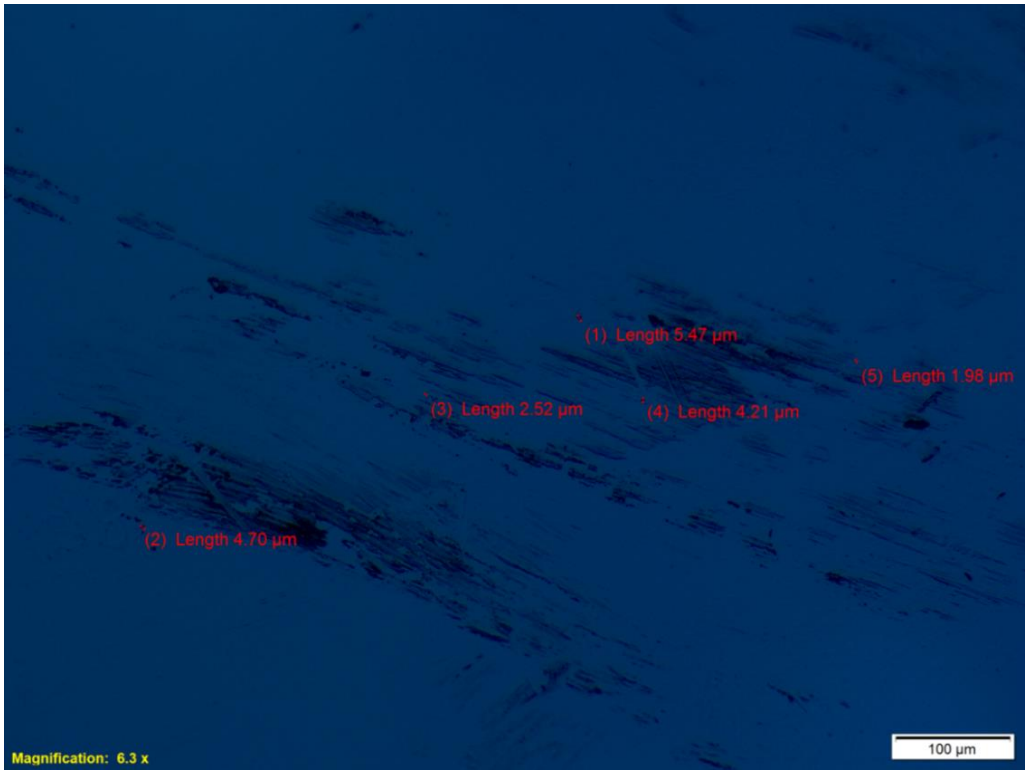


Figure F.2: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2 ml of n-heptane (30 min)



Figure F.3: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 2.5 ml of n-heptane (60 min)



Figure F.4: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 3.5 ml of n-heptane (90 min)

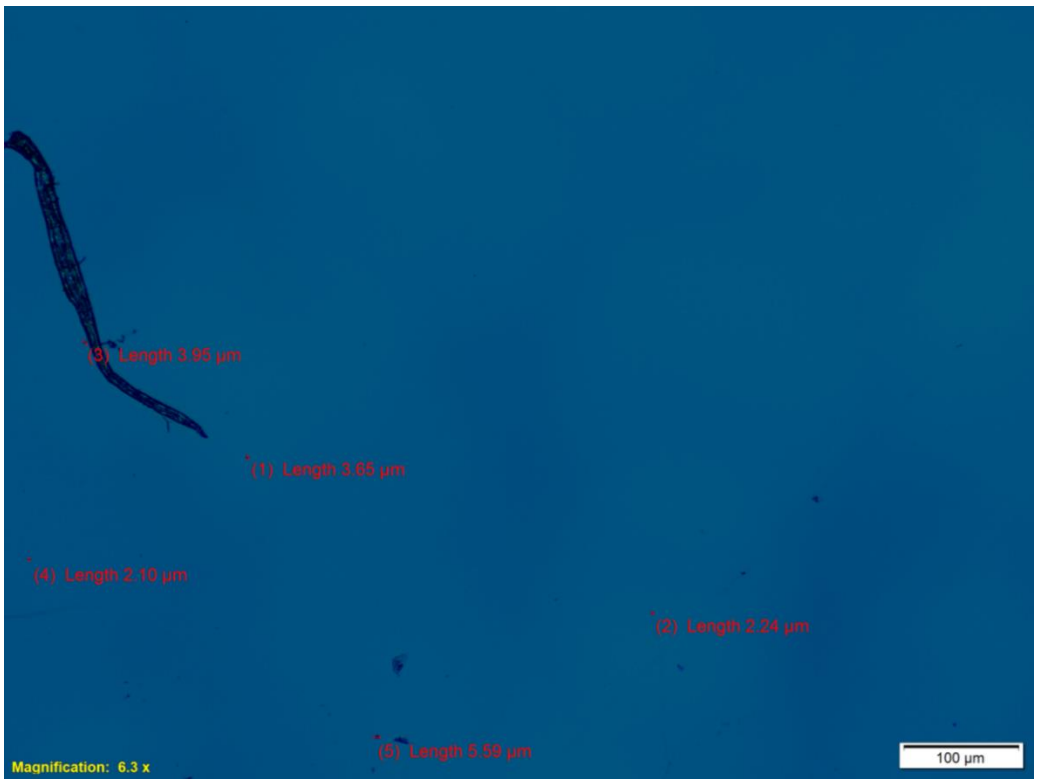


Figure F.5: 0.5g of Crude Oil + 2 ml of 2.5% Salicylic acid + 5 ml of n-heptane (120 min)



Figure F.6: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid (Time zero)



Figure F.7: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 2 ml of n-heptane (30 min)

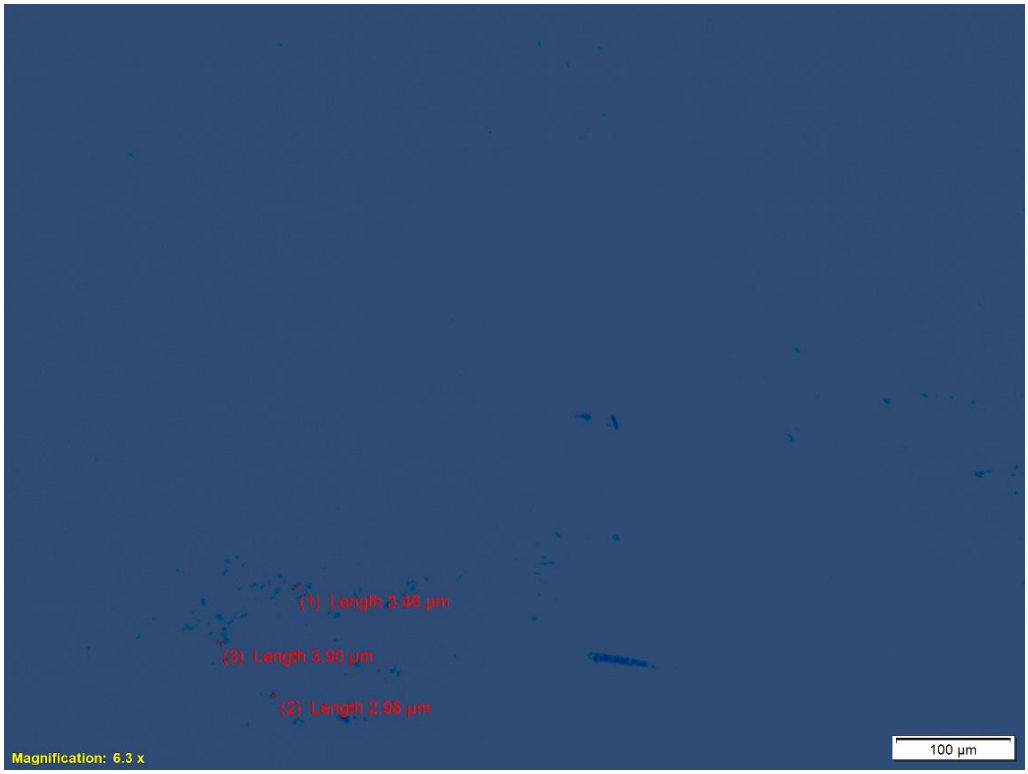


Figure F.8: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 2.5 ml of n-heptane (60 min)

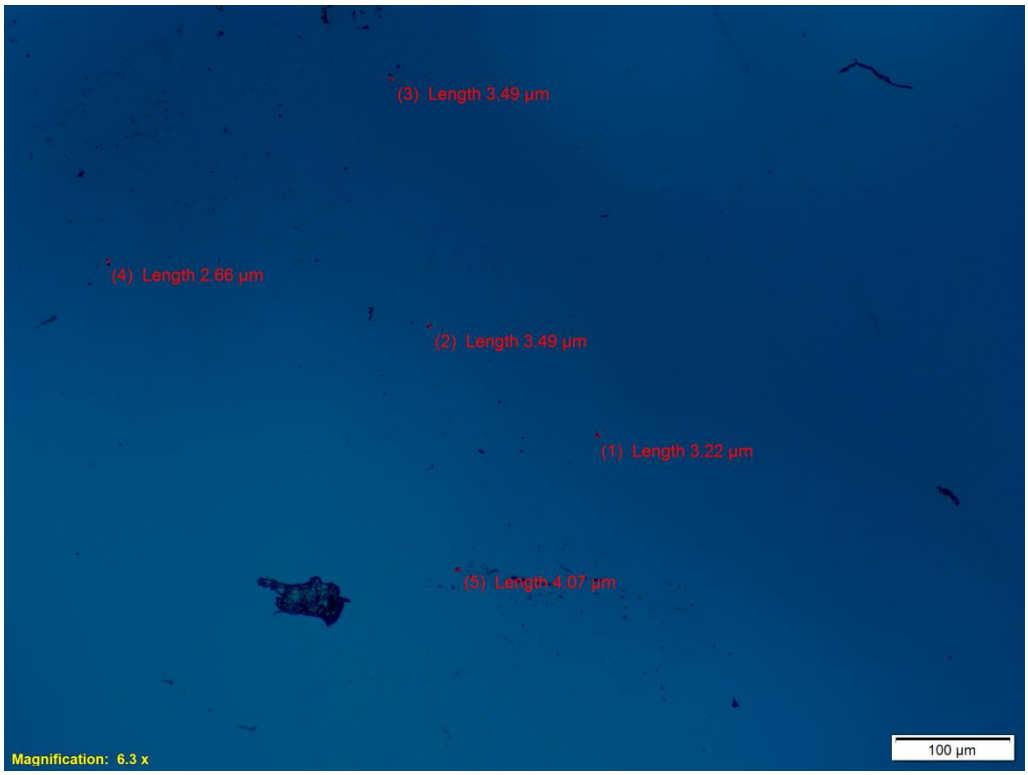


Figure F.9: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 3.5 ml of n-heptane (90 min)



Figure F.10: 0.5g of Crude Oil + 2 ml of 5% Salicylic acid + 5 ml of n-heptane (120 min)

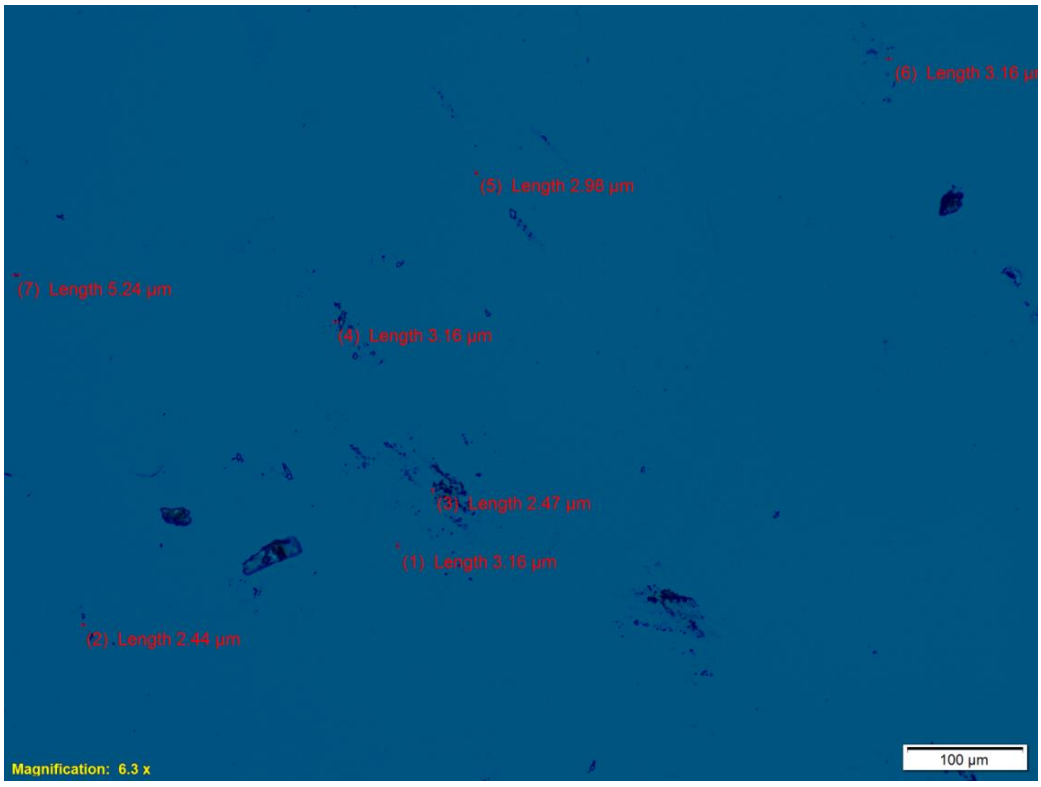


Figure F.11: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid (Time zero)

