CONTROL OF ASPHALTENE PRECIPITATION AND DEPOSITION DURING CARBON DIOXIDE FLOODING ENHANCED OIL RECOVERY

By

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DECLARATION

I, **Jean-Bedel Batchamen Mougnol**, declare that the contents of this thesis represent my unaided work and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology and the Oil and Gas Research Council.

Signed　　　　　　　　　　**Date**

ABSTRACT

Pentane solvent among the two other solvents, hexane and heptane, had a greater ability to extract asphaltene from three crude oils – A, B and C – to precipitate it. The two solvent mixtures (Hexane 75 mL + Pentane 25 mL and 100 mL Pentane + 100 mL Hexane) had the abilities to extract greater yield of asphaltene content from the three different crude oils. Crude oils A and B were analysed to be paraffinic, meanwhile, crude oil C was found to be aromatic. The calculated average of asphaltene content in crude oil A on the ratio of 1:1 solvent-to-solvent mixture were 10.06 g/mL, crude oil B 10.06 g/mL and for crude oil C as 21.33 g/mL. When the solvent-to-solvent mixture ratio was 3:1 the average of the content in crude oil A was 11.8 g/mL, crude oil B 10.13 g/mL and crude oil C 22.65 g/mL. Lastly, the average asphaltene on the single ratio of paraffin solvent in three solvents in crude oil A was 6.86 g/mL, crude oil B 6.06 g/mL and crude oil C 22.73 g/mL. The asphaltene content from the extraction with the solvents was compared with the GC-MS, which further revealed that both analyses resulted in similar conclusions. While CO_2 was found to be more influential in its injection in the crude oil, greater asphaltene contents were noted at a temperature of 25^oC and lesser at 90^oC in all three crude oil types. It can be appreciated that temperature plays a vital role in the process of CO_2 flooding of crude oils. The decrease in the CO_2-to-oil ratio had an increase in the asphaltene content, keeping the flow rate of the CO_2 constant and increasing the amount of crude oil.

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...therefore to my family, everything I have accomplished belongs to you.

DEDICATION

I dedicate this thesis to Mrs Batchamen Honorine and Mr Batchamen Valentin for believing in me.

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SYMBOLS AND ABBREVIATIONS

ADE	Asphaltene Deposition Envelope
APE	Asphaltene Precipitation Envelope
APIg	American Petroleum Institute Gravity
C_5	Pentane
C_6	Hexane
C_7	Heptane
CO_2	Carbon Dioxide
EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
mL	Millilitre
MMP	Miscible Minimum Pressure
OER	Oil Enhanced Recovery
OPEC	Organization petroleum exporters countries
OOIP	Original oil in place
psig	Gauge pressure measured relevant to atmospheric pressure

OUTLINE OF THE THESIS

The research presented in this thesis was conducted at Cape Peninsula University of Technology, South Africa. The GC/MS analysis was conducted at Stellenbosch University, South Africa (Department of chemical engineering) and further analysis was conducted at the geologic department Stellenbosch University.

The thesis comprises of seven chapters.

Chapter 1: Gives a brief introduction, problem statement, objectives and research question of the study.

Chapter 2: Contains the literature review of the thesis and the background of this dissertation.

Chapter 3: Covers the experiment of the asphaltene content from each of the three crude oil types used in this experiment to conduct the analyses. Also covers literature review on asphaltene, results, discussion and conclusion.

Chapter 4: Focuses on the literature review of CO_2 flooding in crude oil and the experiment conducted to sustains the literature review as well the results, discussion and conclusion.

Chapter 5: Focuses on the discussion, conclusions and recommendations.

Chapter 6: Lists the appendices, whereby details regarding calculations and other supplementary information, is listed.

Chapter 7: Lists bibliographical references consulted for the research.

1

INTRODUCTION

This chapter outlines the introduction, problem statement and research questions targeted to achieve the objectives of the project.

1.1 Background

Crude oil as a primary resource in petroleum reservoir is one of the important sources for energy worldwide, as millions of barrels are employed daily in the manufacturing of transportation fuels, chemicals, fertilisers, cosmetics, pharmaceutical and other industries worldwide (Kaplan, 2018). Economically, oil and gas supply power worldwide and will likely continue to do so for the upcoming centuries. In the future, oil production will recover economically from a small reservoir (Zhang *et al*., 2019, Martínez *et al*., 2018). The earlier data used to estimate the oil demand showed that the demand for oil is greater than the production, proving what (Kristoufek, 2018) had predicted.

It is estimated that by 2030 the rest of the world's per-capita demand would be almost two litres a day and its share of total world demand will increase from 39% to 58%. Oil demands should be expected to increase rapidly as it is used as a source of income in most countries (Dargay and Gately, 2010). As crude oil is supposed to be a significant market commodity after gold, the price of oil is monitored globally for increment purposes which may lead to fluctuation and thereby impact global economic trends of reserve oil consumption (Zhang and Wei, 2010). Current evidence suggests that a peak in conventional oil production before 2030 is likely to occur; therefore there is a significant risk of a peak reached even earlier (Sorrell *et al*., 2010). Comparative statistics, under plausible conditions, indicate increased uncertainty about the future oil supply shortfalls (Alquist and Kilian, 2010).

(Baumeister and Peersman, 2013) have explained the possibility of the structural changes in the oil market over time, as they mentioned the relationship between the oil market and the oil supply. The changes in the oil market have an impact on elasticities, the responsiveness of supply and demand to the change in price. The OPEC (Organisation Petroleum Exporters Countries) downfall in the late 1980s and the future market trading are likely to have increased the flexibility of the real price of oil. If a higher fraction of oil transactions are carried out on the spot market, oil supply and demand variations are expected to translate quickly into price changes.

1.2 Origin of crude oil

According to the biogenic theory, crude oil formed from the decaying of old organic matter that has accumulated over an extended period and is covered by layers of mud and sediment imposes enormous pressure and temperature on the organic matter (Chaudhuri, 2016). The formation of petroleum begins when aquatic plant and animal remains are covered by particles of rock and mineral. The environment must be anaerobic, or the oxygen available must be minimal so that the decaying of the organic matter is not rapid. Under these extreme conditions, together with the lack of oxygen (anoxic condition), the materials generally will not decay. Moreover, the layers of sediment will be somehow transformed into sandstone, limestone and other types of sedimentary rocks (Tissot and Welte, 2012).

According to Abdel-Raouf (2012b), the world's oil production is still rich for many years to come, a result of a slow process of nature in bottom seas where deposits of organic compounds have been trapped in the sedimentary rocks. Dargay and Gately (2010) reported that under increasing pressure and temperature, the kerogen (as an additional layer of sediment deposit on top) is transformed into liquid (crude oil) and gaseous (natural gas) hydrocarbons in a process known as *catagenesis*.

1.3 Problem statement

During the production of crude oil, the production rate is retarded by the cohesion force between asphaltene molecules, leaving about 65% of Oils Initially In Place (OIIP) still trapped in the reservoir. Miscible CO_2 flooding as an Enhanced Oil Recovery (EOR) method assists in the reduction of crude oil viscosity and hence leads to improved oil recovery. However, in most oil reservoirs, CO_2 flooding will result in asphaltene crystallisation and deposition due to the instability of asphaltenic-paraffinic compound interactions as temperature and pressure decline. Economically, the deposition of asphaltene is costly due to the required cleaning and maintenance of the production facilities.

The mechanisms of asphaltene in the industry is not yet fully understood as many industries are still experiencing asphaltene deposition especially during tertiary recovery where CO_2 flooding occurs. The factors that trigger this deposition is, however, challenging to monitor due to the asphaltene instability. The deposition of asphaltene can be disrupted by monitoring the factors that trigger its deposition to crystallise. The study of the hydrogen bonding, van der wall forces between the asphaltene and the crude oil can very well establish on the determination and awareness of the asphaltene deposition during carbon dioxide flooding.

According to Leontaritis and Mansoori (1988), the experimental work over the last 40 years suggests that asphaltenes may exist in a colloidal state in the crude oil and further pursue of the subject in this direction by both the industrial and research communities is warranted. Hemmati-Sarapardeh *et al*. (2019) stated that asphaltene precipitation causes different problems in the oil industry. The crystallisation of asphaltene still occurs in many industries which studies have not yet shown how to monitor the asphaltene being precipitated to the surface. Liu *et al.* (2019) mentioned that, attention has been paid to the damage asphaltene deposition causes to the refinery of crude oil, with the tendency of crude oil to be heavier. Further, asphaltene deposition can cause problems such as heat exchanger plugging, catalyst deactivation, and so on in the refining process.

1.4 Research aim and objectives

The research is set to elucidate the mechanism of asphaltenic compound precipitation and the factors that promote its deposition in the reservoir system during carbon dioxide (CO_2) flooding for enhanced oil recovery. The following objectives will be pursued to achieve the aims:

a) to determine the type, nature and the number of asphaltenic compounds in different types of crude oils, and to relate their distribution to the crude API and sourness;
b) to investigate the tendency of asphaltene in crude oil to precipitate in the reservoir system during CO_2 flooding as a function of reservoir temperature and pressure;
c) to investigate the effects of concentration and solubility of CO_2 in crude oil on asphaltene precipitation in the reservoir system during CO_2 flooding; and
d) to investigate asphaltene precipitation onset conditions

1.5 Research questions

This study will provide answers to the following questions to achieve the stated objectives:

a) How does the amount and nature of asphaltenic compounds in different crude oils relate to the API gravity?
b) How much CO_2 will be needed to lower the solubility of asphaltene in crude oil in the reservoir to shift the pH and hence trigger its precipitation?
c) What are the effects of temperature and pressure on asphaltene precipitation in the presence of CO_2?
d) Is there a relationship between asphaltene contents of crude oils and its deposition during CO_2 flooding?

1.6 Scope of study

This research will focus on investigating and controlling the factors of asphaltene precipitation during miscible CO_2 flooding for heavy and light oil in the oil reservoir system. The focus will be on the miscible gas rather than immiscible gas because it has been reported that the miscible gas has higher EOR in the oil production. The use of CO_2 in this research, rather than any other gas, is preferrable as it is homogeneous and miscible in the crude oil, helping to reduce the viscosity of crude oil. Using CO_2 also importantly helps in the reduction of the greenhouse effect, which is less economical and productive in EOR. For a successful outcome in an oil production system pressure, temperature, and composition of oil must be monitored. The lesser the asphaltene content in the light oil, the higher the electrical conductivity due to instability in the oil reservoir. The higher conductivity will cause the asphaltene to precipitate.

1.7 Significance of research

The benefits of this research are as follows:

a) to maximise the oil production recovery during CO_2 flooding by controlling and monitoring the factors that promote asphaltene precipitation-deposition;
b) to minimise costly operational problems associated with the utilisation parameters of oil recovery on asphaltene deposition during CO_2 flooding; and
c) to stabilise asphaltene in crude oil concentration during CO_2 flooding.

2

CHEMISTRY OF ASPHALTENE

Crude oil is an integration source of energy that makes up other fuel components utilised in vehicles, industries, cosmetics, pharmaceuticals and more. The API (American Petroleum Institute) and the viscosity of the crude oil are discussed in this chapter, focussing on their chemical and physical properties. The hydrocarbon content, which makes crude oil, is also defined and discussed, as well as the characterization and precipitation of asphaltene.

2.1 Importance of crude oil

Crude oil, also called *black gold*, is the most important natural resource of industrialised countries. Oil production and transportation can cause severe environmental pollution and disrupt the population of living organisms (Kalhor *et al*., 2017). Crude oil is a complex mixture that contains toxic elements and compounds likely to affect the environment during its production (Wang *et al*., 2018). So while crude oil consumption is projected to increase yearly, problems can arise in the next ten years due to increasing population and its use in the developing countries (Hemmati-Sarapardeh *et al*., 2016). The price of one crude oil barrel (42 gallons or 159 litres) is highly dependent on both its grade – including oil specific gravity, sulphur content and viscosity – and its origins (Demirbas *et al*., 2017). Forecasting volatility is key to the risk-management process and oil price evaluation. High oil prices and volatilities impact global economic growth and eventually the financial markets (Hamilton, 2009).

It is estimated that at the current oil consumption rate (Gupta and Demirbas, 2010), the more significant oil reserves will be depleted in next 50 years, while small reservoirs are already on the verge of depletion. Therefore, the future of short petroleum supply is approaching very fast. A peak in oil production already occurred globally in 2015 (Gupta and Demirbas, 2010) after which the yearly production rate declined at an accelerated percentage. It is estimated that the global oil supply will be dramatically lowered by 2030, resulting in a significant supply gap.

It will be difficult to cover this gap by growing inputs from other alternative energy sources such as biomass, hydro, wind and solar, in such a limited time. Crude oil prices are usually compared to the spot price of West Texas Intermediate (WTI), the source from which the crude oil production is extracted at various composition and hydrocarbon structures depending on the origin source. The alkyl side chains and the number of aromatic rings have a variable of molecular weight, and the aromaticity factor of asphaltenes is disreputable (Cruz *et al*., 2018).

Crude oil depends on the price of brent as traded on the International Commodities Exchange for the delivery in Sullom Voe (Shetland, Scotland). The fall in crude oil prices mainly occurred due to oversupply in the Organization of the Petroleum Exporting Countries (OPEC) (Demirbas *et al*., 2017). Crude oil prices are likely to strengthen if an increase in crude oil inventories is less than anticipated, and vice versa. A rising crude oil inventory would be indicative of increasing supply and decreasing demand conditions. Importantly, unexpected changes in storage levels carry information relevant for price discovery and futures markets (Miao *et al*., 2018).

Qualitative analyses of oil price volatility, based on economic theory, is yet another vital method to understand the essential characteristics of crude oil price fluctuations (Wang *et al.*, 2015). In 2015, the international crude oil prices presented a wave-like decline, while the global crude oil supply was in excess. Analysing the tendencies of international crude oil prices and identifying the change point in the tendency of crude oil price is beneficial for both country enterprises and investors in understanding market tendency, avoiding investment risk and making sound investment decisions. Therefore, in the analysis of crude oil price tendency, the identification of price change points and the prediction of the time for the next change point of crude oil price, has become a scientific issue with important theoretical and practical significance (Chai *et al*., 2018).

2.2 Crude oil types

There are three types of grades of crude oil in the oil reservoir, namely light, medium and heavy (Sedghi and Goual, 2014). Heavy oil has a higher concentration of asphaltene content, leading to its higher density and viscosity (Akbarzadeh *et al.*, 2007). Heavy oil has viscosities ranging from 50 to 50,000 MPa, making it highly porous and permeable in the oil reservoir. Four countries produce heavy oil: Canada, Venezuela, Russia, and the US (in California and Alaska) (Mai and Kantzas, 2009). Heavy oil experienced high pressure during transportation through pipelines (Hart, 2014). Therefore, heavy oil tends to have a low pressure which then results in lowering the recovery factors in comparison to light oil. The production process is unfortunately complicated and expensive. The phase fractionation occurs during the loss of an original valuable fraction through a chemical mechanism that happens during water washing. The phase fractionation mass and the removal of light oil happens physically rather than biologically (Santos *et al*., 2014).

2.3 Crude oil characterisation

Crude oil originates from transformation and decomposition of aquatic, living organisms, mainly from marine or land plants that were buried around 15-500 million years ago (Koseoglu *et al*., 2017). Crude oil is a complex mixture of hydrocarbons and other compounds in a wide range of molecular weights (Khalaf and Mansoori, 2018).

As crude oil is economically significant, increasing in energy demands and maturity of oil fields, alternative technologies should be implemented. High concentrations of asphaltene, resins, nitrogen, sulphur-containing heteroaromatic and several metals, particularly nickel and vanadium, are also present in crude oil (Shibulal *et al*., 2017). Crude oil has been described as a complex mixture of over 6000 potentially different hydrocarbons and metals (Ikanone *et al.*, 2017). Crude oils types, mainly paraffinic, naphthenic and aromatic (Wang *et al*., 2011), can contain more paraffin than naphthene. Whether the crude oil is paraffinic or naphthenic, however, it can contain a large quantity of lighter hydrocarbons and be mobile or contain dissolved gases, while another can contain heavier hydrocarbons and be highly viscous, with little or no dissolved gas (Koseoglu *et al*., 2017).

Crude oil varies in its physical and chemical properties from one geographical region to another and from the field to field (Koseoglu *et al*., 2017). During the analysis of the crude oil, larger molecules with a higher carbon number and molecular mass appear at the earlier stage of the chromatogram while the smallest components appear later and remain longer on the chromatographic column (Ghislain *et al*., 2017). Chemical composition by saturates, aromatics, resins and asphaltenes (SARA) analysis and High-Temperature Gas Chromatography (HTGC) reveal essential data to understand the chemical distribution of crude oil samples.

SARA analysis is a method for characterising crude oils into various chemical groups by preparative column separation and by solubility in various solvents of different polarities. In this method, the crude oil is fractionated into four chemical groups – saturates, aromatics, resins, and asphaltenes – and hence the SARA analysis. Volatile percent and inorganic content in the samples are also measured through SARA analysis (Sharma *et al.*, 2016). Characterisation of crude oils is essential, playing a vital role in understanding the natural behaviour of crude oil that may be associated with flow assurance related issues (Sharma *et al*., 2016). Crude oil analysis can be separated into fractions of saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes (Bissada *et al*., 2016).

Table 2.1 outlines the classification of the crude oils according to their boiling or melting points. The approximate chemical composition in carbon range can identify crude fractions. The chemical composition of the crude fractions can be utilised for engines or in manufacturing cosmetics, pharmaceuticals or machinery, and in the construction of roads or buildings.

Table 2.1: Typical fraction of crude oil (McCain, 1990)

Crude Fraction	Boiling Point*, ºF (melting point)	Approximate Chemical Composition	Uses
Hydrocarbon gas		C_1-C_2	Fuel Gas
	To 100	C_3-C_6	Bottled fuel gas, solvent
Gasoline	100-350	C_5-C_{10}	Motor fuel, solvent
Kerosene	350-450	C_{10}-C_{12}	Jet fuel, cracking stocks
Light gas	450-580	C_{13}-C_{17}	Diesel fuel, furnace fuel
Heavy gas oil	580-750	C_{18}-C_{25}	Lubricant oil, bunker fuel
Lubricants and	750-950	C_{26}-C_{38}	Lubricating oil, Paraffin wax, Petroleum jelly
Waxes*	(100)		
Residuum*	900+ (200+)	C_{38}+	Tars, roofing, compounds, paving asphalts, coke, wood preservatives

2.4 Crude oil components

Crude oil contains hydrocarbons with carbon (85%), hydrogen (H, 10%-14%), a few non-metals (sulphur, nitrogen, oxygen) and metals (nickel, lead, arsenic, and vanadium) (Chaudhuri, 2016). During the ageing process of crude oil, its components are distributed in such a way that the capillary forces are influenced to some degree (Hopkins *et al.*, 2017). Depending on the source, the oil predominantly contains various proportions of straight and branched-chain paraffins, cycloparaffins and naphthene, aromatic and polynuclear aromatic hydrocarbons (Koseoglu *et al.*, 2017).

Crude oil mainly consists of various fractions such as resins, aromatic hydrocarbons, saturates, waxes and asphaltenes (Zanganeh *et al.*, 2018). The use of infrared spectrometry (IR), nuclear magnetic resonance (NMR) and X-ray diffraction studies had concluded that aliphatic alkyl structures are predominant in asphaltene. In the crude oil industry, water-in-oil (W/O) emulsions can be found in almost all processes of production and oil recovery. These emulsions increase the viscosity of the crude oil and affect the flow operations, leading to considerable economic losses during the recovery, treatment and transportation of crude oil.

Water-in-oil emulsions are stabilised by several surface-active species usually found in crude oil, such as resins, asphaltenes, heavy metal solids, organic acids and bases. Asphaltenes are commonly identified as compounds which have a higher tendency to migrate to the W/O interface, introducing a barrier that prevents the droplets from coalescing, yielding high emulsion stability (Zorzenão *et al*., 2018).

The hydrocarbons can be gaseous, liquid or solid under standard temperature and pressure depending on the number of carbon atom arrangement in the molecules (Koseoglu *et al*., 2017). The hydrocarbon content of the crude oil can be grouped into paraffin, naphthenes, aromatics and asphaltenes (Grace, 2013). According to Simanzhenkov and Idem (2003), it has been shown that some heavy fractions from paraffinic oils can contain up to 50% paraffin, 47% naphthenes and up to 3% aromatic compounds.

It is known that the higher the boiling temperature of the crude oil fraction, the smaller the number of paraffinic compounds present in the fraction. McCain (1990) mentioned that crude oil contains a predominance of asphaltene molecules.

Table 2.2 lists the details of crude oil components classified into their paraffin, naphthenes and aromatics sub-divisions.

Table 2.2: Details of crude oil component analysis (Bissada *et al*., 2016)

Paraffins	**Naphthenes**	**Aromatics**
All normal paraffins up to $C_{10}H_{22}$	Cyclopentane	Benzene
Isobutane	Cyclohexane	Toluene
2-Methylbutane	Methylcyclopentane	Ethylbenzene
2-3-Dimethylbutane	1,1-Dimethylcyclopentane	Xylene
2-Methylpentane	1,3-Dimethylcyclohexane	1,2,3- Trimethyl;benzene
3-Methylpentane	1,2,4-Trimethylcyclohexane	
2-methylhexane		
3-methylhexane		
2-Methylheptane		
2,6-Dimethylheptane		
2-Methyloctane		

Table 2.3 shows the percentage of each common element found in all crude oils regardless of their source.

Table 2.3: Crude oil component analysis by weight percentage (Bissada *et al*., 2016)

Element	Percentage by weight
Carbon	84-87
Hydrogen	11-14
Sulphur	0.06-2.0
Nitrogen	0.1-2.0
Oxygen	0.1-2.0

2.4.1 Paraffins

Simanzhenkov and Idem (2003) reported that the *paraffinic hydrocarbons* found in crude oil are methane, ethane, propane and butane. The paraffinic series of these aliphatic hydrocarbons, with a general formula $C_nH_{(2n+2)}$, are long saturated straight chains which carry the full complement of carbon atoms with a single bond, rendering them less reactive. Paraffin is usually in the more substantial fraction of crude oil. They usually have a higher octane number than regular paraffin. Asinger (2016) concluded that standard paraffin is when there is no constituent of olefins in the mixtures. Simanzhenkov and Idem (2003) indicated that light paraffins are usually in gas forms dissolved in the oil reservoir. Some hydrocarbons from C_1 to C_{78} paraffin can be separated from the crude oil. They are all types of paraffin such as n-paraffin and isoparaffins. According to Asinger (2016), paraffinic hydrocarbons can be utilised industrially during the following processes: oxidation, nitration, chlorination, sulphoxidation and sulphochlorination. During sulphoxidation, sulphur oxide and oxygen react with paraffinic hydrocarbons under ultraviolet light or in the presence of peroxides to form aliphatic sulphonic acid.

2.4.2 Naphthenes

Naphthenes, present in crude oil, are monocyclic and polycyclic. The composition of oil can vary from 25 to 75%. Usually, the amount of naphthene in crude oil fractions increases as the boiling point increases. However, there is an exception in the naphthenic hydrocarbons in heavy oil in which, as the boiling point increases, the naphthenic hydrocarbon decreases (Simanzhenkov and Idem, 2003). Naphthenes are cyclic hydrocarbon compounds, consisting of mono-or poly-closed rings. They are also called cycloparaffins or hydrogenated benzenes (Khanna *et al*., 2014).

2.4.3 Aromatics

Aromatics constitute only a small percentage of most crude oils. The common aromatic compound in crude oil is benzene, a popular building block in the petrochemical industry. These are the class of cyclic hydrocarbons that have at least one benzene ring as part of their structure and a general formula of C_nH_{2n-6} ($n > 5$). These hydrocarbons have a pleasant smell, a higher octane number and are much denser than paraffin and naphthenes with the same number of carbons. The aromatics are polyunsaturated, consisting of double bonds (Wauquier, 1995).

2.4.4 Asphaltenes

Asphaltene is one constituent of crude oil with its name discovered by a Frenchman named Boussingault (1837). He discovered that asphaltene has the same characteristics as bitumen (asphalt), found at the time in eastern France and Peru. Asphaltene was consequently named as such since it bears a resemblance to asphalt (Yen and Chilingarian, 2000). Asphaltene has bulky and polar fractions of crude oil which are soluble in aromatic solvents like toluene and benzene, and insoluble in n-alkanes such as n-pentane and n-heptane (Meighani *et al*., 2018). Asphaltenes have been extensively studied due to their tendency to precipitate, even at low concentrations, generating losses during oil production and refining. There are also known for their emulsification power which hampers the separation of water and oil, causing various other problems for the petroleum industry (Aguiar and Mansur, 2015).

Asphaltene is used in its most general sense to refer to the molecular weight of cyclic polyaromatic condensed ring components of crude oil (Idem and Ibrahim, 2002). These favourable interactions are due to some inter-particle forces, individually or collectively, resulting from functionalised groups (including carboxylic, pyrrolic, pyridinic, thiophene and sulphite) on the asphaltenes (Groenzin and Mullins, 2000). Asphaltene is found in crude oil as a colloid mixture and polar molecules formed by the polyaromatic structures containing alkyl chains, such as heteroatoms oxygen (O), sulphur (S), nitrogen (N) and some metals. Asphaltene is composed of several aromatic polynuclear that are surrounded by the hydrocarbon tails (Speight, 2014, Abdel-Raouf, 2012c). Asphaltene is a long molecule, dark brown, friable solids in colour with a density of about 1.2 g/cm^3 that have no definite melting point and usually foams and swells on heating to leave a carbonaceous residue (Fath and Pouranfard, 2014).

Asphaltenes are defined as a solubility class of petroleum fluids that are soluble in aromatic solvents such as toluene, but insoluble in normal alkanes such as n-heptane. Based on this broad definition, asphaltenes consist of thousands of species with different molecular structures.

While the majority of asphaltenes may have a standard architectural structure containing a polycyclic aromatic core and peripheral aliphatic chains, their size and aromaticity vary considerably (Javanbakht *et al.*, 2018). Asphaltenes are defined as the oil fraction that is soluble in toluene, and insoluble in excess short chain n-alkanes, such as n-pentane (Riley *et al*., 2018).

After the production of crude oil, asphaltene is obtained as a deposit, as shown in Figure 2.1. The molecular weight and size are in accordance with the source of crude. This deposition of asphaltene causes severe permeability damages (Shen and Sheng, 2018). Figure 2.1 shows the asphaltene aggregate stack after the production of crude oil (Strausz *et al.,* 1992*)*.

Figure 2.1: Asphaltene stacks of crude oil (Bissada *et al*., 2016)

The asphaltene fraction is comprised of a range of molecules, each consistent with an agreed generic structure: molecules ranging from four to 10 aromatic rings in size with branched alkyl chains, and various heteroatoms, including nitrogen (N), oxygen (O) and sulphur (S) (Riley *et al*., 2018).

Typically, 40 single molecules of asphaltenes of various structural are covalently linked *(Shukla, 2018)*. According to Shukla (2018), as shown in Figure 2.2, for the structural model of typical asphaltene molecules, it is believed that the measurement of high molecular weight belongs not to single asphaltene molecules but molecular aggregates.

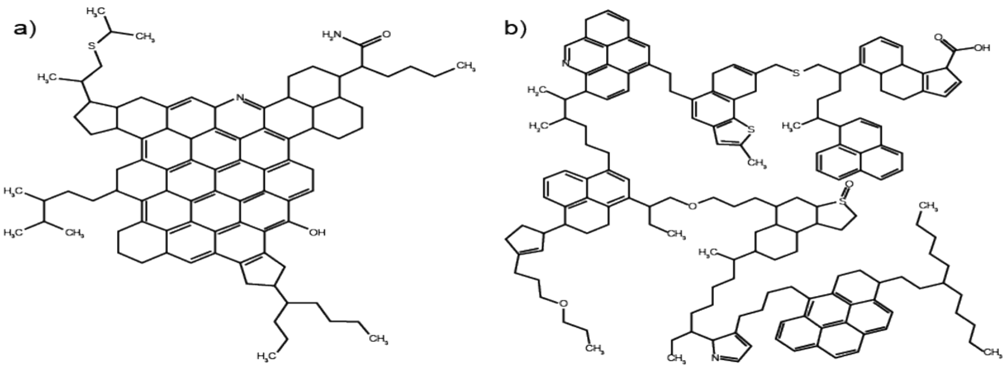


Figure 2.2: Structural model of typical asphaltene molecules in crude oil (Bissada *et al.,* 2016)

It has proven difficult to achieve consistent asphaltene molecular weight measurements as they are a solubility class and not a pure component (Alboudwarej *et al*., 2002). The most common properties of asphaltene are related to their solubility (Nordgård et al., 2009, Ortiz et al., 2010). Asphaltene can be precipitated by dissolving lower alkane molecules such as pentane, hexane and heptane in crude oil with a surface tension lower than that of 25 dyne cm^{-1} at 25°C (77°F). However, they are soluble in liquids such as aromatic compounds, namely benzene, carbon tetrachloride, carbon disulphide and toluene (Shkalikov et al., 2010, Speight, 2014).

Consequently, a smaller mass of asphaltenes will precipitate at higher temperatures. The mechanism of asphaltene precipitation can be described as a process of destabilisation of asphaltene nanoaggregates from the crude oil due to the addition of a precipitant. Their subsequent aggregation and particle growth follow the destabilisation.

When the particles reach the micrometre size, they become detectable by optical microscopy and other techniques (Maqbool *et al*., 2011). Primary asphaltene molecules (or micelles) have the appropriate size between two to five inches. Asphaltene micelles are lyophobic in low molecular weight paraffin hydrocarbons and lyophilic in aromatic hydrocarbons and resins (Sachanen, 1945). Asphaltenes readily absorb both aromatic hydrocarbons and resins. Both resins and aromatic hydrocarbons act as peptising agents for the asphaltene micelles, that is, inhibiting flocculation between the molecules (Ferworn *et al*., 1993).

However, for titrations with heavier alkanes like C_5, asphaltene stability increases with increasing temperature. The asphaltene molecules aggregate due to attractive forces between polyaromatic cores, but their size and shape differ which does not affect the attraction. Additionally, their size decreases with an increase in the hydrogenated polycyclic core, side-chain length and tetralin concentration. The number of side chains also get influenced by the aggregate size, but only in the presence of tetralin.

The effect of tetralin on the solubility of asphaltene indicates that the extent of the tetralin on the number of side alkyl chains influences the structural changes of asphaltene under hydrogenation or dealkylation conditions (Lee and Lee, 2017). According to Strausz *et al*. (1992), asphaltene content has copious quantities of mono to pentacyclic condensed aromatic molecules, constituting the sub-components of crude oil. Most hydrocarbon biomarkers are present in asphaltene in the functionalised form of sulphides, sulphoxides and carboxylic acid, which is colloidal with crude oil.

2.5 Production of crude oil with asphaltenes

The current trend in the petroleum industry is a noticeable shift of technologies towards processing heavier crude oils and residues. These feedstocks are more difficult to process due to the higher content of heavy constituents such as asphaltene and resin, and more significant quantities of non-distillable hydrocarbons having a significant number of heteroatoms and metals in contrast with light crude oils (Trejo *et al.*, 2004). Crude oils that are susceptible to pressure-induced asphaltene precipitation are highly undersaturated; that is, the subsurface formation pressure is much higher than the bubble point which is the pressure and temperature conditions at which the first bubble of gas comes out of solution in oil; thus, crude oil can experience a significant pressure drop without evolving gas (Joshi *et al*., 2001).

2.6 Solubility of crude oil

Investigating the solubility of crude oil is an essential factor in the prediction of asphaltene precipitation. Thermodynamics was the first method in literature to be applied in asphaltene stabilisation regarding reversible solution equilibrium. This method of thermodynamics was easy to implement but not easily observed experimentally. Since then, several researchers have crafted improvement, primarily on the calculation of solubility parameters and characterisation of solid fractions in crude oil (Akbarzadeh *et al*., 2007).

The solubility model is well-established and is based on simplified Flory-Huggins theory. The Flory-Huggins-Zuo Equation of State (FHZ EoS) is a simple theory, highly desirable for oilfield application; this can be achieved by adding the gravity term to the Flory-Huggins theory. The resulting Flory-Huggins-Zuo Equation of State is obtained as shown in Equation 2.1, applicable in the oilfield. For oilfield applications, it is important to specify the asphaltene content as a function of height (hi) in the oil column. For an equilibrated oil column (for which an Equation of State applies), there is no lateral fluid variation (Betancourt *et al*., 2018).

$$\frac{C_a h_2}{C_a h_1} = \frac{OD(h_2)}{OD(h_1)} = \exp\left(-\frac{V_a g \Delta\rho (h_2 - h_1)}{RT}\right) \exp\left(\left(\frac{V_a}{V}\right)_{h_2} - \left(\frac{V_a}{V}\right)_{h_1}\right) exp\left(-\frac{\left[V_a (\partial_a - \partial)^2{}_{h_2} - (\partial_a - \partial)^2{}_{h_1}\right]}{RT}\right) \qquad (2.1)$$

Where Ca (hi) is the asphaltene concentration at height (hi), and OD (hi) is the optical density of the oil in a colour channel; oil colour in the visible-near-infrared (electronic absorption) has been established as linear in asphaltene content.

Va is the molar volume of the asphaltene species of interest from the Yen Mullins model; v is the effective molar volume of the crude oil; g is earth's gravitational acceleration; $\Delta\rho$ is the density difference between asphaltenes and the crude oil; R is the gas constant; T is temperature; and δa and δ are the asphaltene and crude oil Hildebrand solubility parameters respectively (Betancourt *et al*., 2018).

The thermodynamic colloidal model is another model in which asphaltene is considered as a solid particle like colloidal suspension, and absorbed to the resin surface (Zanganeh *et al*., 2018). The loss of side chains can increase in solubility parameters; however, naphthenes have lower solubility parameters similar to aromatics. The molecular weight, density, and solubility parameters of each fraction from essential oils and vacuum residues varied relatively little from source to source (Yarranton *et al*., 2018).

The higher the pressure, the higher the solubility of CO_2 in crude oil. The larger the number of replaced resins by CO_2 molecules, the more a substantial mutual association between asphaltene molecules was observed. The higher the CO_2 content in crude oil, the higher the extraction effect of CO_2 on the crude oil. As the concentration of the solvent is increased, the solubility of the solute significantly decreased, leading to an increase in the amount of the asphaltene precipitation. When the pressure or CO_2 content in the crude oil is further increased to an absolute value, the solubility of CO_2 in crude oil or its extraction effect can achieve a balanced value (also a maximum value), so that the amount of asphaltene precipitation is almost negligible (Chen *et al.*, 2018).

2.7 Crude oil viscosity

Viscosity (thickness or density) is an essential quality of crude oil in which lower density (referred to as light crude) usually yields a higher proportion of the more valuable final petroleum by a simple refining process known as *distillation* (Fattouh, 2010). Heavy crude oils are considered unconventional crude oils because of their high viscosity and density reaching near to or even higher than that of water (Shibulal *et al*., 2017). Crude oil viscosity is a function of several thermodynamic and physical properties such as type and nature of its chemical composition, pressure, bubble point pressure, temperature, oil specific gravity, gas gravity and gas solubility (Hemmati-Sarapardeh *et al*., 2016).

The Least Square Support Machine Vector (LSSM-V) model was designed to predict the viscosity of crude oil (Hemmati-Sarapardeh *et al.*, 2014). The viscosity of oil that lacks volatile components at lower pressure is known as *dead oil*. Determination of crude oil viscosity is a vital parameter for evaluation during the designing of production systems. In the laboratory, the viscosity of crude oil can be analysed by recombining liquids or gases from the separators. As the most accurate method for obtaining values of the reservoir fluid properties from the laboratory data such as pressure, volume, temperature (PVT) is not available, the equation of state (EOS) or empirical correlations can be applied to determine the fluid properties (Hemmati-Sarapardeh *et al.*, 2014). Dead oil viscosity is assumed to be a function of two variables: reservoir oil gravity (API) and reservoir temperature (T).

Equation 2.2 is used to find the viscosity of an unknown crude oil. Where μ is the viscosity; f is the function of the (API,T); od is the oil density; API is the America Petroleum Institute which measured the viscosity of the oil; and T is the reservoir temperature

$$\mu od = f(API, T) \tag{2.2}$$

where μ is the viscosity; f is the function of the (API,T); od is the oil density; API is the America Petroleum Institute which measured the viscosity of the oil; and T is the reservoir temperature.

2.8 Crude oil API gravity content

American Petroleum Institute gravity, a bulk physical property of oils that can be used as a crude oil indicator of thermal maturity, is reported in degrees (API°) (El Bassoussi *et al*., 2018). The most substantial oil has the API value lower than 20^o and for light oil it must be greater than 20^o (Sedghi and Goual, 2014). Heavy oil and residues are viscous with low API gravity ranging from seven to 20. Heavy oil contains many impurities such as asphaltenes, metals, sulphur and nitrogen that pose numerous problems during crude oil production (Alotaibi *et al.*, 2018). The oil samples having API gravities ranging from 20° to 45° are primarily regarded as typical crude oils, whereas those of less than 20° API are usually biodegraded, and above 45° are generally condensate oils. Classified API gravities in the range of massive to light oils are as follow: extra heavy oils: < 10° API, heavy oils: 10° to 22.3° API, medium oils: 22.3° to 31.1° API, light oils: > 31.1° API. All the oil samples recovered from the study area have API° ranging from 30.9° to 44.7° (El Bassoussi *et al.*, 2018) as referenced in Table 2.3.

Light crude oil has a lower specific gravity and a higher than 20^o API value; however, a substantial oil has a stabilised concentration with a higher asphaltene content that leads to its higher density and viscosity. Heavy oil with an API gravity value less than 20^o is commercially unproductive.

It has higher intermolecular force tensions between molecules that stabilise it at room temperature. The viscosity of heavy oil is in the range of 50 to 50,000 mPas, making it highly porous and permeable (Akbarzadeh *et al.*, 2007). Crude oil aromaticity is measured roughly regarding the total aromatic and polyaromatic components (aromatics/resins/asphaltenes) as well as the total metal content (Fe/Ni/Va). Both the crude oil paraffinic content (measured as the saturates) and API gravity increase in the reverse order (Idem and Ibrahim, 2002). Crude oil viscosity is a valuable physical property to the crude oil industry so it should be precisely evaluated for various engineering designs in oil field and refineries (Mansour *et al*., 2018).

Table 2.4 represents the classification of crude oil according to the standard API degree measurement regarding light, medium, heavy or extra heavy.

Table 2.4: Crude oil classification due to their API (Kalam *et al*., 2018)

Classification crude oil	Minimum API (degree)	Maximum API (degree)
Light Oil	31.1	45.4
Medium Oil	22.3	30.2
Heavy Oil	10.0	21.5
Extra Heavy Oil	0.1	6.5

2.9 Hydrocarbons in crude oil

Simanzhenkov and Idem (2003) indicated that naphthenes, aromatics and paraffins are the hydrocarbons found in crude oil. Crude oil is thereby categorised into these three groups of hydrocarbons: paraffin, aromatics and naphthene. In all three categories, branches can be attached to synthesise other hydrocarbons. According to Coutinho *et al.* (2018), there are hundreds of hydrocarbons present in crude oil. Naphthenic hydrocarbons have the formula CnH_2n. All carbon bonds are saturated and as such, naphthenic hydrocarbons in petroleum are relatively stable compounds. Naphthenic hydrocarbons are the most abundant class of hydrocarbons in crude oils. Coutinho *et al.* (2018) also stated that paraffin hydrocarbons are in crude oil. Paraffinic present in smaller or higher amounts in all crude oils, crude oil fractions and products. The cyclic hydrocarbons all have the desirable properties of the alkane’s thermal and chemical stability as well as excellent environmental properties. Wauquier (1995) reported that aromatics constitute only a small percentage of most crude. The most common aromatic in crude oil is benzene, a popular building block in the petrochemical industry. These are the class of cyclic hydrocarbons that have at least one benzene ring as a part of their structure.

Johnny *et al.* (2018) mentioned that hydrocarbon products result in environmental and ecological reverberation, in that most of the hydrocarbon compounds are toxic and relentless in the terrestrial and aquatic environments. Consequently, various physical and chemical methods are used in the removal of contaminants from the environment.

2.10 Sulphur content in crude oil

The third most abundant element in crude oil is sulphur (El Bassoussi *et al*., 2018). Sulphur is highly poisonous and has a foul smell. The crude oil with a low sulphur content (expressed as weight percent) less than unity could be classified as paraffinic, paraffinic-naphthenic or naphthenic. The one with high sulphur (more than unity) belongs to the aromatic intermediate class (El Bassoussi *et al*., 2018). The determination of sulphur using high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS MAS) was first reported by (Huang *et al*., 2008) a method involving the use of high temperature for the detection of sulphur concentration in crude oil. The determination of sulphur has been reported using various analytical techniques, including volumetric (Darjaa *et al.*, 1998), gas chromatography (Machado *et al*., 2011), ion chromatography (Zhong *et al*., 2012), X-ray fluorescence spectrometry (XRF) (Nečemer *et al*., 2003), UV–Vis spectrophotometry (Atanassov *et al*., 2000) and optical emission spectrometry with inductively coupled plasma (ICP-OES) (Young *et al.*, 2011).

The composition changes using polar and high boiling point fractions in heavy oil, as well as refinery processes, can be analysed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) as this elucidates understanding of molecular-level information. It has the capability of analysing the concentration of sulphur and detailing molecular speciation of sulphur contained in any crude oil (Hur *et al*., 2018). Atomic Absorption Spectrometry (AAS) cannot be used for the determination of non-metals such as sulphur because the main absorption lines of this element are below 190 nm (Mior *et al.,* 2013*)*. Crude oil is an organic compound with a minor amount of inorganic species, which can contain from 0,04 up to 5% sulphur. Sulphur is present in the form of thiols. The sulphur content is most importantly used to determine the quality of crude oil of which a significant amount of sulphur in the crude oil lowers the value of oil recovery (Fattouh, 2010). Sulphur content in the crude oil is problematic, however, due to its characterisation as poisonous. Therefore, it should be eliminated during the process of recovering crude oil (Cadorim *et al.,* 2016*)*. Sweet crude oil is considered ‘sweet’ if it contains less than 0.5% sulphur. Sour crude oil contains a total sulphur content of greater than 0.5% (Yasin *et al*., 2013).

3

ASPHALTENE CONTENT OF CRUDE OIL

This chapter focuses on the solvents to extract asphaltene content from crude oil. Three crude oil extract of different API (America Petroleum Institute) gravities were collected and tested for asphaltene and heteroatom content and measured analytically to identify their physical and chemical properties. A comparison was made between the crude oil to solvent ratio, with the two solvent ratios mixed simultaneously. Preference was made on the best optimisation of asphaltene content using paraffin solvents in the extraction of asphaltene compounds from different crude oils, namely A, B, and C. The sulphur content of the three crude oil samples was measured using an appropriate method. The crude oil impurities – known as the heteroatoms content – were analysed using crude oils A, B, and C on an ICP in a laboratory. A conclusion was determined based on relevant analytical findings of their asphaltic/sweetness/sourness and APIg content.

3.1 Methods of asphaltene content

Since asphaltene is colloidal with crude oil, this makes analytical measurements directly in contact with the crude oil and not just the asphaltene. There are several methods which can be used to determine asphaltene content without extraction, including the following: nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), near-infrared (NIR), mid-infrared (MIR), ultraviolet (UV) and fluorescence spectroscopies. There are other techniques available, such as chemo-metrics and multivariate calibration approaches, that can also be used to predict asphaltene content without extraction of asphaltene (Kharrat *et al*., 2013).

Asphaltene content in crude oil depends on the solvent chosen (Mougnol *et al*., 2018). The use of infrared (IR) method on the chemical composition of asphaltene depends on the precipitants used. High-performance liquid chromatography (HPLC) and infrared spectroscopy have also been used for saturating, aromatics, resins and asphaltenes (SARA) characterisation (Fan and Buckley, 2002, Arya *et al.*, 2017). Every type of crude oil has a different type of asphaltene in it that behaves differently. Different asphaltene has different aromatic structures that are not identical (Speight, 1994**)**. There are many hydrocarbons in asphaltene which can adequately define the behaviour and properties of asphaltene molecules in crude oil. Asphaltene molecules mainly consist of naphthenic, aromatic hydrocarbons and alicyclic (Abdel-Raouf, 2012a).

3.2 Asphaltene precipitation region

The change in reservoir fluid composition, temperature and pressure might affect the thermodynamic equilibrium of asphaltenes-resins micelles and thus cause asphaltene precipitation (Ali *et al*., 2015). The precipitation of asphaltene occurs as a result of changes occurring in the reservoir which are determined by pressure, temperature and composition. Drilling, acid stimulation, and hydraulic fracturing activities can also induce precipitation in the near-wellbore region. The region in which precipitations occurs is called asphaltene precipitation envelope (APE) or asphaltene deposition envelope (ADE) (Ghorbani *et al.*, 2016).

Some experimental studies claim reversibility of the asphaltene precipitation with pressure at high temperatures (Hirschberg *et al*., 1984). On the other hand, reversibility concerning the composition at low temperatures is still a relevant topic of debate. As it is believed that dissolution of the precipitated asphaltene is a kinetically slow process, an extended period is thus required for reversibility (Pan *et al*., 1997). Experimental investigations, however, have proven the reversibility of the asphaltene precipitation at high temperatures (reservoir temperatures) concerning pressure or composition (Pan *et al*., 1997, Hemmati-Sarapardeh *et al*., 2013).

3.3 Temperature and pressure effects on asphaltene precipitation

Consequently, a smaller mass of asphaltenes will precipitate at higher temperatures. It can be mentioned in the solubility theory that the total mass of asphaltene nanoaggregates destabilised by the addition of n-alkanes at elevated temperatures is lesser than that at lower temperatures (Maqbool *et al.*, 2011). The higher temperatures could lead to fewer particle collisions resulting in a slower rate of aggregation. It could take the particles a longer time to reach the micrometre size and be detected by optical microscopy (Maqbool *et al.*, 2011).

The precipitant used is also an essential consideration in investigating the role of temperature on the solubility of asphaltenes. The asphaltenes become less soluble in n-propane as temperature increases. However, for other heavier solvents such as pentane (C_5+), a higher stabilisation of asphaltene with an increase in temperature is observed (Wu *et al*., 1998). The higher temperatures and lower viscosity will lead to a shorter onset time for precipitation (Maqbool *et al*., 2011). The viscosity of the crude oil can be decreased by varying temperature which leads to an increase in the diffusion rates in the crude oil as a whole. Increasing temperature can enhance adsorption by breaking up the associations that hold together asphaltene aggregates, thus exposing surface active sites that are buried or bound up within aggregate structures (Adams, 2014). It is accepted that the size of asphaltene aggregates decreases with increased temperature of the supporting medium (Pierre *et al*., 2004).

Several other studies have reported that adsorption decreases with increasing temperature or is unaffected (adsorption is exothermic) (Franco *et al*., 2013). It seems that when injection pressure increases, asphaltene remains dissolved in the reservoir fluid; however, at low pressure, this solubility decreases. Furthermore, the colossal distance between asphaltene particles and the particles of the surrounding fluid cause more precipitation of asphaltene at lower pressures (Alian *et al*., 2011).

3.4 Asphaltene precipitation

In refining and processing operations, asphaltene self-aggregation and precipitation can cause a wide variety of problems, from equipment and flow-line plugging to catalyst deactivation (Gawel *et al*., 2005, Speight, 1999). There are some reservoir fields (Boscan field in Venezuela) with 17 wt% asphaltene, while no asphaltene precipitation was observed in other fields (Hassi-Masoud in Algeria) with 0.15 wt% asphaltene. Numerous production problems arise due to asphaltene precipitation and deposition (Alta'ee *et al*., 2010). Asphaltene precipitation manifests itself in almost all areas of crude oil production, transport and processing. Asphaltene particles destabilised by a variety of factors flocculate precipitate and deposit onto the pore space of rock formations (Nalwaya *et al*., 1999).

Asphaltene forms the most polar fraction of crude oil which therefore decreases the rock permeability and the oil recovery. This causes operational problems and therefore necessitates understanding from studies to prevent the asphaltene precipitation that may lead to blockages of pumps (Kamari *et al*., 2015). The mechanism of asphaltene precipitation can be described as a process of destabilisation of asphaltene nanoaggregates from the crude oil due to the addition of a precipitant (Maqbool *et al*., 2011). The external cause for asphaltene precipitation is the variation of reservoir pressure and temperature, while the variation of oil composition is the internal cause (Dong *et al*., 2014). The effects of these three factors are mainly on the variation of the asphaltene-dissolving capacity of crude oil. The reservoir rock and the composition of formation water further affect the precipitation of asphaltene (Dong *et al*., 2014).

When two densities of different crude oils are mixed, for example, light and heavy oil, this can trigger asphaltene precipitation which will occur over a temperature range (Hung *et al*., 2005). The problematic asphaltenes will precipitate by pressure depletion during oil recovery, so adding an artificial precipitant is necessary to study asphaltene behaviour unless a high temperature and pressure recombined oil is used (Hoepfner *et al*., 2013). Introducing the light and saturated hydrocarbons to the crude oil or change in the number of aromatic and resin fractions may increase the risk of asphaltene precipitation (Meighani *et al*., 2018).

These substances, called *dispersants*, should reduce or retard the precipitation of asphaltenes or diminish the tendency of aggregates to build up on surfaces (Cohrs *et al*., 2012). Good dispersants should also reproduce the interactions that occur between asphaltenes, or instead, be capable of pi-pi interactions and hydrogen bonding. For this purpose, these dispersants need to be Lewis acids or bases, depending on whether the asphaltenes are carried positively or negatively (Chávez-Miyauchi *et al*., 2013). Chang and Fogler (1994) concluded that good dispersants should have an aromatic ring with a polar group and an aliphatic chain. Linear alkylbenzene sulfonic acid and 4-n-octyl benzoic acid are the two dispersants that meet these requirements and thus are already used in the petroleum industry (Kelland, 2014). *Flocculation* is the process of aggregation of fine particles, starting in the reservoir as soon as the pressure of the reservoir drops at the near wellbore (Ali *et al*., 2015).

Two compounds primarily occur during precipitation, namely asphaltene and waxes, so these two components are the most massive compounds in crude oil. Asphaltene is one of the components that cause blockages and many other damages during the production of crude oil where precipitation and deposition occur. Asphaltene precipitation can be monitored and controlled to reduce costs during production and refining processes. During asphaltene precipitation, deposition of asphaltene is constantly monitored (Hung *et al*., 2005). Several standard procedures are available to precipitate asphaltenes from crude oil. The conventional method is first to precipitate the whole asphaltene subfraction from the crude oil by adding an excess of the n-heptane or n-pentane to the crude oil (40 volume of solvent: to 1 volume of oil) (Zorzenão *et al*., 2018).

It is not always easy to control asphaltene precipitation, but some aspects have been studied and analysed to predict the asphaltene precipitation. The focus point of all precipitation happens during the bubble point where the vapour is formed from the liquid and thereby causing asphaltene to precipitate, which can prevent the asphaltene precipitation by monitoring the bubble point. However, the higher the bubble point, usually caused by the factors that trigger asphaltene precipitation, the lower its precipitation (Hung *et al*., 2005). Pentane and heptane solvents provide a different amount of precipitated asphaltene from the same crude oil. However, these precipitated asphaltenes differ notably concerning their aromaticity (hydrogen/carbon atomic ratio) and average molecular weight (Shukla, 2018). Several studies about the colloidal nature of asphaltenes and its self-association phenomenon were reported many years ago (Hung *et al*., 2005). Asphaltenes self-associate and their molecular weight, density and solubility parameter distributions are the internal factors in asphaltene precipitation (Powers *et al*., 2016). Knowing the thermodynamical behaviour of asphaltene molecules and the sample produced by crude oil will render an essential understanding of the asphaltene precipitation that occurs in both light and heavy crude oil (Rogel *et al*., 2015).

The more the paraffinic the crude oil is, the lower the asphaltene content which therefore brings to an understanding that precipitation occurs in light oil more than heavy oil. Additionally, light paraffin typically gets blended with the more substantial crude oil, inducing asphaltene precipitation (Rogel *et al*., 2016). Polyaromatic cores in crude oil can interact with other aromatic compounds and polar groups in asphaltenes leading to asphaltene precipitation (Ilyin *et al*., 2016). In general, these changes and their effects are relatively well-understood based on experimental evidence as well as thermodynamic modelling. However, the reason why some crude oils produce deposits while others do not, even under similar conditions, is still a matter of intense research. In particular, it has been challenging to link asphaltene chemical characteristics with their solubility/deposition behaviour (Rogel *et al*., 2015). Asphaltene precipitation is determined by measuring the amount of precipitate regarding the crude oil weight at different ratios (volumes) of precipitants (Meighani *et al*., 2018).

3.5 Asphaltene structures and molecular weight/size

Asphaltene molecular weight has been widely investigated for quite some time. From an industrial application point of view, asphaltene molecular weight is important for setting up a heavy oil refining strategy so that the process is both efficient and economically viable. If the measured average molecular weight of asphaltene is high and is the true molecular weight, then a substantial amount of energy will be needed to break the molecule into light products during the refining process (Khalaf and Mansoori, 2018). Vapour pressure osmometric (VPO) can be used to measure the molecular weight of asphaltene; however, the measuring of the molecular weight is not accurate (Cunico *et al*., 2004).

Nanofiltration can be used to investigate the size of asphaltene aggregate precipitated during CO_2 /CH_4 injection. Nanomembranes of 200 nm, 100 nm and 30 nm were used to filter the oil sample, injected by a mole fraction of CO_2 and CH_4 gas. It was observed that asphaltene aggregate size at various injected CO_2 and CH_4 concentrations were obtained. Then these were compared with the pore size distribution data of shale that was measured by mercury intrusion porosimetry. The results showed that the higher CO_2 and CH_4 concentrations caused more asphaltene precipitation and growth in asphaltene aggregate size (Shen and Sheng, 2016). Density is mainly sensitive to the hydrocarbon type rather than molecular weight. For example, the densities of n-alkanes with molecular weights greater than 170 g/mol do not significantly change with increasing carbon number (up to 310 g/mol) (Yarranton *et al*., 2018). The structure of asphaltene with four to 10 fused rings has been a challenge to determine whether asphaltene is monomeric (one fused ring systems per molecule) or polymeric (more than one ring) (Badre *et al*., 2006).

The asphaltene on their monomeric and polymeric structure is represented in Figure 3.1, where 1.5 nm and 2 nm is a representative structure of an asphaltene monomeric. Moreover, 5 nm is an asphaltene polymeric.

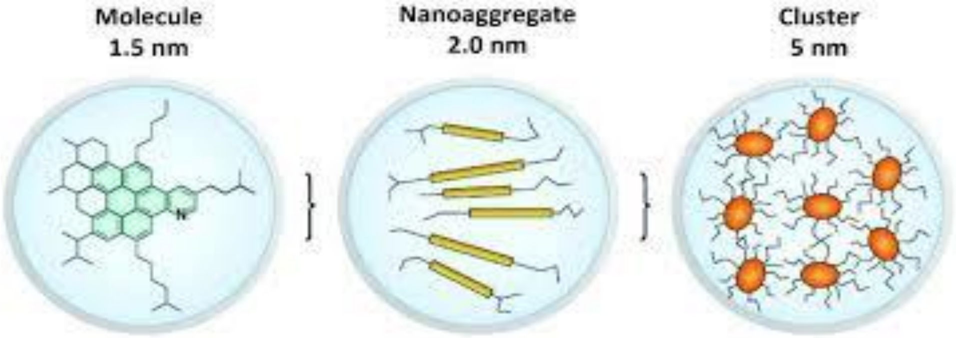


Figure 3.1: Asphaltene monomeric and polymeric structure (Rashid *et al*., 2019)

The Fluorescence Depolarization (FD) or the Transmission Electrons Microscope (TEM) can be used to investigate the size of the asphaltene molecules. The asphaltene molecular weight is roughly 750 g/mol, ranging in size from roughly 500-1000 g/mol in petroleum asphaltene (Groenzin and Mullins, 2000). Many instruments were used in the discussion of the asphaltene molecular size, for instance, the use of ionisation spectroscopy, and field ionisation mass spectroscopy (FIMS) gave a mean value of the molecular weight of asphaltene range at 700 g/mol (Buch *et al*., 2003). The model compound analysis shows that the size range corresponds to approximately 500 to 1000 g/mol in agreement with mass spectroscopy results (Groenzin and Mullins, 2000). Moreover, the diameter of the asphaltene molecules was found to be in the range of 10-20 Å (Groenzin and Mullins, 2000). All asphaltenes presented approximately the same molar mass range, around 400 g/mol (Aguiar and Mansur, 2015).

3.6 Types of hydrocarbons in asphaltene

Every source of crude oil has a different type of asphaltene and aromatic structure within it, which behaves differently in chemical composition (Speight, 1994). There are many hydrocarbons in asphaltenes which can adequately define the behaviour and properties of asphaltene molecules in crude oil, consisting primarily of naphthenic, aromatic hydrocarbons, and aromatic ring systems with alicyclic chains (Abdel-Raouf, 2012a). The asphaltene molecule has a similar structure to kerogen with the smallest size and less condensed aromatic nuclei. Asphaltene is a macromolecular compound that consists of different hydrocarbon content from different crude oils. The hydrocarbon content in asphaltene is classified according to the different crude oil type.

Asphaltene does not have a molecular structure that is universally understandable; it can only be identified on the origin of the crude oil type. Every crude oil type has its own elementary and chemical compositions of hydrocarbon content (Snowdon *et al*., 2016). The type of asphaltenes, their concentration and the level of self-association have a significant impact on the viscosity of crude oils (Giraldo *et al*., 2013).

3.7 Asphaltene dissolution by a strong organic acid

Asphaltene reactions, due to their stabilisation, can be very well understood in comparison with the conducting polymers like the polymeranaline (PANI). They both have similarity in their fused benzene rings and the heteroatomic atoms like nitrogen, oxygen, and sulphur whose lone electron pairs can be protonated in the sense of donating or change atoms positively (HONORS, 2017).

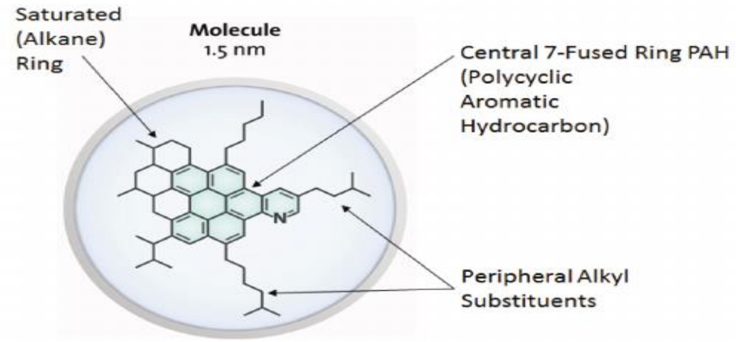


Figure 3.2: Asphaltene with fused benzene rings and heteroatoms attached (Mullins *et al.,* 2015)

It was determined that the protonation reaction occurred when an addition of a strong acid named dodecylbenzene (DBSA) is reacted with asphaltene. The long-chained tails of the acidic molecules can create solvation shells around the large and highly aromatic asphaltene molecules. The solvation or dissolution is a process of an ion or molecules dissolving in a solvent where hydrogen and van der Waals forces are driving factors. This solvation shell created by DBSA can allow asphaltene to dissolve even in traditional asphaltene precipitants like heptane (HONORS, 2017).

3.8 Absorption and adsorption of asphaltene

The expectation is that the stronger the interaction of the solvent with the asphaltenes and resins, the more intense the absorption of the resulting solution will be (Aguiar and Mansur, 2015). Adsorption of asphaltenes onto a surface is determined by both their chemical and structural characteristics (Gray *et al*., 2011). As the adsorption behaviour that exists in the presence of high asphaltene concentrations is complex, it has not yet been adequately described analytically (Gaboriau and Saada, 2001).

The source of asphaltenes, adsorption conditions, charge behaviour and hydrophilicity of the particles are essential for determining which types of asphaltenes adsorb, the properties of the adsorbed asphaltene aggregates, and how the resulting surfaces become modified. A mechanism for how the stability of asphaltenes affects particle behaviour was recently proposed, stating that as the stability of the asphaltenes, within the oil matrix, approaches or exceeds the point of flocculation, the resulting asphaltene-coated particles also become significantly destabilised (Adams, 2014).

With fewer asphaltene molecules in a solution, the adsorption is rapid. In the case of oil-water interfaces, the timescales are similar for various oils, but the variation with asphaltene concentration is qualitatively different: adsorption becomes faster with increasing concentrations of oils that are useful in asphaltene solvents. The presence of surfactant changes the adsorption process significantly (Jeribi *et al*., 2002). Asphaltene adsorption is a negative phenomenon to be avoided in reservoirs, pipes and production equipment. Asphaltene could form aggregates which can be adsorbed onto reservoir rocks and mineral surfaces (Castillo *et al*., 2017).

3.9 Solubility and insolubility of asphaltenes

The asphaltene insolubility does not affect or reach the surface because of the more substantial the asphaltene compounds, the more difficult the solubility, resulting in difficulty on its deposition on the surface. The higher the molecular weight of an asphaltene the less soluble it is (De Boer *et al*., 1995). The inhibitors can be used to detect the asphaltene contents and analyse its solubility. For example, the solvent n-heptane was used as an inhibitor to detect the solubility of crude oil (Vananton, 1997). The reason why some crude oils deposit while others do not, in the same conditions, is because of their solubility which can be best described as the phenomena of asphaltene precipitation and deposition (Rogel *et al*., 2015). Temperature and pressure mainly cause solubility of asphaltene. The lower the solubility, the higher the asphaltene precipitation under the stated condition, thereby resulting in the asphaltene deposition on the surface (De Boer *et al*., 1995).

Higher molecular weight, boiling point and density will result in less solubility of asphaltene (Hasanvand *et al*., 2015). The solubility can, therefore, define a particular asphaltene. The lower the asphaltene solubility, the higher its deposition on the surface (Rogel *et al*., 2015). The solubility of asphaltene depends upon the mutual balance between the asphaltene fraction and the lighter fractions of the crude oil (Abdel-Raouf, 2012c). Flory-Huggins model is the most common method applied to solubility approach. Asphaltene solubility can be obtained, especially at higher solvent ratios, and separation of resin molecules is likely a reason for higher precipitation of asphaltene at high-pressure conditions (Meighani *et al*., 2018).

Generally, in light oil reservoirs, asphaltene solubility is low, rendering asphaltene unstable and increasing the possibility of precipitation (Alian *et al*., 2011).

The solvents in Table 3.1 have been categorised as eco-friendly solvents which are currently utilised for various industrial applications such as purification, pre-formulation studies and dosage form design of pharmaceuticals/drugs in pharmaceutical industries. Moreover, they can be utilised during the extraction of asphaltene precipitation in various quantities depending on their solubility (Kalam *et al*., 2018).

Table 3.1: Solubility of asphaltene in various solvents (Speight, 1994) where δ = solubility parameter, y = surface tension, and v = molar volume

Solvent	$\delta = yv^{-1/3}$	Solubility (wt%)
	Normal hydrocarbons	
Pentane	3.2	0
Hexane	3.5	18.3 (20.1)
Heptane	3.8	30.1 (32.5)
Octane	3.9	38.9 (42.0)
Nonane	4.0	40.3 (44.4)
Decane	4.1	43.2 (46.7)

The solubility parameter values of crude oil-solvent mixtures were calculated from the weighted average of the solubility parameters of pure solvents using ultraviolet-visible (UV–Vis) spectroscopy (Aguiar and Mansur, 2015). The precipitant n-alkane has the ability to reduce the overall solubility parameter of the system which therefore causes a higher driving force for asphaltene destabilisation and aggregation by the influence of temperature. The higher temperatures and the lower solubility of asphaltenes will lead to faster aggregation and shorter onset time for the detection of precipitation. The precipitant used is also an essential consideration in investigating the role of temperature on the solubility of asphaltenes (Vargas *et al*., 2009). (Maqbool *et al*., 2011) have used the-SAFT equation of state to model how asphaltene solubility can either increase or decrease with increasing temperature.

According to (da Silva *et al*., 2014), different grades of crude oil have different solubilities due to changes in liquid composition, density and viscosity; this can be affected by temperature range. The higher the asphaltenic content, the greater the viscosity. When different crude oils are blended, asphaltene precipitation can be promoted due to its instability in an oil mixture. The gas solubility is an active function of the pressure, the temperature, the API gravity and the gas gravity.

The gas solubility reaches its maximum value at the bubble point pressure, and all the available gases are dissolved in the oil (Tarek, 2007). When a gas dissolves, it does so because its molecules interact with the solvent molecules. As temperature rises, the solubility of a gas decreases, leading to the solubility of the oil to increase as pressure increases.

The gas is the influence on the solubility of the oil. The heat is released when these new attractive interactions form, as dissolving most gases in liquids is an exothermic process (Hassan *et al*., 2016). As the oil-precipitant mixture is heated, its lighter fractions, predominantly alkanes, expand and efficiently reduce the solubility parameter of this mixture, rendering the asphaltenes less soluble in it. This process is analogous to a reservoir situation where the asphaltenes become more unstable as the crude oil is depressurised from the reservoir pressure to the bubble point pressure (Kraiwattanawong *et al*., 2007). The solubility of asphaltenes, the most substantial fraction in any crude oil, depends on the delicate balance between this fraction and the lighter fractions of the crude. Any disturbance in this balance could lead to asphaltene self-aggregation (Leontaritis and Mansoori, 1988).

3.10 Asphaltene conductivity

Figure 3.1 represents the conductivity of asphaltene. The slope change could mean a transition in the crude oil micro-structure which governs the macroscopic properties. These results prove that the apparatus will be useful for providing more particular knowledge of the crude oil (Charin *et al*., 2017). The strong interactions of ions with colloidal species and their influence on aggregation and flocculation processes justify a study of asphaltene-ion system conductivity (Behar *et al.*, 1998). The electrical conductivity of crude oil can be a function of various physical and chemical properties. In addition to large fraction content and viscosity, other competing variables, such as the nature of each compound regarding its effect on charge transfer, may govern the conductivity of crude oils. The crude oil conductivity varies exponentially with temperature (Charin *et al., 2017).* Figure 3.1 shows that the slope of the Arrhenius plot has changed for all crude oils, at about 70 to 90^{o}C.

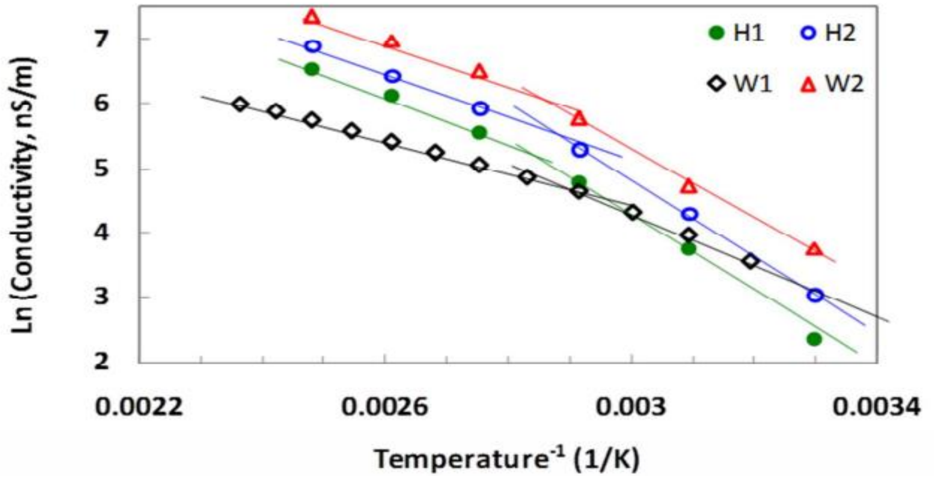


Figure 3.3: Arrhenius plot for the AV measurement up to 150°C. A slope change of Arrhenius plot also is observed (Charin *et al*., 2017).

The electric conductance in aliphatic hydrocarbons is most likely related to the presence of polar impurities or trapped electrons present in the liquid or generated at the electrode surface. The crude oil electrical conductivity against temperature showed exponential behaviour. Crude oils rich in polar compounds tend to be more conductive than other crude oils. However, at lower temperatures, the effect of crude oil viscosity was significant (Charin *et al*., 2017).

The set up in Figure 3.4 was developed to measure the conductivity of various crude oils at the reservoir conditions. The experimental apparatus consists of the jacket high-pressure vessel (SS316L) with maximum working pressure and temperature of 130 bar and 3500°C, respectively. Moreover, a high-pressure syringe pump (Teledyne Isco, model 260D) was employed to maintain pressure to the cell using nitrogen as an inert gas.

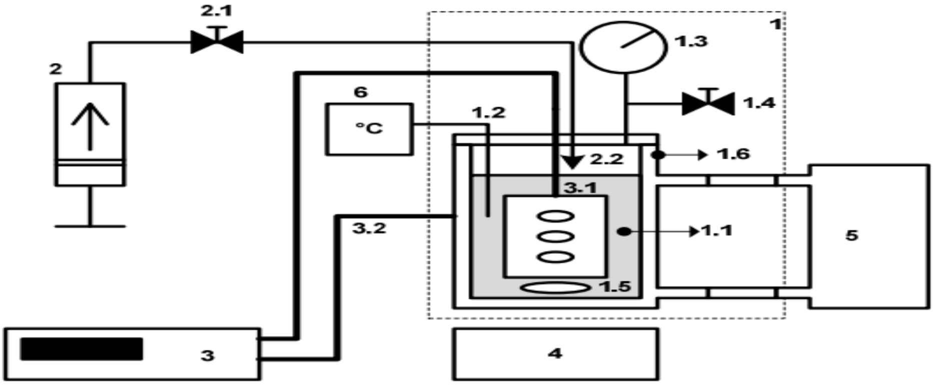
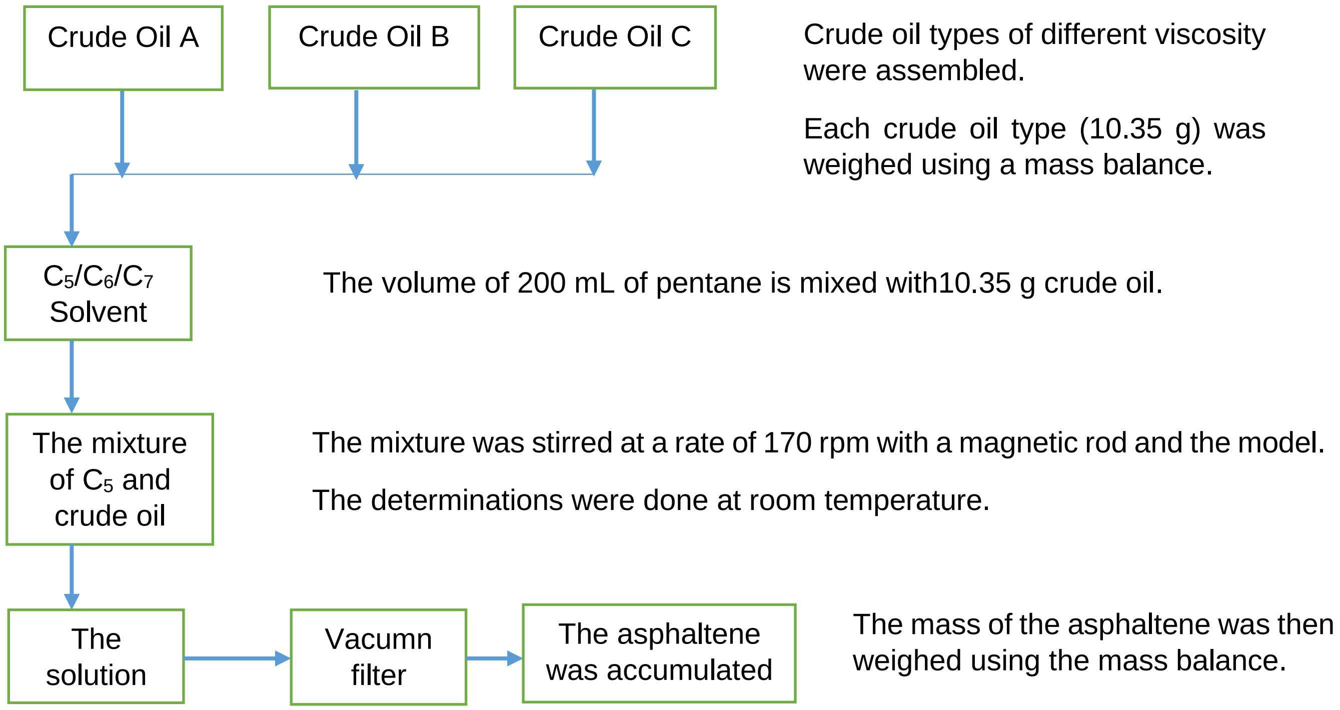


Figure 3.4: Experimental setup for measurement of petroleum electrical conductivity (Charin *et al.*, 2017) with conductivity cell (1.1), petroleum sample (1.2), temperature transducer Pt100 (1.3), pressure gauge (1.4), discharge valve (1.5), magnetic bar (1.6), heating jacket (2), syringe pump (2.1), valve (2.2), inert gas N_2 (3), pico-ammeter (3.1), internal electrode (3.2), external electrode (4), magnetic stirrer (5), and path for controlling temperature with circulating silicone oil (6)

3.11 Methodology

The flow diagram below represents the experiment set up conducting the accumulation of asphaltene content from 3 crude oil types. It is the break down of the experiment during the laboratory experiment on how each procedure was conducted. However on the flow diagram below only a single experiment is shown, in which similarity procedure was imitated to elucidate the same objectives on procuring asphaltene content.