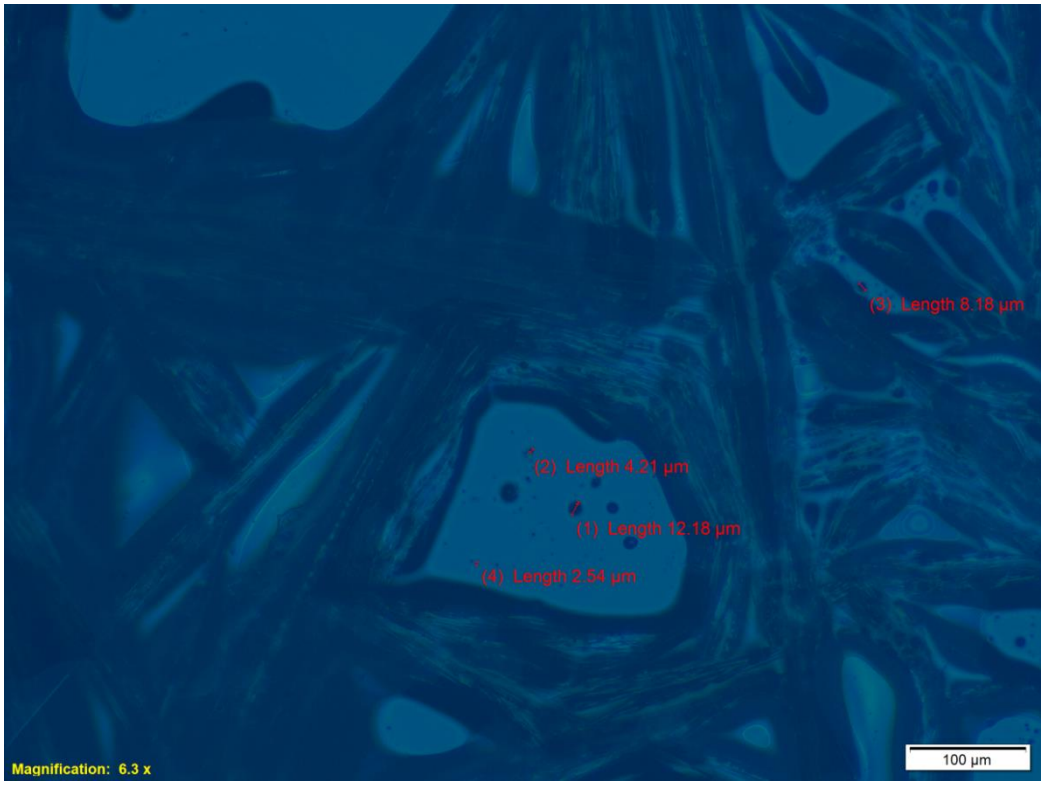


Figure F.12: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 2 ml n-heptane (30 min)



Figure F.13: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 2.5 ml n-heptane (60 min)



Figure F.14: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 3.5 ml n-heptane (90 min)

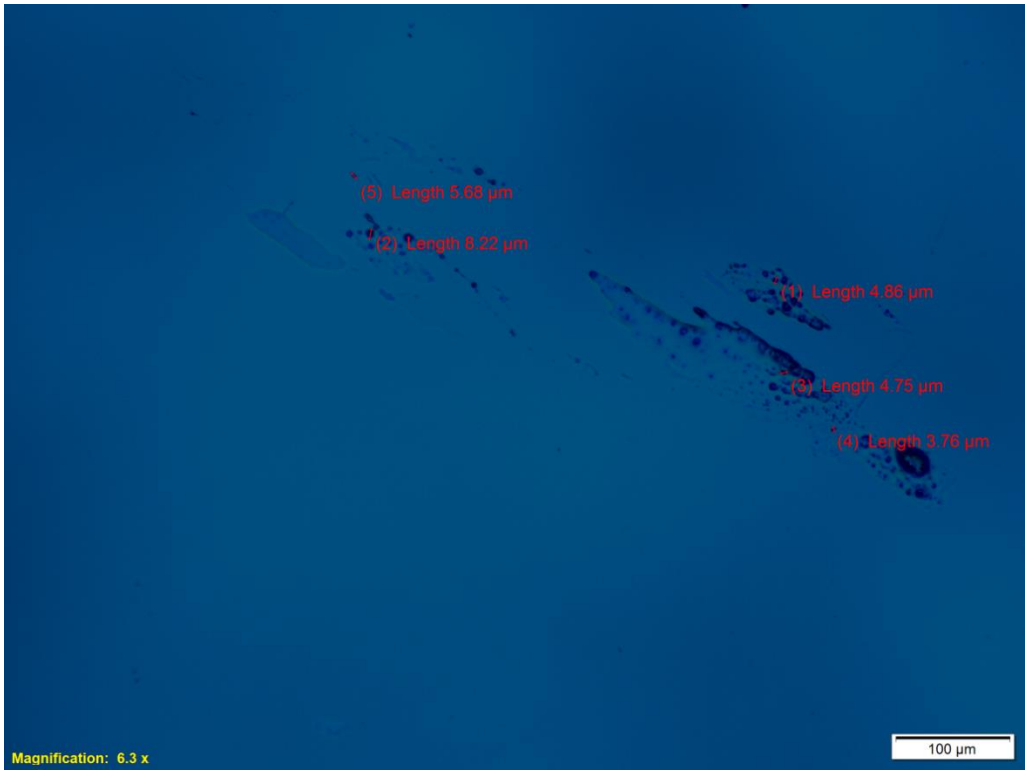


Figure F.15: 0.5g of Crude Oil + 2 ml of 10% Salicylic acid + 5 ml n-heptane (120 min)

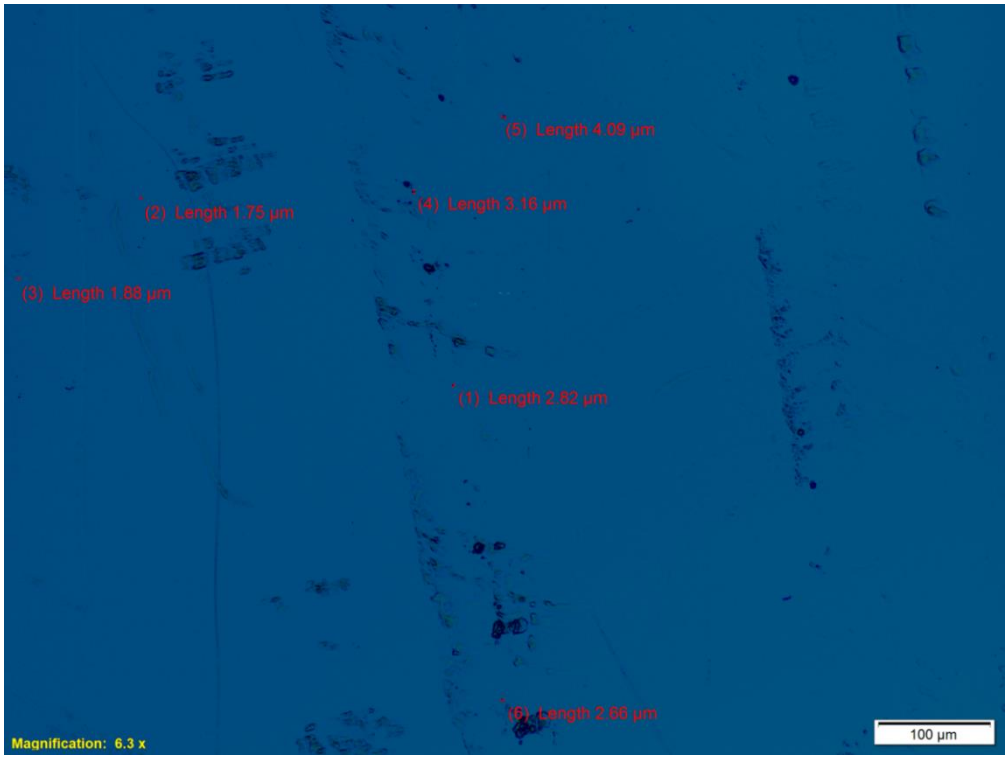


Figure F.16: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid (Time zero)

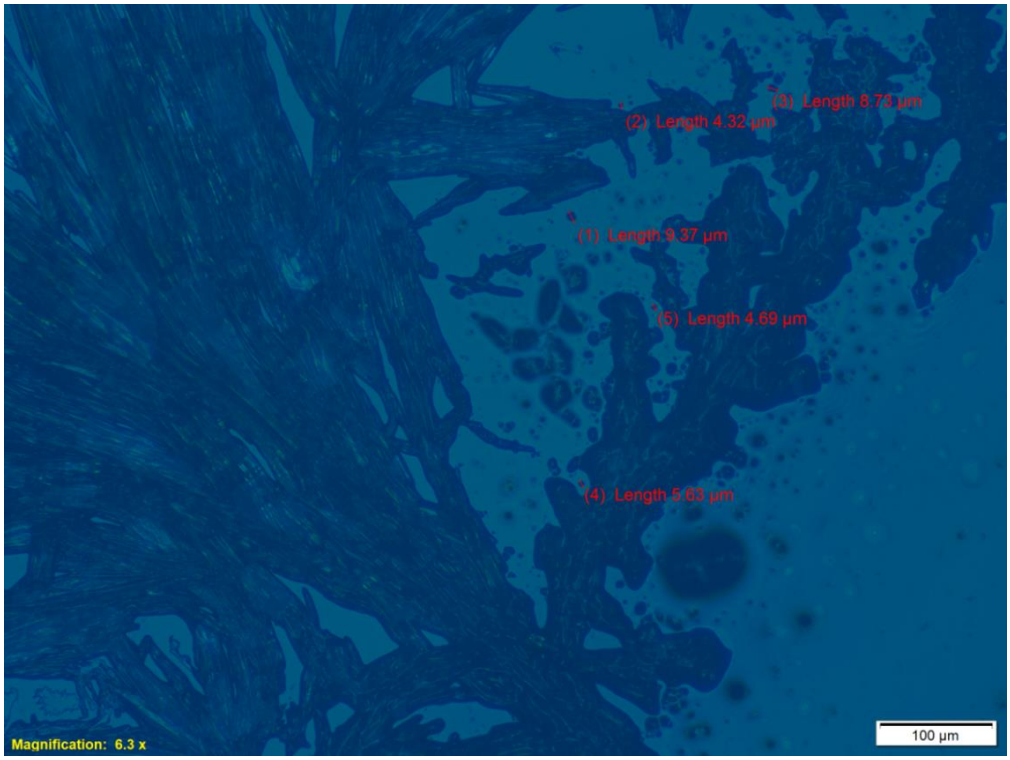


Figure F.17: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 2 ml of n-heptane (30 min)

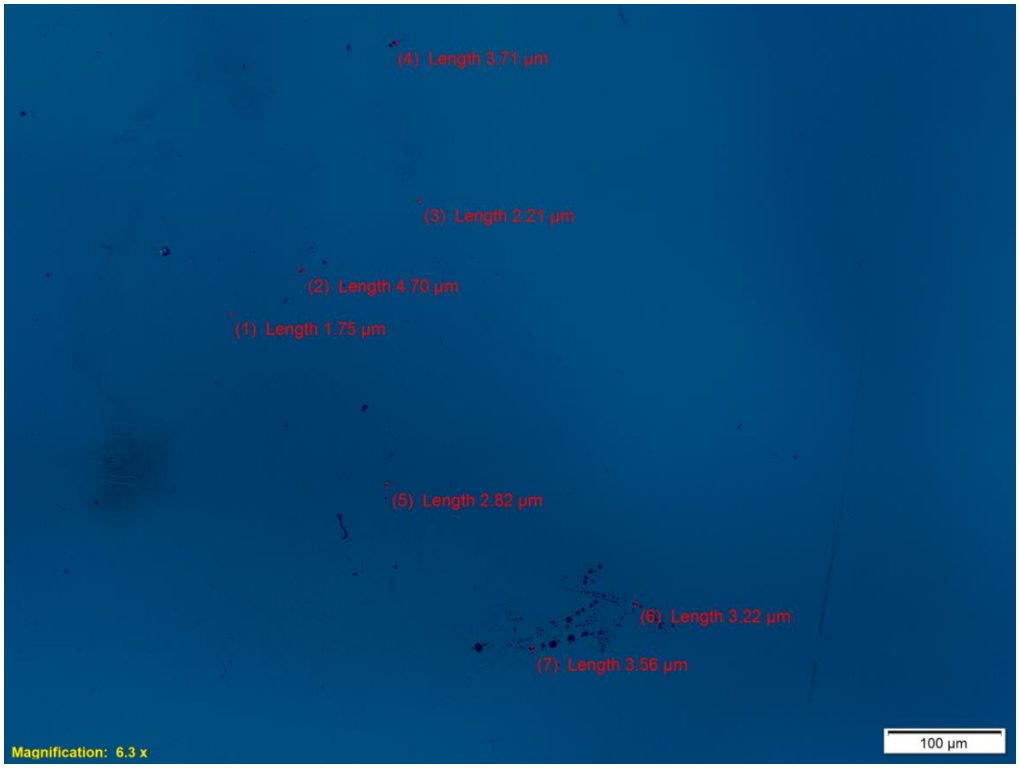


Figure F.18: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 2.5 ml of n-heptane (60 min)



Figure F.19: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 3.5 ml of n-heptane (90 min)

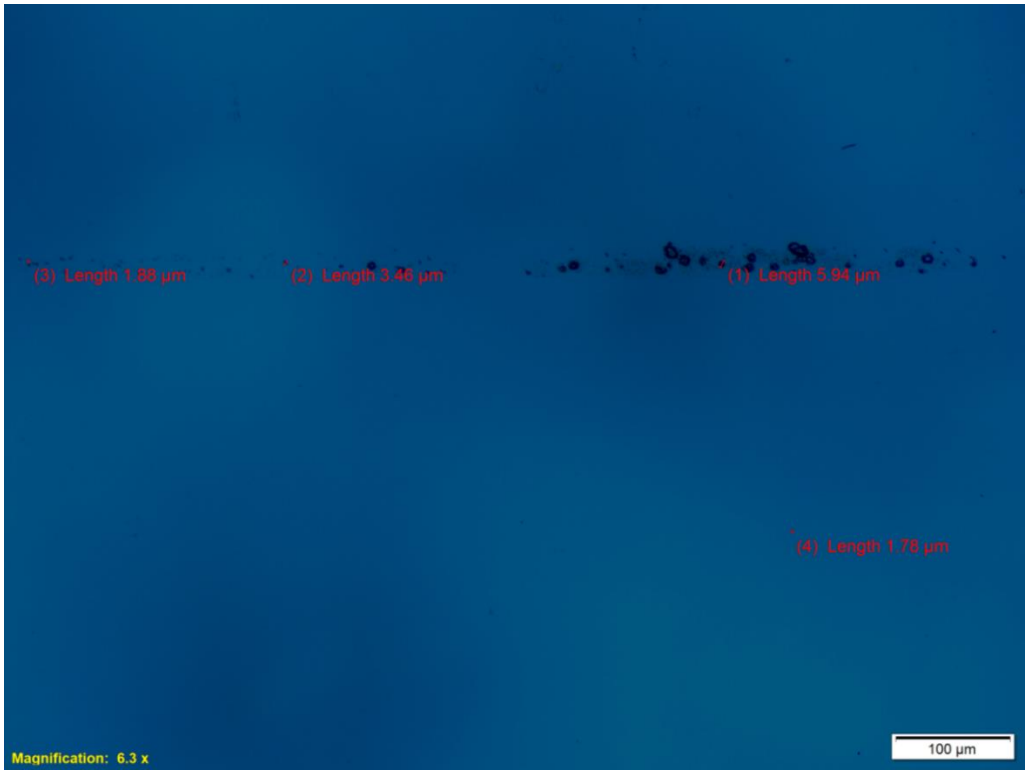


Figure F.20: 0.5g of Crude Oil + 2 ml of 15% Salicylic acid + 5 ml of n-heptane (120 min)