The experiment was all conducted at room temperature observed in figure 3.5. The material safety data sheet (MSDS) of each solvent and crude oil was provided and studied before proceeding.



Crude oil types of different viscosity were assembled.

Each crude oil type (10.35 g) was weighed using a mass balance.

The volume of 200 mL of pentane is mixed with10.35 g crude oil.

The mixture was stirred at a rate of 170 rpm with a magnetic rod and the model.

The determinations were done at room temperature.

The mass of the asphaltene was then weighed using the mass balance.

Figure 3.5: Block of flow diagram showing experimental approach

Three types of crude oils – A, B and C – were used in the determination of asphaltene precipitation.

Three sets of experiments were conducted using different solvents such as pentane (C_5), hexane (C_6) and heptane (C_7). The oil-solvent mixtures were prepared in the following ratios: 40:1 (5 g of crude oil into a 200 mL solvent); 30:1 (5 g of crude oil into a 150 mL solvent); and 20:1 (5 g of crude into oil 100 mL solvent). Furthermore, a 20:1*mixture (2.5 g of crude oil into 50 mL) was also prepared.

All the above mixtures were stirred at 170 revolutions per minute (rpm) using a magnetic stirrer before undergoing filtration.

Each crude oil-solvent ratio solution was vacuum filtered using the water pressurising pump to extract asphaltene from the solution mixture. The experiment was conducted at room temperature (25^{o}C).

The second experiment was conducted by mixing two solvents before the crude was dissolved. The solvents were mixed at a 1:1 ratio (100 mL of one solvent mixed into 100 mL of the second solvent) to give a total volume of 200 mL. Then, 5 g of each crude oil type was dissolved in the above solvent mixture. A similar experiment was conducted by mixing two solvents at 3:1 ratio (75 mL of one solvent mixed into 25 mL of the second solvent) to give a total volume of 100 mL. 2.5 g of each crude oil type dissolved in the 3:1 solvent mixture. The solvent-to-solvent ratio of 3:1 was readily flocculated with the crude oil to aggravate the asphaltene content to precipitate.

All solvents mixtures were filtered using the filter paper. The process of the filtration took place in the vacuum filter in which 0.22 µm filter paper was used during the filtration of the asphaltene particles from each crude oil, A, B and C. The tap water pressurised the drying process of the asphaltene particles. The solution remaining in the beaker was named maltene, the remainder of bioproduct during the filtration.

Equation 3.1 below represents the calculation of asphaltene content which was used to calculate the asphaltene content of each crude oil type and tabulated.

$$\text{Asphaltene content} = \frac{\text{Weight of dried asphaltene (g)}}{\text{The volume of the crude oil used (mL)}} \times 100 \qquad (3.1)$$

After obtaining asphaltene content, further analysis for heteroatoms was conducted using gas chromatography-mass spectrum (GC/MS), indulging coupled plasma (ICP) for impurities in the three crude oil types. The separation was performed on a gas chromatograph (6890N, Agilent technologies network) coupled to an Agilent technologies inert XL EI/CI Mass Selective Detector (MSD) (5975B, Agilent Technologies Inc., Palo Alto, CA). The GC-MS system was coupled to a CTC Analytics PAL auto-sampler. Separation of fatty acids was performed on a non-polar ZB-Semi- volatile (30 m, 0.25 mm ID, 0.25 µm film thickness) Zebron 7HG-G027-11-GGA capillary column. The gas used was helium (He) as a drying gas, at a flow rate of 1 mL/min. The temperature of the injector was kept constant at 250°C. Finally, 1µl of the sample was injected in a split ratio set at 5:1 split ratio.

The temperature of the oven was manipulated at 40°C for three minutes, and finally ramped up to 325°C at a rate of 6°C/min and held for 10 minutes.

The MSD was operated in a full scan mode, and the source and quad temperatures were maintained at 230°C and 150°C, respectively. The transfer line temperature was maintained at 250°C.

The mass spectrometer was operated under electron impact mode at ionisation energy of 70 eV, scanning from 35 to 500 m/z. The solvent delay was set at four minutes.

The procedures were conducted three times for each solvent and after that, the average of the asphaltene content was calculated using Equation 3.1, with results tabulated in Tables 3.10-3.12.

3.11.1 Experimental

All chemicals utilised were of analytical grade (AR grade). Pentane (C_5H_{12}) (Merck,100%), hexane (C_6H_{14}) (Merk,100%) and heptane (C_7H_{16}) (Merk, 100%) were used as the precipitants on the asphaltene extraction on the crude oils. The alkanes (paraffin) are non-polar solvents and are miscible solvents with other non-polar substances with similarities properties. Alkanes are suitable for the extraction of asphaltene on the crude oil used in these experiments because asphaltene is polar. The properties and characteristics of the solvents used are indicated in Table 3.2.

Table 3.2: Properties of the solvents used in for the experimental

Molecular Name	Formula	Molar weight	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State at (20°C)
Pentane	C_5H_{12}	72.15	–130	36	0.626 g/mL	Liquid
Hexane	C_6H_{14}	86.18	–95	69	0.659 g/mL	Liquid
Heptane	C_7H_{16}	100.20	–91	98	0.684 g/mL	Liquid

Three crude oil types A, B and C were supplied with their material safety data sheets (MSDS) by Chevron Company, Cape Town, South Africa. The magnetic stirrer was named Zeal Tech, model (09201); Standard: Rod, Teflon Magnet.

The solvent-oil mixtures, of which their preparation mixtures were discussed in Tables 3.3-3.6, can be tabulated as follows:

Table 3.3: Preparation set up for mixtures of solvent to oil ratio (40:1) at 25ºC

	Solvents	**Mass of the crude oil (g)**			**The volume of the solvent (g)**		
		Run1	Run2	Run3	Run1	Run2	Run3
Crude Oil A	(C_5)	5	5	5	200	200	200
	(C_6)	5	5	5	200	200	200
	(C_7)	5	5	5	200	200	200

For all three crude oil types weighing at 5 g and the three solvents at the same temperature as above, a similar experiment was conducted with solvent volumes 150 mL and 100 mL

Table 3.4 represents the preparation of the mixtures when 2.5 g crude oil for the three crude oil types is dissolved in a 50 mL solvent.

Table 3.4: Preparation set up for mixtures of solvent to oil ratio (20:1)* at 25ºC

	Solvents	**Mass of the crude oil (g)**			**The volume of the solvent (g)**		
		Run1	Run2	Run3	Run1	Run2	Run3
Crude Oil A	(C_5)	2.5	2.5	2.5	50	50	50
	(C_6)	2.5	2.5	2.5	50	50	50
	(C_7)	2.5	2.5	2.5	50	50	50

A similar procedure was repeated for the other crude oil A and B at constant crude oil mass of 5 g conducted at the same constant solvent volume of 50 mL for each solvent.

Two solvents were mixed at a 1:1 ratio and 5 g of crude oil were dissolved in the solution, with results indicated in Table 3.5.

Table 3.5: Preparation set up of oil mixed with two solvents at a ratio (1:1) at 25ºC

	Solvents	**Mass of the crude oil (g)**			**The volume of the solvent (g)**		
		Run1	Run2	Run3	Run1	Run2	Run3
Crude Oil A	(C_5+C_6)	5	5	5	(C_5+C_6)	(C_5+C_6)	(C_5+C_6)
	(C_6+C_5)	5	5	5	(C_6+C_5)	(C_6+C_5)	(C_6+C_5)
	(C_5+C_7)	5	5	5	(C_5+C_7)	(C_5+C_7)	(C_5+C_7)

For all three crude oil types weighing 5 g and the three solvents at the same temperature as above, a similar experiment was conducted with solvent volume 100 mL of each solvent to a total volume of 200 mL.

Table 3.6 reveals that 75 g of each solvent mixed with 25 g of another solvent mixed simultaneously with results of the total solvent volume of 100 mL.

Table 3.6: Preparation set up of oil with two solvents mixed at a ratio (3:1) at 25^{o}C

	Solvents	**Mass of the crude oil (g)**			**The volume of the solvent (mL)**		
		Run1	Run2	Run3	Run1	Run2	Run3
Crude Oil A	(C_5+C_6)	2.5	2.5	2.5	(C_5+C_6)	(C_5+C_6)	(C_5+C_6)
	(C_6+C_5)	2.5	2.5	2.5	(C_6+C_5)	(C_6+C_5)	(C_6+C_5)
	(C_6+C_7)	2.5	2.5	2.5	(C_6+C_7)	(C_6+C_7)	(C_6+C_7)

Table 3.7 clearly emphasised the three main compounds found in each crude oil type, the percentage of each compound found, and therefore the analysis in comparison of the asphaltene extraction from a variety of solvents.

Table 3.7: Tabulated results of the compounds found in each crude oil type

Compounds Name	**Crude oil A** **132** Compounds (GC-MS)	**Crude oil B** **135** Compounds (GC-MS)	**Crude oil C** **138** Compounds (GC-MS)
Paraffins	78 **(59.09%)**	85 **(62.96%)**	42 **(30.43%)**
Aromatics	25 **(18.94%)**	28 **(20.74%)**	63 **(45.65%)**
Naphthene	17 **(12.88%)**	13 **(9.63%)**	0 **(0%)**

3.11.2 Analysis of metals and non-metals using ICP

The following procedure was conducted before the analysis of the ICP.

The sample of 0.25 g was weight in the microwave vessels, and then the volume of nitric acid (HNO_3), 3 mL H_2O_2 (peroxide) and volume of water (H_2O) of 2.5 mL were added in the mixtures. It was left for 20 minutes on an open surface for pre-digestion before sealing the vessels and proceeding to the heating programme (oil digestion).Instrument: MARS microwave digester

Model: MARS 5

Microwave Method

Power Level – 1600W, 100%

Ramp Time – 25 minutes (time taken to heat the sample from 20°C to 210°C)

Pressure - 800 psi

Temp – 210°C

Hold time – 10 minutes (time that the sample speny in the microwave under above conditions)

Cool down time was 25 minutes (default setting of the microwave after microwaving). Weighed out 9 mL of deionised water in a sample bottle cleaned in 10% HNO_3 and adding 1 mL of the digest to it. The sample is then ready for analysis.

Crude oil C, after the user of the indulged couple plasma (ICP), shows greater metals content in nickel (Ni), iron (Fe), vanadium (V) and non-metals content such as sulphur (S) and nitrogen (N), as tabulated in Table 3.8.

Table 3.8: Metal and non-metal content in crude oils A, B and C using ICP

	Al mg/L	**Fe mg/L**	**Ni mg/L**	**V mg/L**	**S mg/L**	**N %**
Accuracy %	***104***	***102***	***105***	***98***	***103***	***101***
Digestion oil A	<1	<0,3	<0,3	0.4	565	0.11
Digestion oil B	<1	<0,3	<0,3	0.4	551	0.07
Digestion oil C	<1	1.8	3.5	4.8	2391	0.39

Nitrogen was not analysed on ICP as the other elements. An elemental analyser was used for nitrogen which is the method used for combustion of the sample to turn all the nitrogen into a gas form. Accuracy stated in the result sheet is the method accuracy based on the quality control sample analysed in the run of the samples. This has no relevancy to purity.

For crude oil A the density was 0.965 g/cm^3 (965 000 mg/dm^3). The total Sulphur content in

Crude oil A was $(565\ mg/l)/(965\ 000\ mg/l)\ \times 100\ = \mathbf{0.059}\ \%$ (3.1)

Crude oil B was $(551\ mg/l)/(972\ 000\ mg/l)\ \times 100\ = \mathbf{0.057}\ \%$ (3.2)

Crude oil C was $(2391\ mg/l)/(985\ 000\ mg/l)\ \times 100\ = \mathbf{0.243}\ \%$ (3.3)

The three crude oil A, B and C were found to be sweet crudes due to their sulphur content of below 0.5%.

3.12 Results and discussion

Table 3.9 represents the percentage concentration (m/v) of the asphaltene content in the three types of crude oil using n-pentane as a solvent, with Equation 3.1 used to calculate the asphaltene content.

Table 3.9: Tabulation of asphaltene content from three crude oils at a solvent volume of 200 mL

	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	5.1 g	5.1 g	4.8 g	4.8 g	4.9 g	5.2 g	5.0 g	5.1 g	5.0 g
Volume solvent	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL
mass asphaltenes deposited	0.29 g	0.39 g	0.31 g	0.35 g	0.33 g	0.37 g	1.18 g	1.13g	1.17 g
Average mass	**0.33 g**			**0.35 g**			**1.16 g**		
Average asphaltene content % (g/mL)	**6.6 g/mL**			**6.8 g/mL**			**23.2 g/mL**		

A similar calculation for the other solvents on the three crude oil types was done, with results tabulated in Appendix A.

Table 3.10 is the tabulation of the three crude oil results on their asphaltene content using Equation 3.1.

Table 3.10: Crude oils A, B and C asphaltene content from solvent to oil ratio

	Solvents	**Ratio (40:1) 200 mL into 5 g**	**Ratio (30:1) 150 mL into 5 g**	**Ratio (20:1) 100 mL into 5 g**	**Ratio (20:1)* 50 mL into 2.5 g**
Crude Oil A	Pentane (C_5)	6.6	11	9.2	13.2
	Hexane (C_6)	4	10.6	6.6	6
	Heptane (C_7)	3.6	2.6	4.2	4.8
Crude Oil B	Pentane (C_5)	6.8	8.8	10.2	9.2
	Hexane (C_6)	6.4	5.4	6	6.4
	Heptane (C_7)	3	3.4	3.6	3.6
Crude Oil C	Pentane (C_5)	23.2	23.3	24.1	23.9
	Hexane (C_6)	22.3	22.1	23.1	22.6
	Heptane (C_7)	22.2	21.7	22.4	21.9

3.12.1 Asphaltene content using pentane, hexane and heptane as solvents

From Table 3.10, and looking at crude oil A results, it was observed that the value of the asphaltene content in C_5 increase from 6.6 g/mL at ratio (40:1) to 11 g/mL at ratio (30:1); and in C_6 an increase at the asphaltene content value of 4 g/mL at ratio (40:1) to 10.6 g/mL at a ratio (30:1) This showed a larger increase in trend since the solvent is decreased from 200 mL to 150 mL. It was noticed that in some other ratios, such as (30:1) to (20:1), there was a decrease in asphaltene content which could result in some of the van Waal forces that influence the asphaltene precipitation. It can not be concluded that the greater or lower the solvents will result in the higher yield of asphaltene precipitation. Crude oil B had similar results in asphaltene content with crude oil A which emphasises the similarity of their chemical compositions or structures. Lastly, crude oil C revealed a greater yield in the asphaltene content, suggesting that the crude oil C viscosity and density were greater than in crude oil A and B. The greater volume of the solvent is believed to have less influence in the asphaltene content.

The asphaltene content obtained from crude oil A, presented in Table 3.10, can also be represented in a graph.

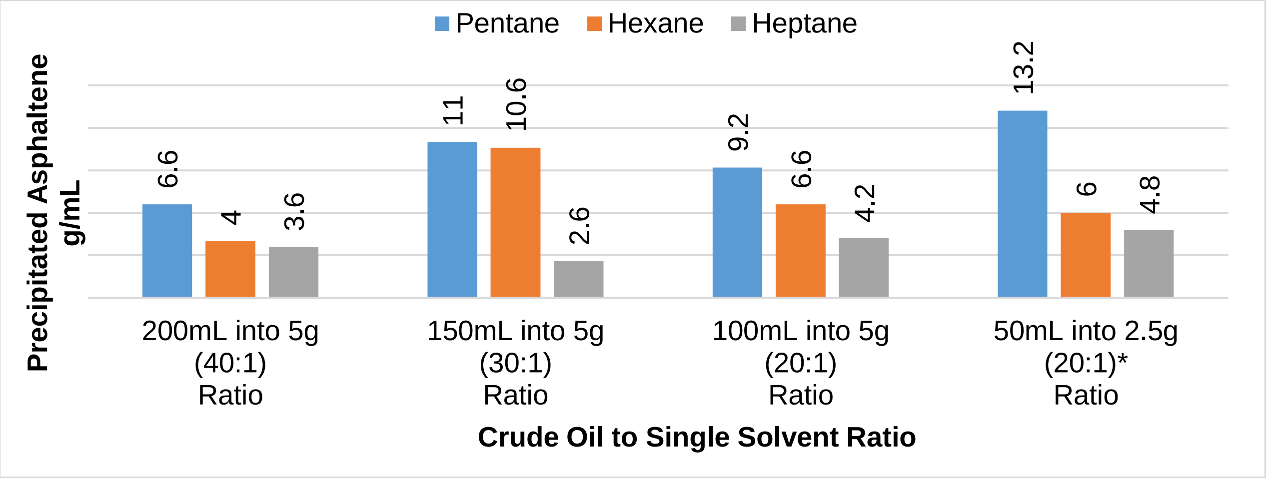


Figure 3.6: Asphaltene content from the single solvent determinations of crude oil A

Referring to Figure 3.6, hexane solvent had similarity in the trend as pentane where the solvent-to-oil ratio (40:1) in (C_6) of asphaltene content of 4 g/mL increased to 10.6 g/mL at the ratio (30:1). The solvent-to-oil ratio still using hexane decreased in asphaltene content from 10.6 g/mL at the ratio (30:1) to 6.6 g/mL at ratio (20:1) and 6 g/mL at a ratio (20:1)* which therefore reveals the descending of the asphaltene content on the oil-to-solvent ratios. Also from Figure 3.7, the following can be discussed about heptane.

The asphaltene content decreased from 3.6 g/mL (40:1) to 2.6 g/mL (30:1) with a sudden increase to 4.2 g/mL (20:1) and a further increase to 4.8 g/mL at ratio (20:1)* . Crude oils A and B show a similarity in graphical trends.

The figure below presents the asphaltene content obtained by crude oil C that clearly explains the results tabulated in Table 3.10.

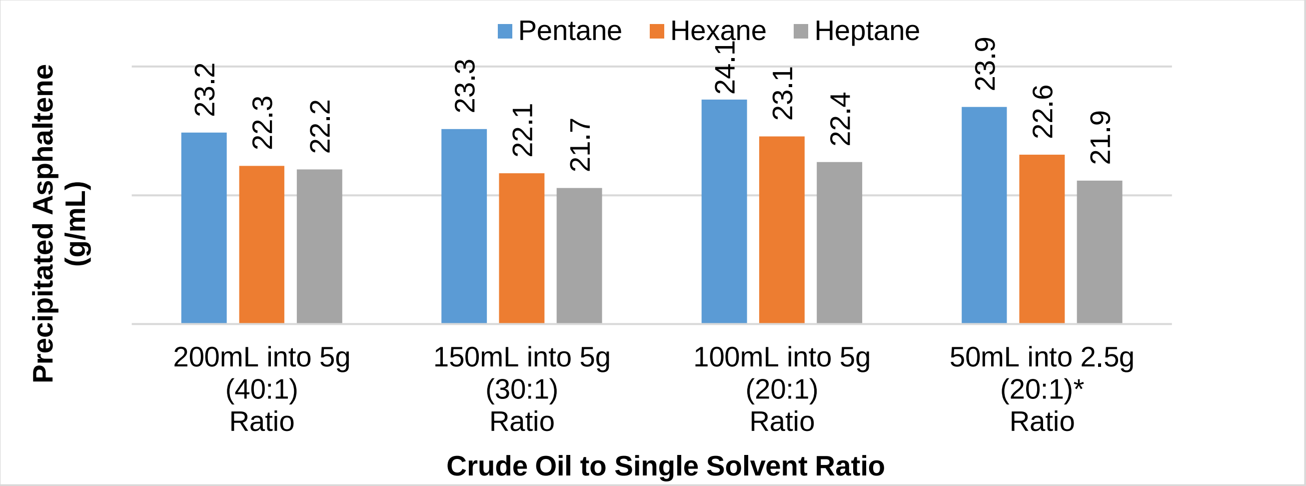


Figure 3.7: Asphaltene content from the single solvent determinations of crude oil C

A very high asphaltene content was obtained from crude oil C. For all the ratios investigated, it was observed that asphaltene content ranges from 21.7 g/mL to 24.1 g/mL. From each solvent-to-oil (40:1), the asphaltene content decreased from C_5 to C_7 which after that followed by another solvent-to-oil ratio (30:1), (20:1) and (20:1) at the similar graphical trends.

Figure 3.8 represents the combination of the two crude oil samples, A and C, which elucidate both crude oil type's similarity and differences.

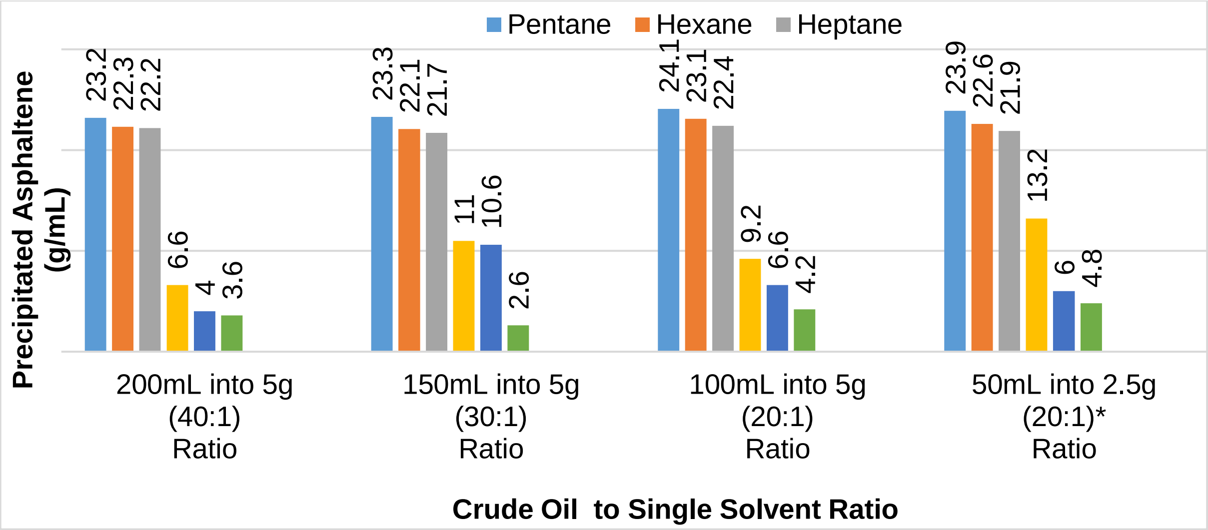


Figure 3.8: Comparison of asphaltene content from crude oil C (see Fig 3.7) to asphaltene content of crude oil A (Fig 3.6) when the three pure solvents are used

The asphaltene content in crude oil C is vastly different from crude oils A and B, as summarised in the Table 3.10. Heptane, with a lower solubility, has the weaker ability to extract asphaltene particles, as shown in Figure 3.7, for all three crude oil types A, B and C.

Table 3.11: Asphaltene content from crude oils A, B and C (mass of oil = 5 g) using a combination of two solvents in the ratio (3:1) (C_5 = Pentane, C_6= Hexane, C_7 = Heptane at 25^{o}C)

	Solvents	**Asphaltene content when two solvents are mixed**
Crude Oil A	(C_5) 75 mL + (C_6) 25 mL	13.20
	(C_5) 75 mL + (C_7) 25 mL	10.80
	(C_6) 75 mL + (C_5) 25 mL	15.20
	(C_6) 75 mL + (C_7) 25 mL	9.60
	(C_7)75 mL + (C_5) 25 mL	12.80
	(C_7) 75 mL + (C_6) 25 mL	9.20
Crude Oil B	(C_5) 75 mL + (C_6) 25 mL	12.00
	(C_5) 75 mL + (C_7) 25 mL	7.60
	(C_6) 75 mL + (C_5) 25 mL	14.80
	(C_6) 75 mL + (C_7) 25 mL	8.80
	(C_7) 75 mL + (C_5) 25 mL	8.00
	(C_7) 75 mL + (C_6) 25 mL	9.60
Crude Oil C	(C_5) 75 mL + (C_6) 25 mL	24.90
	(C_5) 75 mL + (C_7) 25 mL	25.09
	(C_6) 75 mL +(C_5) 25 mL	25.20
	(C_6) 75 mL + (C_7) 25 mL	20.31
	(C_7) 75 mL + (C_5) 25 mL	16.80
	(C_7) 75 mL + (C_6) 25 mL	23.60

Table 3.11 lists the asphaltene content when two solvents are mixed at ratio 3:1. For crude oil A and looking at C_5:C_6 and C_5:C_7 it was observed that there is a decrease in the asphaltene content respectively (13.20-10.80). Similarly, the above trend was noted if the mixture changed from C_6:C_5 to C_6:C_7 (15.20-9.60) and from C_7:C_5 to C_7:C_6 (12.80-9.20). Crude oil B had a similar trend to crude oil A which can further be observed in the table. Crude oil C reveals completely different trends from the two other crude oil where from C_5:C_6, C_5:C_7 and C_6:C_7 increases consistently (24.90-25.09-25.20) in the asphaltene content.

The asphaltene content obtained from crude oil A is illuminated in Table 3.11.

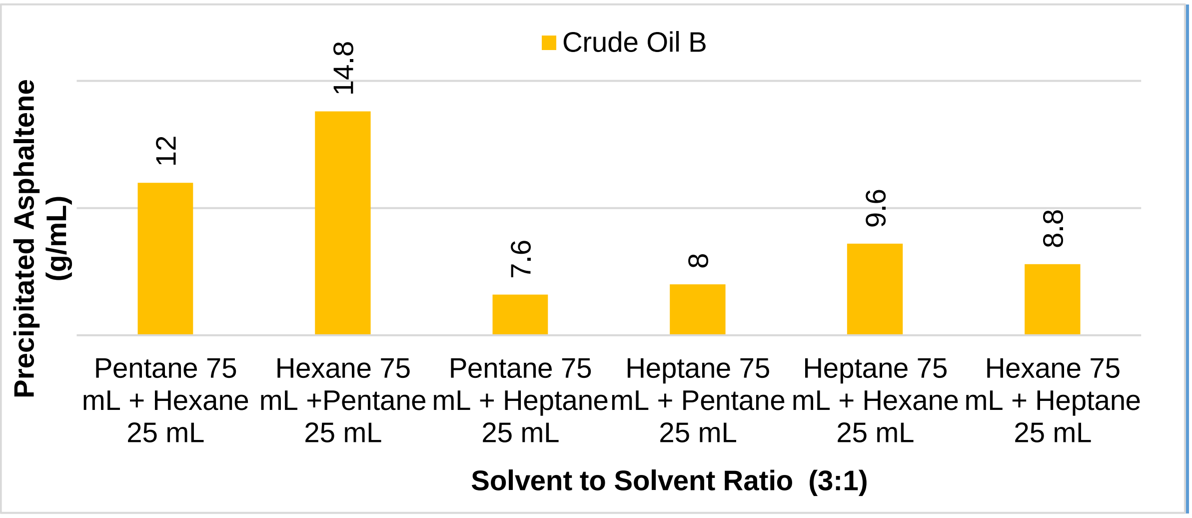


Figure 3.9: Asphaltene content from solvent-to-solvent ratio (3:1) of crude oil B

The asphaltene content increased from 12 to 14.8 where a sudden decrease halted to 7.6 g/mL at solvent-to-solvent ratio (C_5) 75 mL + (C_7) 25 mL. The asphaltene content in a solvent-to-solvent ratio in both the two other crude oil types A and C was observed the same throughout the graphic presentation.

Figure 3.10, represents asphaltene content from crude oil C, presented graphically below and further explained by the results tabulated in Table 3.11.

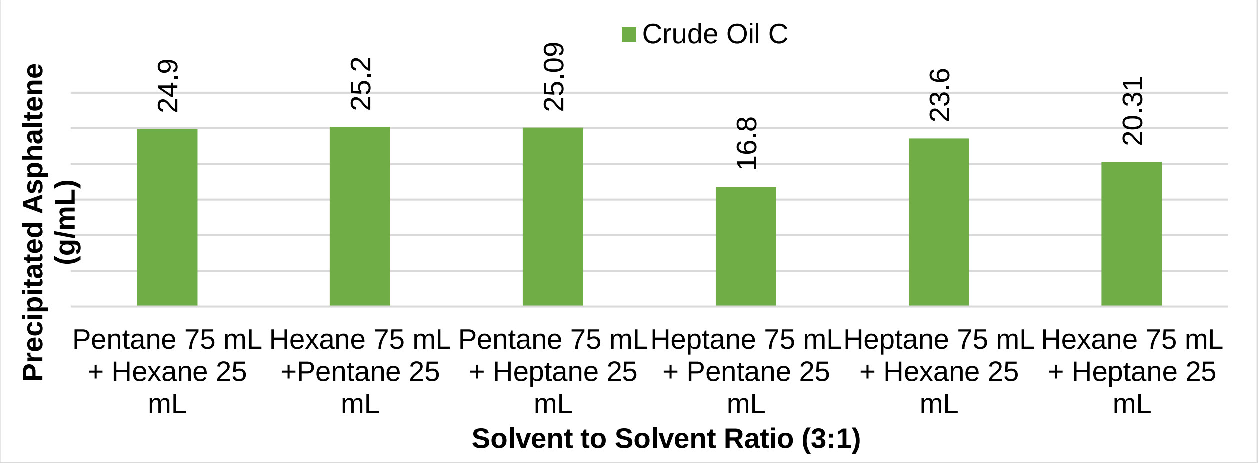


Figure 3.10: Asphaltene content from the solvent-to-solvent ratio (3:1) of crude oil C

The asphaltene content was obtained at intervals at a different solvent-to-solvent ratio at a constant crude oil mass. It is observed that from the solvent-to-solvent ratio of (3:1) during (C_5) 75 mL + (C_6) 25 mL, asphaltene content of 12 g/mL increased to 14.8 g/mL at a solvent-to-solvent ratio of (C_6) 75 mL + (C_5) 25 mL. The asphaltene content ranges from 14.80 - 8 g/mL.

Figure 3.11 reveals the correlation of both crude oils B and C, indicated on the plane bar graph their similarities and differences observed.

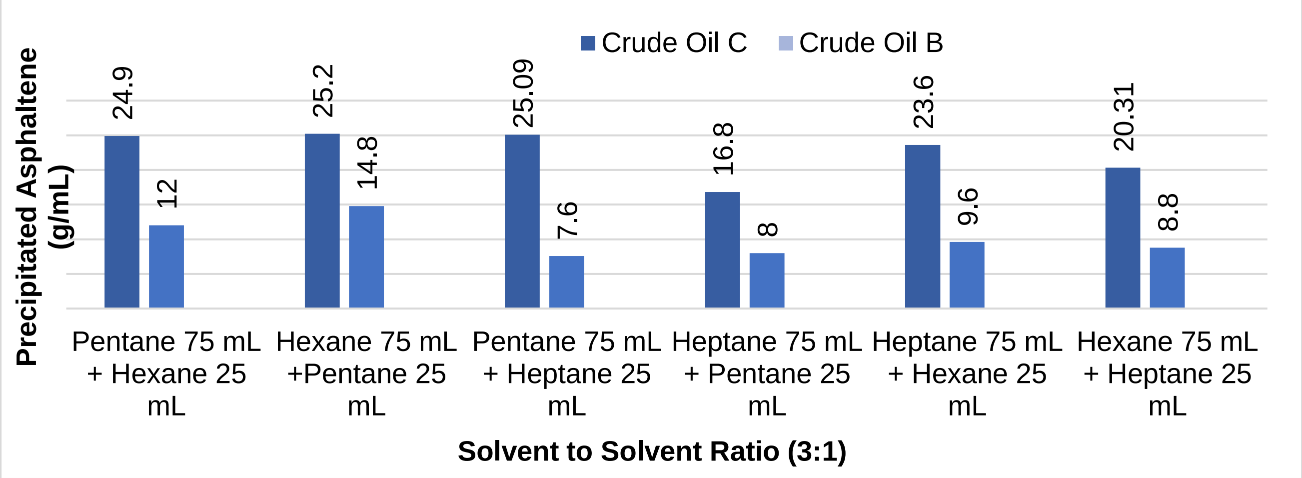


Figure 3.11: Asphaltene content from solvent-to-solvent ratio (3:1) of crude oils B and C

It is reflected that crude oil C on the ratio (3:1) had a greater advantage on the asphaltene content as compared to crude oil B of the same solvent-to-solvent ratio. Both crude oils B and C ranged between 25.09-7.6 g/mL.

The range difference between the two crude oil types can clearly emphasise the difference in molecular structures or molecular weight of either the solvent or the mixture.

Table 3.12 is a tabulation of a ratio (1:1) of the three solvents. The mixtures of the three solvents during the extraction of the asphaltene content from the three crude oil types A, B and C were used to investigate the best ratio to trigger higher yield of the asphaltene to precipitate at constant parameters such as temperature.

Table 3.12: Asphaltene content of crude oils A, B and C when the solvent-to-solvent ratio is 1:1 and mass of crude oil = 5 g

Solvents	Asphaltene content
Crude Oil A	
100 g (C_5)+ 100 g (C_6)	11.6
100 g (C_5)+ 100 g (C_7)	10.8
100 g (C_6)+ 100 g (C_7)	7.8
Crude Oil B	
100 g (C_5)+ 100 g (C_6)	11.6
100 g (C_5)+ 100 g (C_7)	9.6
100 g (C_6)+ 100 g (C_7)	9
Crude Oil C	
100 g (C_5)+ 100 g (C_6)	22.4
100 g (C_5)+ 100 g (C_7)	21.4
100 g (C_6)+ 100 g (C_7)	20.2

Figure 3.12 on the ratio (1:1) has a constant trend of depression of asphaltene content from 11.6 to 7.8 g/mL.

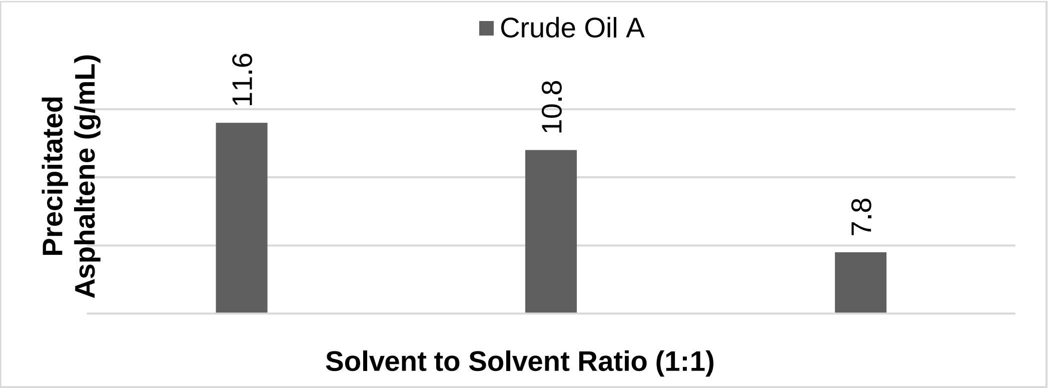


Figure 3.12: Asphaltene content from solvent-to-solvent ratio (1:1) of crude oil A

The asphaltene content was noticed to be favoured on the 100 g (C_5) + 100 g (C_6), where the greater asphaltene content was observed at 11.6 g/mL.

The asphaltene content for crude oil B has been introduced below which is further explained by the results obtained in Table 3.13.

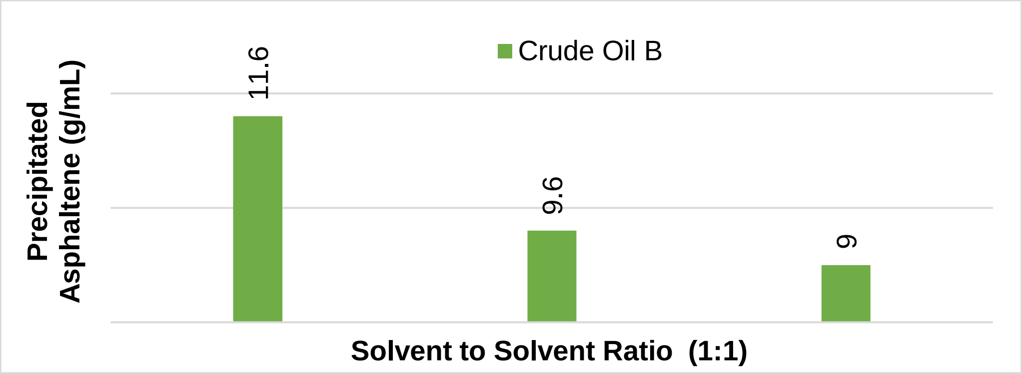


Figure 3.13: Asphaltene content from solvent-to-solvent ratio (1:1) of crude oil B

The asphaltene content decreased thoroughly from 11.6 g/mL to 9.6 g/mL and after that to 9 g/mL where the asphaltene content was obtained less at a solvent-to-solvent ratio 100 g (C_6) + 100 g (C_7).

The graph below represents the interpretation of Table 3.13 in which the asphaltene content is presented.

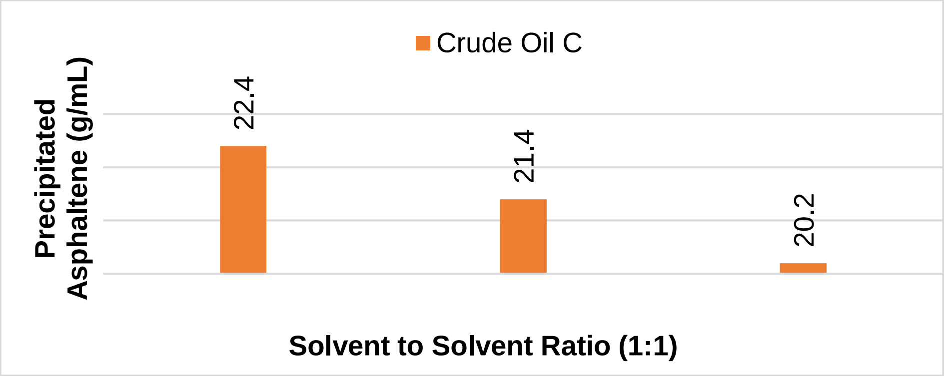


Figure 3.14: Asphaltene content from solvent-to-solvent ratio (1:1) of crude oil C

Figure 3.14, lastly, showed the vast differences in asphaltene content, yet follows the same trend as the other crude oils A and B.

Three crude oils A, B and C merged in Figure 3.15, in which each solvent-to-solvent ratio was therefore explained and analysed on the asphaltene content.

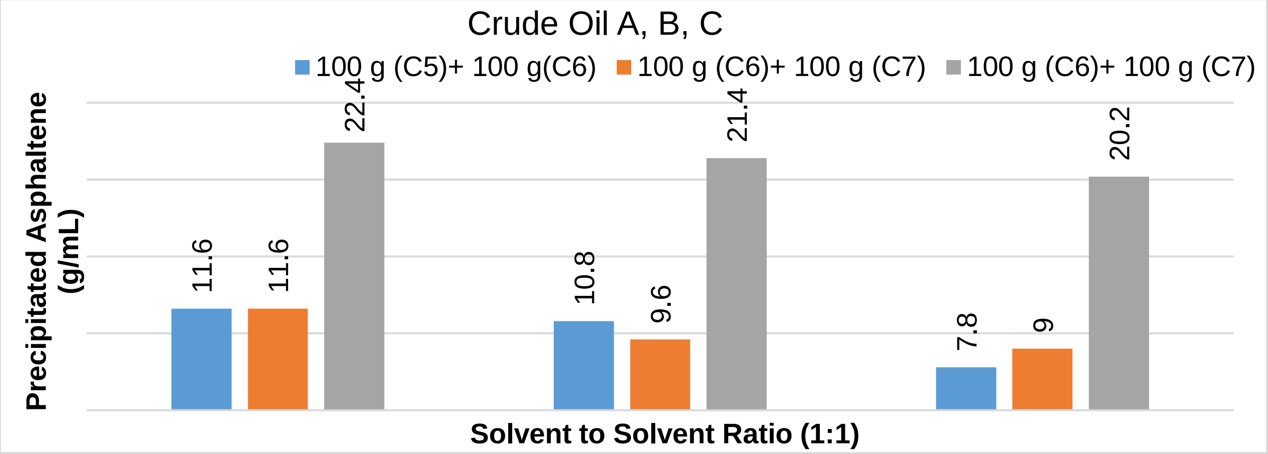


Figure 3.15: Asphaltene content from the solvent-to-solvent ratio (1:1) of crude oils A, B and C

Crude oils A and B have a greater similarity in the asphaltene content as compared to crude oil C. The solvent-to-solvent ratio (1:1) on the 100 g (C_6) + 100 g (C_7) had a lesser asphaltene content as compared to 22.4 g/mL on the solvent to solvent ratio 100 g (C_5) + 100 g (C_6) in crude oil C.

3.12.2 Observation on the colour of asphaltene content

The overall observation was that pentane solvents during the extraction of asphaltene result in a brown powder colour as compared to the two other solvents. Hexane had a black in colour and slightly shiny on the filter. Heptane solvents, on the hand, were noted for having a shiny, crystals asphaltene dispersed on the filter paper.

3.12.3 Asphaltene precipitation influenced by time

It was recorded that the time had a greater influence in the asphaltene precipitation which was caused by the solvents. The shorter time had a greater asphaltene content and a higher flow rate during the filtration. Pentane had a shorter onset time, followed by hexane and lastly heptane. Heptane solvent had retardation on the filtration which the asphaltene content using heptane solvent was not as great as pentane solvent.

3.13 Conclusion

The lower the molecular weight, the more asphaltene content extraction. Crude oil C had higher viscosity and was believed to have higher asphaltene content and impurity content. However, it is necessary to understand and evaluate the aggregation of asphaltene in mixed solvents, its molecular nature, and its interaction energies that are responsible for the behaviour of asphaltene. At a high n-paraffin concentration, the preferred stacking of asphaltene molecules was face-to-face because of high aromatic interactions between the aromatic cores. The presence of hydrogen bond interactions enhanced the stability of the aggregate. The size of the asphaltene deposit increases significantly with elapsed time, and size distribution becomes wider at higher precipitant concentration. A higher concentration of asphaltene precipitant could lead to a higher deposition rate.

The results also indicate that higher flow rate causes faster growth of asphaltene deposits in capillary flow. Larger sizes of asphaltene deposits are formed, and the number of asphaltene deposits decreases with the elapsed time at a higher flow rate. This could indicate faster deposition kinetics at higher flow rates. The GC-MS analysis concluded that crude oils A and B are both paraffinic compound. However crude oil C is aromatic crude which differs from other crude oils. It can be understood that during the extraction of asphaltene using different solvents, both crude oil graphical representation has similar properties in which GC-MS had proven. Crude oil C has the higher the sulphur content and its aromatic content revealed its sweetness.

4

CARBON DIOXIDE FLOODING IN EOR

This chapter outlines the investigation of CO_2 flooding in the reservoir system. Miscible and immiscible flooding is chosen to achieve a higher rate factor in the recovery of oil. The effect and properties of the surfactant is studied as well to determine why CO_2 is an injectant of choice in EOR (enhance oil recovery). The influence on the factors that promote precipitation of asphaltene such as CO_2 flooding, temperature and pressure is investigated.

4.1 Enhanced oil recovery

Enhanced oil recovery (EOR) is an implementation method applied to extract oil from the oil reservoir and therefore is ordinarily used after primary and secondary oil recovery. It is used when the oil is trapped in the reservoir rocks to improve oil recovery (IOR). There are three levels used in the oil production systems: primary, secondary and tertiary recovery (Sheng, 2013). The major EOR processes are categorised into thermal, gas flood and chemical flood recovery methods (Zanganeh *et al.*, 2018). Different techniques can be used for different grades of oil; for instance, heavy, medium, and light oil have different EOR techniques for oil production. In situ combustion has been proposed as a potential enhanced oil recovery (EOR) technique for heavy oil reservoirs (Zheng *et al*., 2013).

Primary, secondary and tertiary (EOR) recovery methods follow a natural progression of oil production; however, it is cost-effective to produce from hydrocarbon reservoirs. Enhanced oil recovery processes attempt to recover oil beyond secondary methods (Kokal and Al-Kaabi, 2010) and according to (Li *et al*., 2000), the first oil recovery (natural oil) required no external energy to produce the oil or gas from the oil reservoir. It is the first stage in which oil production occurred, but with a limited amount of oil. It is usually the cheapest and natural way of extracting oil from the reservoir without any expenditure on machinery. However, according to (Emegwalu, 2010), the difference in pressure from high to low is the cause of extraction of oil from the reservoir to the surface. It is stated by (Liu *et al*., 2008) that approximately 10-19% of oil from original oil in place (OOIP) is extracted to the surface while 80% is still trapped in the sediments rocks. The secondary recovery is a physical method where this time the use of artificial energy is applicable in the oil reservoir. After primary recovery, water alternating gas (WAG) injection, the mixture of gas and water combined, can be conducted to extract oil from the oil reservoir to the surface (Emegwalu, 2010). However the purpose of water and gas is to increase the pressure of the reservoir to push the oil out, usually occurring when there is insufficient pressure underground.

(Holmberg *et al.*, 2002). As water will be able to sweep the oil away from the reservoir to the surface, this is the reason why water is efficient in this method of the second stage oil recovery. The oil is driven to the wellhead where it will be easy to flow to the surface (Emegwalu, 2010). Even during this process of extraction, not all the oil from the pores is extracted. There will be still some amount of oil trapped in the sediment rocks, with recovery between 25-45% of OOIP (Mohan, 2009). The residual oil saturation after primary and secondary recovery is about 50-60% of the original oil in place (OOIP) (Zanganeh *et al*., 2018).

Tertiary recovery is used in EOR after primary and secondary recovery has been conducted. It is the final stage where the use of carbon dioxide or any other miscible or immiscible gas is preferred to sweep the oil from the oil recovery. Carbon dioxide flooding is useful in oil production and any gas such as nitrogen or methane can also be used. The carbon dioxide can displace a higher amount of oil and lower the viscosity of the oil in the reservoir. They are other EOR techniques which can either be used in secondary or tertiary recovery such as polymer flooding, steam flooding and more (Schramm, 2000). The oil recovery is influenced by geologic features such as rock and fluid characteristics, porosity, permeability, and structural or stratigraphic features such as faults and other barriers to oil or gas movement (Verma, 2015).

4.2 The properties of carbon dioxide (CO_2) during flooding

Carbon dioxide is a colourless, odourless, inert and non-combustible gas with a molar mass of 44 g/mol (Mathiassen, 2003), stable at low temperatures and pressures, but during flooding, CO_2 depends on temperature. Below the critical temperature, CO_2 can either be a liquid or gas over a wide range of pressures. Above the critical temperature, CO_2 will exist as a gas regardless of the pressure. Its viscosity strongly depends on pressure and temperature. The carbon dioxide viscosity increases as pressure increases at a given temperature of the reservoir. During CO_2 flooding, the displacement of crude oil with water is more efficient than with natural gas (Mathiassen, 2003).

4.3 Carbon dioxide flooding in crude oil

Carbon dioxide flooding is the process in which CO_2 floods in the reservoir at a specific RPM (rate per min) to overcome the viscosity of the crude oil and challenges in the production system (Forthuber and Valdez, 2003). Carbon dioxide flooding is an effective method for geological sequestration of greenhouse gas and enhancing oil recovery. In the CO_2 flooding process, it becomes difficult for asphaltene to remain dissolved in crude oil, resulting in its precipitation (Dong *et al*., 2014).

Asphaltene itself is not problematic, but asphaltene precipitation is a big concern. Precipitation may happen during different phases of production, especially in CO_2 flooding. It is well known that light and medium oil reservoirs are good candidates for CO_2 injection as a tertiary recovery after water flooding (Alian *et al*., 2011).

The injection of CO_2 in crude oil causes reduction of viscosity and higher density in the crude oil. It extracts light hydrocarbons, reduces interfacial tension (IFT) and oil-swelling and it is also suitable for either immiscible and miscible displacement (Cao and Gu, 2013). The CO_2 flooding process, depending on the highest possible operating pressure and minimum miscible conditions, can be performed at both miscibility and immiscibility conditions (Wang and Gu, 2011). Carbon dioxide flooding behaves much like a vaporising gas drive, as described initially by Hutchinson and Braun (Orr Jr *et al.*, 1981). During a flood, vapour phase CO_2 mixes with oil and extracts light and intermediate hydrocarbons. After multiple contacts, the CO_2-rich phase vaporises enough hydrocarbons to develop a composition that can displace oil efficiently (Orr Jr *et al.*, 1981).

Carbon dioxide flooding may result in some production problems which may lead to the formation of calcium carbonate ($CaCO_3$) scaling. When CO_2 dissolves in water under reservoir pressure, it depresses the water pH to 2 to 3 units, resulting in a formation of acidic water (Yuan *et al*., 2001). During the process, the acidic water is then mixed with calcium from the limestone, concentrating the calcium more than initially. As the concentration of calcium increases, it results in a flow out of water that travels to the plant site where the pressure is then further monitored and investigated. The increase in pH will result in calcium carbonate increase; therefore reaction of an acid and carbonate will result in water, salt and carbon dioxide as products. Calcium carbonate can be monitored as an internal factor found in the reservoir using pressure to control the pH shifts (Yuan *et al*., 2001).

The results of CO_2 gas injection revealed that the amount of asphaltene deposition was increased to a great extent as the CO_2 mole percent was increased. For example, changing CO_2 composition from 5 to 20 mol% resulted in 56% more asphaltene deposition at 140 bar and 90°C (Zanganeh *et al.*, 2018). The gas solubility reaches its maximum value at the bubble point pressure, and all the available gases are dissolved in the oil (Tarek, 2007). When a gas dissolves, it does so because its molecules interact with the solvent molecules. As temperature rises, the solubility of gas decreases which therefore leads to the solubility of the oil to increase as pressure increases. The gas thus influences the solubility of the oil. The heat is released when these new attractive interactions form, as dissolving most gases in liquids is an exothermic process (Hassan *et al*., 2016).

4.4 Advantages and disadvantages of CO_2 flooding in the reservoir

Carbon dioxide flooding has been successfully used commercially for EOR since 1970 (Stewart *et al.*, 2018). Mathiassen (2003) stated that carbon dioxide has both advantages and disadvantages in an EOR process. The advantage of CO_2 compared to other gases is that it can extract hydrocarbons up to C_{30} which are the more solid hydrocarbons (Mathiassen, 2003). It has the capability of expanding oil to a greater extent than methane, as well causing the oil to swell due to its solubility. Carbon dioxide has the following advantageous characteristics in the oil flooding process (Mathiassen, 2003):

- It reduces oil viscosity.
- It increases the oil density.
- It is soluble in water.
- It reduces water density
- It achieves miscibility at pressures of only 100 to 300 bar.
- It promotes swelling.

However, disadvantages of CO_2 in the miscible flooding include changes in the reservoir wettability, wellbore and formation damage and avoidance of adverse effects of the following factors need improvement (da Silva *et al.*, 2014):

- addition of foaming solutions together with $CO_{2;}$
- shutting down production wells to regular flow;
- perforating techniques (which techniques); and
- alternating water only with water and gas injection (WAG).

4.5 Miscible and immiscible flooding

Miscible and immiscible gas flooding is one of the enhanced oil recovery (EOR) techniques that has been widely used to investigate the contribution of gas flooding that generates asphaltene precipitation (Speight, 2014). There are two types of carbon dioxide – miscible and immiscible flooding – with different functions in the oil reservoir. However, both can enhance oil recovery in the reservoir (Abedini and Torabi, 2014). Carbon dioxide miscible or immiscible flooding may trigger the precipitation and deposition of asphaltene which brings a decrease of crude oil recovery that causes it to reduce permeability and porosity of the reservoir rocks (Seifried *et al.*, 2015).

When the reservoir pressure is less than the minimum miscibility pressure (MMP), the gas injection would be an immiscible injection process with low efficiency (Fanchi, 2005); however miscible flooding is when two or more fluids are a colloid mixture to form a homogeneous phase whereas immiscible flooding cannot form a homogeneous mixture. Therefore, both miscible and immiscible flooding increase enhanced oil recovery in all type of crude oil. Carbon dioxide flooding is one of the essential methods for enhanced oil recovery (EOR) because it not only increases oil recovery efficiency but also causes a reduction in greenhouse gas emissions. The injected CO_2 at miscible conditions increased oil recovery for crude oil compared to flooding only with CO_2. Transverse dispersion of CO_2 helps in eliminating or at least reducing the effect of viscous instabilities (Hamouda and Chughtai, 2018). Carbon dioxide flooding by immiscible flooding has been increasingly employed to enhance oil recovery (EOR) operations to minimise the challenges that occur in the heavy crude oil operations when the API degree is below 20 (Seifried *et al*., 2015).

4.6 Flood phase behaviour

Carbon dioxide use is one of the greenest and low-cost methods in EOR processes. This method affects oil production by reducing oil viscosity and interfacial tension, extraction of hydrocarbons or oil swelling, and also causes some other problems such as asphaltene deposition (Bakyani *et al*., 2018). While carbon dioxide injection is one of the essential methods currently being used in enhanced oil recovery, it may change the properties of the crude oil and increase the possibility of asphaltene precipitation. Carbon dioxide, in addition to temperature and pressure, helps to improve oil recovery which successfully allows the production of asphaltene to occur. Also, carbon dioxide is the preferred gas to easily extract hydrocarbons from the rocks reservoir as it increases the surface area of the well by decreasing the viscosity of the oil. Reservoirs such as lithologies, siliciclastic, carbonate and others are suitable for CO_2 EOR application only if the permeability of porosity is present that will allow the fluid to accumulate than flow (Yin and Yen, 2000).

When CO_2 is injected into the oil reservoir, it will contribute to the asphaltene precipitation by changing composition of the asphaltene. Changes in composition frequently happen in gas injection processes employed in enhanced oil recovery (EOR). Gas injection includes processes such as miscible flooding with CO_2, N_2 or natural gas (Rodriguez, 2008). Increasing the injection pressure of CO_2 leads to a smaller asphaltene deposit. Dynamic flow experiments depict that due to the presence of asphaltene inside the core samples, porosity and permeability of rocks would be reduced. It was reported that at higher pressures (2600 psig), fewer asphaltene deposits were noted because of the lower permeability and porosity (Alian *et al.*, 2011). Asphaltene precipitation and deposition may affect the vast region in the reservoir, starting from the wellbore and extending over long distances from its origin.

In contrast, the reservoir damage due to wax deposition is rather limited to a short distance, maximum 1 foot away from the wellbore. Just like asphaltene deposition, a wax deposition is a reversible process which can be eliminated by thermal treatment methods (Civan, 2000).

4.7 Deposition of asphaltene

Asphaltenes are of great industrial significance because of their tendency to deposit in porous rock formations, wellbores, production lines and refineries. Pressure depletion is the primary cause of arterial deposition in a wellbore (Hoepfner *et al*., 2013).

Deposition of crude oil components into piping for topside facilities during the refining process and petroleum recovery operations is a multi-million-dollar concern for the crude oil industry: the replacement of clogged pipes can cost millions of dollars. In petroleum recovery, such deposits precipitate out of solution, mainly due to depressurisation relative to the reservoir pressure. Asphaltenes, present in crude oils in the range of 0-20% or more, have a substantial effect on chemical properties of the crude oil. Asphaltene comprises the heaviest and the most polar fractions and are enriched in heteroatoms (N, S, and O), typically to a few mass %.

The higher or lower the pH in fluids and other factors such as a decrease in pressure, temperature changes and the injection of the incompatible fluids may trigger the deposition of asphaltene (Villard *et al*., 2016). The higher the asphaltene solubility, the higher its deposition on the surface (Rogel *et al*., 2015). The lower the ratio of resins to asphaltene, the higher the asphaltene precipitation (Ali *et al*., 2015). The expensive cost of treatments to remove the asphaltene deposition results in more attention of the industry and academic researchers seeking solutions to inhibit or reduce asphaltene precipitation in recent years (Zanganeh *et al*., 2018). Asphaltene deposition can be predicted through modelling such as Flory-Huggins polymer solution and the equation of state (EOS) (refer to section 2). Using linear relations of EOS will help to determine the asphaltene deposition and how much it will deposit under certain conditions such as variations in pressure, miscible gas and CO_2 flooding (Vafaie-Sefti and Mousavi-Dehghani, 2006).

Figure 4.1 shows how the reduction of pressure in the reservoir has caused the instability which therefore resulted in the deposition of the asphaltene in the pipe.

Figure 4.1: Asphaltene deposition in tubing and reservoir (Borden, 2013)

4.8 Prevention of deposition of asphaltene

Asphaltene deposition can be controlled using predictive, corrective or preventive methods. In the predictive method, a combination of thermodynamic and kinetic models, mostly derived from the polymer solution, colloidal stability and FRACTAL aggregation theories, are used (Idem and Ibrahim, 2002).

This is to predict composition, pressure and temperature conditions for the onset of asphaltene precipitation after the introduction of experimentally determined oil characteristics (typically fluid composition and physicochemical properties). However, it has been noticed that purely thermodynamic predictive models are not sufficient in real reservoir simulations (Idem and Ibrahim, 2002).

The removal of the precipitated asphaltene after being deposited can be either mechanically or chemically removed by the addition of aromatic solvents. This is the remedy that can be applied when the damages have already been encountered in the production field (Idem and Ibrahim, 2002). The most effective asphaltene precipitation preventive action, though, is the reservoir pressure maintenance above the asphaltene precipitation onset. Some of the asphaltene dispersants and precipitation inhibitors constitute the prevention of asphaltene precipitation and deposition occurrence (Idem and Ibrahim, 2002).

4.9 Factors influencing asphaltene precipitation and deposition during CO_2 flooding

There are many factors influencing asphaltene precipitation, but the three significant factors below are the most important, needing to be monitored and controlled during crude oil production:

- temperature;
- pressure; and
- oil composition.

These factors influence asphaltene precipitation, causing significant losses due to damages and cost-effectiveness on the maintenance of the reservoir (Loureiro, 2015). While changing the temperature and composition of crude oil causes asphaltene precipitation, a decrease in pressure is the most critical influence factor (Hasanvand, 2015). At higher temperatures, the onset time for asphaltene precipitation is shorter which means that at higher temperatures, asphaltene precipitation is more comfortable to occur. Moreover, the temperature effect on asphaltene stability was explored based on considering the difference in asphaltene property (Maqbool *et al*., 2011). Correspondingly, the compositions of crude oil and reservoir permeability are positively correlated with the amount of asphaltene precipitation (Chen *et al*., 2018).

4.10 Instrumentation used

Figure 4.2 is used on the carbon dioxide flooding where gas has been manipulated at a constant flow rate, which thereby passes into a vacuum and is mixed with the crude oil. The process of the CO_2 being injected into the crude oil is called *carbon dioxide flooding.*

The air inlet is the injection of CO_2 into the tube glass. The conductivity cell contains the solvent of choice (pentane, hexane or heptane).

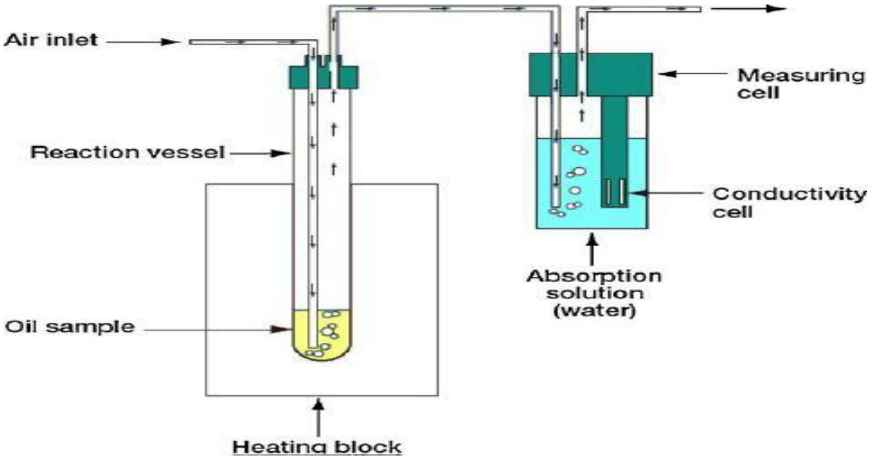


Figure 4.2: Principles of measurement for the rancimat test method for CO_2 flooding (EN 14112 and IS15607)

4.11 Results and discussion

The determination of asphaltene content with CO_2 flooding was investigated under the following conditions: pressure = 17.2 MPa; CO_2 flow rate 0.5 mL/min for 48 hours: volume of oil 10.35 mL with varying temperature 25°C, 30°C, 60°C and 90°C. 200 mL of pentane (C_5), hexane (C_6) and heptane (C_7) used of each determination.

The asphaltene content obtained using crude oil A is presented in Table 4.1.

Table 4.1: Asphaltene content from a temperature range of 25°C-90°C during CO_2 flooding using crude oil A volume of 10.35 mL

Temperature °C	Solvent	Asphaltene Content g/mL	Solvent	Asphaltene Content g/mL	Solvent	Asphaltene Content g/mL
25	C_5	4.72	C_6	4.68	C_7	4.56
30	C_5	4.27	C_6	4.21	C_7	4.16
60	C_5	4.42	C_6	4.38	C_7	4.25
90	C_5	4.68	C_6	4.57	C_7	4.39

The table above represents the result of the three solvents. It was observed that at 25°C and 90°C the asphaltene content was higher than at the other temperatures for all solvents. Furthermore, for all solvent, a higher of asphaltene was obtained at 25°C. At this temperature, pentane gave the highest yield of asphaltene content. When the temperature increases from 30°C to 60°C, the asphaltene content increase for all three solvents.

Figures 4.3-4.4 indicate the graphical interpretation of the asphaltene content after using carbon dioxide (CO_2) flow rate of 0.5 mL/min for crude oils A, B and C when pentane of each solvent at different temperatures.

Table 4.2: Asphaltene content obtained after CO_2 flooding when temperature is varied from 25°C-90°C using crude oils A, B and C. Volume of each crude oil = 10.35 mL and solvent used = pentane

		Asphaltene Content g/mL		
Temperature °C	Solvent	Crude oil A	Crude oil B	Crude oil C
25	C_5	4.72	4.92	5.13
30	C_5	4.27	4.76	4.79
60	C_5	4.42	4.81	4.88
90	C_5	4.68	4.87	4.96

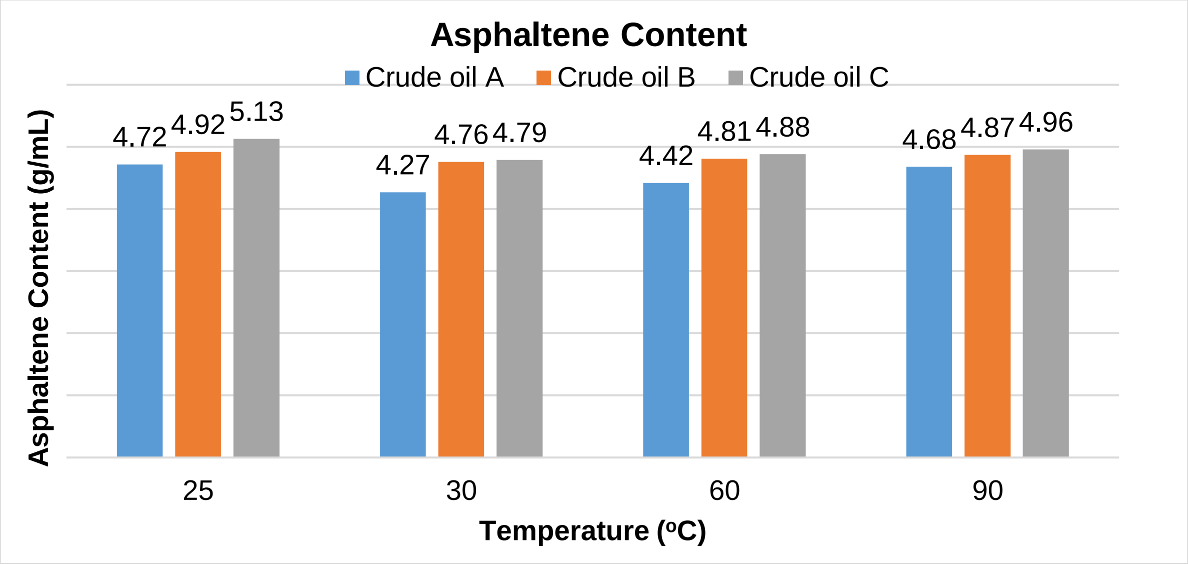


Figure 4.3: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using C_5 for crude oils A, B and C

Similar results were observed for hexane and heptanes for all three crude oils. The results are represented in Appendix C from Tables C1 to C3.

The asphaltene content in crude oil increased with the rise in temperature. This was because the solubility of CO_2 decreased with the increase of temperature, and the effect of CO_2 on asphaltene decreased, resulting in a decrease of the amount of asphaltene precipitated. Consequently, the asphaltene content in crude oil increased. However, due to the mechanism of CO_2 injection in the crude oil, asphaltene precipitation is extremely sensitive to CO_2 even though the contribution from asphaltene content in the oil cannot be ignored. The higher the injection of CO_2, the higher the asphaltene precipitation. It helps to shift the pH in the reservoir, under moisture or wettability conditions, which therefore triggers the asphaltene precipitation.

The results showed that hydrocarbon injection increases the amount of asphaltene precipitation. However, CO_2 injection did not affect the stability of asphaltene particles. Further, the instability of asphaltene particles by reducing the temperature during CO_2 injection was reported. The higher polarity solvent causes a more substantial reduction in viscosity of the diluted heavy crude oil, which CO_2 is related to as the solvent to encourage the production of crude in the result of asphaltene precipitation. Asphaltenes become increasingly unstable with temperature increase. Lower temperatures led to the formation of highly porous and loose aggregate structures with relatively low fractal dimensions. The asphaltene precipitation was revealed to be at a higher yield at 25°C because, at that stability, the asphaltene molecules are stable and the van der Waals forces between asphaltene molecules are not particularly strong.

Asphaltene content from different molar ratios

At this time the flowrate increase by 10 from 0.5 mL/min to 5 mL/min for 48 hours: volume of oil 500 mL; 10.00 mL; 6.66 mL; 5.55 mL at various molar ratio. 200 mL of pentane (C_5), hexane (C_6) and heptane (C_7) used of each asphaltene determination at room temperature.

Molar Ratio % = $(Carbon\ Dioxide\ Flow\ rate\ Used)/(Crude\ Oil\ Volume\ Used\ ) \times 100$

E.g: $(5\ mL/min)/10\ mL \quad \times\ 100 = 50\ \%$

Similar calculations was repeated respectively for all the crude oil on their molar ratio and tabulated from C_4 to C_6 on the appendix C.

Table 4.2 clearly shows the results of each crude oil tabulated on each CO_2 to oil ratio percentage using pentane solvent. It can be seen that the asphaltene content in crude oil decreased with an increase of the molar ratio of CO_2 to crude oil. This was because when the relative content of CO_2 increased, more of the light components of crude oil were extracted into the CO_2 phase, causing the increased asphaltene precipitation.

Table 4.3: Asphaltene content of crude oils A, B and C after interacting with CO_2 at different CO_2 to crude oil ratios using pentane as a solvent

CO_2 to oil ratio, %	1	50	75	90
Contents of asphaltene, wt% (**Crude oil A**)	4.88	4.81	4.59	3.41
Contents of asphaltene, wt% (**Crude oil B**)	4.91	4.87	4.62	3.44
Contents of asphaltene, wt% (**Crude oil C**)	5.62	5.24	5.17	4.93

Figure 4.4 represents the graphic representation of Table 4.2 and other tables on the appendix C, Table C4, Table C5 and Table C6 on how CO_2 to oil ratio using pentane on the three crude oil types is being interpreted and analysed.

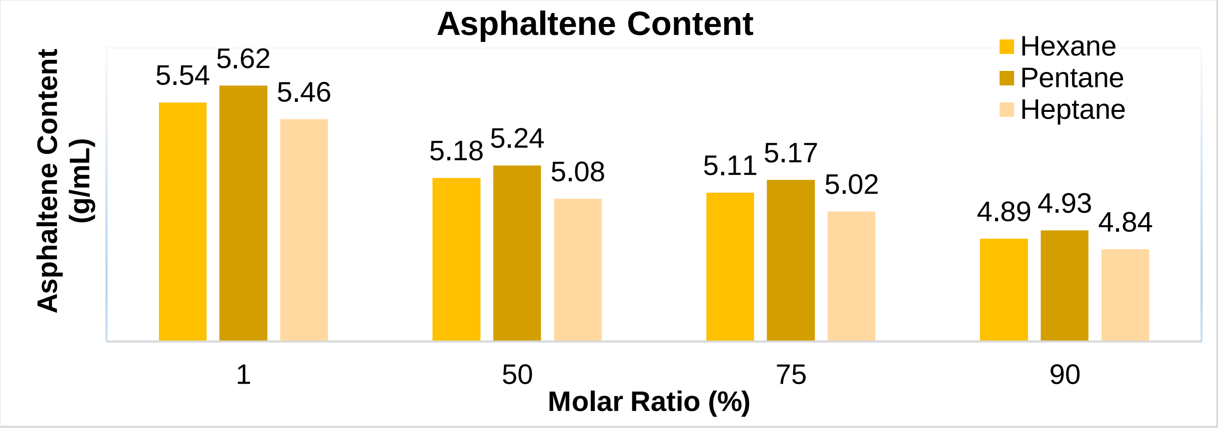


Figure 4.4: Asphaltene content using C_5, C_6, C_7 during CO_2 flooding on the different molar ratios for crude oil A, B and C

The asphaltene content in crude oil decreased with an increase of the molar ratio of CO_2 to crude oil. This was because when the relative content of CO_2 increased, more of the light components of crude oil were extracted into the CO_2 phase, causing the increased asphaltene precipitation. Asphaltene precipitation induced by CO_2 therefore causes oil-water IFT to increase. Carbon dioxide flooding processes trigger asphaltene precipitation and reduce the asphaltene by dissolving it in crude oil. Carbon dioxide gas increases the mobility of the oil and thus raises the productivity of the reservoir.