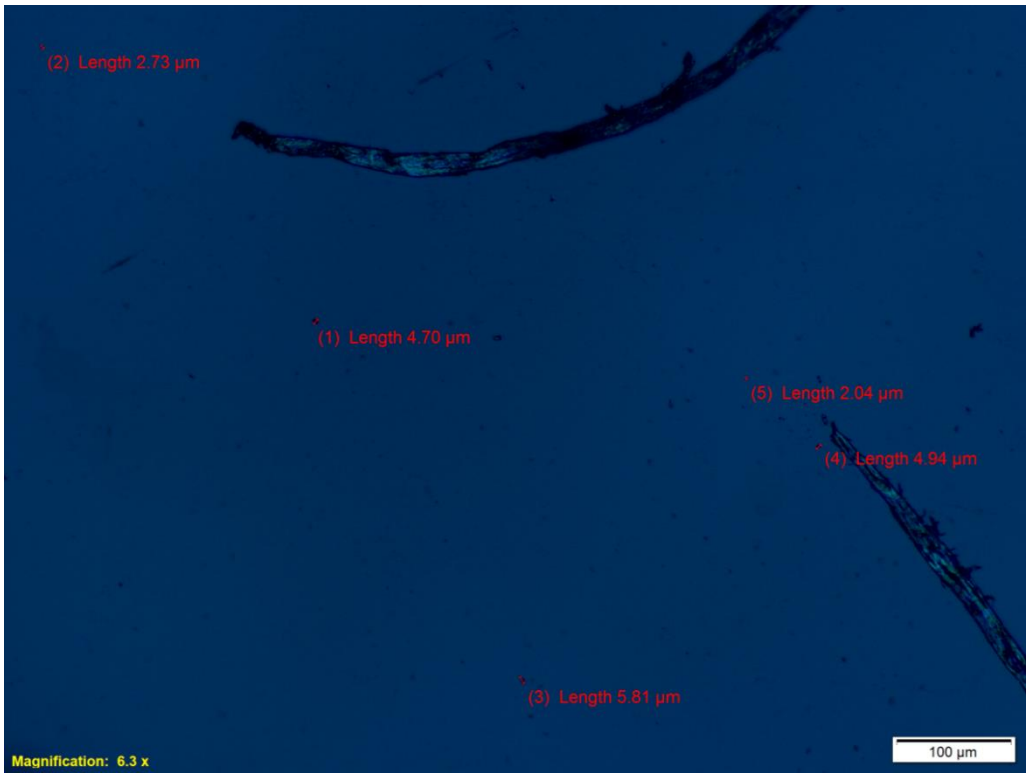


Figure F.21: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid (Time zero)

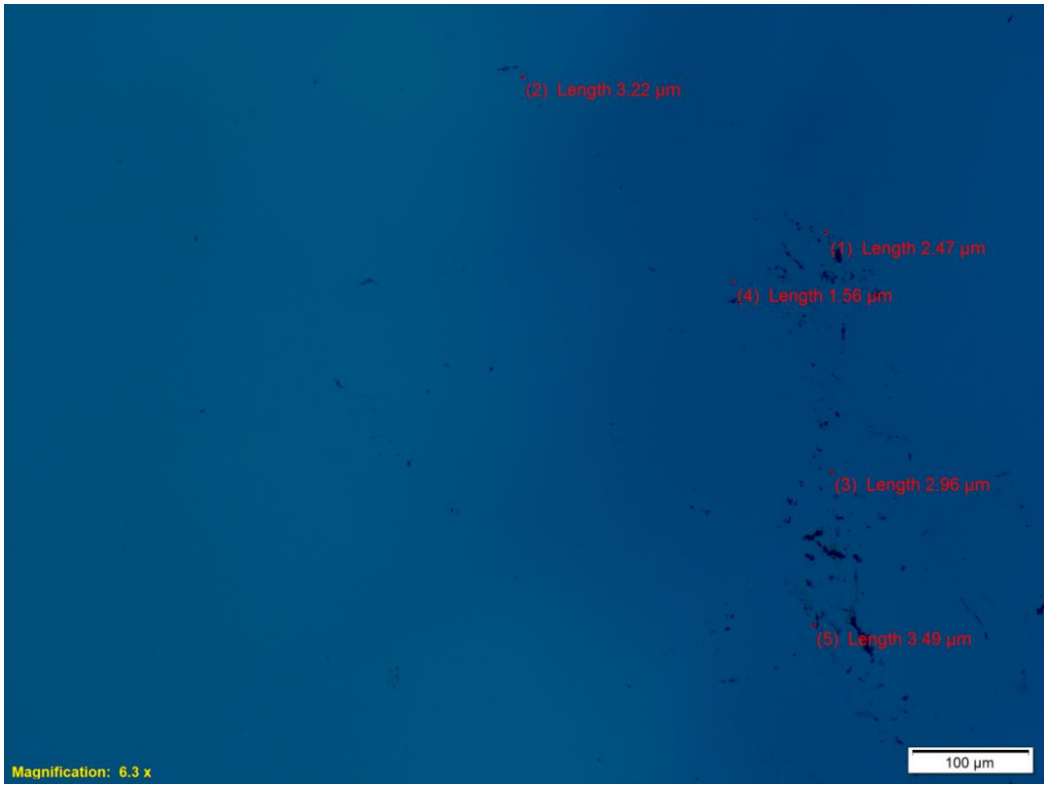


Figure F.22: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 2 ml of n-heptane (30 min)

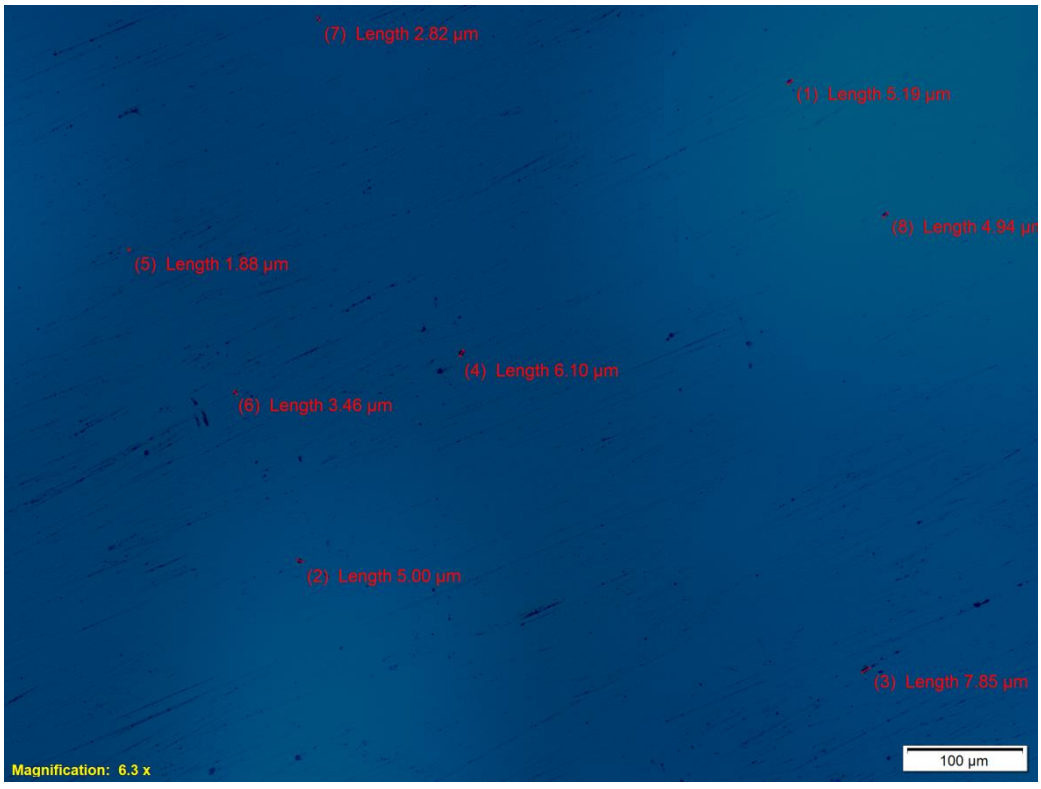


Figure F.23: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 2.5 ml of n-heptane (60 min)

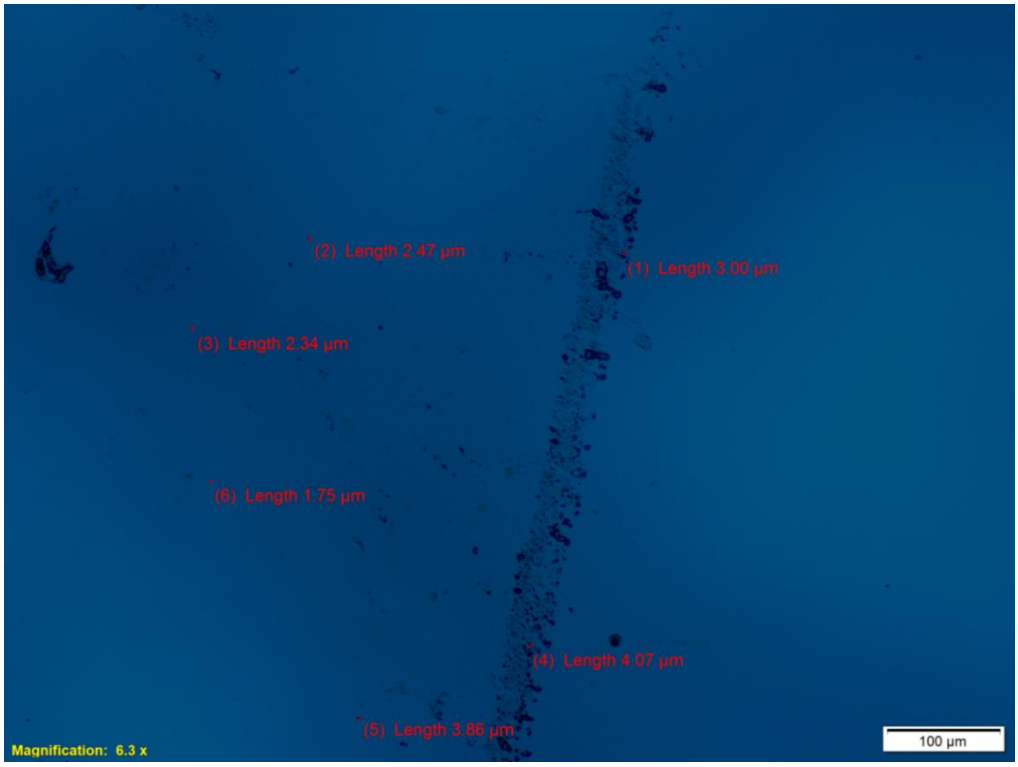


Figure F.24: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 3.5 ml of n-heptane (90 min)

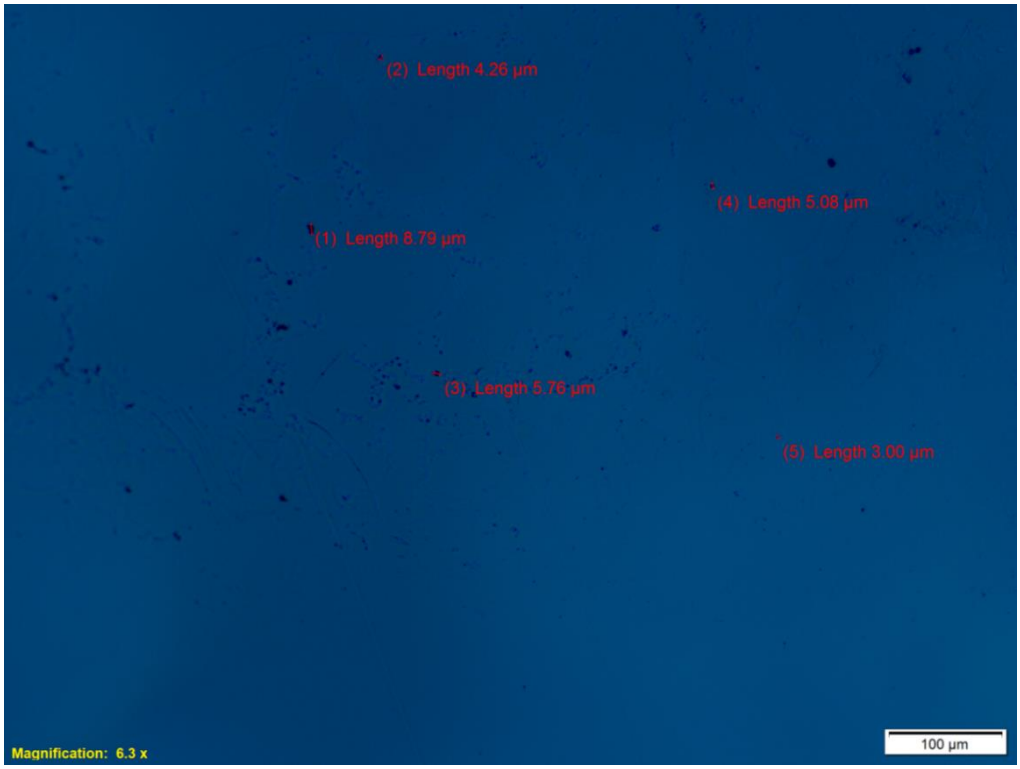


Figure F.25: 0.5g of Crude Oil + 2 ml of 20% Salicylic acid + 5 ml of n-heptane (120 min)



Figure F.26: 0.5g of Crude Oil + 2 ml of 25% salicylic acid (Time zero)