Hydrogen bonding between the asphaltene molecules is more likely due to heteroatoms in the functional groups. However, since asphaltenes consist mainly of carbon and hydrogen atoms, it is also important to consider van der Waals interaction forces. Although van der Waals forces are weak, its overall contribution could be significant once the asphaltene molecules are highly packed.

4.12 Conclusions

The CO_2 flooding into different crude oil types A, B and C which have different API gravities revealed that asphaltene content depends on the temperature and the ratio of CO_2 flooding to the crude oil. These two factors have a greater influence on the asphaltene precipitation content. The CO_2 influences the solubility of asphaltene and therefore leads to the asphaltene deposition. The solvents used (pentane, hexane and heptane) play a role in the CO_2 flooding, as it was noticed that pentane extracted more asphaltene. The lesser CO_2 to oil ratio percentage, the higher the asphaltene content. The propensity for CO_2 to induce asphaltene precipitation increases with oil API, but paraffinic decreases with oil aromaticity and asphaltene content. This is a complete reversal of the situation for n-heptane induced asphaltene precipitation.

5

CONCLUSIONS AND RECOMMENDATIONS

5.1 General conclusions

It can be understood from the practical results that the alkanes of lower molecular weight can extract higher asphaltene contents. Crude oil A, B, and C show different results of the asphaltene content obtained on the GC/MS. Crude oil A and B showed similarities on the properties investigated whereas crude oil C reflected a higher asphaltene content as well as impurities during the extraction. It was observed that in crude oil A and B, compounds eluted at the same retention times which proved that the compounds have similar properties. The asphaltene molecules and the solvent are involved in a robust electrochemical reaction during the mixture of the crude oil and the solvents in which the physiochemistry occurred when extraction took place.

The alkane solvents play a vital role during extraction of asphaltene. The amount of solvent used can undoubtedly influence the quantitative asphaltene precipitated. From the experiments conducted in the project, pentane can extract more asphaltene due to its lower molecular weight as compared to hexane and heptane. When two solvents were mixed in different ratios, it was noticed that the asphaltene content from the ratio (3:1), (C_5+C_6) has the higher optimal value of each crude oil types (A, B and C). The solvent to the solvent ratio (1:1) (C_5+C_6) was obtained to extract higher asphaltene content with all three crude oil types A, B and C as compared to (C_6+C_7) and (C_5+C_7).

It can be mentioned that alkanes create a greater physio-sorption on the asphaltene from the crude oil in which asphaltene forces tend to weaken and precipitate as less solvent is added to the mixtures of asphaltene and solvent ratio. Different solvents have proven to have different asphaltene content results due to their solubility and molecular weight. There are other compounds which can extract more asphaltene than pentane due to their molecular weight or carbon atom attachments; however, in this project, pentane has been proven to be sufficient and cheaper for the crystallisation of asphaltene. The use of alkanes as a solvent than any other compounds such as nitrogen, methane and others is due to its cost-effectiveness. It is cheap and sufficient during the enhanced oil recovery in the oil production. Due to the viscosity and the higher asphaltenes content on the crude oil, the adsorption of asphaltene is not as rapid as when there is lesser asphaltene amount. The APIg of the crude oil is inversely proportional to the adsorption of the asphaltene. Pentane which has linear carbon chains trigger the greater forces in adsorption of asphaltene.

The lower the solubility of the solvent the greater the asphaltene content will be extracted. Alkanes can break down the covalent bonding that is held between crude oil and the asphaltene during its mixtures on the chemisorption. The asphaltene precipitation can be explained by polarisation and solubility of the asphaltene to the solvent. The presence of the amphiphile head group on the asphaltene will increase polarity. This will strengthen the attraction of amphiphile to asphaltenes through acid and base interaction; the amphiphile effectiveness on asphaltene stabilisation is therefore increased. The amphiphile with short tails will be embedded in and co-precipitated with asphaltene. The higher ratio of resins in asphaltene will minimise the asphaltene precipitation to occur.

The effect of the polarity/aggregation on the interface behaviour has been described by using the fractionation of asphaltenes. This procedure entails the separation of asphaltene portions using different solvents or different solvent/crude oil volume ratios which resulted in a different degree of extraction of asphaltene amount. Due to the individual properties of the different crude oil types, it was concluded that crude oil C has the higher sulphur content of 2391 mg/L followed by crude oil A of 565 mg/L and crude oil B of 551 mg/L. This can be explained by the viscosity of each crude oil type in correlation to their asphaltenes content. The sulphur content found in the crude oil C was four times greater than the two other crude oil. The more the sulphur content, the sweetness of the oil. The analysis conducted proved that the best commercial oils would be crude oil A and B and most expensive one will be crude oil C.

From the GC/MS analysis, it was observed that the chromatogram of crude oil C was different from crude oil A or B. The lower volume of the solvent caused greater adsorption towards the asphaltene particles in the crude oil. The alkanes with the higher solubilities extract less asphaltene. Both crude oils A and B had both paraffinic and naphthenic compounds. Paraffin is the dominant compound in both crude oil A and B meaning they both had a higher percentage of paraffinic compounds as compared to crude oil C.

Crude oil C revealed no naphthenic compounds and showed a greater percentage of aromatics and some paraffinic compounds. The carbon dioxide flooding was found to be successful in this project. However temperature had a great influence in the asphaltene precipitation. It was investigated that CO_2 flooding had a greater impact on the solubility of each crude oil types in which therefore the asphaltene precipitation was triggered. The temperature was a factor during the conversion of the crude oil to precipitate asphaltene. At a temperature of 25^oC, it was found among all the crude oil types that asphaltene was settled at a higher yield caused the molecules of the asphaltene to be mobilised. Asphaltene was stabilised at the temperature of 25^oC which therefore encountered that the precipitation of asphaltene to be greater.

Carbons did change the crude oil behaviour and equilibrium condition which favour precipitation of asphaltene. The time required to precipitate asphaltenes can vary from a few minutes to several months, depending on the precipitant concentration used and that no single concentration can be identified as the critical precipitant concentration for asphaltene precipitation. Both upstream and downstream processes involve temperature variations, which can cause the precipitation of asphaltenes and can lead to deposition and fouling problems during the production, transportation, and processing of crude oils.

The higher temperatures the precipitation onset time for asphaltenes is shorter and their solubility is higher. The effect of the expansion of hydrocarbons, oxidation of crude oil, and the loss of light hydrocarbons due to evaporation, all of which are possible when the temperature is increased. This project provides a unified approach to understand the variety of factors that change as a result of temperature variation and evaluates their contributions to changes in asphaltene precipitation kinetics and their solubility. It was further proof that, as molar ratio increases, the asphaltene content decrease, which was caused by the internal forces between the asphaltene molecules. Constant CO_2 flooding with a change of the crude oil volumes with having on the decrease in solubility.

5.2 Recommendations

From this project on the investigation of the asphaltenes, it can be concluded that a specific solvent can trigger asphaltene to crystallise and deposit due to its molecular structure, solubility and the mutual balance on the polarity between the crude oil and the asphaltene content in that crude oil. The volume of the solvent influences the extraction ability of the asphaltene crystallisation. The current study proved that lower solvent volume had a more significant capacity of asphaltene extraction — the less the solvent volume will have a higher mutual balance as compared to the significant amount of asphaltene been dissolved in the crude oil. The asphaltene is more in contact to contact during the lesser the volume. The end of hydrogen tails amphiphilic is more in contact with the end of the solvent of a lesser volume than the higher volume. Too much injection of carbon dioxide will cause the acidic of the reservoir. Therefore CO_2 should be carefully monitored. During the molar ratio of CO_2 and oil, too much injection of CO_2 will reduce the asphaltene content.

The lower the solvent towards the asphaltene precipitation the greater the asphaltene particles. As the solvent decrease from 200 mL to 50 mL at a constant crude oil mass shows greater asphaltene particles. Therefore, the solubility during the mixture of crude oil and the solvent reveal greater adsorption forces (energy). The lower the overall solubility of the mixture of crude oil and solvent range between 3.5 wt% to 3.2 wt% the greater the asphaltene particles. Many articles have mentioned that paraffin is the cause of the asphaltene to precipitate and the cause of blockage on the pipeline during the production of crude oil.

However, during this research finding, it reveals that the aromatic compound is the cause of asphaltene precipitation. During the analyses of this research, it was found that aromatics content in crude oil results in greater asphaltene content. The phenomena are not fulling understood, however, it can be concluded based on the amphiphilic (hydrophilic + lipophilic), more of the lipophilic content in the amphiphilic can be the cause of the asphaltene content. As temperature increase above 90°C, the asphaltene content reaches the same asphaltene content value at room temperature (25°C). Heptane solvent on the CO_2 flooding had a greater increase on the asphaltene as temperature increases. The more the solubility solvent on the CO_2, the greater the asphaltene content.

6

APPENDICES

Appendix A- Crude oil analysis using GC-MS

Table A1: Analyses of crude oil A using GC/MS

RT	Area Pct	Library/ID
4.3075	3.3598	Toluene
4.4385	0.9768	3-Methylheptane
4.6247	0.8705	Dimethylcyclohexane
4.6798	0.7564	Cis-1,3-Dimethylcyclohexane Or Trans-1,3 Dimethylcyclohexane
4.8177	0.2135	Unknown
4.8936	0.3342	Cis-1-Ethyl-2-Methylcyclopentan
5.1073	3.1076	Octane
5.2659	0.2576	Cis,Trans-1,3-Dimethylcyclohexane
5.8382	0.3802	2,6-Dimethylheptane
6.0037	1.0001	Ethylcyclohexane
6.114	0.31	Cyclohexane, 1,1,3-Trimethyl-
6.576	0.6134	Heptane, 2,3-Dimethyl
6.707	0.489	Methyllaurate
6.7898	0.2956	Octane, 4-Methyl
6.8449	0.5781	Octane, 2-Methyl
6.9829	1.4194	Benzene, 1,3-Dimethyl
7.0173	1.2038	Benzene, 1,4-Dimethyl
7.4104	0.2613	Cyclopentane, Butyl
7.5207	0.3404	1-Ethyl-3-Methylcyclohexane
7.6172	0.9282	Cis-1-Ethyl-3-Methyl-Cyclohexane
7.8724	2.4666	Nonane
8.0723	0.3882	1,2,3,5-Tetramethylcyclohexane
8.424	0.3884	Cis-3-Hexenyl Formate
8.5136	0.2441	Nonane, 4-Methyl
8.7274	0.4914	Cyclohexane, Propyl
8.8101	0.6832	Octane, 3,6-Dimethyl
8.9618	0.4389	Heptane, 3-Ethyl-2-Methyl
9.3755	0.4172	Benzene, Propyl
9.5962	1.1985	Benzene, 1-Ethyl-3-Methyl
9.7065	0.6688	Nonane, 2-Methyl
9.8375	0.4743	1,2,4-Trimethylbenzene
9.8858	0.3652	Nonane, 3-Methyl
10.0719	0.3528	Benzene, 1-Ethyl-2-Methyl
10.2581	0.2896	Cyclohexane, 1-Methyl-2-Propyl-

10.534	0.9275	1,2,4-Trimethylbenzene
10.7477	2.3666	Decane
11.2786	0.3352	C3-Benzene
11.32	0.5521	Decane, 4-Methyl
11.6234	0.2742	Cyclohexane, Butyl
12.1061	0.2398	Benzene, 1-Methyl-3-Propyl
12.2647	0.5538	Decane, 5-Methyl
12.3543	0.4656	Decane, 4-Methyl
12.4853	0.553	Decane, 2-Methyl
12.6508	0.3239	Decane, 3-Methyl
12.7818	0.1691	Benzene, 4-Ethyl-1,2-Dimethyl
12.8508	0.2561	Benzene, 1-Methyl-2-(1-Methylethyl)
13.03	0.3109	1-Methyl-2-Phenylcyclopropane 2
13.4782	2.4107	Undecane
13.8575	0.4688	Benzene, 1,2,4,5-Tetramethyl
13.9609	0.1722	Benzene, 1-Ethyl-2,4-Dimethyl
14.1195	0.1913	Dodecane, 2,6,10-Trimethyl
14.2574	0.2914	2-Methyldecalin (Probably Trans)
14.3746	0.1856	Cyclohexane, Pentyl
14.7539	0.1639	Benzene, 1-Ethyl-2,4-Dimethyl
14.8159	0.2297	6-Methylundecane
14.8504	0.1484	Undecane, 5-Methyl
14.9607	0.3236	Undecane, 5-Methyl
15.0986	0.5238	Undecane, 2-Methyl
15.2503	0.3418	Undecane, 3-Methyl
15.5468	0.3183	Undecane, 2,4-Dimethyl
15.6709	0.4845	Naphthalene
16.0295	2.3587	Dodecane
16.3053	0.5065	Undecane, 2,6-Dimethyl
16.9811	0.2178	Cyclohexane, Hexyl
17.2362	0.1777	Dodecane, 6-Methyl
17.2776	0.2007	Dodecane, 5-Methyl
17.4017	0.2723	Dodecane, 4-Methyl
17.5396	0.4594	Dodecane, 2-Methyl
17.7258	0.8952	Tridecane, 7-Methyl
18.4222	2.8853	Tridecane
18.7256	0.489	Naphthalene, 2-Methyl
19.4151	0.3007	Cyclohexane, 1,1'-Methylenebis
19.5737	0.164	Tridecane, 5-Methyl
19.6978	0.1996	Tridecane, 4-Methyl
19.8288	0.4864	Tridecane, 2-Methyl
19.9736	0.251	Tridecane, 3-Methyl
20.0839	1.03	Nonane, 3,7-Dimethyl
20.67	2.4247	Tetradecane
20.8355	0.2481	Naphthalene, 1,5-Dimethyl

20.8769	0.3216	Naphthalene, 1,5-Dimethyl
21.132	0.5498	Naphthalene, 2,3-Dimethyl
21.2699	0.6967	Decahydro-4,4,8,9,10-Pentamethylnaphthalene
21.5733	0.1972	Naphthalene, 1,4-Dimethyl
21.6974	0.6959	Cyclohexane, Octyl
21.9112	1.2127	Hexadecane
21.9871	0.3073	Tetradecane, 2-Methyl
22.0629	0.3692	Decahydro-4,4,8,9,10-Pentamethylnaphthalene
22.1319	0.2583	Tetradecane, 3-Methyl-
22.78	2.4436	Pentadecane
23.3316	0.148	Naphthalene, 1,4,5-Trimethyl
23.4764	0.2036	Naphthalene, 1,4,6-Trimethyl
23.766	0.4059	Naphthalene, 1,6,7-Trimethyl
23.8488	0.2619	Methyl-Ethyl-Naphthalene
24.0211	0.3957	Hexadecane
24.1591	0.2597	Pentadecane, 3-Methyl
24.7797	2.1358	Hexadecane
25.6415	0.9222	Pentadecane, 2,6,10-Trimethyl
25.8346	0.1792	Tetradecane
25.9587	0.1767	Hexadecane, 2-Methyl
26.0897	0.1939	Hexadecane, 3-Methyl
26.6827	2.6282	Heptadecane
26.7379	1.8725	Pentadecane, 2,6,10,14-Tetramethyl
27.4205	0.2038	Hexadecane, 2,6,10,14-Tetramethyl
27.7929	0.4242	Pentadecane
28.4824	2.1688	Octadecane
28.5721	0.8061	Hexadecane, 2,6,10,14-Tetramethyl
29.5374	0.2443	Docosane, 7-Hexyl
29.958	0.2584	Hexadecane, 2,6,10,14-Tetramethyl
30.1993	2.1347	Nonadecane
31.1785	0.4186	Palmitic Acid
31.344	0.2325	Eicosane, 3-Methyl
31.8404	2.1275	Heneicosane
32.923	0.2055	Tricosane
33.4057	2.0827	Docosane
33.9366	0.2297	Heptadecene-(8)-Carbonic Acid-(1)
34.3227	0.3285	Octadecanoic Acid
34.9089	2.1135	Octadecanoic Acid
36.3431	2.0611	Hexadecane
37.7221	1.9891	Tetracosane
39.0529	1.8858	Pentacosane
40.3355	1.6578	Octacosane
41.5697	1.5914	Pentacosane
42.7557	1.2572	Hexadecane
43.9141	1.1148	Nonacosane

45.0243	0.9509	Triacontane
45.6793	0.2556	13(16),14-Labdien-8-Ol
46.0999	0.8781	Octacosane
46.424	0.3492	Phenanthrene, 9-Dodecyltetradecahydro
46.5826	0.2256	Phenanthrene, 9-Dodecyltetradecahydro
47.148	0.5548	Octacosane
48.1685	0.478	Octacosane
49.1614	0.2242	Tetracosane

Table A2: Analyses of crude oil B using GC/MS

RT	Area Pct	Library/ID
4.3074	2.9776	Toluene
4.4384	0.8587	3-Methylheptane
4.6246	0.7962	cis-1,3-Dimethylcyclohexane or trans-1,3-Dimethylcyclohexane
4.6867	0.6632	Cyclohexane, 1,4-dimethyl
4.8177	0.195	Unknown
4.9004	0.3121	Cyclopentane, 1-Ethyl-2-Methyl
5.1073	2.7689	Octane
5.2659	0.2431	Cyclohexane, 1,4-dimethyl
5.8382	0.3546	2,6-Dimethylheptane
6.0037	0.9091	Ethylcyclohexane
6.114	0.2926	Cyclooctane, (1-methylpropyl)
6.576	0.5719	Heptane, 2,3-Dimethyl
6.707	0.4598	Methyllaurate
6.7897	0.2862	Octane, 4-methyl
6.8518	0.5228	Dodecane, 4,6-dimethyl
6.9828	1.2914	Benzene, 1,3-dimethyl
7.0173	1.1388	Octane, 3-methyl
7.4103	0.252	Cyclopentane, butyl
7.5206	0.3251	Cyclohexane, 1-ethyl-4-methyl-, trans
7.6103	0.8842	Benzene, 1,4-dimethyl
7.8723	2.2834	Nonane
8.0723	0.3737	Cyclohexane, 1-ethyl-4-methyl-, cis
8.4308	0.3713	Pentalene, octahydro-2-methyl
8.5136	0.232	Nonane, 4-methyl
8.7273	0.4715	Cyclohexane, propyl
8.8101	0.6422	Octane, 2,6-dimethyl
8.9618	0.4185	Heptane, 3-ethyl-2-methyl
9.3824	0.3963	Undecane, 5,7-dimethyl
9.5341	0.2463	Benzene, propyl
9.5961	0.8984	Benzene, 1-ethyl-4-methyl
9.7065	0.6452	Nonane, 2-methyl
9.8375	0.4578	1,2,4-Trimethylbenzene
9.8857	0.3564	Nonane, 3-methyl

10.0719	0.3402	Decane
10.2581	0.2618	Cyclohexane, 1-methyl-2-propyl
10.5339	0.8013	1,2,4-Trimethylbenzene
10.7477	2.1916	Decane
11.2786	0.3156	1,2,4-Trimethylbenzene
11.32	0.5252	Decane, 4-methyl
11.6234	0.257	Cyclohexane, butyl
12.106	0.2287	Benzene, 1-methyl-3-propyl
12.2646	0.5432	Decane, 5-methyl
12.3543	0.4638	Decane, 4-methyl
12.4922	0.5461	Decane, 2-methyl
12.6508	0.32	Decane, 3-methyl
12.7818	0.1748	Benzene, 1-methyl-2-(1-methylethyl)
12.8507	0.2741	Benzene, 1-Methyl-3-(1-Methylethyl)
13.03	0.3616	1-Methyl-2-Phenylcyclopropane 2
13.4782	2.4495	Undecane
13.8574	0.4959	2-Methyldecalin
13.9609	0.1726	1,2,3,4-Tetramethylbenzene
14.1195	0.1972	Undecane, 5-Methyl
14.2574	0.298	2-Methyldecalin (Probably Trans)
14.3746	0.1887	Cyclohexane, Pentyl
14.7538	0.1685	Benzene, 1,2,3,5-Tetramethyl
14.8159	0.2336	Heptane, 3-Ethyl-2-Methyl
14.8504	0.1511	Undecane, 5-Methyl
14.9607	0.3251	Undecane, 5-Methyl
15.0986	0.5218	Undecane, 2-Methyl
15.2503	0.3412	Undecane, 3-Methyl
15.5468	0.1821	Spiro[5.6]Dodecane
15.6709	0.477	Naphthalene
16.0295	2.3394	Dodecane
16.3053	0.4783	Undecane, 2,6-Dimethyl
16.981	0.1739	Cyclohexane, Hexyl
17.2361	0.1583	Dodecane, 6-Methyl
17.2844	0.1828	Undecane, 2,4-Dimethyl
17.4016	0.1879	Dodecane, 4-Methyl
17.5395	0.4393	Dodecane, 2-Methyl
17.7257	0.8686	Tridecane, 7-Methyl
18.4152	2.8416	Tridecane
18.7255	0.4014	Naphthalene, 2-Methyl
19.4151	0.2945	Cyclohexane, 1,1'-Methylenebis
19.5736	0.1541	Tridecane, 5-Methyl
19.6909	0.1753	Tridecane, 4-Methyl
19.8288	0.4863	Tridecane, 2-Methyl
19.9736	0.2402	Tridecane, 3-Methyl
20.0839	1.0643	Nonane, 3,7-Dimethyl

20.67	2.5275	Tetradecane
20.8355	0.2856	Naphthalene, 1,5-Dimethyl
20.8769	0.3332	Naphthalene, 1,5-Dimethyl
21.132	0.5647	Naphthalene, 2,3-Dimethyl
21.5664	0.1736	Naphthalene, 1,2-Dimethyl
21.6974	0.586	Cyclohexane, Octyl
21.9111	1.202	Dodecane
21.987	0.2964	Tetradecane, 2-Methyl
22.0628	0.3644	Decahydro-4,4,8,9,10-Pentamethylnaphthalene
22.1318	0.24	Tetradecane, 3-Methyl
22.7799	2.5575	Pentadecane
23.3247	0.1679	Naphthalene, 1,4,6-Trimethyl
23.4695	0.251	Naphthalene, 1,4,6-Trimethyl
23.6695	0.1321	Tridecane
23.7729	0.4507	Naphthalene, 2,3,6-Trimethyl
23.8487	0.3001	Naphthalene, 2,3,6-Trimethyl
24.028	0.4593	Tridecane, 6-Propyl
24.1521	0.3247	Pentadecane, 3-Methyl
24.5658	0.2841	Naphthalene, 2,3,6-Trimethyl
24.7796	2.3033	Hexadecane
25.6415	1.0071	Pentadecane, 2,6,10-Trimethyl
25.8346	0.1961	Tetradecane
25.9518	0.1971	Tridecane, 2-Methyl
26.0897	0.1718	Hexadecane, 3-Methyl
26.6827	2.7775	Heptadecane
26.7379	2.1048	Pentadecane, 2,6,10,14-Tetramethyl
27.4205	0.2026	Hexatriacontane
27.7928	0.3951	Tridecane
27.9239	0.1056	Pentadecane,
28.4824	2.3303	Octadecane
28.572	0.9766	Hexadecane, 2,6,10,14-Tetramethyl
29.5374	0.2224	Hexadecane
29.958	0.2766	Hexatriacontane
30.1993	2.3009	Nonadecane
31.3439	0.1459	Nonadecane, 3-Methyl
31.8404	2.419	Eicosane
32.923	0.2986	Hexadecane
33.4056	2.2015	Eicosane
34.9019	2.2817	Tetracosane
35.7845	0.1548	Eicosane
36.343	2.1452	Eicosane, 7-Hexyl
37.7221	2.0842	Tetracosane
39.0529	1.9618	Pentacosane
40.3285	1.7228	Hexacosane
41.5628	1.672	Pentacosane

42.7557	1.4239	Octacosane
43.9072	1.1653	Pentacosane
45.0173	0.9991	Pentacosane
45.6724	0.2781	Tiacontane
46.0999	0.9411	Pentacosane
46.4171	0.3817	Anthracene, 9-Cyclohexyltetradecahydro
46.5757	0.2502	24-Norcholane, 23-[2-Methyl-1-(1-Methylethyl)Cyclopropyl]-, (5.Alpha.)
47.1411	0.5912	Octacosane
48.1616	0.517	Pentacosane
49.1545	0.2525	Heptacosane
50.1336	0.1478	Octacosane

Table A3: Analyses of crude oil C using GC/MS

RT	Area Pct	Library/ID
6.9759	0.0622	M-Xylene
7.6103	0.1562	P-Xylene
7.8448	0.1677	Nonane
9.5824	0.4006	Benzene, 1-Ethyl-3-Methyl
9.6927	0.2281	Nonane, 2-Methyl
9.8306	0.071	1,3,5-Trimethylbenzene
10.5201	0.7627	1,2,4-Trimethylbenzene
10.7132	0.912	Decane
11.2717	0.3225	Benzene, 1-Ethyl-4-Methyl
11.3062	0.2881	Nonane, 2,6-Dimethyl
11.6441	0.4502	1H-Indene, 2,3-Dihydro
12.0026	0.1808	Benzene, 1,3-Diethyl
12.0992	0.3727	Benzene, 1-Methyl-4-Propyl
12.2784	0.9411	Benzene, 4-Ethyl-1,2-Dimethyl
12.3543	0.2956	Decane, 4-Methyl
12.4784	0.5264	Decane, 2-Methyl
12.637	0.3058	Decane, 3-Methyl
12.768	0.3492	Benzene, 2-Ethyl-1,4-Dimethyl
12.8439	0.3863	Benzene, 1-Methyl-3-(1-Methylethyl)
13.0162	0.9556	Benzene, 1-Ethyl-2,4-Dimethyl
13.4368	1.5468	Undecane
13.5127	0.3695	Benzene, 1-Methyl-4-(1-Methylethyl)
13.8506	0.7544	1,2,3,4-Tetramethylbenzene
13.9471	0.686	P-Xylene, 2,5-Dimethyl-
14.1057	0.2041	Tetracosane, 2,6,10,15,19,23-Hexamethyl
14.347	0.3165	Benzene, (1,1-Dimethylpropyl)
14.4642	1.1373	Benzene, 2-Ethenyl-1,4-Dimethy
14.5746	0.2736	M-Xylene, 2-Ethyl
14.6849	1.3086	1H-Indene, 2,3-Dihydro-1-Methyl
14.747	0.4891	1,2,3,4-Tetramethylbenzene

14.8021	0.6761	Benzene, (1-Methylnonadecyl)
14.8366	0.3137	Undecane, 5-Methyl
14.9538	0.9431	Benzoic Acid, 2,5-Dimethyl
15.0848	0.8218	Undecane, 2-Methyl
15.1538	0.2516	Benzene, Diethylmethyl
15.2434	0.4655	Undecane, 3-Methyl
15.34	0.4371	Benzene, (1,1-Dimethylpropyl)
15.602	0.6182	1H-Indene, 2,3-Dihydro-4,6-Dimethyl
15.6709	2.6982	Naphthalene
15.7744	0.8103	1H-Indene, 2,3-Dihydro-4,7-Dimethyl
15.8916	2.0613	Benzene, (2-Methyl-1-Butenyl)
15.995	1.6241	Benzene, 2,4-Dimethyl-1-(1-Methylethyl)
16.1605	0.3536	Benzene, 1,3-Dimethyl-5-(1-Methylethyl)
16.2915	0.5949	Dodecane, 6-Methyl
16.4087	0.4563	Benzene, (1,2,2-Trimethylpropyl)
16.5121	0.3766	4-Nonene, 5-Butyl
16.5742	0.5616	Naphthalene, 1,2,3,4-Tetrahydro-1,1-Dimethyl
16.6569	0.2429	Undecane, 3,8-Dimethyl
16.7811	1.1711	5-Ethylindan
16.8569	0.3098	Benzene, 1,4-Dimethyl-2-(2-Methylpropyl)
16.9465	0.5299	1H-Indene, 2,3-Dihydro-1,1,5-Trimethyl
17.0224	0.5817	1H-Indene, 2,3-Dihydro-1,1,5-Trimethyl
17.0707	0.3109	Piperazine, 1-Phenyl
17.2086	2.1909	1H-Indene, 2,3-Dihydro-4,7-Dimethyl
17.3947	0.6664	Dodecane, 4-Methyl
17.4499	0.4193	Benzene, Hexyl
17.4982	0.8264	1H-Indene, 2,3-Dihydro-1,6-Dimethyl
17.5327	0.9384	Diallylmethylchlorosilane
17.6361	0.8367	1H-Indene, 2,3-Dihydro-1,2-Dimethyl
17.6843	0.9873	Dodecane, 3-Methyl
17.8429	0.6764	Benzene, 1,4-Dimethyl-2-(2-Methylpropyl)
17.8981	0.7076	Benzene, 1,3-Dimethyl-5-(1-Methylethyl)
17.9464	0.6656	1H-Indene, 2,3-Dihydro-4,7-Dimethyl
18.0912	0.4814	1H-Indene, 2,3-Dihydro-1,4,7-Trimethyl
18.1739	1.2051	Naphthalene, 1,2,3,4-Tetrahydro-5,7-Dimethyl
18.2429	1.093	1H-Indene, 2,3-Dihydro-1,1,3-Trimethyl
18.3739	6.0661	Naphthalene, 2-Methyl
18.5531	0.7402	2-Methylbenzo[B]Thiophene
18.6635	1.1757	Benzo[B]Thiophene, 2-Methyl
18.7187	2.347	Naphthalene, 2-Methyl
18.8083	0.6144	Benzene, 1,3,5-Trimethyl-2-(1-Propenyl)
18.891	0.6492	5,6,7,8-Tetrahydroquinoxaline
18.9876	0.7478	1H-Indene, 2,3-Dihydro-1,4,7-Trimethyl
19.0289	0.3086	Tetralin, 1-Ethyl
19.1393	0.5028	Tridecane, 3-Methyl

19.2634	0.5985	1,4-Dimethyltetralin
19.3254	0.3352	Benzene, 1-(1-Methylethenyl)-3-(1-Methylethyl)
19.4013	0.7722	Trans-1-(3,4-Dimethylphenyl)-But-2-ENE
19.4978	0.4251	6-Methyltridecane
19.5805	0.8691	5-Methyltridecane
19.684	0.3382	Tridecane, 4-Methyl
19.8219	1.2681	Tridecane, 2-Methyl
19.9598	0.6644	Tridecane, 3-Methyl
20.0701	0.9215	6-Propyltetraline
20.4494	1.0886	1H-Indene, 2,3-Dihydro-1,1,3-Trimethyl
20.5735	1.1277	2-Ethylnaphthalene
20.6217	1.6597	Tetradecane
20.8217	2.2873	Naphthalene, 2,6-Dimethyl
20.8631	1.389	Naphthalene, 1,6-Dimethyl
21.1251	3.1738	Naphthalene, 2,3-Dimethyl
21.2216	1.8927	Naphthalene, 1,7-Dimethyl
21.5526	1.5171	Naphthalene, 2,3-Dimethyl
21.6767	0.9094	1,2-Benzenedicarboxylic Acid, Dimethyl Ester
21.8491	1.2597	Naphthalene, 1,4-Dimethyl
21.9663	0.3559	Dodecane
22.0698	0.3338	1,5,8-Trimethyl
22.4628	0.4841	Acenaphthylene, 1,2-Dihydro
22.58	0.5978	Propylnaphthalene
22.6765	0.2985	2-Isopropylnaphthalene
22.7317	1.1542	Pentadecane
22.9041	1.5526	Naphthalene, 2-(1-Methylethyl)
23.0351	0.2919	Zentrobor-1
23.0765	0.2664	2,3,6-Trimethylnaphthalene
23.1937	0.3563	2,5,7-Trimethyl-1-Thiaindene
23.2489	0.227	Naphthalene, 1,4,6-Trimethyl
23.3109	0.6613	Naphthalene, 2,3,6-Trimethyl
23.4557	0.8926	Naphthalene, 2,3,6-Trimethyl
23.5385	0.257	Benzo[B]Thiophene, 2,5,7-Trimethyl-
23.7315	0.7206	Naphthalene, 1,4,6-Trimethyl
23.835	0.616	Naphthalene, 1,6,7-Trimethyl
24.0211	0.386	Naphthalene, 1,6,7-Trimethyl
24.0763	0.252	Naphthalene, 1,6,7-Trimethyl
24.1246	0.4347	Naphthalene, 1,4,6-Trimethyl
24.3935	0.1201	Azulene, 2,4,6-Trimethyl-
24.5107	0.2524	1,2-Benzenedicarboxylic Acid, Diethyl Ester
24.5521	0.197	Naphthalene, 1,4,6-Trimethyl
24.7313	1.3436	Hexadecane
24.8486	0.5238	1,1'-Biphenyl, 2-Methyl
25.152	0.1753	2,6,6-Trimethyl-3,4-Benzotricyclo
25.5657	0.3554	1,1'-Biphenyl, 2,2'-Dimethyl

26.6275	0.5149	Heptadecane
26.8206	0.181	1,1'-Biphenyl, 4,4'-Dimethyl
28.4272	0.3244	Octadecane
30.1442	0.2263	Nonadecane
31.7784	0.2507	Eicosane
33.3505	0.2873	Heneicosane
34.8468	0.3939	Eicosane
36.2879	0.3372	Octadecane
37.6738	0.4309	Tetracosane
39.0046	0.4995	Pentacosane
40.2871	0.6081	Heneicosane
41.5214	0.6608	Tricosane
42.7143	0.6278	Heptacosane
43.8658	0.5055	Heptacosane
44.9828	0.4387	Heptacosane
46.0654	0.3804	Heptacosane
47.1204	0.2497	Heptacosane
49.0442	0.2024	4,5.Alpha.-Epoxy-3-Methoxy-17-Methyl-7.Alpha.-4-Phenyl-1,3-Butadienyl)-6.Beta.,7.Beta.-(Oxymethylene) Morphinan

Table A4: Paraffin content in crude oil A

RT	Library/ID	RT	Library/ID	RT	Library/ID
4.4385	3-Methylheptane	15.5468	Undecane, 2,4-dimethyl	26.6827	Heptadecane
5.1073	Octane	16.0295	Dodecane	26.7379	Pentadecane, 2,6,10,14-tetramethyl
5.8382	2,6-Dimethylheptane	16.3053	Undecane, 2,6-dimethyl	27.4205	Hexadecane, 2,6,10,14-tetramethyl
6.576	Heptane, 2,3-dimethyl	17.2362	Dodecane, 6-methyl	27.7929	Pentadecane
6.7898	Octane, 4-methyl	17.2776	Dodecane, 5-methyl	28.4824	Octadecane
6.8449	Octane, 2-methyl	17.4017	Dodecane, 4-methyl	28.5721	Hexadecane, 2,6,10,14-tetramethyl
7.8724	Nonane	17.5396	Dodecane, 2-methyl	29.5374	Docosane, 7-hexyl
8.5136	Nonane, 4-methyl	17.7258	Tridecane, 7-methyl	29.958	Hexadecane, 2,6,10,14-tetramethyl
8.8101	Octane, 3,6-dimethyl	18.4222	Tridecane	30.1993	Nonadecane
8.9618	Heptane, 3-ethyl-2-methyl	19.5737	Tridecane, 5-methyl	31.344	Eicosane, 3-methyl
9.7065	Nonane, 2-methyl	19.6978	Tridecane, 4-methyl	31.8404	Heneicosane
9.8858	Nonane, 3-methyl	19.8288	Tridecane, 2-methyl	32.923	Tricosane
10.7477	Decane	19.9736	Tridecane, 3-methyl	33.4057	Docosane
11.32	Decane, 4-methyl	20.0839	Nonane, 3,7-dimethyl	36.3431	2,6 methyl Hexadecane
12.2647	Decane, 5-methyl	20.67	Tetradecane	37.7221	Tetracosane
12.3543	Decane, 5,1-methyl	21.9112	Hexadecane	39.0529	Pentacosane
12.4853	Decane, 2-methyl	21.9871	Tetradecane, 2-methyl	40.3355	Octacosane

12.6508	Decane, 3-methyl	22.78	Pentadecane	41.5697	3,1-propyl Pentacosane
13.4782	Undecane	24.0211	Propyl, Hexadecane	42.7557	2-dimethyl Hexadecane
14.1195	Dodecane, 2,6,10-trimethyl	24.1591	Pentadecane, 3-methyl	43.9141	Nonacosane
14.8159	6-Methylundecane	24.7797	Hexadecane	45.0243	Triacontane
14.8504	Undecane, 5-methyl	25.6415	Pentadecane, 2,6,10-Trimethyl	46.0999	Dimetyl, Octacosane
14.9607	Undecane, 3-methyl	25.8346	Tetradecane	47.148	1.5-dimetyl Octacosane
15.0986	Undecane, 2-methyl	25.9587	Hexadecane, 2-methyl	48.1685	2-metyl Octacosane
15.2503	Undecane, 3-methyl	26.0897	Hexadecane, 3-methyl	49.1614	Butyl, Tetracosane

Table A5: Aromatic content in crude oil A

RT	Library/ID	RT	Library/ID
4.3075	Toluene	13.8575	Benzene, 1,2,4,5-tetramethyl
6.9829	Benzene, 1,3-dimethyl	13.9609	Benzene, 1-ethyl-2,4-dimethyl
7.0173	Benzene, 1,4-dimethyl	14.7539	Benzene, 2-ethyl-2,5-dimethyl
9.3755	Benzene, propyl	15.6709	Naphthalene
9.5962	Benzene, 1-ethyl-3-methyl	18.7256	Naphthalene, 2-methyl
9.8375	1,2,4-Trimethylbenzene	20.8355	Naphthalene, 1,5-dimethyl
10.0719	Benzene, 1-ethyl-2-methyl	20.8769	Naphthalene, 1,3-dimethyl
10.534	1,2,4-Trimethylbenzene	21.132	Naphthalene, 2,3-dimethyl
11.2786	C3-Benzene	21.5733	Naphthalene, 1,4-dimethyl
12.1061	Benzene, 1-methyl-3-propyl	23.3316	Naphthalene, 1,4,5-trimethyl
12.7818	Benzene, 4-ethyl-1,2-dimethyl	23.4764	Naphthalene, 1,4,6-trimethyl
12.8508	Benzene, 1-methyl-2-(1-methylethyl)	23.766	Naphthalene, 1,6,7-trimethyl
		23.8488	Methyl-ethyl-Naphthalene

Table A6: Naphthene content in crude oil A

RT	Library/ID	RT	Library/ID
4.6247	cis-1,3-Dimethylcyclohexane	8.7274	Cyclohexane, propyl
4.6798	cis-1,4-Dimethylcyclohexane	13.03	1-Methyl-2-Phenylcyclopropane 2
4.8936	cis-1-Ethyl-2-methylcyclopentane	8.0723	1,2,3,5-tetramethylcyclohexane
5.2659	cis,trans-1,3-Dimethylcyclohexane	10.2581	Cyclohexane, 1-methyl-2-propyl-
6.0037	Ethylcyclohexane	11.6234	Cyclohexane, butyl
6.114	Cyclohexane, 1,1,3-trimethyl	14.3746	Cyclohexane, pentyl
7.4104	Cyclopentane, butyl	16.9811	Cyclohexane, hexyl
7.5207	1-Ethyl-3-methylcyclohexane	21.6974	Cyclohexane, octyl
7.6172	cis-1-Ethyl-3-methyl-cyclohexane		

Table A7: Paraffin content in crude oil B

RT	Library/ID	RT	Library/ID
4.4384	3-Methylheptane	20.67	Tetradecane
5.1073	Octane	21.6974	Cyclohexane, octyl
6.576	Heptane, 2,3-dimethyl	21.9111	2,1-Methyl Dodecane
6.7897	Octane, 4-methyl	22.1318	Tetradecane, 3-methyl
6.8518	Dodecane, 4,6-dimethyl	22.7799	Pentadecane
7.0173	Octane, 3-methyl	23.6695	Tridecane ,4,1-dimethyl
7.8723	Nonane	24.028	Tridecane, 6-propyl
8.5136	Nonane, 4-methyl	24.1521	Pentadecane, 3-methyl
8.7273	Cyclohexane, propyl	24.7796	Hexadecane
8.8101	Octane, 2,6-dimethyl	25.6415	Pentadecane, 2,6,10-Trimethyl
8.9618	Heptane, 3-ethyl-2-methyl	25.8346	Tetradecane
9.3824	Undecane, 5,7-dimethyl	25.9518	Tridecane, 3-methyl
9.7065	Nonane, 2-methyl	26.0897	Hexadecane, 3-methyl
9.8857	Nonane, 3-methyl	26.6827	Heptadecane
10.0719	Decane	26.7379	Pentadecane, 2,6,10,14-tetramethyl
10.7477	2-Trimetyl, Decane	27.4205	Hexatriacontane
11.32	Decane, 4-methyl	27.7928	Tridecane
12.2646	Decane, 5-methyl	27.9239	Pentadecane,
12.3543	Decane, 4-dimethyl	28.4824	Octadecane
12.4922	Decane, 2-methyl	28.572	Hexadecane, 2,6,10,14-tetramethyl
12.6508	Decane, 3-methyl	29.5374	Hexadecane
13.4782	Undecane	29.958	Hexatriacontane
14.1195	Undecane, 5-methyl	30.1993	Nonadecane
14.8159	Heptane, 3-ethyl-2-methyl	31.3439	Nonadecane, 3-methyl
14.8504	Undecane, 5-methyl	31.8404	Eicosane
14.9607	Undecane, 6-methyl	32.923	Hexadecane
15.0986	Undecane, 2-methyl	33.4056	Eicosane
15.2503	Undecane, 3-methyl	34.9019	Tetracosane
16.0295	Dodecane	35.7845	Eicosane
16.3053	Undecane, 2,6-dimethyl	36.343	Eicosane, 7-hexyl
16.981	Cyclohexane, hexyl	37.7221	Tetracosane
17.2361	Dodecane, 6-methyl	39.0529	Pentacosane
17.2844	Undecane, 2,4-dimethyl	40.3285	2,4-dimethyl, Hexacosane
17.4016	Dodecane, 4-methyl	41.5628	2,1-dimethyl, Pentacosane
17.5395	Dodecane, 2-methyl	42.7557	Octacosane
17.7257	Tridecane, 7-methyl	43.9072	3-methyl, Pentacosane
18.4152	Tridecane	45.0173	1,6-propyl, Pentacosane
19.5736	Tridecane, 5-methyl	45.6724	Tiacontane
19.6909	Tridecane, 4-methyl	46.0999	1,3-methyl, Pentacosane
19.8288	Tridecane, 2-methyl	47.1411	Octacosane
19.9736	Tridecane, 3-methyl	48.1616	Pentacosane, 4-methyl
20.0839	Nonane, 3,7-dimethyl	49.1545	Heptacosane, 5-methyl
		50.1336	Octacosane

Table A8: Aromatic content in crude oil B

RT	Library/ID	RT	Library/ID
4.3074	Toluene	15.6709	Naphthalene
6.9828	Benzene, 1,3-dimethyl	18.7255	Naphthalene, 2-methyl
7.6103	Benzene, 1,4-dimethyl	20.8355	Naphthalene, 1,5-dimethyl
9.5341	Benzene, propyl	20.8769	Naphthalene, 1,5-dimethyl
9.5961	Benzene, 1-ethyl-4-methyl	21.132	Naphthalene, 2,3-dimethyl
9.8375	1,2,4-Trimethylbenzene	21.263	Decahydro-4,4,8,9,10-pentamethylnaphthalene
10.5339	1,2,4-Trimethylbenzene	21.5664	Naphthalene, 1,2-dimethyl
11.2786	1,2,4-Trimethylbenzene	21.987	Tetradecane, 2-methyl
12.106	Benzene, 1-methyl-3-propyl	22.0628	Decahydro-4,4,8,9,10-pentamethylnaphthalene
12.7818	Benzene, 1-methyl-2-(1-methylethyl)	23.3247	Naphthalene, 1,4,6-trimethyl
12.8507	Benzene, 1-methyl-3-(1-methylethyl)	23.4695	Naphthalene, 1,4,3-trimethyl
13.03	1-Methyl-2-Phenylcyclopropane 2	23.7729	Naphthalene, 2,3,6-trimethyl
13.9609	1,2,3,4-Tetramethylbenzene	23.8487	Naphthalene, 2,3,5-trimethyl
14.7538	Benzene, 1,2,3,5-tetramethyl	24.5658	Naphthalene, 2,3,6-trimethyl

Table A10: Naphthene content in crude oil B

RT	Library/ID	RT	Library/ID
4.6246	cis-1,3-Dimethylcyclohexane	7.4103	Cyclopentane, butyl
4.6867	Cyclohexane, 1,4-dimethyl	7.5206	Cyclohexane, 1-ethyl-4-methyl
4.9004	Cyclopentane, 1-Ethyl-2-Methyl	8.0723	Cyclohexane, 1-ethyl-2-methyl
5.2659	Cyclohexane, 1,4-dimethyl	10.2581	Cyclohexane, 1-methyl-2-propyl
5.8382	2,6-Dimethylheptane	11.6234	Cyclohexane, butyl
6.0037	Ethylcyclohexane	14.3746	Cyclohexane, pentyl
6.114	Cyclooctane, (1-methylpropyl)		

Table A11: Paraffin content in crude oil C

RT	Library/ID	RT	Library/ID
7.8448	Nonane	19.9598	Tridecane, 3-methyl
9.6927	Nonane, 2-methyl	20.6217	Tetradecane
10.7132	Decane	21.9663	Dodecane
11.3062	Nonane, 2,6-dimethyl	22.7317	Pentadecane
12.3543	Decane, 4-methyl	24.7313	Hexadecane
12.4784	Decane, 2-methyl	26.6275	Heptadecane
12.637	Decane, 3-methyl	28.4272	Octadecane

13.4368	Undecane	30.1442	Nonadecane
14.1057	Tetracosane, 2,6,10,15,19,23-hexamethyl	31.7784	Eicosane
14.8366	Undecane, 5-methyl	33.3505	Heneicosane
15.0848	Undecane, 2-methyl	34.8468	1,3-methyl, Eicosane
15.2434	Undecane, 3-methyl	36.2879	Octadecane
16.2915	Dodecane, 6-methyl	37.6738	Tetracosane
16.6569	Undecane, 3,8-dimethy	39.0046	Pentacosane
17.3947	Dodecane, 4-methyl	40.2871	1,2-trimetyl, Heneicosane, 4-dimethyl
17.6843	Dodecane, 3-methyl	41.5214	Tricosane
19.1393	Tridecane, 3-methyl	42.7143	Heptacosane
19.4978	6-Methyltridecane	43.8658	2,1-Methyl, Heptacosane
19.5805	3-Methyltridecane	44.9828	2,2-Methyl, Heptacosane
19.684	Tridecane, 4-methyl	46.0654	2,3-Methyl, Heptacosane
19.8219	Tridecane, 2-methyl	47.1204	2,4-Methyl, Heptacosane

Table A12: The aromatic content in the crude oil C

RT	Library/ID	RT	Library/ID
6.9759	m-Xylene	17.8429	Benzene, 1,4-dimethyl-2-(2-methylpropyl)
7.6103	p-Xylene	17.8981	Benzene, 1,3-dimethyl-5-(1-methylethyl)
9.5824	Benzene, 1-ethyl-3-methyl	18.1739	Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl
9.8306	1,3,5-Trimethylbenzene	18.3739	Naphthalene, 2-methyl
10.5201	1,2,4-Trimethylbenzene	18.7187	2,1-Methyl, Naphthalene,
11.2717	Benzene, 1-ethyl-4-methyl	18.8083	Benzene, 1,3,5-trimethyl-2-(1-propenyl)
12.0026	Benzene, 1,3-diethyl	20.8217	Naphthalene, 2,6-dimethyl
12.0992	Benzene, 1-methyl-4-propyl	20.8631	Naphthalene, 1,6-dimethyl
12.2784	Benzene, 4-ethyl-1,2-dimethyl	21.1251	Naphthalene, 2,3-dimethyl
12.768	Benzene, 2-ethyl-1,4-dimethyl	21.2216	Naphthalene, 1,7-dimethyl
12.8439	Benzene, 1-methyl-3-(1-methylethyl)	21.5526	Naphthalene, 2,3-dimethyl
13.0162	Benzene, 1-ethyl-2,4-dimethyl	21.6767	1,2-Benzenedicarboxylic acid, dimethyl ester
13.5127	Benzene, 1-methyl-4-(1-methylethyl)	21.8491	Naphthalene, 1,4-dimethyl
13.8506	1,2,3,4-tetramethylbenzene	22.58	propylnaphthalene
13.9471	p-Xylene, 2,5-dimethyl	22.6765	2-Isopropylnaphthalene
14.347	Benzene, (1,1-dimethylpropyl)	22.9041	Naphthalene, 2-(1-methylethyl)
14.4642	Benzene, 2-ethenyl-1,4-dimethy	23.0765	2,3,6-Trimethylnaphthalene

14.5746	m-Xylene, 2-ethyl	23.2489	Naphthalene, 1,4,6-trimethyl
14.6849	1H-Indene, 2,3-dihydro-1-methyl	23.3109	Naphthalene, 2,3,6-trimethyl
14.747	1,2,3-Tetramethylbenzene	23.4557	Naphthalene, 2,3,6-trimethyl
14.8021	Benzene, (1-methylnonadecyl)	23.5385	Benzo[b]thiophene, 2,5,7-trimethyl-
15.34	Benzene, (1,1-dimethylpropyl)	23.7315	Naphthalene, 1,4,6-trimethyl
15.6709	Naphthalene	23.835	Naphthalene, 1,6,7-trimethyl
15.8916	Benzene, (2-methyl-1-butenyl)	24.0211	Naphthalene, 1,6,7-trimethyl
15.995	Benzene, 2,4-dimethyl-1-(1-methylethyl)	24.0763	Naphthalene, 1,6,8-trimethyl
16.1605	Benzene, 1,3-dimethyl-5-(1-methylethyl)	24.1246	Naphthalene, 1,4,6-trimethyl
16.4087	Benzene, (1,2,2-trimethylpropyl)	24.5107	1,2-Benzenedicarboxylic acid, diethyl ester
16.5742	Naphthalene, 1,2,3,4-tetrahydro-1,1-dimethyl	24.5521	Naphthalene, 1,4,6-trimethyl
16.8569	Benzene, 1,4-dimethyl-2-(2-methylpropyl)	24.8486	1,1'-Biphenyl, 2-methyl
17.0707	Piperazine, 1-phenyl	25.152	2,6,6-trimethyl-3,4-benzotricyclo
17.4499	Benzene, hexyl	25.5657	1,1'-Biphenyl, 2,2'-dimethyl
		26.8206	1,1'-Biphenyl, 4,4'-dimethyl

During the analysis of the components in crude oil C, it was found that they were no present off naphthene. The predominant compounds in this crude oil were aromatic compounds which then followed by paraffin.

Appendix B- Calculations of asphaltene content

The density of each crude oil A, B and C were analysed using a density meter.

Crude oil A = 0.965 g/cm^3

Crude oil B = 0.972 g/cm^3

Crude oil C = 0.985 g/cm^3

Table B1: Sample calculations on the asphaltene content

	Solvents	**Ratio (40:1) 200 mL into 5 g**	**Ratio (30:1) 150 mL into 5 g**	**Ratio (20:1) 100 mL into 5 g**	**Ratio (20:1)* 50 mL into 2.5 g**
Crude Oil A	**Pentane (C_5)**	6.6	11.0	9.2	13.2
	Hexane (C_6)	4.0	10.6	6.6	6.0
	Heptane (C_7)	3.6	2.6	4.2	4.8
Crude Oil B	**Pentane (C_5)**	6.8	8.8	10.2	9.2
	Hexane (C_6)	6.4	5.4	6	6.4
	Heptane (C_7)	3.0	3.4	3.6	3.6
Crude Oil C	**Pentane (C_5)**	23.2	23.3	24.1	23.9
	Hexane (C_6)	22.3	22.1	23.1	22.6
	Heptane (C_7)	22.2	21.7	22.4	21.9

The average mass of the asphaltene deposit: $\mathbf{A}_{\mathbf{ma}} = \frac{\text{run1+ run2+ run3}}{\text{total number of runs}}$

Equation 3.1 was used to calculate the asphaltene content of each crude oil using different solvents.

Extraction of asphaltenes from crude oil using ratio (40:1)

(Using 5 g of oil with 200 mL of solvents)

The wettability is the number of moistures lost during the drying process.

Mass of the asphaltenes deposit = mass of dry asphaltene with filter paper - a mass of filter paper

Crude oil A **Run 1**-(**Pentane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.39 g)

Run 2-Filter paper (1.08 g); Dry asphaltene with filter paper (1.47 g)

Run 3-Filter paper (1.11 g); Dry asphaltene with filter paper (1.42 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.22 g) – a mass of dry asphaltene content with filter paper (1.39 g) = **0.83 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.28 g) – a mass of dry asphaltene content with filter paper (1.47 g) = **0.81 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.31 g) – a mass of dry asphaltene content with filter paper (1.42 g) =**0.89 g**

Crude oil B **Run 1**-(**Pentane**) Filter paper (1.09 g); Dry asphaltene with filter paper (1.44 g)

Run 2-Filter paper (1.13 g); Dry asphaltene with filter paper (1.46 g)

Run 3-Filter paper (1.07 g); Dry asphaltene with filter paper (1.44 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.95 g) – a mass of dry asphaltene content with filter paper (1.44 g) = **0.51 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.98 g) – a mass of dry asphaltene content with filter paper (1.46 g) =**0.51 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.93 g) – a mass of dry asphaltene content with filter paper (1.44 g) = **0.49 g**

Crude oil C **Run 1-** (**Pentane**) Filter paper (1.11 g); Dry asphaltene with filter paper (2.29 g)

Run 2-Filter paper (1.08 g); Dry asphaltene with filter paper (2.21 g)

Run 3-Filter paper (1.09 g); Dry asphaltene with filter paper (2.26 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.26 g) – a mass of dry asphaltene content with filter paper (2.29 g) = **0.970 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.16 g) – a mass of dry asphaltene content with filter paper (2.21 g) = **0.950 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.26 g) = **0.950 g**

Extraction of asphaltenes from crude oil using ratio (40:1)

(Using 5 g of oil with 200 mL of solvents)

Crude oil A **Run 1**-(**Hexane**) Filter paper (1.08 g); Dry asphaltene with filter paper (1.28 g)

Run 2- Filter paper (1.08 g); Dry asphaltene with filter paper (1.29 g)

Run 3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.30 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.71 g) – a mass of dry asphaltene content with filter paper (1.28 g) =**0.43 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.79 g) – a mass of dry asphaltene content with filter paper (1.29 g) = **0.50 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.81 g) – a mass of dry asphaltene content with filter paper (1.30 g) =**0.51 g**

Crude oil B **Run1** (**Hexane**) Filter paper (1.11 g); Dry asphaltene with filter paper (1.43 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.44 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (1.37 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.84 g) – a mass of dry asphaltene content with filter paper (1.43 g) = **0.41 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.91 g) – a mass of dry asphaltene content with filter paper (1.44 g) = **0.47 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.88 g) – a mass of dry asphaltene content with filter paper (1.37 g) = **0.51 g**

Crude oil C **Run1** (**Hexane**) Filter paper (1.13 g); Dry asphaltene with filter paper (2.25 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (2.21 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (2.22 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.25 g) = **0.960 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.09 g) – a mass of dry asphaltene content with filter paper (2.21 g) = **0.880 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.16 g) – a mass of dry asphaltene content with filter paper (2.22 g) = **0.940 g**

Table B2: Sample calculations on the asphaltene content on hexane

SOLVENT: N-HEXANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	5.2 g	4.96 g	5.02 g	5.0 g	5.01 g	5.0 g	4.9 g	5.08 g	5.1 g
Volume solvent	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL
mass asphaltenes deposited	0.20 g	0.21 g	0.19 g	0.32 g	0.35 g	0.28 g	1.12 g	1.11 g	1.13 g
Average mass	**0.20 g**			**0.32 g**			**1.115 g**		
Average asphaltene content	**4 g/mL**			**6.4 g/mL**			**22.3 g/mL**		

Extraction of asphaltenes from crude oil using ratio (40:1)

(Using 5 g of oil with 200 mL of solvents)

Crude oil A **Run 1**-(**Heptane**) Filter paper (1.06 g); Dry asphaltene with filter paper (1.26 g)

Run 2- Filter paper (1.07 g); Dry asphaltene with filter paper (1.25 g)

Run 3- Filter paper (1.09 g); Dry asphaltene with filter paper (1.25 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.71 g) – a mass of dry asphaltene content with filter paper (1.28 g) =**0.45 g**.

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.70 g) – a mass of dry asphaltene content with filter paper (1.29 g) = **0.41 g.**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.74 g) – a mass of dry asphaltene content with filter paper (1.30 g) =**0.44 g**.

Crude oil B **Run 1**-(**Heptane**) Filter paper (1.09 g); Dry asphaltene with filter paper (1.25 g)

Run 2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.27 g)

Run 3- Filter paper (1.07 g); Dry asphaltene with filter paper (1.18 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.70 g) – a mass of dry asphaltene content with filter paper (1.25 g) =**0.45 g**.

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.77 g) – a mass of dry asphaltene content with filter paper (1.27 g) = **0.50 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.79 g) – a mass of dry asphaltene content with filter paper (1.18 g) =**0.61 g**

Crude oil C **Run1** (**Heptane**) Filter paper (1.11 g); Dry asphaltene with filter paper (2.12 g)

Run2- Filter paper (1.11 g); Dry asphaltene with filter paper (2.22 g)

Run3- Filter paper (1.07 g); Dry asphaltene with filter paper (2.28 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.10 g) – a mass of dry asphaltene content with filter paper (2.12 g) = **0.98 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.16 g) – a mass of dry asphaltene content with filter paper (2.22 g) =**0.94 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.28 g) = **0.93 g**

Table B3: Sample calculations on the asphaltene content on heptane

SOLVENT: N-HEPTANE									
	CRUDE OIL A			**CRUDE OIL B**			**CRUDE OIL C**		
Mass oil used	5.01 g	5.02 g	5.01 g	5.03 g	5.01 g	5.03 g	5.07 g	4.96 g	4.98 g
Volume solvent	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL	200 mL
mass asphaltenes deposited	0.20 g	0.18 g	0.16 g	0.16 g	0.18 g	0.11 g	1.01 g	1.11 g	1.21 g
Average mass	**0.18 g**			**0.15 g**			**1.11 g**		
Average asphaltene content	**3.6 g/mL**			**3 g/mL**			**22.2 g/mL**		

Extraction of asphaltenes from crude oil using ratio 30:1

(Using 5 g of oil with 150 mL of solvents)

Pentane at 5 g into 150 mL, (Ratio 30:1)

Mass of the asphaltenes deposit = mass of dry asphaltene with filter paper – a mass of filter paper

Crude oil A **Run1**- (**Pentane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.67 g)

Run2- Filter paper (1.11 g); Dry asphaltene with filter paper (1.60 g)

Run3- Filter paper (1.08 g); Dry asphaltene with filter paper (1.67 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.44 g) – a mass of dry asphaltene content with filter paper (1.67 g) =**0.77 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.48 g) – a mass of dry asphaltene content with filter paper (1.60 g) =**0.88 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.46 g) – a mass of dry asphaltene content with filter paper (1.67 g) =**0.79 g**

Crude oil B **Run1**- (**Pentane**) Filter paper (1,08 g); Dry asphaltene with filter paper (1.55 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.55 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (1.50 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.02 g) – a mass of dry asphaltene content with filter paper (1.55 g) =**0.47 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.09 g) – a mass of dry asphaltene content with filter paper (1.55 g) =**0.54 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.06 g) – a mass of dry asphaltene content with filter paper (1.50 g) =**0.56 g**

Crude oil C **Run1**- (**Pentane**) Filter paper (1.10 g); Dry asphaltene with filter paper (2.271 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (2.263 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (2.266 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.20 g) – a mass of dry asphaltene content with filter paper (2.271 g) =**0.929 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.19 g) – a mass of dry asphaltene content with filter paper (2.263 g) =**0.927 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.25 g) – a mass of dry asphaltene content with filter paper (2.266 g) =**0.984 g**

Table B4: Sample calculations on the asphaltene content on pentane at 150 mL

SOLVENT: N-PENTANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	5.01 g	5.0 g	4.99 g	5.0 g	5.0 g	5.0 g	4.99 g	5.3 g	5.0 g
Volume solvent	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL
mass asphaltenes deposited	0.57 g	0.49 g	0.59 g	0.47 g	0.45 g	0.40 g	1.171 g	1.163 g	1.166 g
Average mass	**0.55 g**			**0.44 g**			**1.167 g**		
Average asphaltene content	**11 g/mL**			**8.8 g/mL**			**23.3 g/mL**		

Extraction of asphaltenes from crude oil using ratio 30:1

(using 5 g of oil with 150 mL of solvents)

Hexane at 5 g into 150 mL, (Ratio 30:1)

Crude oil A **Run1**- (**Hexane**) Filter paper (1.12 g); Dry asphaltene with filter paper (1.65 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.67 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (1.59 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.79 g) – a mass of dry asphaltene content with filter paper (1.65 g) =**0.14 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.82 g) – a mass of dry asphaltene content with filter paper (1.67 g) =**0.15 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.74 g) – a mass of dry asphaltene content with filter paper (1.59 g) =**0.15 g**

Crude oil B **Run1**- (**Hexane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.41 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.34 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.37 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.02 g) – a mass of dry asphaltene content with filter paper (1.41 g) =**0.61 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.09 g) – a mass of dry asphaltene content with filter paper (1.34 g) =**0.75 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.12 g) – a mass of dry asphaltene content with filter paper (1.37 g) =**0.75 g**

Crude oil C **Run1**- (**Hexane**) Filter paper (1.10 g); Dry asphaltene with filter paper (2.201 g)

Run2- Filter paper (1.11 g); Dry asphaltene with filter paper (2.219 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (2.205 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.20 g) – a mass of dry asphaltene content with filter paper (2.201 g) =**0.999 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.18 g) – a mass of dry asphaltene content with filter paper (2.219 g) =**0.961 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.19 g) – a mass of dry asphaltene content with filter paper (2.205 g) =**0.985 g**

Table B5: Sample calculations on the asphaltene content on hexane at 150 mL

SOLVENT: N-HEXANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	4.98 g	5.0 g	5.01 g	5.0 g	5.01 g	5.0 g	4.98 g	5.08 g	5.01 g
Volume solvent	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL
mass asphaltenes deposited	0.53 g	0.57 g	0.49 g	0.31 g	0.24 g	0.26 g	1.101 g	1.109 g	1.105 g
Average mass	**0.53 g**			**0.27 g**			**1.105 g**		
Average asphaltene content	**10.6 g/mL**			**5.4 g/mL**			**22.1 g/mL**		

Extraction of asphaltenes from crude oil using ratio 30:1

(using 5 g of oil with 150 mL of solvents)

Crude oil A **Run1**- (**Heptane**) Filter paper (1.11 g); Dry asphaltene with filter paper (1.26 g)

Run2- Filter paper (1.06 g); Dry asphaltene with filter paper (1.19 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (1.21 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.89 g) – a mass of dry asphaltene content with filter paper (1.26 g) =0.63 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.87 g) – a mass of dry asphaltene content with filter paper (1.19 g) =0.68 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.98 g) – a mass of dry asphaltene content with filter paper (1.21 g) =0.77 g

Crude oil B **Run1**- (**Heptane**) Filter paper (1.06 g); Dry asphaltene with filter paper (1.25 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.23 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.29 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.90 g) – a mass of dry asphaltene content with filter paper (1.25 g) =0.65 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.94 g) – a mass of dry asphaltene content with filter paper (1.23 g) =0.71 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.91 g) – a mass of dry asphaltene content with filter paper (1.29 g) =0.62 g

Crude oil C **Run1**- (**Heptane**) Filter paper (1.12 g); Dry asphaltene with filter paper (2.196 g)

Run2- Filter paper (1.07 g); Dry asphaltene with filter paper (2.155 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (2.194 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.14 g) – a mass of dry asphaltene content with filter paper (2.196 g) =**0.944 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.12 g) – a mass of dry asphaltene content with filter paper (2.155 g) =**0.965 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.11 g) – a mass of dry asphaltene content with filter paper (2.194 g) =**0.916 g**

Table B6: Sample calculations on the asphaltene content on heptane at 150 mL

SOLVENT: N-HEPTANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	5.01 g	5.0 g	4.99 g	5.0 g	5.0 g	5.0 g	5.7 g	5.03 g	4.99 g
Volume solvent	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL	150 mL
mass asphaltenes deposited	0.15 g	0.13 g	0.11 g	0.19 g	0.14 g	0.18 g	1.076 g	1.085 g	1.094 g
Average mass	**0.13 g**			**0.17 g**			**1.085 g**		
Average asphaltene content	**2.6 g/mL**			**3.4 g/mL**			**21.7 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1

(Using 5 g of oil with 100 mL of solvents

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Pentane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.52 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.51 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (1.64 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.01 g) – a mass of dry asphaltene content with filter paper (1.52 g) =**0.49 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.11 g) – a mass of dry asphaltene content with filter paper (1.51 g) =**0.60 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.13 g) – a mass of dry asphaltene content with filter paper (1.64 g) =**0.49 g**

Crude oil B **Run1**- (**Pentane**) Filter paper (1.12 g); Dry asphaltene with filter paper (1.68 g)

Run2- Filter paper (1.12 g); Dry asphaltene with filter paper (1.61 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.59 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.24 g) – a mass of dry asphaltene content with filter paper (1.68 g) =**0.56 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.29 g) – a mass of dry asphaltene content with filter paper (1.61 g) =**0.68 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.21 g) – a mass of dry asphaltene content with filter paper (1.59 g) =**0.60 g**

Crude oil C **Run1**- (**Pentane**) Filter paper (1.08 g); Dry asphaltene with filter paper (2.284 g)

Run2- Filter paper (1.08 g); Dry asphaltene with filter paper (2.286 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (2.305 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.23 g) – a mass of dry asphaltene content with filter paper (2.284 g) =**0.944 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.286 g) =**0.924 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.19 g) – a mass of dry asphaltene content with filter paper (2.305 g) =**0.885 g**

Table B7: Sample calculations on the asphaltene content on pentane at 100 mL

SOLVENT: N-PENTANE									
	CRUDE OIL A			**CRUDE OIL B**			**CRUDE OIL C**		
Mass oil used	4.99 g	4.99 g	5.02 g	5.01 g	5.02 g	5.0 g	5.01 g	5.02 g	5.04 g
Volume solvent	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL
mass asphaltenes deposited	0.42 g	0.41 g	0.55 g	0.56 g	0.49 g	0.48 g	1.204 g	1.206 g	1.205 g
Average mass	**0.46 g**			**0.51 g**			**1.205 g**		
Average asphaltene content	**9.2 g/mL**			**10.2 g/mL**			**24.1 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1

(Using 5 g of oil with 100 mL of solvent

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Hexane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.45 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.40 g)

Run3- Filter paper (1.12 g); Dry asphaltene with filter paper (1.45 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.18 g) – a mass of dry asphaltene content with filter paper (1.45 g) =0.73 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.14 g) – a mass of dry asphaltene content with filter paper (1.40 g) =0.74 g

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.31 g) – a mass of dry asphaltene content with filter paper (1.45 g) =0.86 g

Crude oil B **Run1**- (**Hexane**) Filter paper (1.09 g); Dry asphaltene with filter paper (1.39 g)

Run2- Filter paper (1.12 g); Dry asphaltene with filter paper (1.49 g)

Run3- Filter paper (1.07 g); Dry asphaltene with filter paper (1.30 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.24 g) – a mass of dry asphaltene content with filter paper (1.39 g) =**0.85 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.97 g) – a mass of dry asphaltene content with filter paper (1.49 g) =**0.58 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.16 g) – a mass of dry asphaltene content with filter paper (1.30 g) =**0.86 g**

Crude oil C **Run1**- (**Hexane**) Filter paper (1.11 g); Dry asphaltene with filter paper (2.268 g)

Run2- Filter paper (1.12 g); Dry asphaltene with filter paper (2.279 g)

Run3- Filter paper (1.10 g); Dry asphaltene with filter paper (2.248 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.268 g) =**0.942 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.25 g) – a mass of dry asphaltene content with filter paper (2.279 g) =**0.971 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.23 g) – a mass of dry asphaltene content with filter paper (2.248 g) =**0.982 g**

Table B8: Sample calculations on the asphaltene content on hexane at 100 mL

SOLVENT: N-HEXANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	5.01 g	5.06 g	4.99 g	5.01 g	5.0 g	5.0 g	5.1 g	5.09 g	4.98 g
Volume solvent	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL
mass asphaltenes deposited	0.35 g	0.31 g	0.33 g	0.30 g	0.37 g	0.23 g	1.158 g	1.159 g	1.148 g
Average mass	**0.33 g**			**0.30 g**			**1.155 g**		
Average asphaltene content	**6.6 g/mL**			**6 g/mL**			**23.1 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1

(Using 5 (g) of oil with 100 mL of solvent

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Heptane**) Filter paper (1.06 g); Dry asphaltene with filter paper (1.25 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.27 g)

Run3- Filter paper (1.13 g); Dry asphaltene with filter paper (1.39 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.07 g) – a mass of dry asphaltene content with filter paper (1.25 g) =**0.82 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.11 g) – a mass of dry asphaltene content with filter paper (1.27 g) =**0.84 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.13 g) – a mass of dry asphaltene content with filter paper (1.39 g) =**0.74 g**

Crude oil B **Run1**- (**Heptane**) Filter paper (1.11 g); Dry asphaltene with filter paper (1.29 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.31 g)

Run3- Filter paper (1.07 g); Dry asphaltene with filter paper (1.22 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.15 g) – a mass of dry asphaltene content with filter paper (1.29 g) =**0.86 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.18 g) – a mass of dry asphaltene content with filter paper (1.31 g) =**0.87 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.08 g) – a mass of dry asphaltene content with filter paper (1.22 g) =**0.86 g**

Crude oil C **Run1**- (**Heptane**) Filter paper (1.11 g); Dry asphaltene with filter paper (2.27 g)

Run2- Filter paper (1.11 g); Dry asphaltene with filter paper (2.20 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (2.20 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.17 g) – a mass of dry asphaltene content with filter paper (2.27 g) =**0.90 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.17 g) – a mass of dry asphaltene content with filter paper (2.20 g) =**0.97 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.19 g) – a mass of dry asphaltene content with filter paper (2.20 g) =**0.99 g**

Table B9: Sample calculations on the asphaltene content on heptane at 100 mL

SOLVENT: N-HEPTANE									
	CRUDE OIL A			**CRUDE OIL B**			**CRUDE OIL C**		
Mass oil used	5.0 g	5.0 g	5.0 g	5.01 g	4.99 g	5.0 g	5.2 g	4.98 g	5.4 g
Volume solvent	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL
mass asphaltenes deposited	0.19 g	0.18 g	0.26 g	0.18 g	0.21 g	0.15 g	1.16 g	1.09 g	1.11 g
Average mass	**0.21 g**			**0.18 g**			**1.12 g**		
Average asphaltene content	**4.2 g/mL**			**3.6 g/mL**			**22.4 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1*