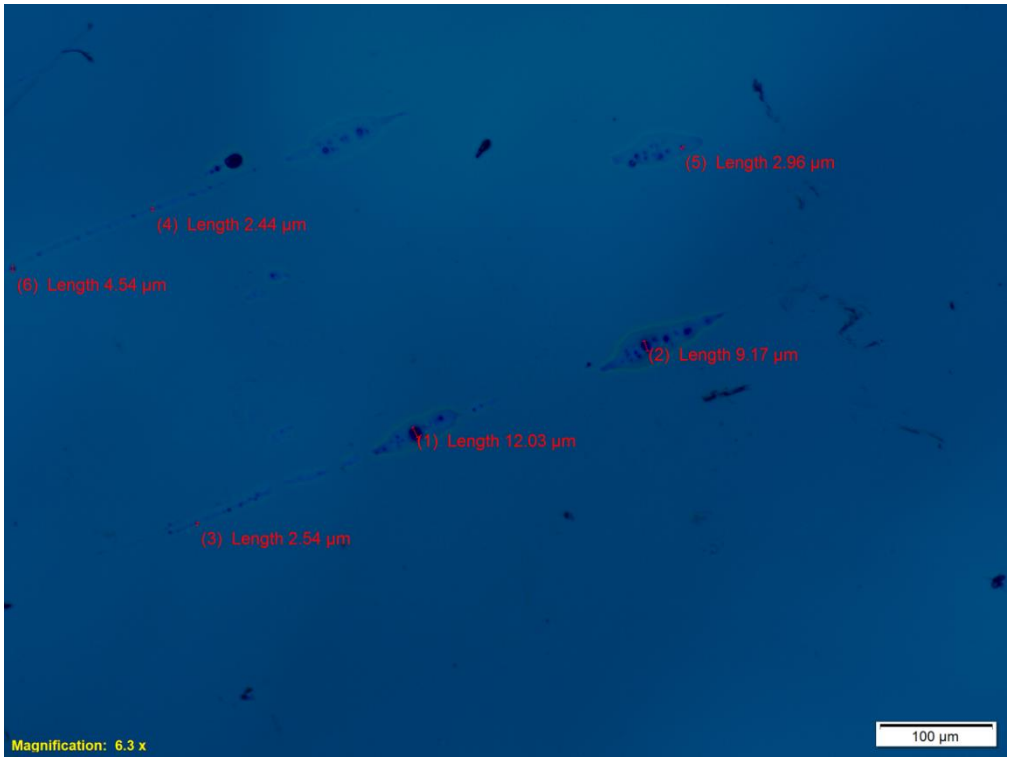


Figure F.27: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 2 ml of n-heptane (30 min)

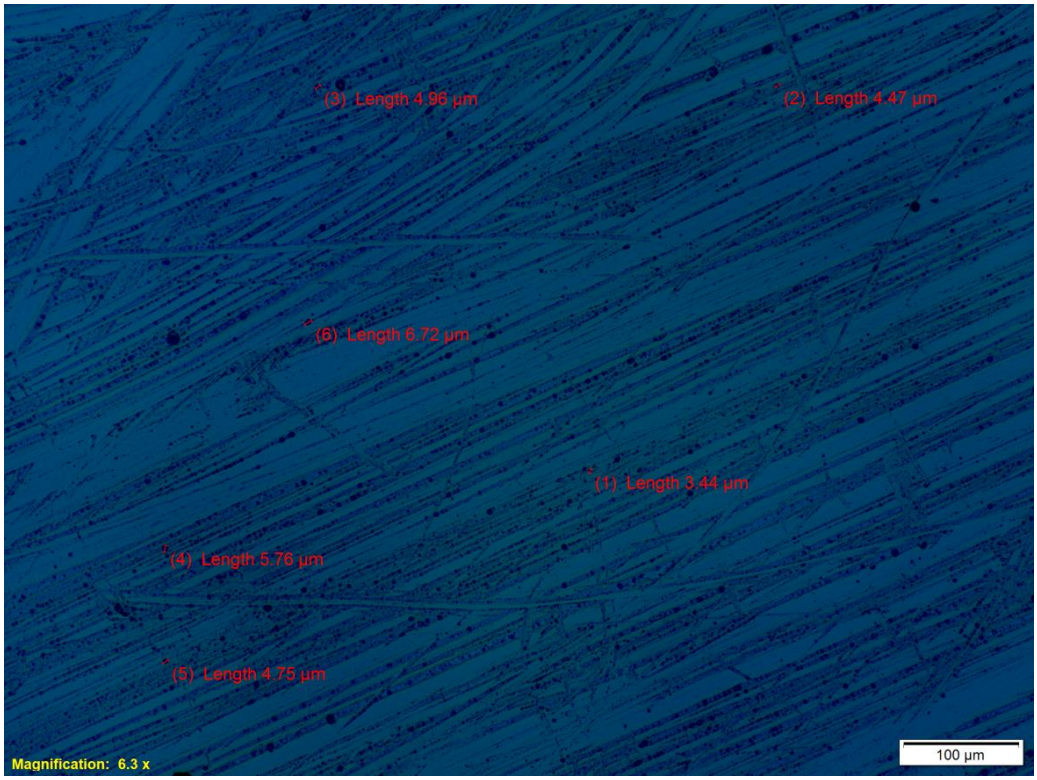


Figure F.28: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 2.5 ml of n-heptane (60 min)



Figure F.29: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 3.5 ml of n-heptane (90 min)

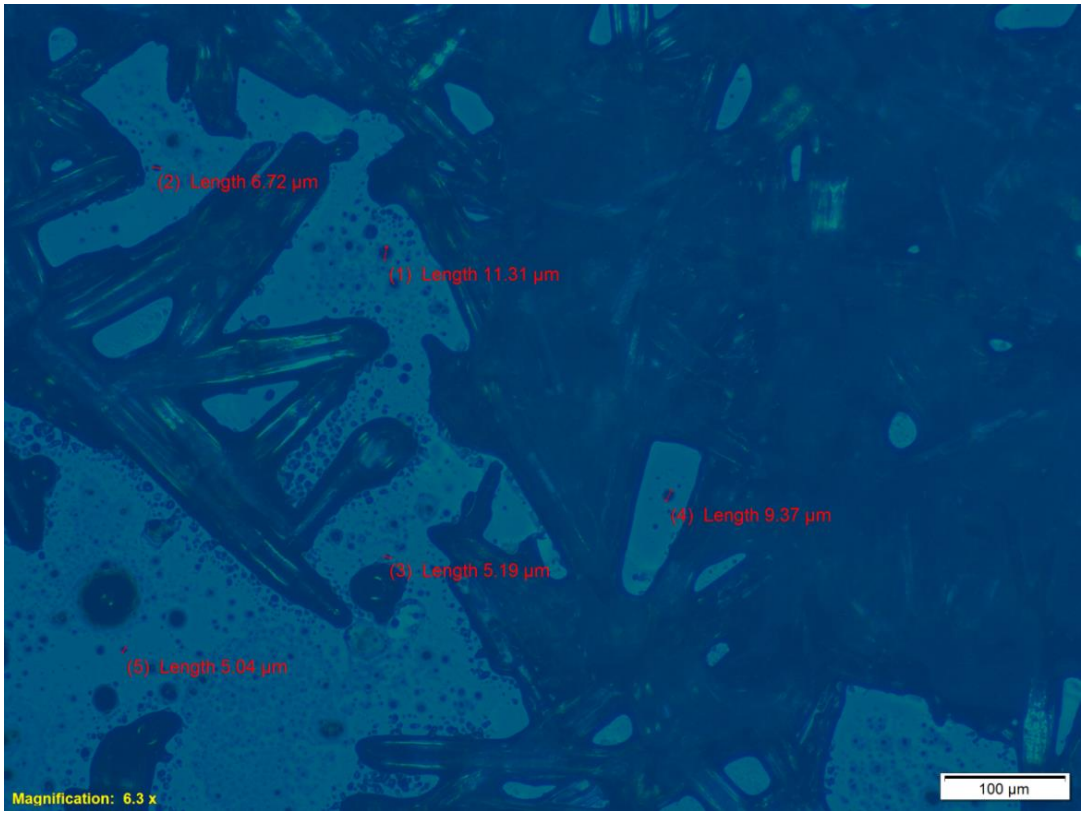


Figure F.30: 0.5g of Crude Oil + 2 ml of 25% Salicylic acid + 5 ml of n-heptane (120 min)

APPENDIX G: Crude Oil - n-heptane - Iso-Phthalic acid mixture at 80 ^{o}C

Figure G: Effect of addition of n-heptane on the mixture (Crude Oil + Iso-Phthalic acid) on asphaltene aggregation at 80 ºC



Figure G.1: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid (Time zero)

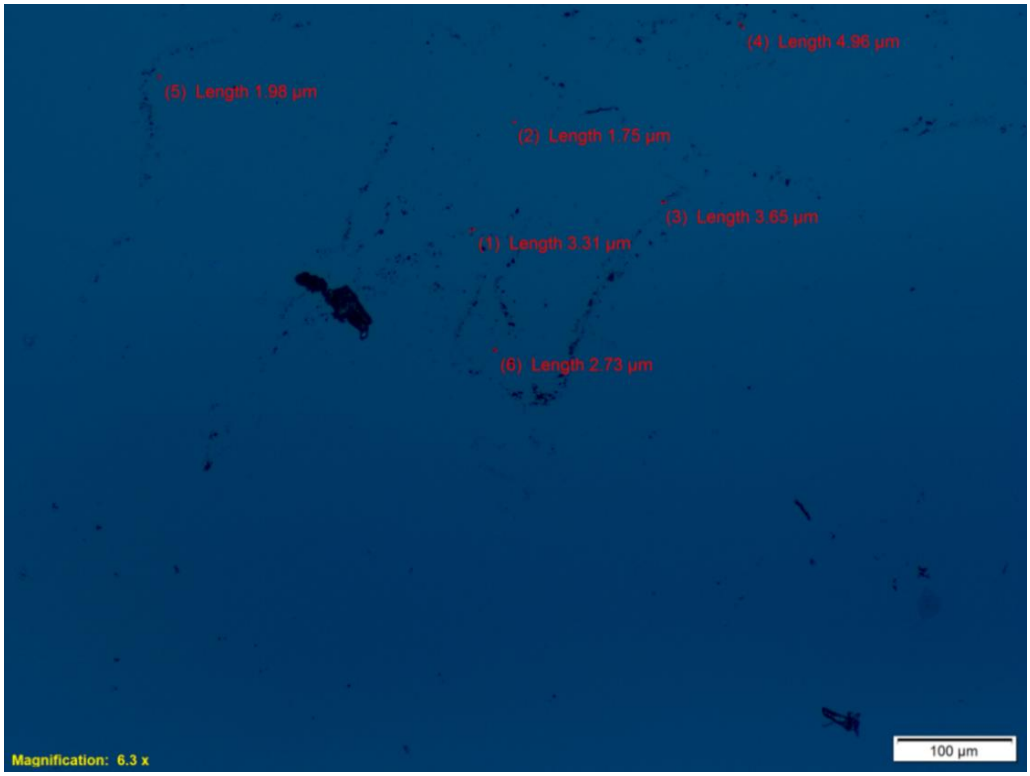


Figure G.2: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 2 ml of n-heptane (30min)



Figure G.3: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)



Figure G.4: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

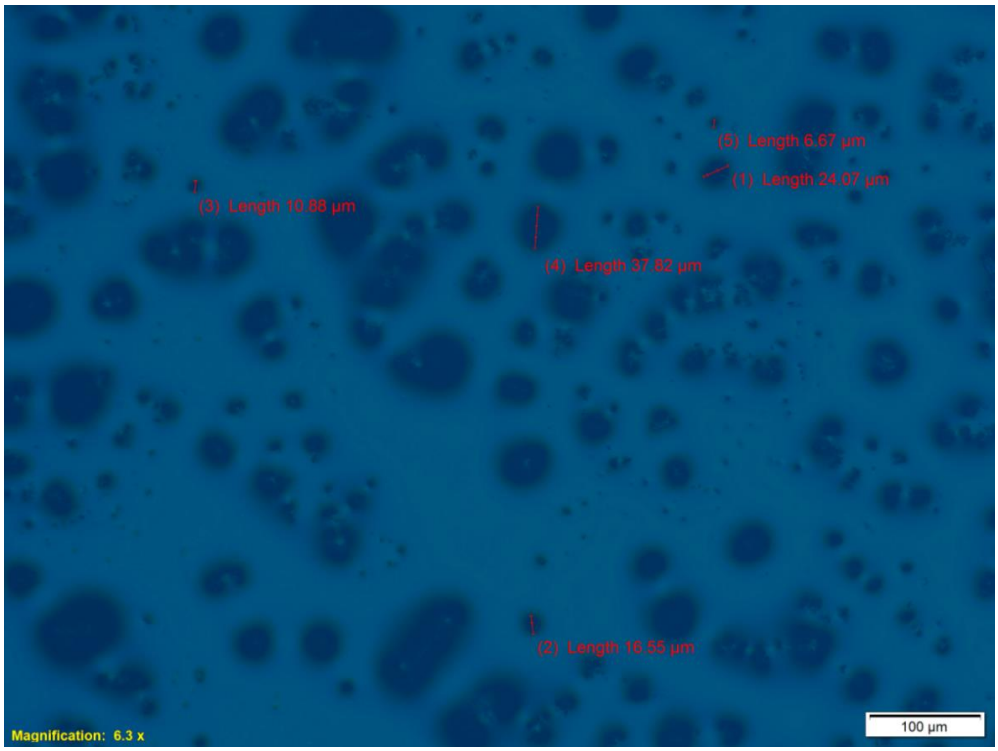


Figure G.5: 0.5g of Crude Oil + 2 ml of 2.5% Iso-Phthalic acid + 5 ml of n-heptane (120 min)



Figure G.6: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid (Time zero)