(Using 2.5 g of oil with 100 mL of solvent

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Pentane**) Filter paper (1.12 g); Dry asphaltene with filter paper (1.79 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.71 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (1.80 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.92 g) – a mass of dry asphaltene content with filter paper (1.79 g) =**0.13 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.09 g) – a mass of dry asphaltene content with filter paper (1.71 g) =**0.38 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.89 g) – a mass of dry asphaltene content with filter paper (1.80 g) =**0.09 g**

Crude oil B **Run1**- (**Pentane**) Filter paper (1.10 g); Dry asphaltene with filter paper (1.52 g)

Run2- Filter paper (1.08 g); Dry asphaltene with filter paper (1.56 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.59 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.05 g) – a mass of dry asphaltene content with filter paper (1.52 g) =**0.53 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.11 g) – a mass of dry asphaltene content with filter paper (1.56 g) =**0.55 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.07 g) – a mass of dry asphaltene content with filter paper (1.59 g) =**0.48 g**

Crude oil C **Run1**- (**Pentane**) Filter paper (1.11 g); Dry asphaltene with filter paper (2.302 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (2.299 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (2.305 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.302 g) =**0.908 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.23 g) – a mass of dry asphaltene content with filter paper (2.299 g) =**0.931 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.305 g) =**0.905 g**

Table B10: Sample calculations on the asphaltene content on pentane at 50 mL

SOLVENT: N-PENTANE									
	CRUDE OIL A			CRUDE OIL B			CRUDE OIL C		
Mass oil used	2.5 g	2.49 g	2.51 g	2.51 g	2.51 g	2.55 g	2.52 g	2.51 g	2.50 g
Volume solvent	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL
mass asphaltenes deposited	0.67 g	0.62 g	0.71 g	0.42 g	0.48 g	0.48 g	1.192 g	1.199 g	1.194 g
Average mass	**0.66 g**			**0.46 g**			**1.195 g**		
Average asphaltene content	**13.2 g/mL**			**9.2 g/mL**			**23.9 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1*

(Using 2.5 g of oil with 100 mL of solvent

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Hexane**) Filter paper (1.09 g); Dry asphaltene with filter paper (1.27 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.43 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.39 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.72 g) – a mass of dry asphaltene content with filter paper (1.27 g) =**0.45 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.89 g) – a mass of dry asphaltene content with filter paper (1.43 g) =**0.46 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.79 g) – a mass of dry asphaltene content with filter paper (1.39 g) =**0.40 g**

Crude oil B **Run1**- (**Hexane**) Filter paper (1.08 g); Dry asphaltene with filter paper (1.38 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.43 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.44 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.69 g) – a mass of dry asphaltene content with filter paper (1.38 g) =**0.31** g

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.78 g) – a mass of dry asphaltene content with filter paper (1.43 g) =**0.35 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.92 g) – a mass of dry asphaltene content with filter paper (1.44 g) =**0.48 g**

Crude oil C **Run1**- (**Hexane**) Filter paper (1.12 g); Dry asphaltene with filter paper (2.23 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (2.25 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (2.21 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.19 g) – a mass of dry asphaltene content with filter paper (2.23 g) =**0.96 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.17g) – a mass of dry asphaltene content with filter paper (2.25g) =**0.92 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.21 g) – a mass of dry asphaltene content with filter paper (2.23 g) =**0.98 g**

Table B11: Sample calculations on the asphaltene content on hexane at 50 mL

SOLVENT: N-HEXANE									
	CRUDE OIL A			**CRUDE OIL B**			**CRUDE OIL C**		
Mass oil used	2.49 g	2.52 g	2.48 g	2.5 g	2.5 g	2.51 g	2.51 g	2.6 g	2.51 g
Volume solvent	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL
mass asphaltenes deposited	0.28 g	0.34 g	0.28 g	0.30 g	0.33 g	0.33 g	1.11 g	1.16 g	1.12 g
Average mass	**0.3 g**			**0.32 g**			**1.13 g**		
Average asphaltene content	**6 g/mL**			**6.4 g/mL**			**22.6 g/mL**		

Extraction of asphaltenes from crude oil using ratio 20:1*

(Using 2.5 g of oil with 100 mL of solvent

Mass of the asphaltenes deposit = mass of dry asphaltene – a mass of filter paper

Crude oil A **Run1**- (**Heptane**) Filter paper (1.12 g); Dry asphaltene with filter paper (1.34 g)

Run2- Filter paper (1.10 g); Dry asphaltene with filter paper (1.37 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.34 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (1.82 g) – a mass of dry asphaltene content with filter paper (1.34 g) =**0.48 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.05 g) – a mass of dry asphaltene content with filter paper (1.37 g) =**0.68 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.14 g) – a mass of dry asphaltene content with filter paper (1.34 g) =**0.80 g**

Crude oil B **Run1**- (**Heptane**) Filter paper (1.11 g); Dry asphaltene with filter paper (1.25 g)

Run2- Filter paper (1.09 g); Dry asphaltene with filter paper (1.30 g)

Run3- Filter paper (1.11 g); Dry asphaltene with filter paper (1.30 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.09 g) – a mass of dry asphaltene content with filter paper (1.25 g) =**0.84 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.15 g) – a mass of dry asphaltene content with filter paper (1.30 g) =**0.85 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (2.08 g) – a mass of dry asphaltene content with filter paper (1.30 g) =**0.78 g**

Crude oil C **Run1**- (**Heptane**) Filter paper (1.10 g); Dry asphaltene with filter paper (2.199 g)

Run2- Filter paper (1.08 g); Dry asphaltene with filter paper (2.169 g)

Run3- Filter paper (1.09 g); Dry asphaltene with filter paper (2.187 g)

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.15 g) – a mass of dry asphaltene content with filter paper (2.199 g) =**0.951 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.08 g) – a mass of dry asphaltene content with filter paper (2.169 g) =**0.911 g**

Mass of wettability content lost = mass of wet asphaltene with filter paper (3.17 g) – a mass of dry asphaltene content with filter paper (2.187 g) =**0.983 g**

Table B12: Sample calculations on the asphaltene content on heptane at 50 mL

SOLVENT: N-HEPTANE									
	CRUDE OIL A			**CRUDE OIL B**			**CRUDE OIL C**		
Mass oil used	2.47 g	2.54 g	2.53 g	2.52 g	2.48 g	2.52 g	2.51 g	2.49 g	2.54 g
Volume solvent	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL	50 mL
mass asphaltenes deposited	0.22 g	0.27 g	0.23 g	0.14 g	0.21 g	0.19 g	1.099 g	1.089 g	1.097 g
Average mass	**0.24 g**			**0.18 g**			**1.095 g**		
Average asphaltene content	**4.8 g/mL**			**3.6 g/mL**			**21.9 g/mL**		

Appendix C- Tabulation of CO_2 flooding and molar ratio

The table belows are the tabulation of the results obtained during CO_2 flooding in different temperature at differing solvent and crude oil types.

Table C1: Asphaltene content from temperature range of 25ºC – 90ºC during CO_2 for crude oil A

Temperature (ºC)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)
25	C_5	4.72	C_6	4.68	C_7	4.56
30	C_5	4.27	C_6	4.21	C_7	4.16
60	C_5	4.42	C_6	4.38	C_7	4.25
90	C_5	4.68	C_6	4.57	C_7	4.39

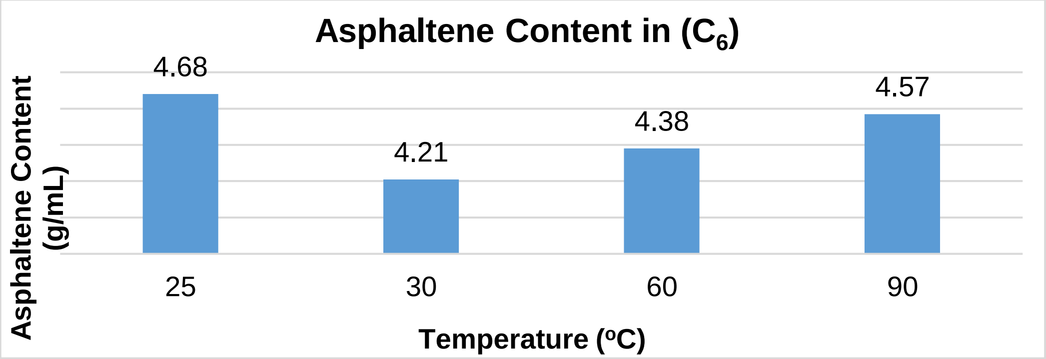


Figure C1: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_6) for crude oil A

Table C2: Asphaltene content from temperature range of 25ºC – 90ºC during CO_2 for crude oil B

Temperature (ºC)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)
25	C_5	4.92	C_6	4.83	C_7	4.77
30	C_5	4.76	C_6	4.66	C_7	4.51
60	C_5	4.81	C_6	4.76	C_7	4.63
90	C_5	4.87	C_6	4.71	C_7	4.68

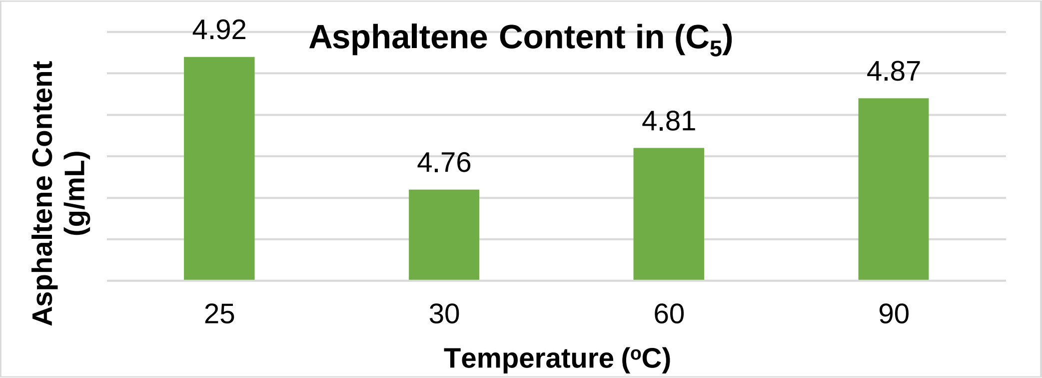


Figure C2: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_5) for crude oil B

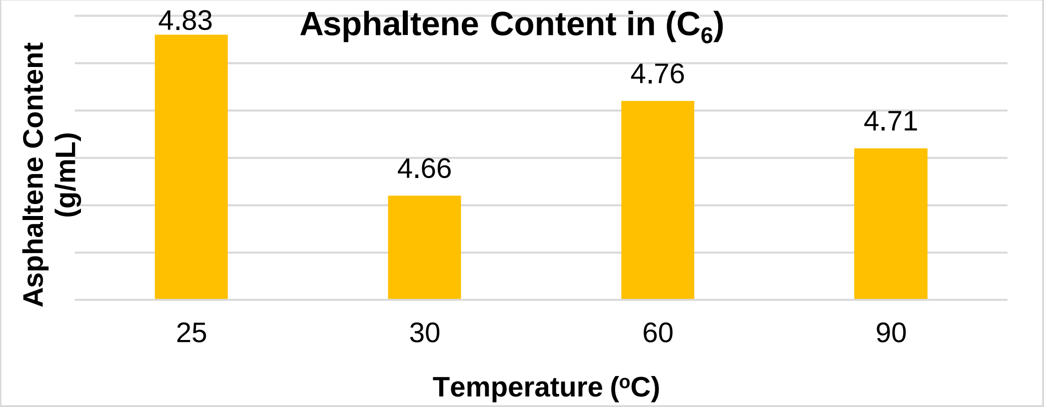


Figure C3: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_6) for crude oil B

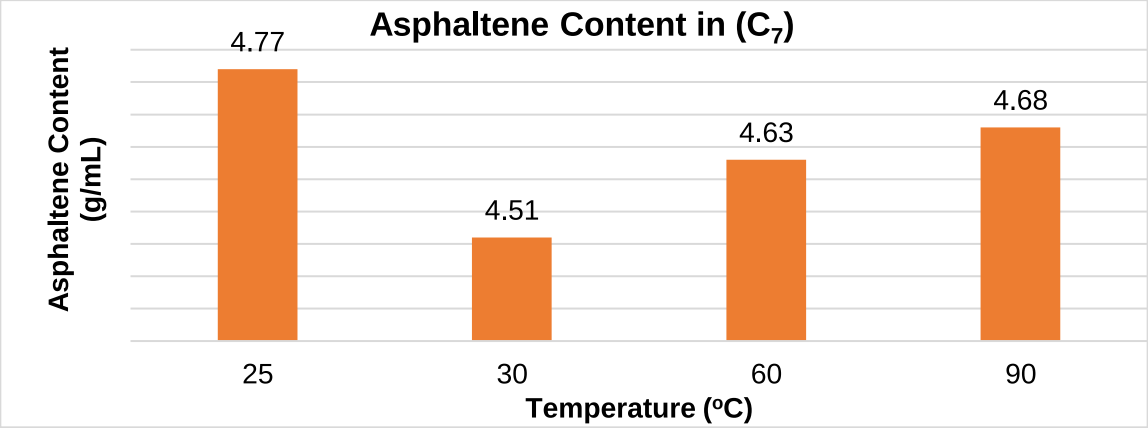


Figure C4: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_7) for crude oil B

Table C3: Asphaltene content from temperature range of 25°C – 90°C during CO_2 for crude oil C

Temperature (°C)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)	Solvent	Asphaltene Content (g/mL)
25	C_5	5.13	C_6	4.97	C_7	4.81
30	C_5	4.79	C_6	4.60	C_7	4.37
60	C_5	4.88	C_6	4.78	C_7	4.66
90	C_5	4.96	C_6	4.87	C_7	4.78

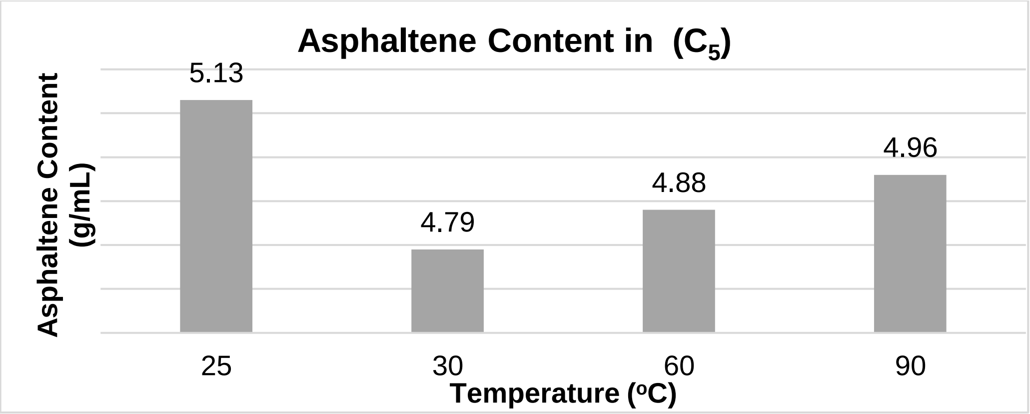


Figure C5: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_5) for crude oil C

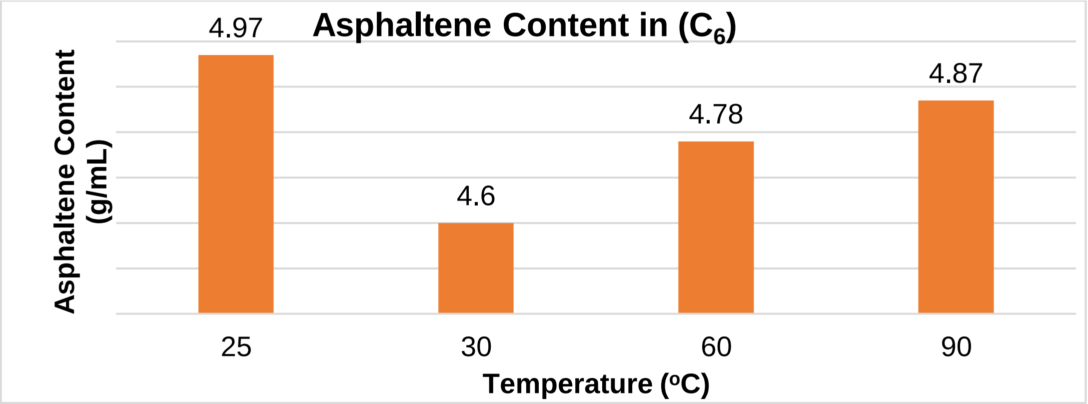


Figure C6: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_6) for crude oil C

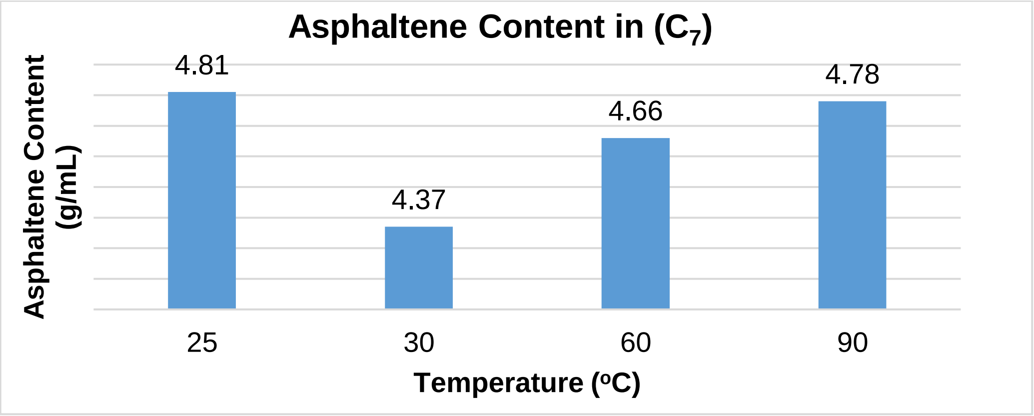


Figure C7: Asphaltene content from the CO_2 flooding at a flow rate of 0.5 mL/min using (C_7) for crude oil C

Table C4: Asphaltene contents of crude oil A, B and C after interacting with CO_2 at different CO_2 to crude ratios C_5

CO_2 to oil ratio, %	1	50	75	90
Contents of asphaltene, wt% (**Crude oil A**)	4.88	4.81	4.59	3.41
Contents of asphaltene, wt% (**Crude oil B**)	4.91	4.87	4.62	3.44
Contents of asphaltene, wt% (**Crude oil C**)	5.62	5.24	5.17	4.93

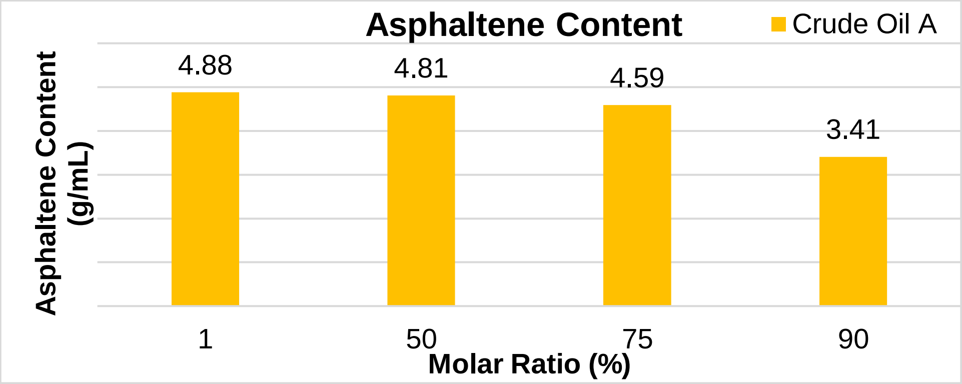


Figure C8: Asphaltene content on C_5 during CO_2 flooding on the different molar ratio for crude oil A

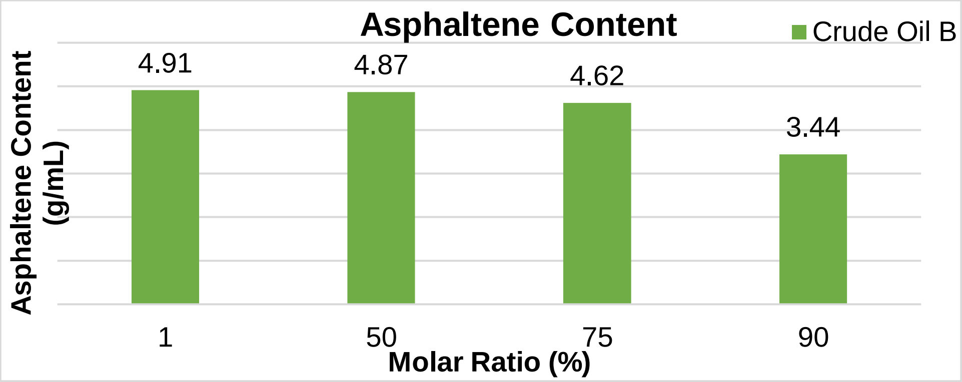


Figure C9: Asphaltene content on C_5 during CO_2 flooding on the different molar ratio for crude oil B

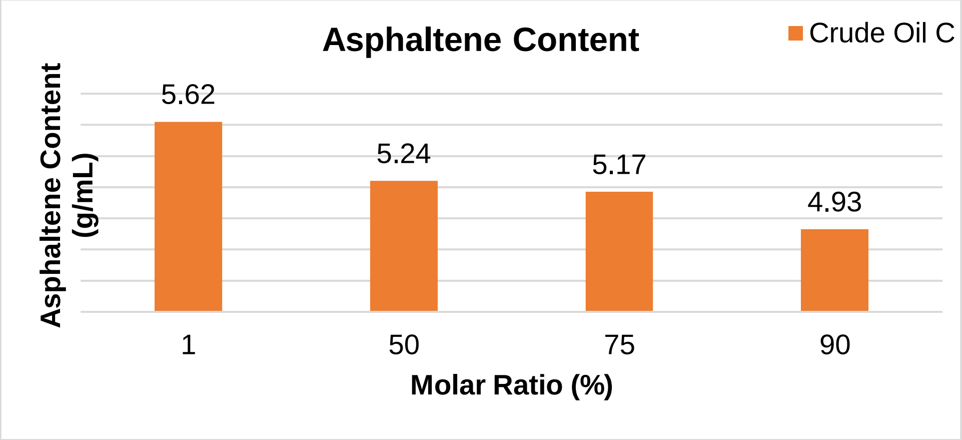


Figure C10: Asphaltene content on C_5 during CO_2 flooding on the different molar ratio for crude oil C

Table C5: Asphaltene content of crude oils A, B and C after interacting with CO_2 at different CO_2 to crude ratios C_6

CO_2 to oil ratio, %	1	50	75	90
Contents of asphaltene, wt% (**Crude oil A**)	4.85	4.78	4.53	3.35
Contents of asphaltene, wt% (**Crude oil B**)	4.87	4.77	4.61	3.4
Contents of asphaltene, wt% (**Crude oil C**)	5.54	5.18	5.11	4.89

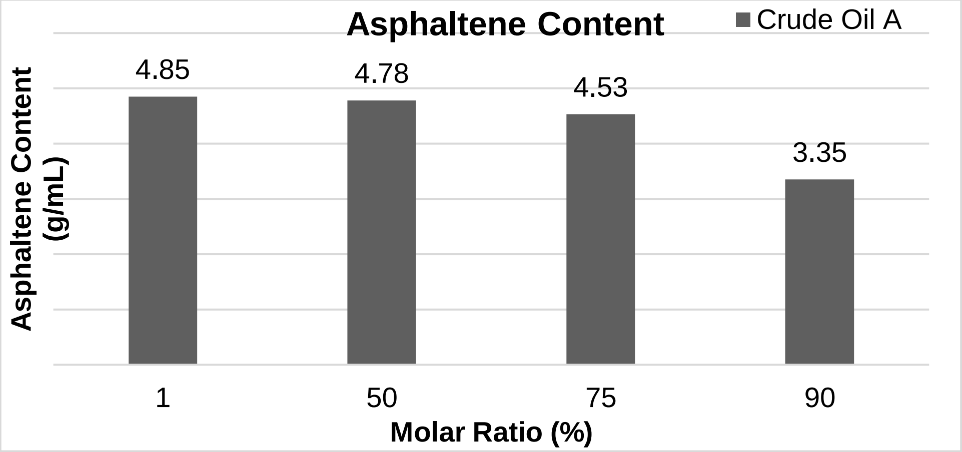


Figure C11: Asphaltene content on C_6 during CO_2 flooding on the different molar ratio for crude oil A

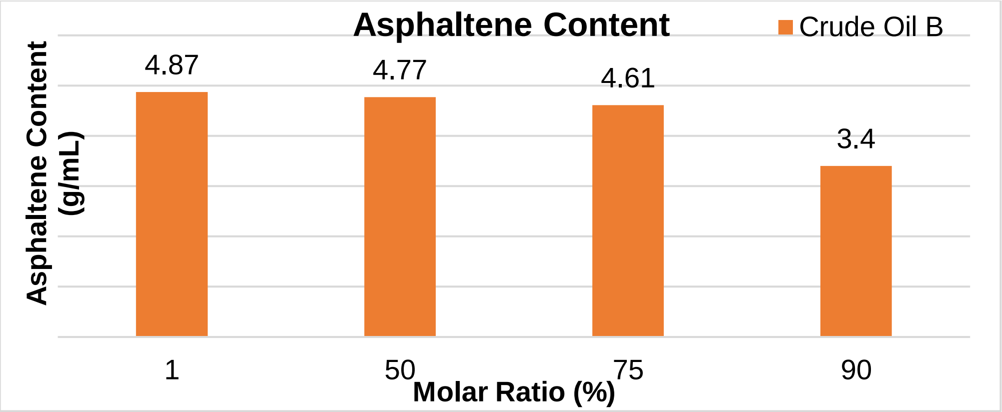


Figure C12: Asphaltene content on C_6 during CO_2 flooding on the different molar ratio for crude oil B

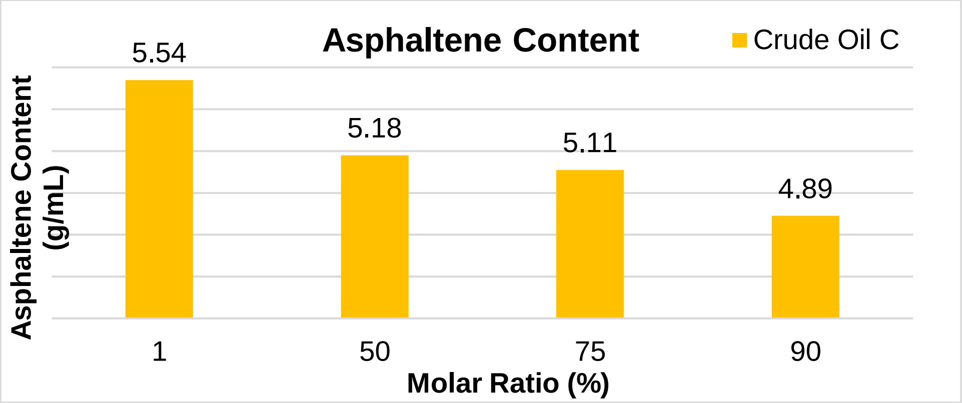


Figure C13: Asphaltene content on C_6 during CO_2 flooding on the different molar ratio for crude oil C

Table C6: Asphaltene content of crude oils A, B and C after interacting with CO_2 at different CO_2 to crude ratios C_7

CO_2 to oil ratio, %	1	50	75	90
Contents of asphaltene, wt% (**Crude oil A**)	4.8	4.71	4.49	3.32
Contents of asphaltene, wt% (**Crude oil B**)	4.83	4.74	4.57	3.35
Contents of asphaltene, wt% (**Crude oil C**)	5.46	5.08	5.02	4.84

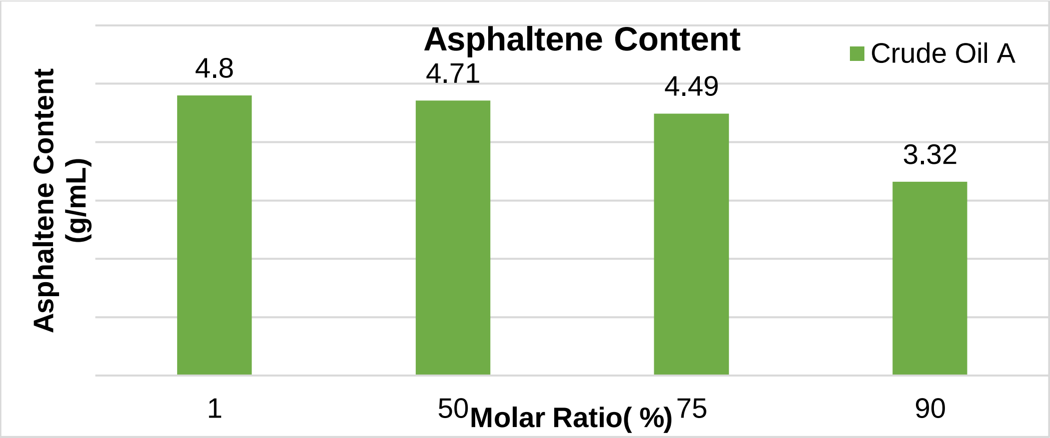


Figure C14: Asphaltene content on C_7 during CO_2 flooding on the different molar ratio for crude oil A

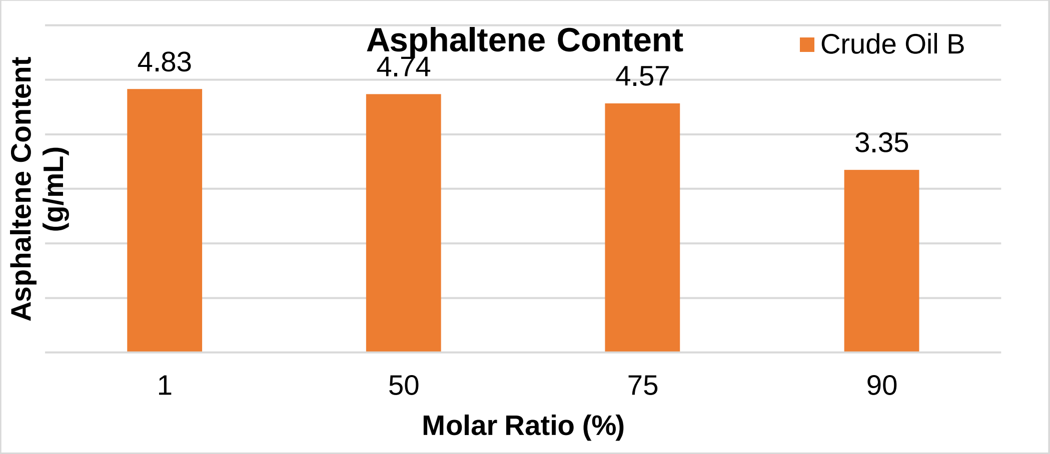


Figure C15: Asphaltene content on C_7 during CO_2 flooding on the different molar ratio for crude oil B

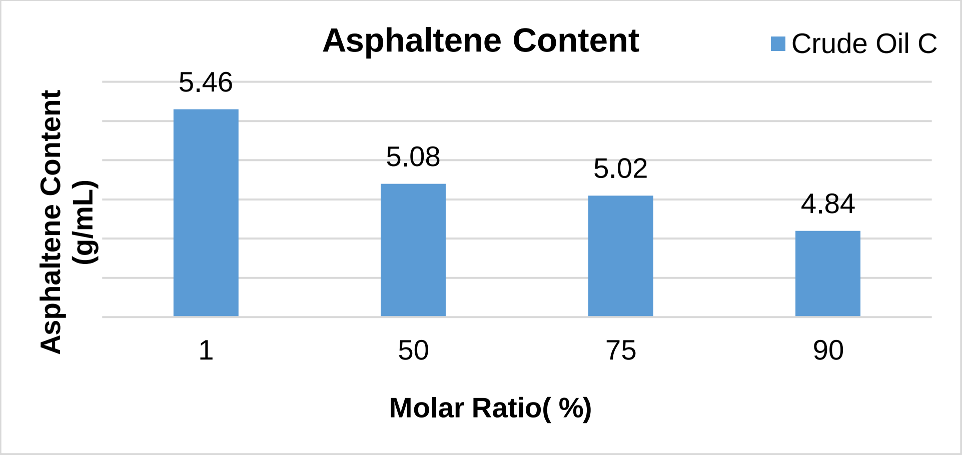


Figure C16: Asphaltene content on C_7 during CO_2 flooding on the different molar ratio for crude oil C