Figure G.7: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

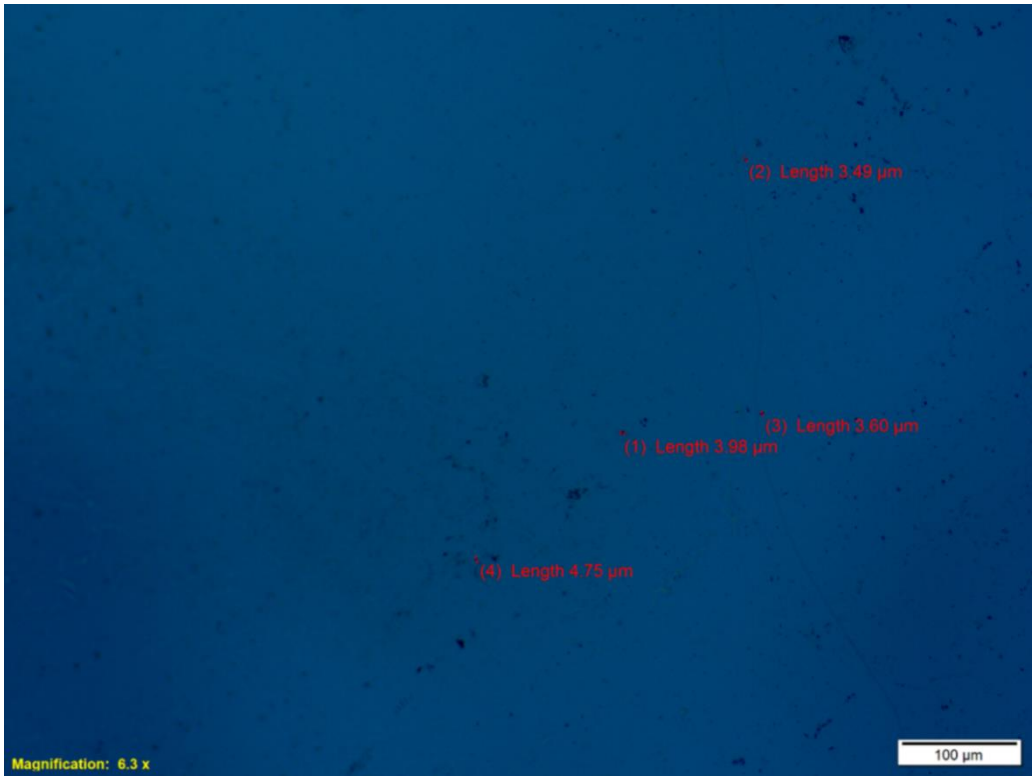


Figure G.8: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

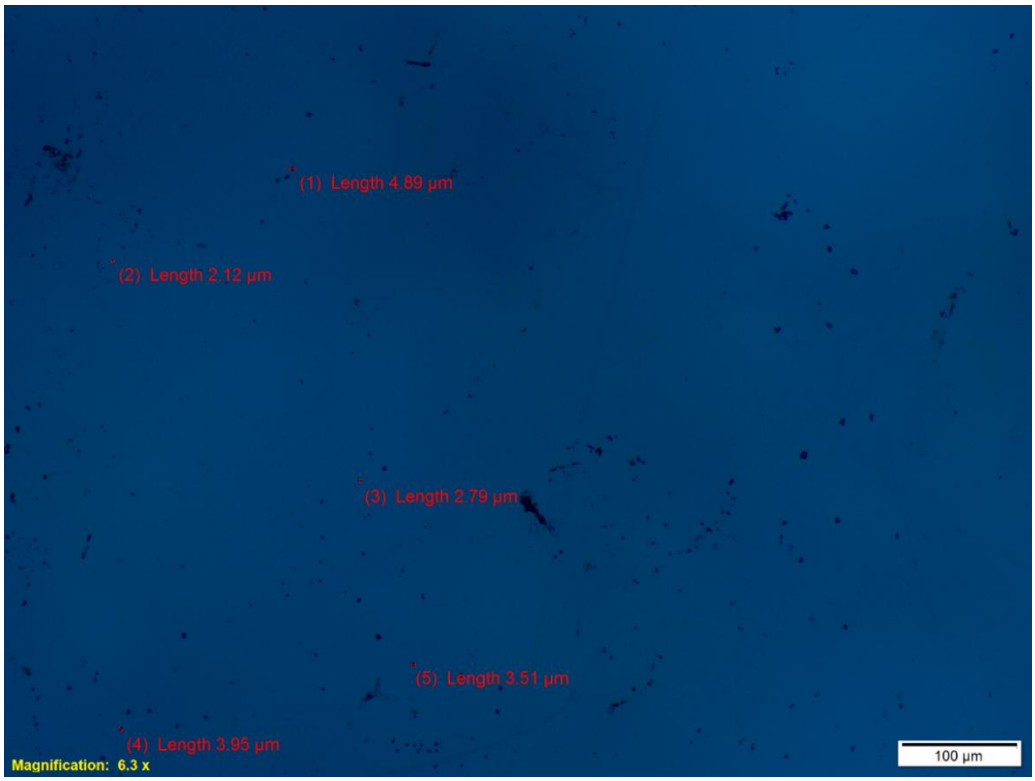


Figure G.9: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

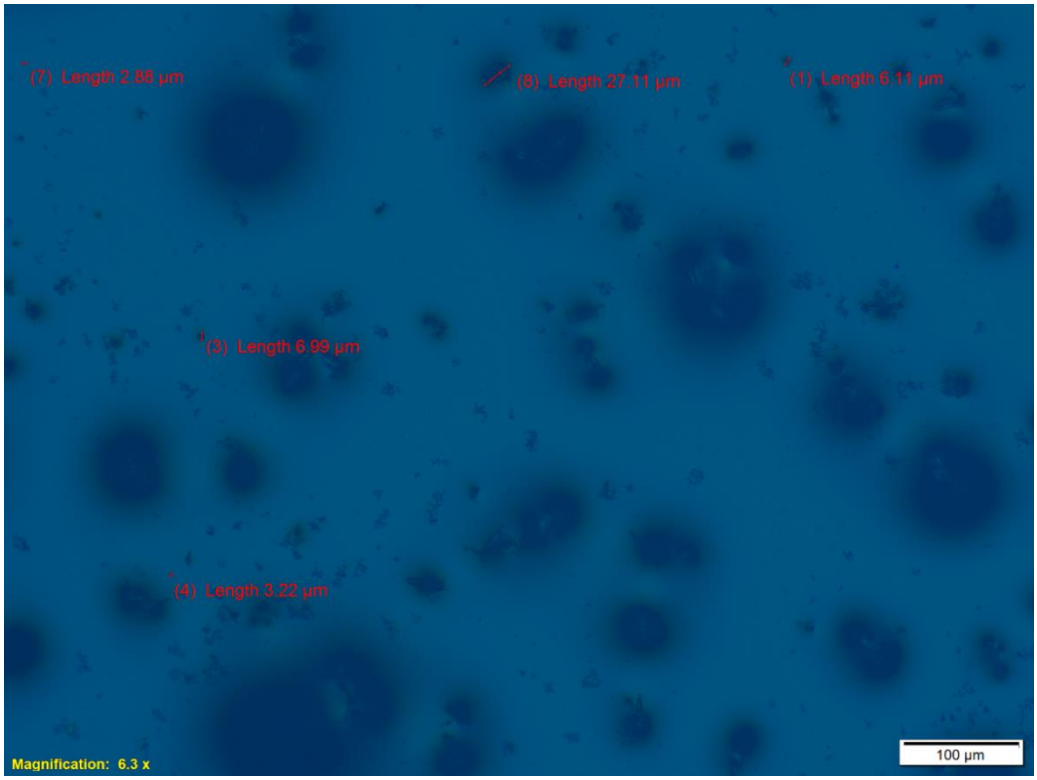


Figure G.10: 0.5g of Crude Oil + 2 ml of 5% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

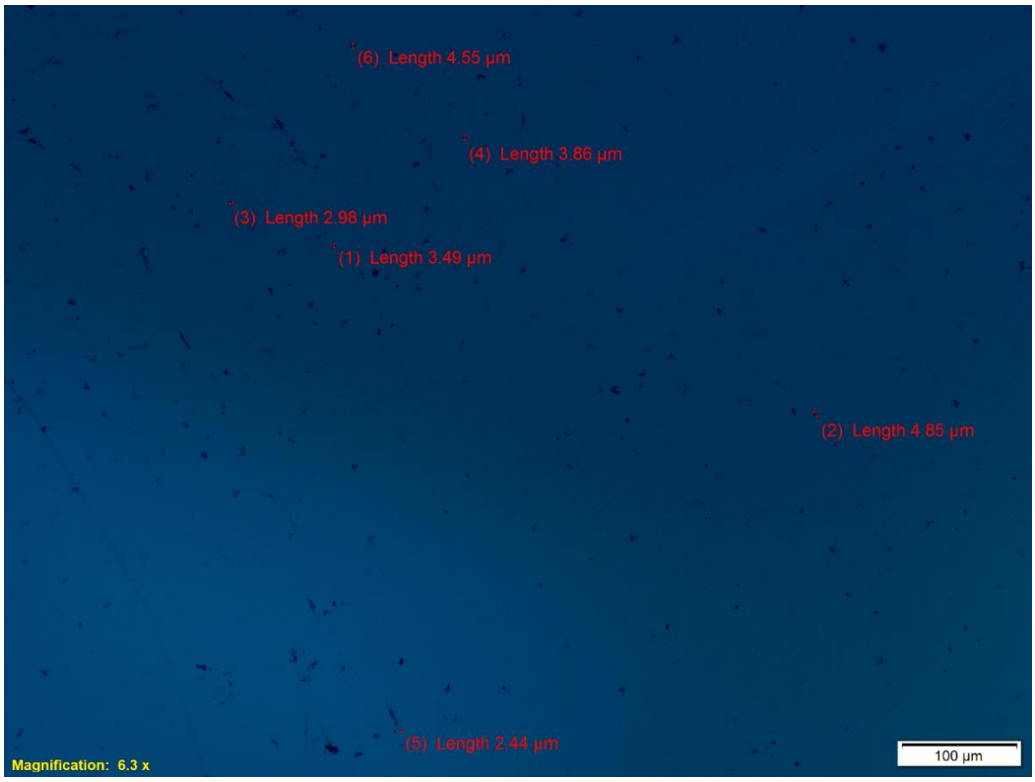


Figure G.11: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid (Time zero)

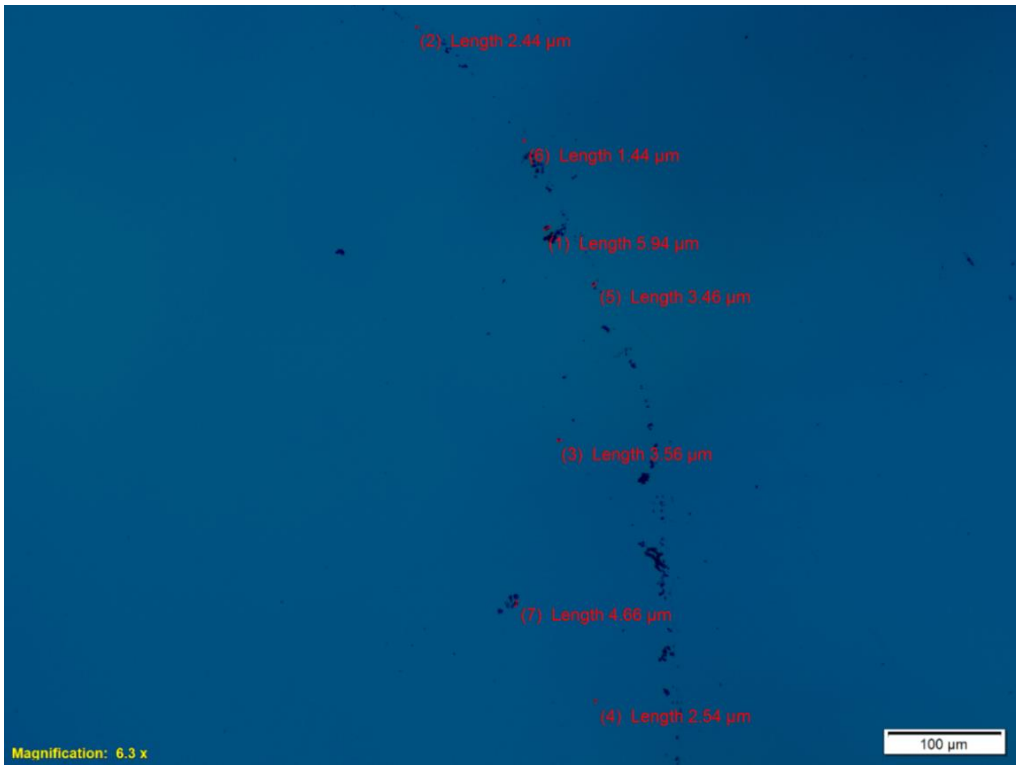


Figure G.12: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 2 ml of n-heptane (30 min)

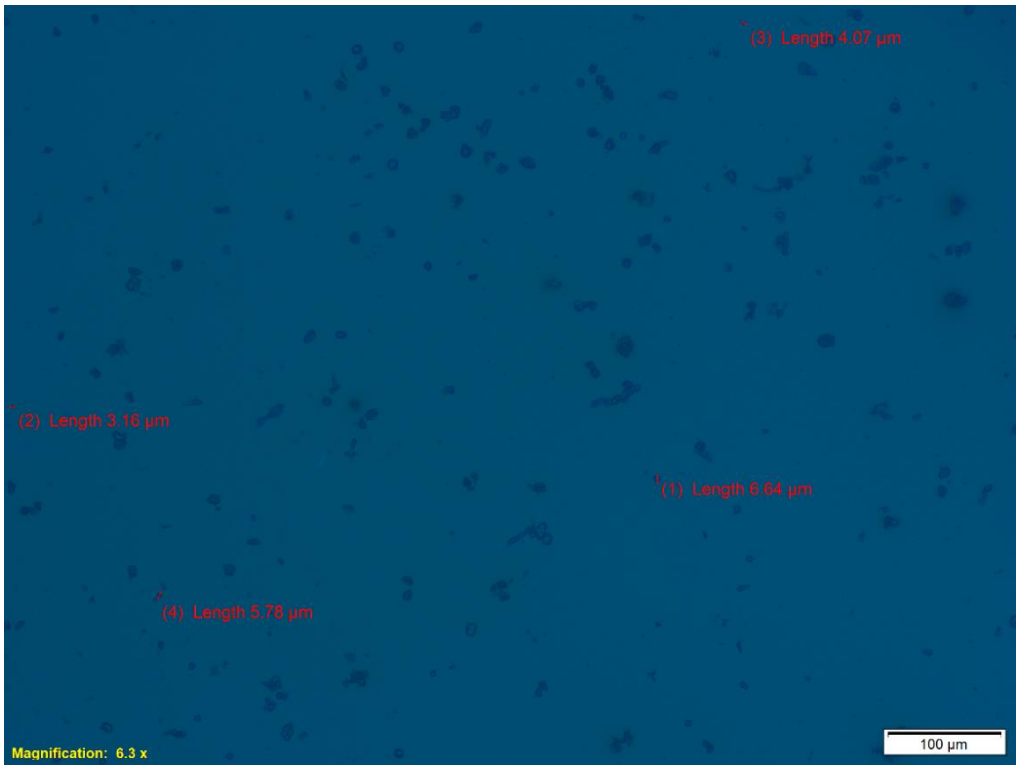


Figure G.13: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)



Figure G.14: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

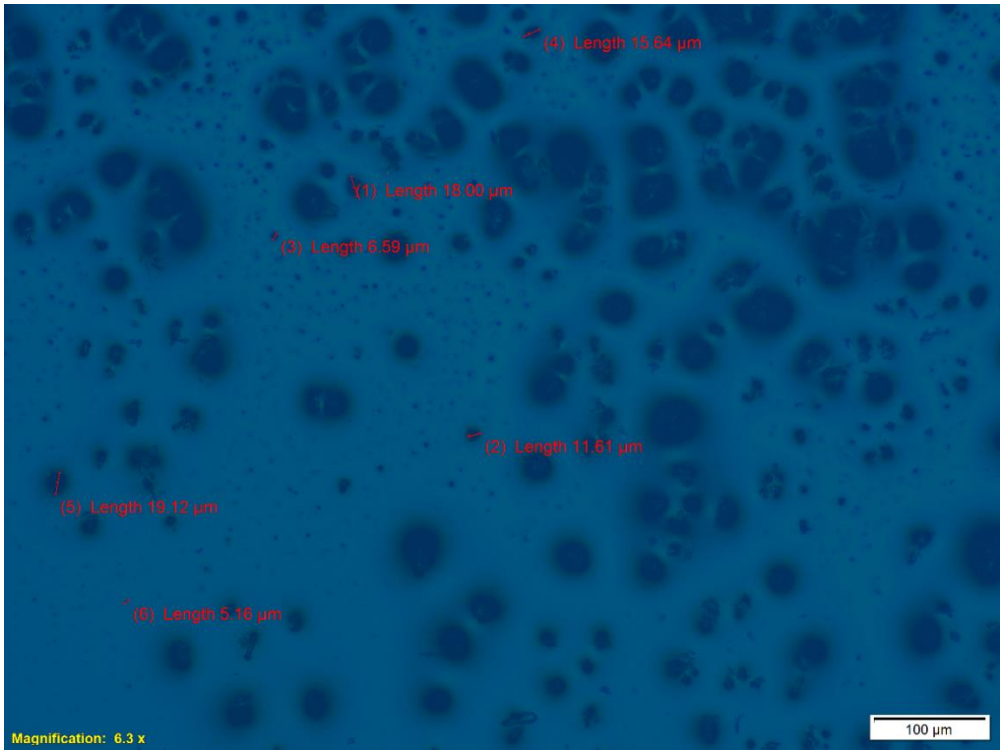


Figure G.15: 0.5g of Crude Oil + 2 ml of 10% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

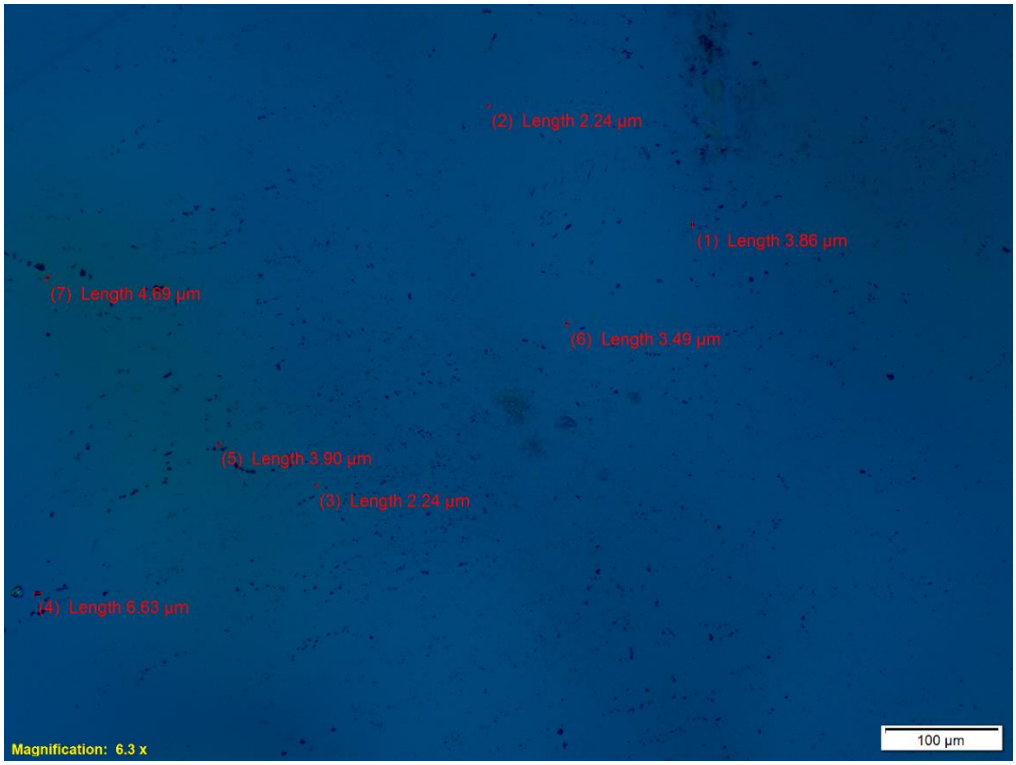


Figure G.16: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid (Time zero)



Figure G.17: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2 ml of n-heptane (30 min)



Figure G.18: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

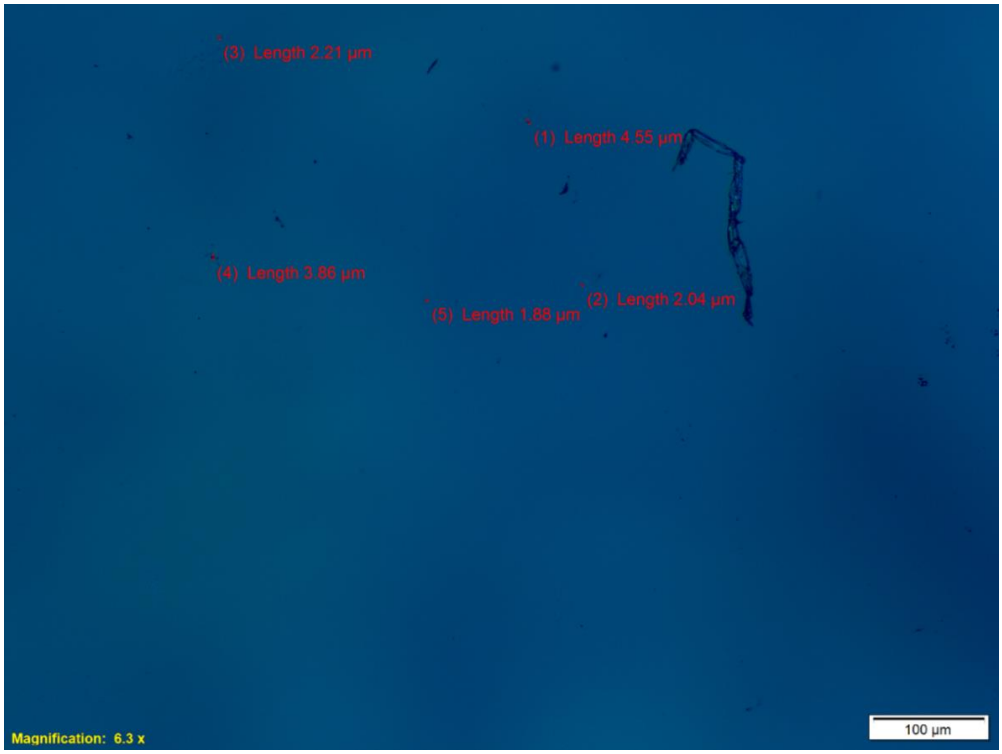


Figure G.19: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

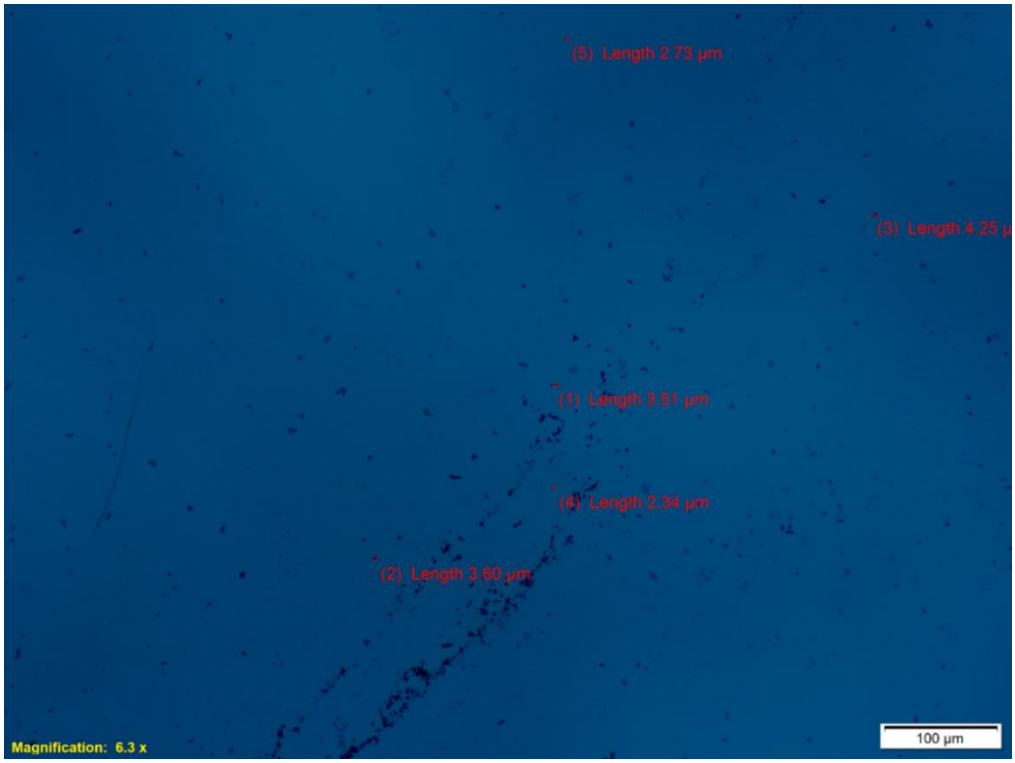


Figure G.20: 0.5g of Crude Oil + 2 ml of 15% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

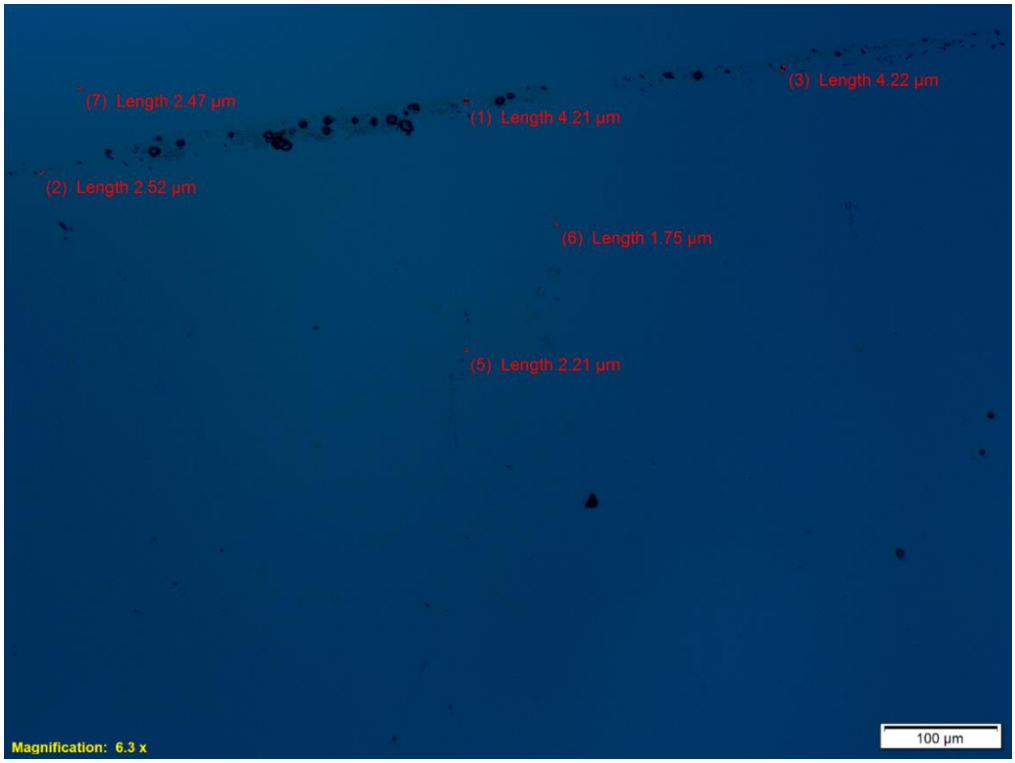


Figure G.21: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid (Time zero)

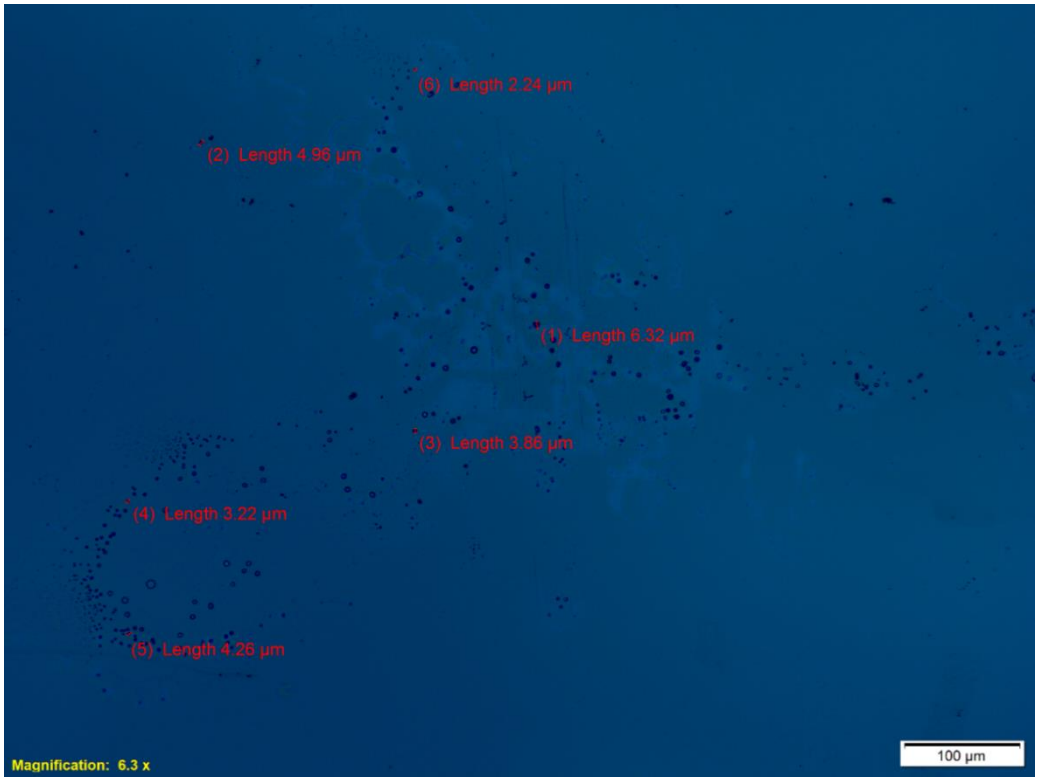


Figure G.22: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2ml of n-heptane (30 min)



Figure G.23: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)



Figure G.24: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)



Figure G.25: 0.5g of Crude Oil + 2 ml of 20% Iso-Phthalic acid + 5 ml of n-heptane (120 min)



Figure G.26: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid (Time zero)

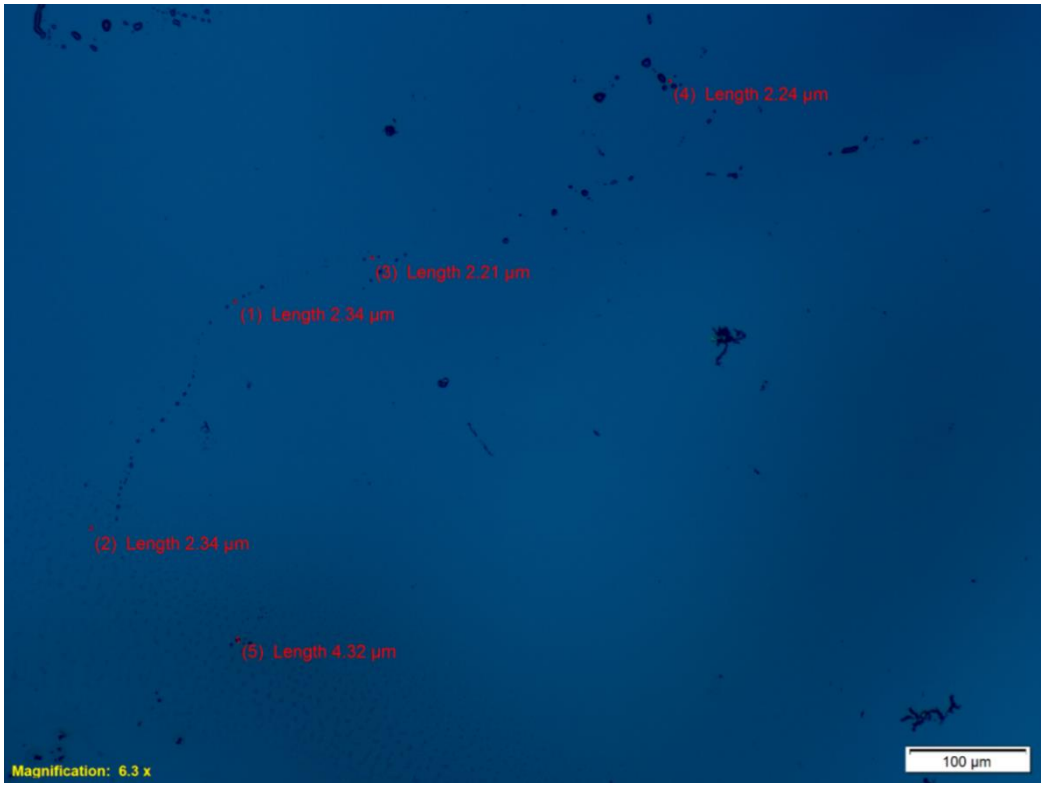


Figure G.27: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2 ml of n-heptane (30 min)



Figure G.28: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 2.5 ml of n-heptane (60 min)

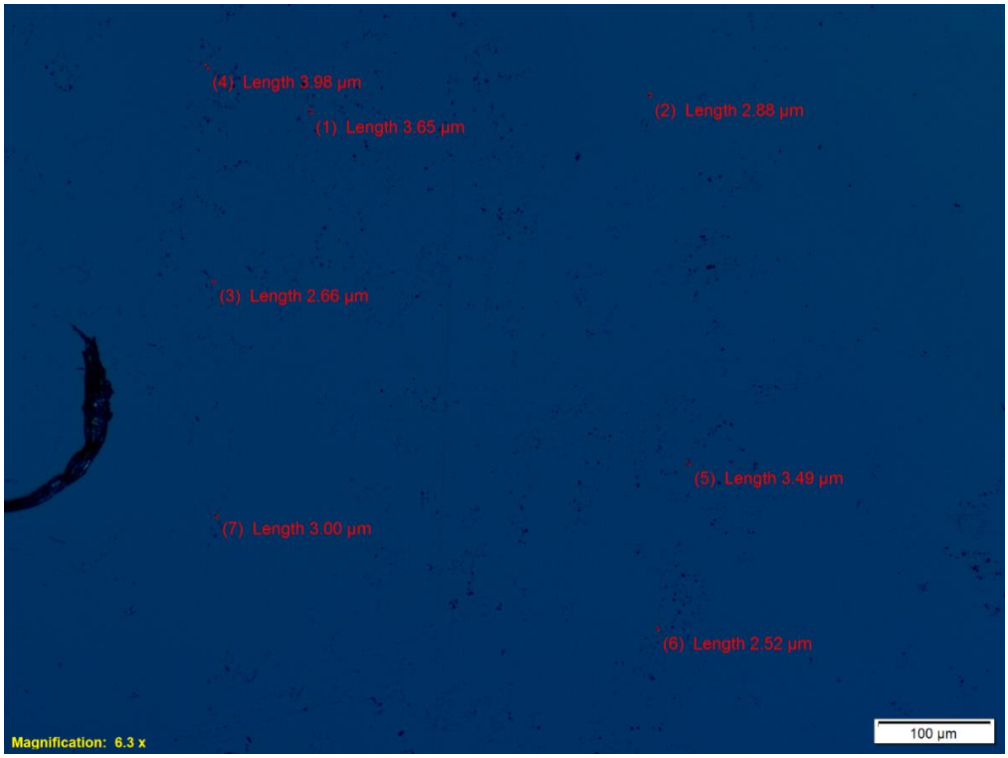


Figure G.29: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 3.5 ml of n-heptane (90 min)

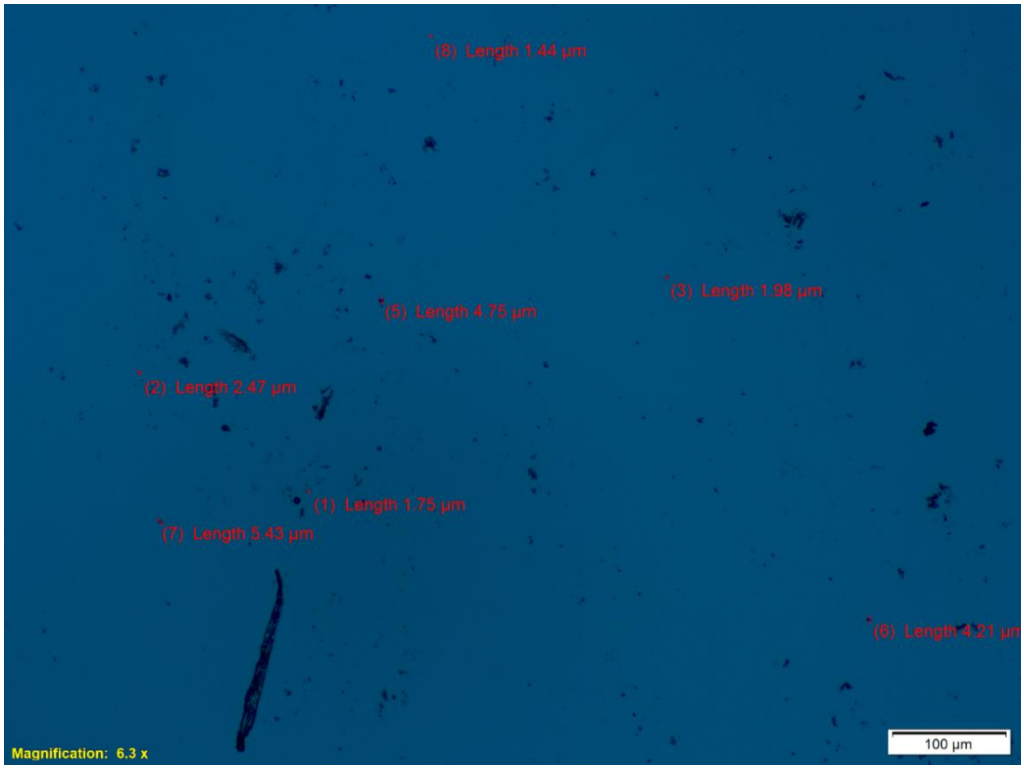


Figure G.30: 0.5g of Crude Oil + 2 ml of 25% Iso-Phthalic acid + 5 ml of n-heptane (120 min)

APPENDIX H: Crude Oil - n-heptane mixture at 35 ºC

Figure H: Asphaltene aggregation stages with the presence of n-heptane at 35 ºC

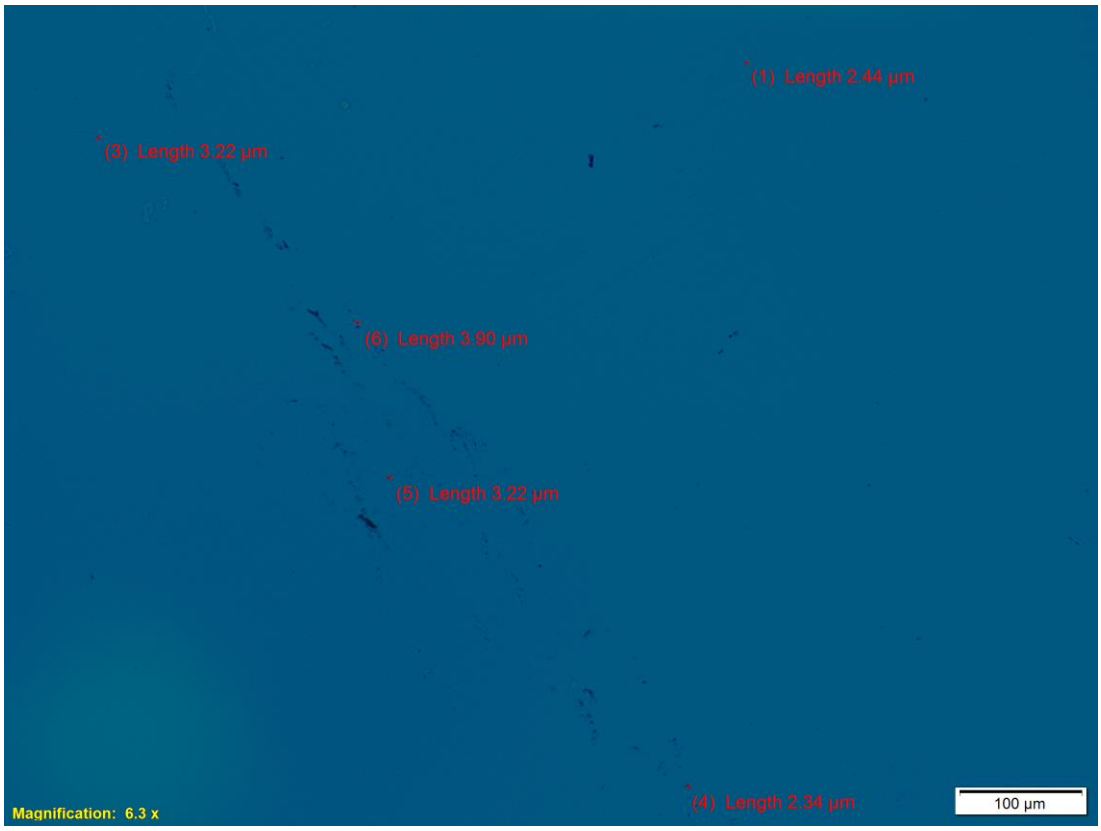


Figure H.1: 0.5g of Crude Oil + 2 ml of n-heptane (30 min)



Figure H.2: 0.5g of Crude Oil + 2.5 ml of n-heptane (60 min)



Figure H.3: 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min)

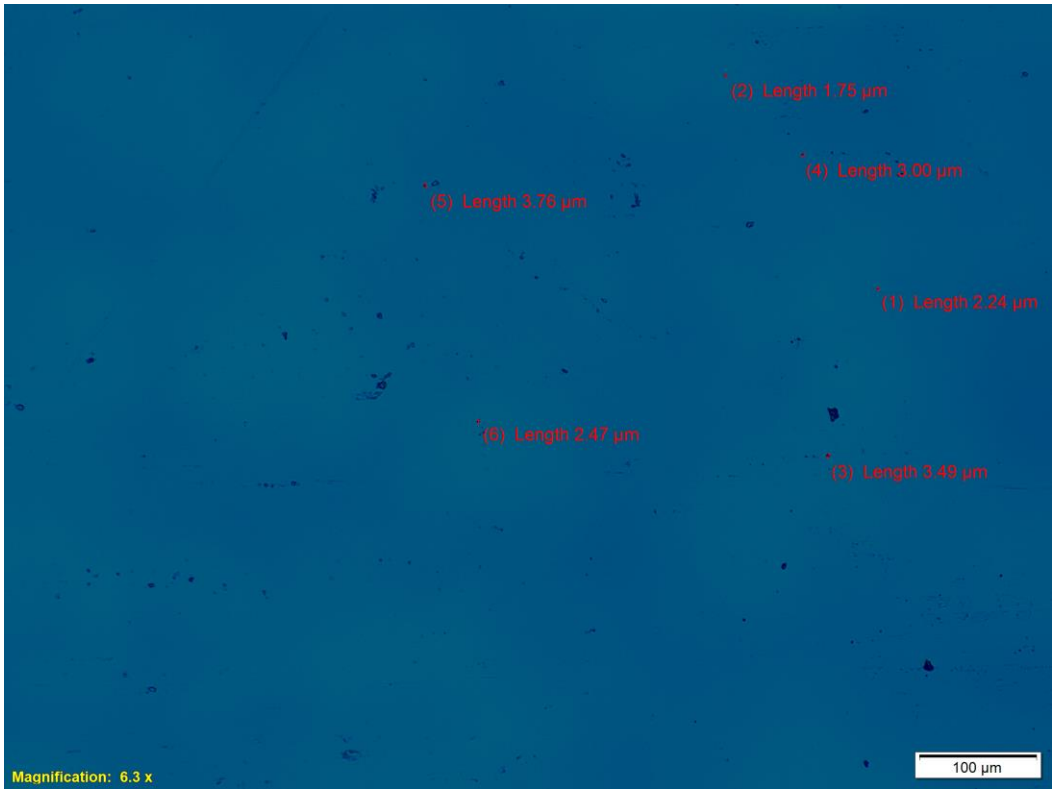


Figure H.4: 0.5g of Crude Oil + 5 ml of n-heptane (120 min)

APPENDIX I: Crude Oil - n-heptane mixture at 65 ºC

Figure I: Asphaltene aggregation stages with the presence of n-heptane at 65 ºC

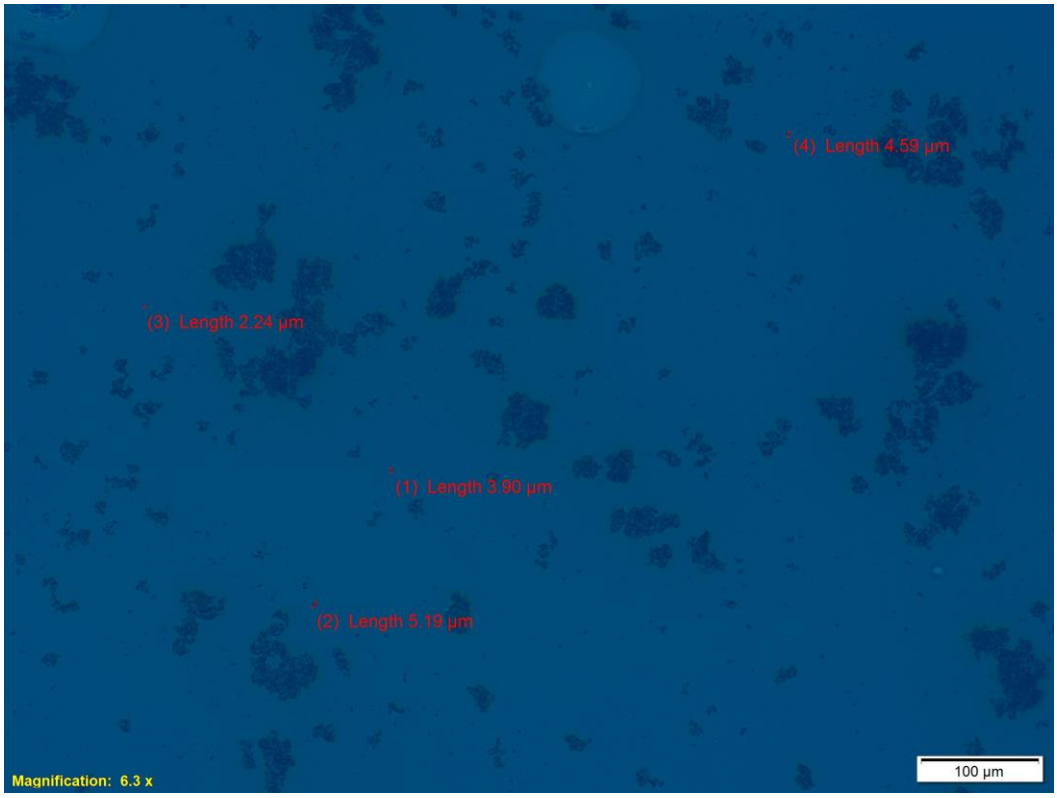


Figure I.1: 0.5g of Crude Oil + 2 ml of n-heptane (30 min)

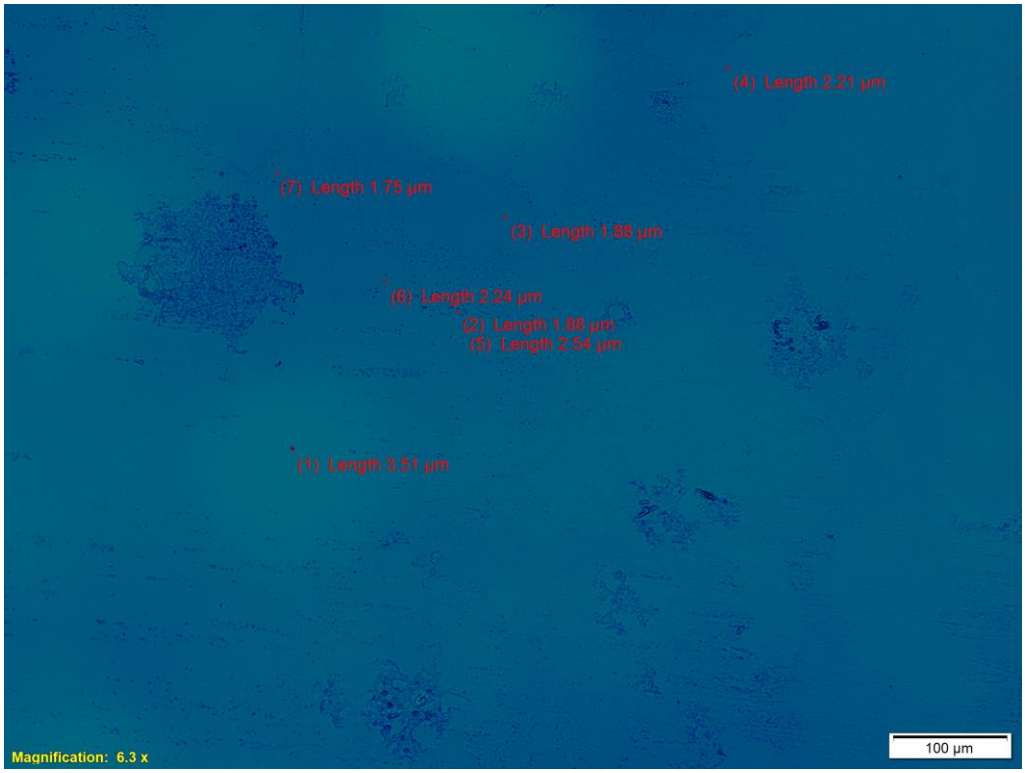


Figure I.2: 0.5g of Crude Oil + 2.5 ml of n-heptane (60 min)

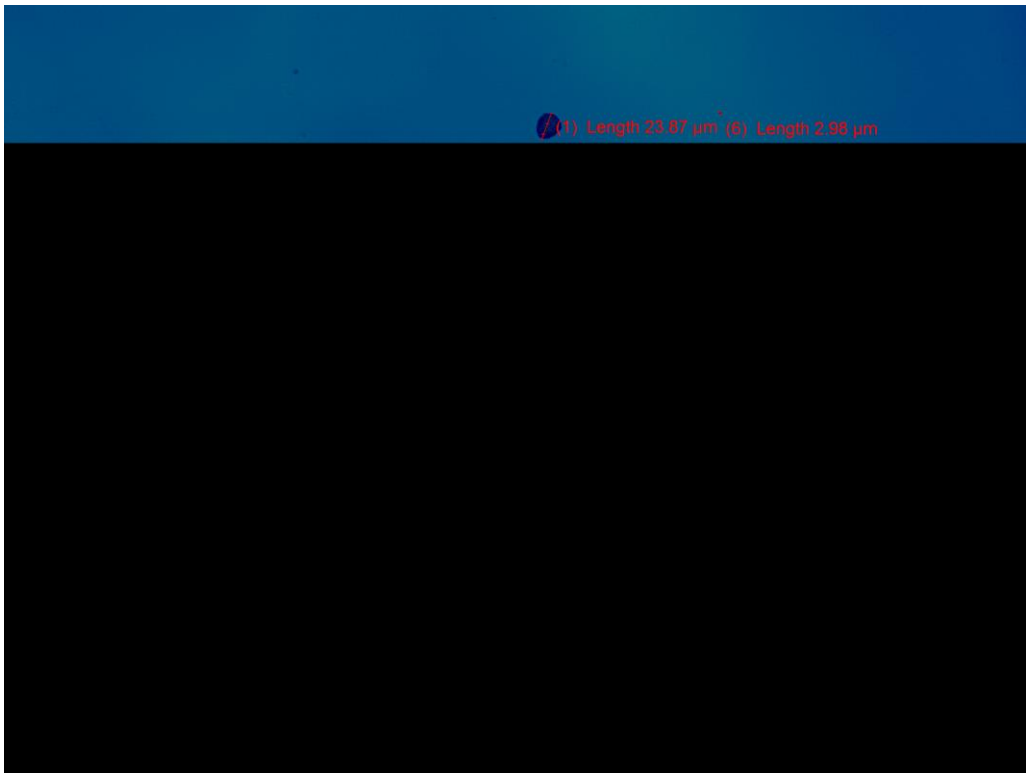


Figure I.3: 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min)

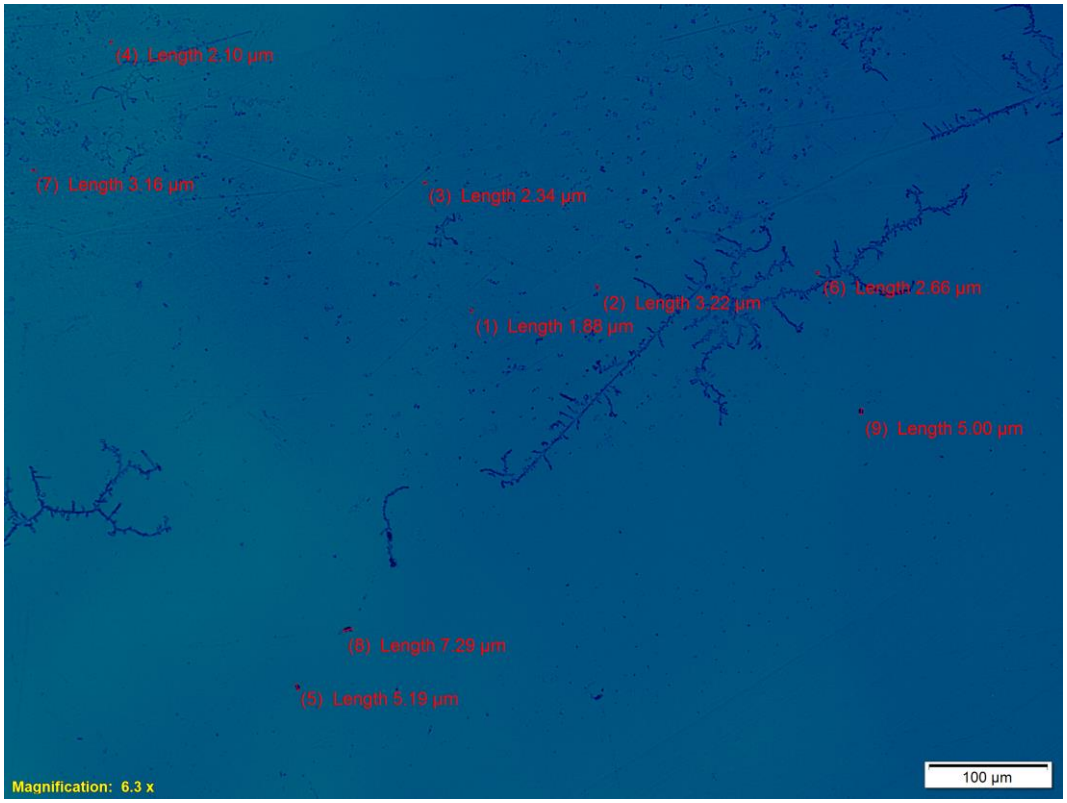


Figure I.4: 0.5g of Crude Oil + 5 ml of n-heptane (120 min)

APPENDIX J: Crude Oil - n-heptane mixture at 80 ºC

Figure J: Asphaltene aggregation stages with the presence of n-heptane at 80 ºC



Figure J.1: 0.5g of Crude Oil + 2 ml of n-heptane (30 min)



Figure J.2: 0.5g of Crude Oil + 2.5 ml of n-heptane (60 min)

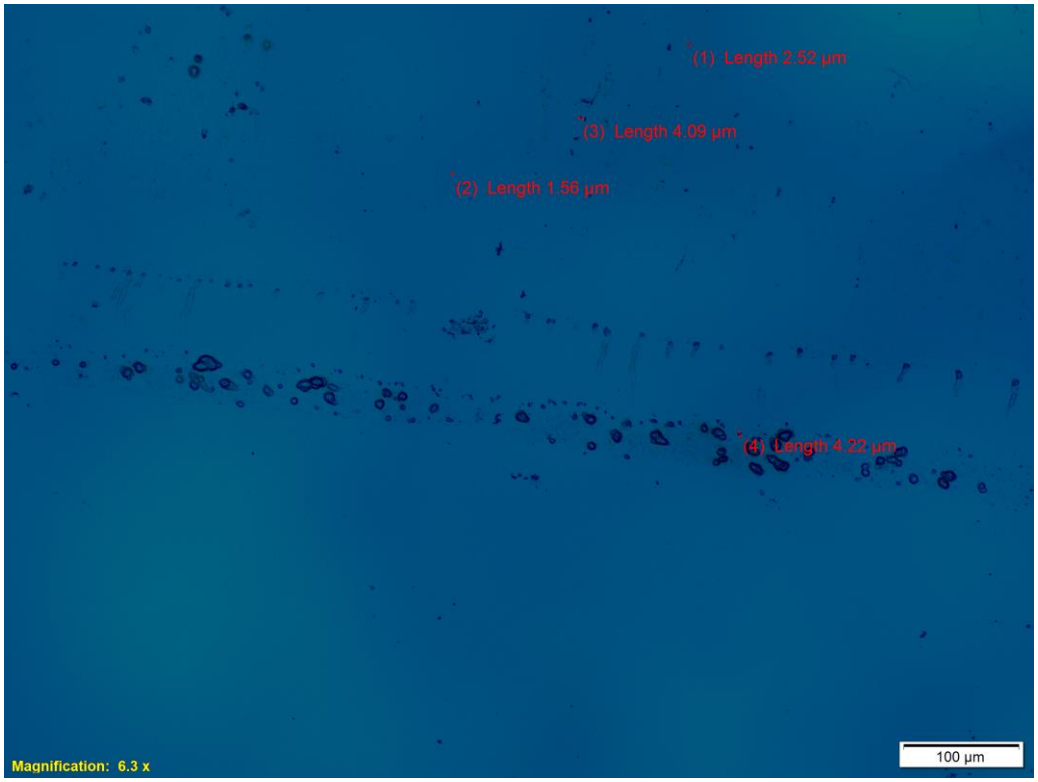


Figure J.3: 0.5g of Crude Oil + 3.5 ml of n-heptane (90 min)



Figure J.4: 0.5g of Crude Oil + 5 ml of n-heptane (120 min)