Appendix D- GC-MS chromotograms for crude oil A,B and C

Spectrum and Chromatograms of Crude Oil Samples A, B and C

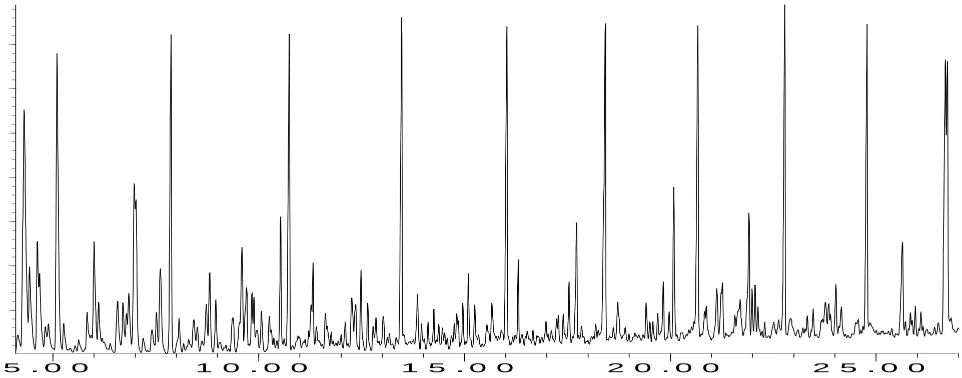


Figure D1: Asphaltene spectrum from crude oil A

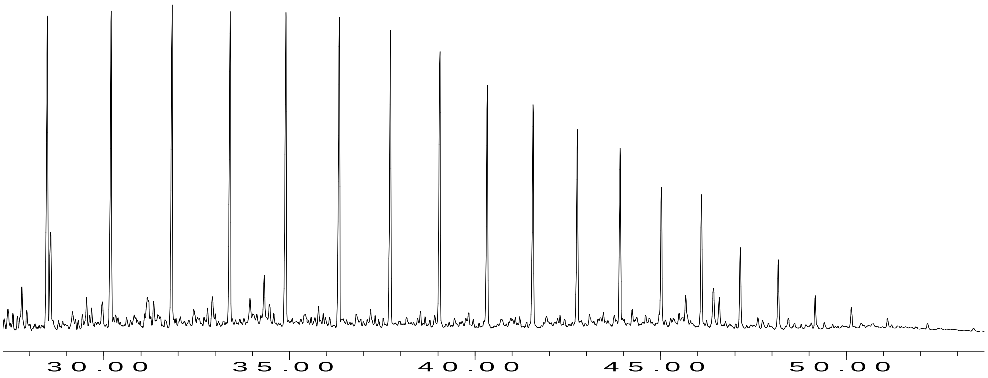


Figure D2: Asphaltene spectrum from crude oil A

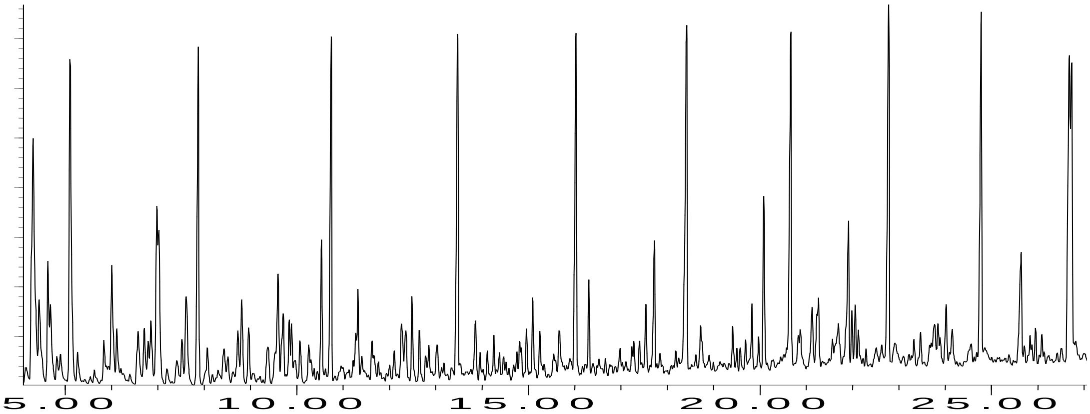


Figure D3: Asphaltene spectrum from crude oil B

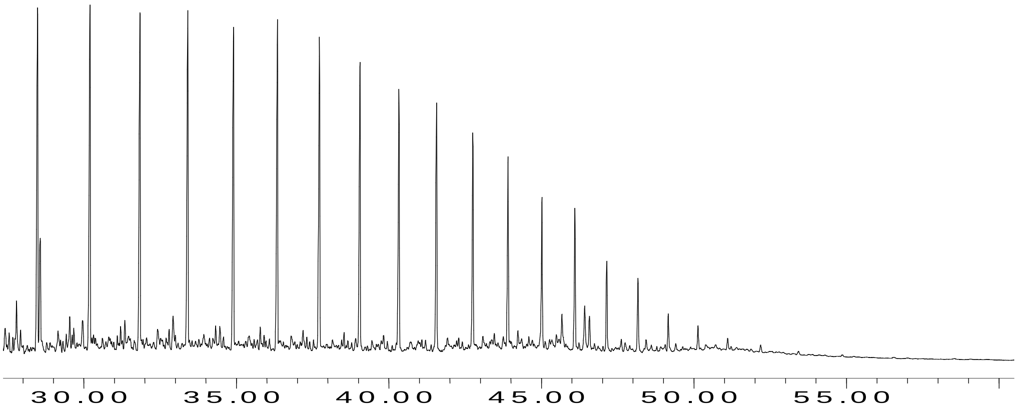


Figure D4: Asphaltene spectrum from crude oil B

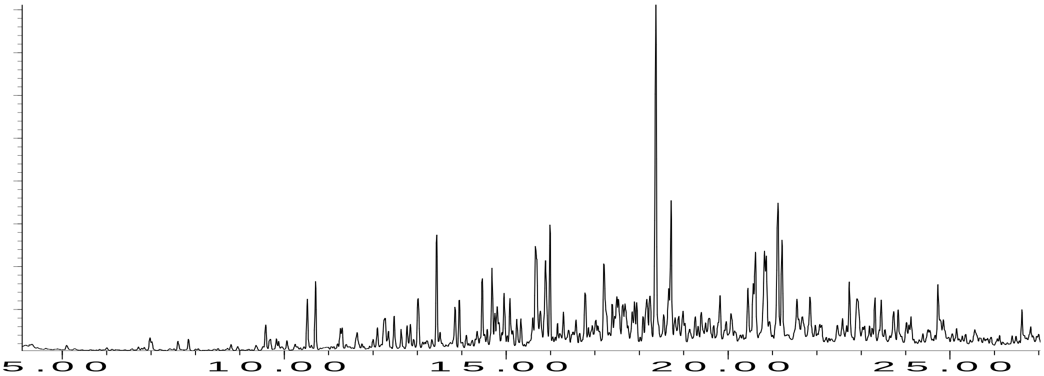


Figure D5: Asphaltene spectrum from crude oil C

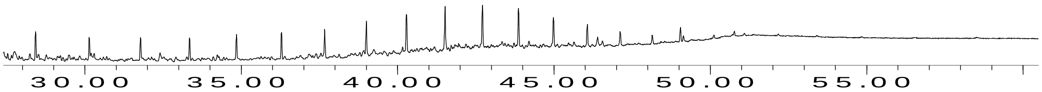


Figure D6: Asphaltene spectrum from crude oil C

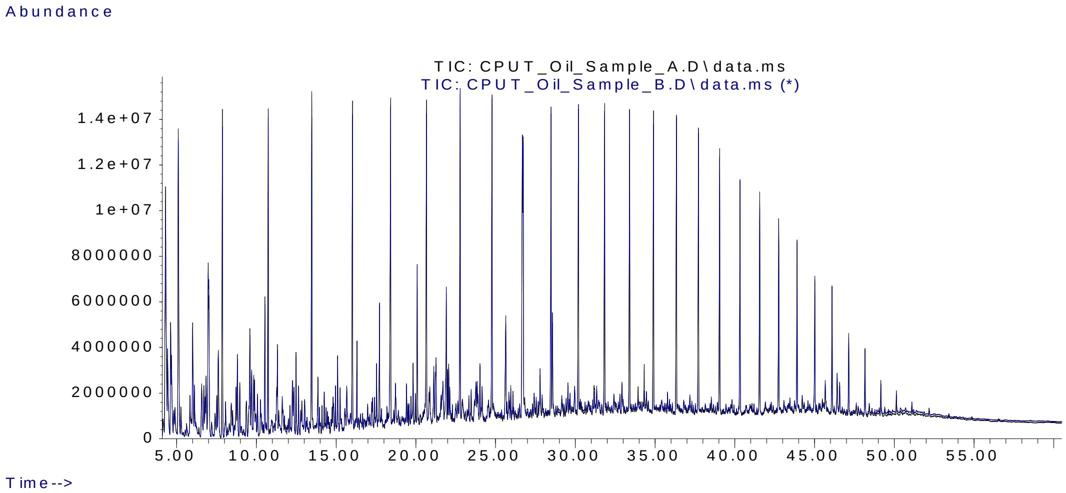


Figure D7: Asphaltene spectrum from crude oil A

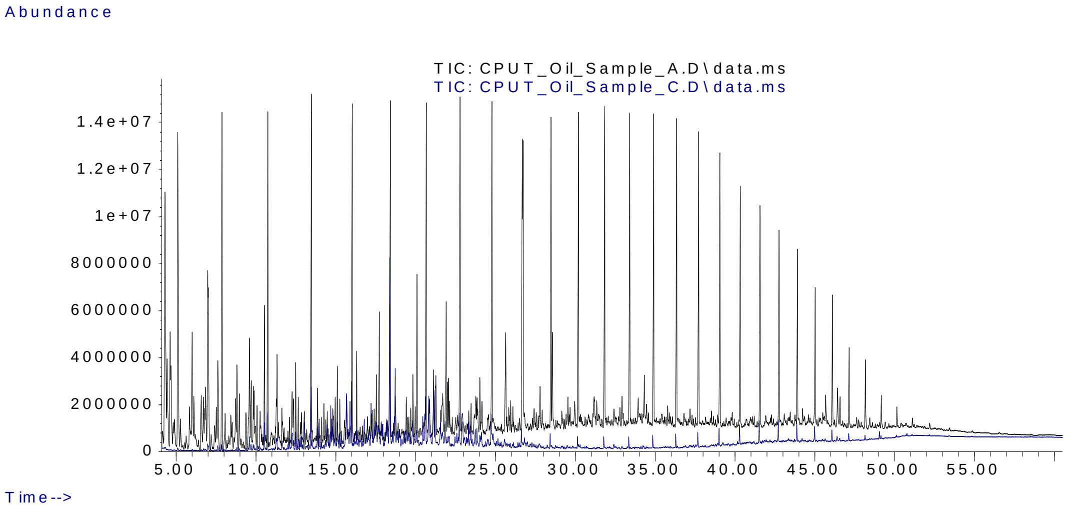


Figure D8: Asphaltene spectrum from crude oil B

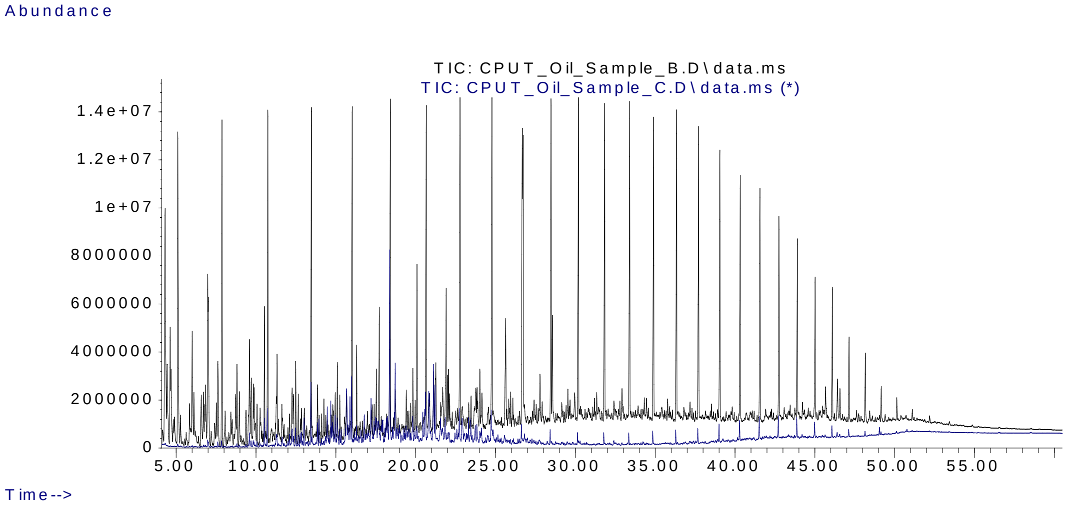


Figure D9: Asphaltene spectrum from crude oil B

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References

ABDEL-RAOUF, M. 2012a. Factors affecting the stability of crude oil emulsions. *Crude oil emulsions–composition, stability and characterization. Croatia: Intech***,** 183-204.

ABDEL-RAOUF, M. E.-S. 2012b. *Crude Oil Emulsions: Composition Stability and Characterization*, InTech.

ABDEL-RAOUF, M. E.-S. 2012c. Factors affecting the stability of crude oil emulsions. *Crude oil emulsions-Composition stability and characterization.* intech.

ABEDINI, A. & TORABI, F. 2014. On the CO_2 storage potential of cyclic CO_2 injection process for enhanced oil recovery. *Fuel,* 124**,** 14-27.

ADAMS, J. J. 2014. Asphaltene adsorption, a literature review. *Energy & Fuels,* 28**,** 2831-2856.

AGUIAR, J. I. & MANSUR, C. R. 2015. Study of the interaction between asphaltenes and resins by microcalorimetry and ultraviolet–visible spectroscopy. *Fuel,* 140**,** 462-469.

AKBARZADEH, K., HAMMAMI, A., KHARRAT, A., ZHANG, D., ALLENSON, S., CREEK, J., KABIR, S., JAMALUDDIN, A., MARSHALL, A. G. & RODGERS, R. P. 2007. Asphaltenes—problematic but rich in potential. *Oilfield Review,* 19**,** 22-43.

ALBOUDWAREJ, H., BECK, J., SVRCEK, W., YARRANTON, H. & AKBARZADEH, K. 2002. Sensitivity of asphaltene properties to separation techniques. *Energy & Fuels,* 16**,** 462-469.

ALI, M., DAHRAJ, N. U. & HAIDER, S. A. Study of Asphaltene Precipitation during CO_2 Injection in Light Oil Reservoirs. SPE/PAPG Pakistan section Annual Technical Conference, 2015. Society of Petroleum Engineers.

ALIAN, S. S., OMAR, A. A., ALTA'EE, A. F. & HANI, I. 2011. Study of Asphaltene Precipitation induced formation Damage during CO_2 injection for a Malaysian light oil. *World Academy of Science, Engineering and Technology, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering,* 5**,** 482-486.

ALOTAIBI, F. M., GONZÁLEZ-CORTÉS, S., ALOTIBI, M. F., XIAO, T., AL-MEGREN, H., YANG, G. & EDWARDS, P. P. 2018. Enhancing the production of light olefins from heavy crude oils: Turning challenges into opportunities. *Catalysis Today*.

ALQUIST, R. & KILIAN, L. 2010. What do we learn from the price of crude oil futures? *Journal of Applied Econometrics,* 25**,** 539-573.

ALTA'EE, A. F., SAAID, I. & MASOUDI, R. 2010. Carbon Dioxide Injection and Asphaltene Precipitation in Light Oil Reservoirs.

ARYA, A., LIANG, X., VON SOLMS, N. & KONTOGEORGIS, G. M. 2017. Modeling of Asphaltene Precipitation from Crude Oil with the Cubic Plus Association Equation of State. *Energy & Fuels,* 31**,** 2063-2075.

ASINGER, F. 2016. *Paraffins: chemistry and technology*, Elsevier.

ATANASSOV, G., LIMA, R., MESQUITA, R., RANGEL, A. & TÓTH, I. 2000. Spectrophotometric determination of carbon dioxide and sulphur dioxide in wines by flow injection. *Analusis,* 28**,** 77-82.

BADRE, S., GONCALVES, C. C., NORINAGA, K., GUSTAVSON, G. & MULLINS, O. C. 2006. Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen. *Fuel,* 85**,** 1-11.

BAKYANI, A. E., NAMDARPOOR, A., SARVESTANI, A. N., DAILI, A., GANJI, S. Y. & ESMAEILZADEH, F. 2018. A Simulation Approach for Screening of EOR Scenarios in Naturally Fractured Reservoirs. *International Journal of Geosciences,* 9**,** 19.

BAUMEISTER, C. & PEERSMAN, G. 2013. The role of time-varying price elasticities in accounting for volatility changes in the crude oil market. *Journal of Applied Econometrics,* 28**,** 1087-1109.

BEHAR, E., HASNAOUI, N., ACHARD, C. & ROGALSKI, M. 1998. Study of asphaltene solutions by electrical conductivity measurements. *Revue de L'institut francais du petrole,* 53**,** 41-50.

BETANCOURT, S. S., JOHANSEN, Y. B., FORSYTHE, J. C., RINNA, J., CHRISTOFFERSEN, K., SKILLINGSTAD, P. L., ACHOUROV, V., CANAS, J., CHEN, L. & POMERANTZ, A. E. 2018. Gravitational Gradient of Asphaltene Molecules in an Oilfield Reservoir with Light Oil. *Energy & Fuels,* 32**,** 4911-4924.

BISSADA, K. A., TAN, J., SZYMCZYK, E., DARNELL, M. & MEI, M. 2016. Group-type characterization of crude oil and bitumen. Part I: Enhanced separation and quantification of saturates, aromatics, resins and asphaltenes (SARA). *Organic Geochemistry,* 95**,** 21-28.

BORDEN, K. 2013. The Challenges of Processing and Transporting Heavy Crude. *Oil and Gas Facilities,* 2**,** 22-26.

BOUSSINGAULT, J.-B. Mémoire sur l’influence des défrichements dans la diminution des cours d’eau. Annales de chimie, 1837. 113-141.

BUCH, L., GROENZIN, H., BUENROSTRO-GONZALEZ, E., ANDERSEN, S. I., LIRA-GALEANA, C. & MULLINS, O. C. 2003. Molecular size of asphaltene fractions obtained from residuum hydrotreatment☆. *Fuel,* 82**,** 1075-1084.

CADORIM, H. R., PEREIRA, É. R., CARASEK, E., WELZ, B. & DE ANDRADE, J. B. 2016. Determination of sulfur in crude oil using high-resolution continuum source molecular absorption spectrometry of the SnS molecule in a graphite furnace. *Talanta,* 146**,** 203-208.

CAO, M. & GU, Y. 2013. Oil recovery mechanisms and asphaltene precipitation phenomenon in immiscible and miscible CO_2 flooding processes. *Fuel,* 109**,** 157-166.

CASTILLO, J., VARGAS, V., PISCITELLI, V., ORDOÑEZ, L. & ROJAS, H. 2017. Study of asphaltene adsorption onto raw surfaces and iron nanoparticles by AFM force spectroscopy. *Journal of Petroleum Science and Engineering,* 151**,** 248-253.

CHAI, J., LU, Q., HU, Y., WANG, S., LAI, K. K. & LIU, H. 2018. Analysis and Bayes statistical probability inference of crude oil price change point. *Technological Forecasting and Social Change,* 126**,** 271-283.

CHANG, C.-L. & FOGLER, H. S. 1994. Stabilization of asphaltenes in aliphatic solvents using alkylbenzene-derived amphiphiles. 2. Study of the asphaltene-amphiphile interactions and structures using Fourier transform infrared spectroscopy and small-angle X-ray scattering techniques. *Langmuir,* 10**,** 1758-1766.

CHARIN, R. M., CHAVES, G. M. T., KASHEFI, K., ALVES, R. P., TAVARES, F. W. & NELE, M. 2017. Crude Oil Electrical Conductivity Measurements at High Temperatures: Introduction of Apparatus and Methodology. *Energy & Fuels,* 31**,** 3669-3674.

CHAUDHURI, U. R. 2016. *Fundamentals of petroleum and petrochemical engineering*, CRC Press.

CHÁVEZ-MIYAUCHI, T. E., ZAMUDIO-RIVERA, L. S., BARBA-LÓPEZ, V., BUENROSTRO-GONZALEZ, E. & MARTÍNEZ-MAGADÁN, J. M. 2013. N-aryl amino-alcohols as stabilizers of asphaltenes. *Fuel,* 110**,** 302-309.

CHEN, J., LI, T. & WU, S. 2018. Influence of pressure and CO_2 content on the asphaltene precipitation and oil recovery during CO_2 flooding. *Petroleum Science and Technology***,** 1-6.

CIVAN, F. 2000. Reservoir Formation Damage-Fundamentals, Modeling, Assessment, and Migration, Gulf Pub. *Co., Houston, TX, 742p*.

COHRS, C., KRULL, M., FEUSTEL, M. & RAUSCH, H. 2012. Additives for crude oils. Google Patents.

COUTINHO, D. M., FRANÇA, D., VANINI, G., MENDES, L. A. N., GOMES, A. O., PEREIRA, V. B., ÁVILA, B. M. & AZEVEDO, D. A. 2018. Rapid hydrocarbon group-type semi-quantification in crude oils by comprehensive two-dimensional gas chromatography. *Fuel,* 220**,** 379-388.

CRUZ, E. E. B., RIVAS, N. V. G., GARCÍA, U. P., MARTINEZ, A. M. M. & BANDA, J. A. M. 2018. Characterization of Crude Oils and the Precipitated Asphaltenes Fraction using UV Spectroscopy, Dynamic Light Scattering and Microscopy. *Recent Insights in Petroleum Science and Engineering.* InTech.

CUNICO, R. L., SHEU, E. Y. & MULLINS, O. C. 2004. Molecular weight measurement of UG8 asphaltene using APCI mass spectroscopy. *Petroleum science and technology,* 22**,** 787-798.

DA SILVA, N., OLIVEIRA, V. D. R., SOUZA, M., GUERRIERI, Y. & COSTA, G. 2014. New method to detect asphaltene precipitation onset induced by CO_2 injection. *Fluid Phase Equilibria,* 362**,** 355-364.

DARGAY, J. M. & GATELY, D. 2010. World oil demand’s shift toward faster growing and less price-responsive products and regions. *Energy Policy,* 38**,** 6261-6277.

DARJAA, T., YAMADA, K., SATO, N., FUJINO, T. & WASEDA, Y. 1998. Determination of sulfur in metal sulfides by bromine water-CCl4 oxidative dissolution and modified EDTA titration. *Fresenius' journal of analytical chemistry,* 361**,** 442-444.

DE BOER, R., LEERLOOYER, K., EIGNER, M. & VAN BERGEN, A. 1995. Screening of crude oils for asphalt precipitation: theory, practice, and the selection of inhibitors. *SPE Production & Facilities,* 10**,** 55-61.

DEMIRBAS, A., OMAR AL-SASI, B. & NIZAMI, A.-S. 2017. Recent volatility in the price of crude oil. *Energy Sources, Part B: Economics, Planning, and Policy,* 12**,** 408-414.

DONG, Z.-X., WANG, J., LIU, G., LIN, M.-Q. & LI, M.-Y. 2014. Experimental study on asphaltene precipitation induced by CO_2 flooding. *Petroleum Science,* 11**,** 174-180.

EL BASSOUSSI, A. A., EL-SABAGH, S. M., HARB, F. M. & EL NADY, M. M. 2018. Characterization and correlation of crude oils from some wells in the North Western Desert, Egypt. *Petroleum Science and Technology***,** 1-8.

EMEGWALU, C. C. 2010. *Enhanced oil recovery for Norne Field's E-segment using surfactant flooding.* Norges teknisk-naturvitenskapelige universitet, Fakultet for ingeniørvitenskap og teknologi, Institutt for petroleumsteknologi og anvendt geofysikk.

FAN, T. & BUCKLEY, J. S. 2002. Rapid and accurate SARA analysis of medium gravity crude oils. *Energy & Fuels,* 16**,** 1571-1575.

FANCHI, J. R. 2005. *Principles of applied reservoir simulation*, Gulf Professional Publishing.

FATH, A. H. & POURANFARD, A.-R. 2014. Evaluation of miscible and immiscible CO_2 injection in one of the Iranian oil fields. *Egyptian Journal of Petroleum,* 23**,** 255-270.

FATTOUH, B. 2010. The dynamics of crude oil price differentials. *Energy Economics,* 32**,** 334-342.

FERWORN, K. A., SVRCEK, W. Y. & MEHROTRA, A. K. 1993. Measurement of asphaltene particle size distributions in crude oils diluted with n-heptane. *Industrial and Engineering Chemistry Research;(United States),* 32.

FORTHUBER, F. A. & VALDEZ, R. 2003. Carbon dioxide pump, pumping system, and method of controlling the same. Google Patents.

FRANCO, C., PATIÑO, E., BENJUMEA, P., RUIZ, M. A. & CORTÉS, F. B. 2013. Kinetic and thermodynamic equilibrium of asphaltenes sorption onto nanoparticles of nickel oxide supported on nanoparticulated alumina. *Fuel,* 105**,** 408-414.

GABORIAU, H. & SAADA, A. 2001. Influence of heavy organic pollutants of anthropic origin on PAH retention by kaolinite. *Chemosphere,* 44**,** 1633-1639.

GAWEL, I., BOCIARSKA, D. & BISKUPSKI, P. 2005. Effect of asphaltenes on hydroprocessing of heavy oils and residua. *Applied Catalysis A: General,* 295**,** 89-94.

GHISLAIN, T., MOLNÁRNÉ GURICZA, L. & SCHRADER, W. 2017. Characterization of crude oil asphaltenes by coupling size-exclusion chromatography directly to an ultrahigh-resolution mass spectrometer. *Rapid Communications in Mass Spectrometry,* 31**,** 495-502.

GHORBANI, M., ZARGAR, G. & JAZAYERI-RAD, H. 2016. Prediction of asphaltene precipitation using support vector regression tuned with genetic algorithms. *Petroleum,* 2**,** 301-306.

GIRALDO, J., NASSAR, N. N., BENJUMEA, P., PEREIRA-ALMAO, P. & CORTÉS, F. B. 2013. Modeling and prediction of asphaltene adsorption isotherms using Polanyi’s modified theory. *Energy & Fuels,* 27**,** 2908-2914.

GRACE, R. D. 2013. *Oil: an overview of the petroleum industry*, Elsevier.

GRAY, M. R., TYKWINSKI, R. R., STRYKER, J. M. & TAN, X. 2011. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy & Fuels,* 25**,** 3125-3134.

GROENZIN, H. & MULLINS, O. C. 2000. Molecular size and structure of asphaltenes from various sources. *Energy & Fuels,* 14**,** 677-684.

GUPTA, R. B. & DEMIRBAS, A. 2010. *Gasoline, diesel, and ethanol biofuels from grasses and plants*, Cambridge University Press.

HAMILTON, J. D. 2009. Causes and Consequences of the Oil Shock of 2007-08. National Bureau of Economic Research.

HAMOUDA, A. A. & CHUGHTAI, S. 2018. Miscible CO_2 Flooding for EOR in the Presence of Natural Gas Components in Displacing and Displaced Fluids. *Energies,* 11**,** 391.

HART, A. 2014. A review of technologies for transporting heavy crude oil and bitumen via pipelines. *Journal of Petroleum Exploration and Production Technology,* 4**,** 327-336.

HASANVAND, M. Z., AHMADI, M. A. & BEHBAHANI, R. M. 2015. Solving asphaltene precipitation issue in vertical wells via redesigning of production facilities. *Petroleum,* 1**,** 139-145.

HASSAN, M., GAJBHIYE, R. N., SULTAN, A. S. & ABU-KHAMSIN, S. Measurement of Bubble Point Pressures of n-Decane, CO_2 and N_2 Mixtures. SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, 2016. Society of Petroleum Engineers.

HEMMATI-SARAPARDEH, A., AMINSHAHIDY, B., PAJOUHANDEH, A., YOUSEFI, S. H. & HOSSEINI-KALDOZAKH, S. A. 2016. A soft computing approach for the determination of crude oil viscosity: light and intermediate crude oil systems. *Journal of the Taiwan Institute of Chemical Engineers,* 59**,** 1-10.

HEMMATI-SARAPARDEH, A., AYATOLLAHI, S., GHAZANFARI, M.-H. & MASIHI, M. 2013. Experimental determination of interfacial tension and miscibility of the CO_2–crude oil system; temperature, pressure, and composition effects. *Journal of Chemical & Engineering Data,* 59**,** 61-69.

HEMMATI-SARAPARDEH, A., SHOKROLLAHI, A., TATAR, A., GHARAGHEIZI, F., MOHAMMADI, A. H. & NASERI, A. 2014. Reservoir oil viscosity determination using a rigorous approach. *Fuel,* 116**,** 39-48.

HEMMATI-SARAPARDEH, A., DABIR, B., AHMADI, M., MOHAMMADI, A. H. & HUSEIN, M. M. 2019. Modelling asphaltene precipitation titration data: A committee of machines and a group method of data handling. *The Canadian Journal of Chemical Engineering,* 97**,** 431-441.

HIRSCHBERG, A., DEJONG, L., SCHIPPER, B. & MEIJER, J. 1984. Influence of temperature and pressure on asphaltene flocculation. *Society of Petroleum Engineers Journal,* 24**,** 283-293.

HOEPFNER, M. P., LIMSAKOUNE, V., CHUENMEECHAO, V., MAQBOOL, T. & FOGLER, H. S. 2013. A fundamental study of asphaltene deposition. *Energy & Fuels,* 27**,** 725-735.

HOLMBERG, K., JÖNSSON, B., KRONBERG, B. & LINDMAN, B. 2002. *Surfactants and polymers in aqueous solution*, Wiley Online Library.

HONORS, L. D. 2017. Research Experience.

HOPKINS, P., WALROND, K., OMLAND, I., STRAND, S., PUNTERVOLD, T. & AUSTAD, T. The Influence of Crude Oil Flooding and Ageing on Carbonate Core Wettability During Core Restoration. IOR 2017-19th European Symposium on Improved Oil Recovery, 2017.

HUANG, M. D., BECKER-ROSS, H., FLOREK, S., HEITMANN, U., OKRUSS, M. & PATZ, C.-D. 2008. Determination of sulfur forms in wine including free and total sulfur dioxide based on molecular absorption of carbon monosulfide in the air–acetylene flame. *Analytical and bioanalytical chemistry,* 390**,** 361-367.

HUNG, J., CASTILLO, J. & REYES, A. 2005. Kinetics of asphaltene aggregation in toluene−heptane mixtures studied by confocal microscopy. *Energy & Fuels,* 19**,** 898-904.

HUR, M., WARE, R. L., PARK, J., MCKENNA, A. M., RODGERS, R. P., NIKOLAU, B. J., WURTELE, E. S. & MARSHALL, A. G. 2018. Statistically Significant Differences in Composition of Petroleum Crude Oils Revealed by Volcano Plots Generated from Ultrahigh Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectra. *Energy & Fuels*.

IDEM, R. O. & IBRAHIM, H. H. 2002. Kinetics of CO_2-induced asphaltene precipitation from various Saskatchewan crude oils during CO_2 miscible flooding. *Journal of petroleum science and engineering,* 35**,** 233-246.

IKANONE, C. E. O., AKINLOYE, O. A., UGBAJA, R. N., OMOTAINSE, S. O., AJAYI, O. L. & SHOPEIN, T. M. 2017. Effect of sub-acute exposure to bonny light crude oil on plasma biochemistry and liver histopathology of albino rat. *Animal Research International,* 14**,** 2652.

ILYIN, S., ARININA, M., POLYAKOVA, M., BONDARENKO, G., KONSTANTINOV, I., KULICHIKHIN, V. & MALKIN, A. 2016. Asphaltenes in heavy crude oil: Designation, precipitation, solutions, and effects on viscosity. *Journal of Petroleum Science and Engineering,* 147**,** 211-217.

JAVANBAKHT, G., SEDGHI, M., WELCH, W. R., GOUAL, L. & HOEPFNER, M. P. 2018. Molecular polydispersity improves prediction of asphaltene aggregation. *Journal of Molecular Liquids*.

JERIBI, M., ALMIR-ASSAD, B., LANGEVIN, D., HENAUT, I. & ARGILLIER, J. 2002. Adsorption kinetics of asphaltenes at liquid interfaces. *Journal of colloid and interface science,* 256**,** 268-272.

JOHNNY, N. A., PETER, A. S., DAVID, A. A. & MAURICE, E. 2018. Hydrocarbonoclastic potentials of Enterobacteriaceae isolated from the crude oil polluted Iko river estuary and freshwater ecosystem of the Niger Delta Region of Nigeria.

JOSHI, N. B., MULLINS, O. C., JAMALUDDIN, A., CREEK, J. & MCFADDEN, J. 2001. Asphaltene precipitation from live crude oil. *Energy & Fuels,* 15**,** 979-986.

KALAM, M. A., KHAN, A. A., ALSHAMSAN, A., HAQUE, A. & SHAKEEL, F. 2018. Solubility of a poorly soluble immunosuppressant in different pure solvents: Measurement, correlation, thermodynamics and molecular interactions. *Journal of Molecular Liquids,* 249**,** 53-60.

KALHOR, A. X., MOVAFEGHI, A., MOHAMMADI-NASSAB, A. D., ABEDI, E. & BAHRAMI, A. 2017. Potential of the green alga Chlorella vulgaris for biodegradation of crude oil hydrocarbons. *Marine pollution bulletin,* 123**,** 286-290.

KAMARI, A., SAFIRI, A. & MOHAMMADI, A. H. 2015. Compositional model for estimating asphaltene precipitation conditions in live reservoir oil systems. *Journal of Dispersion Science and Technology,* 36**,** 301-309.

KAPLAN, R. S. 2018. A Perspective on Oil. *speech of,* 19.

KELLAND, M. A. 2014. *Production chemicals for the oil and gas industry*, CRC press.

KHALAF, M. H. & MANSOORI, G. A. 2018. A new insight into asphaltenes aggregation onset at molecular level in crude oil (an MD simulation study). *Journal of Petroleum Science and Engineering,* 162**,** 244-250.

KHANNA, S., SINGH, K., NASSER, S. & SHARMA, S. 2014. Chemistry of crude oils. *Internal Journal of Advance Research and Innovation,* 2**,** 525-532.

KHARRAT, A. M., INDO, K. & MOSTOWFI, F. 2013. Asphaltene content measurement using an optical spectroscopy technique. *Energy & Fuels,* 27**,** 2452-2457.

KOKAL, S. & AL-KAABI, A. 2010. Enhanced oil recovery: challenges & opportunities. *World Petroleum Council: Official Publication,* 64.

KOSEOGLU, O. R., AL-HAJJI, A. & MULLER, H. 2017. CHARACTERIZATION OF CRUDE OIL BY FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY. US Patent 20,170,363,602.

KRAIWATTANAWONG, K., FOGLER, H. S., GHARFEH, S. G., SINGH, P., THOMASON, W. H. & CHAVADEJ, S. 2007. Thermodynamic solubility models to predict asphaltene instability in live crude oils. *Energy & fuels,* 21**,** 1248-1255.

KRISTOUFEK, L. 2018. Are the crude oil markets really becoming more efficient over time? Some new evidence. *Energy Economics*.

LEE, H. & LEE, Y.-K. 2017. Effects of the asphaltene structure and the tetralin/heptane solvent ratio on the size and shape of asphaltene aggregates. *Physical Chemistry Chemical Physics,* 19**,** 13931-13940.

LEONTARITIS, K. J. & MANSOORI, G. A. 1988. Asphaltene deposition: a survey of field experiences and research approaches. *Journal of Petroleum Science and Engineering,* 1**,** 229-239.

LI, G.-Z., MU, J.-H., LI, Y. & YUAN, S.-L. 2000. An experimental study on alkaline/surfactant/polymer flooding systems using nature mixed carboxylate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 173**,** 219-229.

LIU, G., YANG, J., SONG, J. & XU, X. 2019. Inhibition of asphaltene precipitation in blended crude oil using novel oil-soluble maleimide polymers. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects***,** 1-11.

LIU, S., ZHANG, D., YAN, W., PUERTO, M., HIRASAKI, G. J. & MILLER, C. A. 2008. Favorable attributes of alkaline-surfactant-polymer flooding. *SPE Journal,* 13**,** 5-16.

MACHADO, M. E., CARAMÃO, E. B. & ZINI, C. A. 2011. Investigation of sulphur compounds in coal tar using monodimensional and comprehensive two-dimensional gas chromatography. *Journal of Chromatography A,* 1218**,** 3200-3207.

MAI, A. & KANTZAS, A. 2009. Heavy oil waterflooding: effects of flow rate and oil viscosity. *Journal of Canadian Petroleum Technology,* 48**,** 42-51.

MANSOUR, E., DESOUKY, S., EL AILY, M. & HELMI, M. 2018. The effect of asphaltene content on predicting heavy dead oils viscosity: Experimental and modeling study. *Fuel,* 212**,** 405-411.

MAQBOOL, T., SRIKIRATIWONG, P. & FOGLER, H. S. 2011. Effect of temperature on the precipitation kinetics of asphaltenes. *Energy & Fuels,* 25**,** 694-700.

MARTÍNEZ, J. M. P., ABADIE, L. M. & FERNÁNDEZ-MACHO, J. 2018. A multi-resolution and multivariate analysis of the dynamic relationships between crude oil and petroleum-product prices. *Applied energy,* 228**,** 1550-1560.

MATHIASSEN, O. M. 2003. CO_2 as injection gas for enhanced oil recovery and estimation of the potential on the Norwegian continental shelf. *Trondheim, Norway*.

MCCAIN, W. D. 1990. *The properties of petroleum fluids*, PennWell Books.

MEIGHANI, H. M., GHOTBI, C., BEHBAHANI, T. J. & SHARIFI, K. 2018. Evaluation of PC-SAFT model and Support Vector Regression (SVR) approach in prediction of asphaltene precipitation using the titration data. *Fluid Phase Equilibria,* 456**,** 171-183.

MIAO, H., RAMCHANDER, S., WANG, T. & YANG, J. 2018. The impact of crude oil inventory announcements on prices: Evidence from derivatives markets. *Journal of Futures Markets,* 38**,** 38-65.

MIOR, R., MORÉS, S., WELZ, B., CARASEK, E. & DE ANDRADE, J. B. 2013. Determination of sulfur in coal using direct solid sampling and high-resolution continuum source molecular absorption spectrometry of the CS molecule in a graphite furnace. *Talanta,* 106**,** 368-374.

MOHAN, K. Alkaline surfactant flooding for tight carbonate reservoirs. SPE Annual Technical Conference and Exhibition, 2009. Society of Petroleum Engineers.

MOUGNOL, J.-B. B., RABIU, A., OBANIJESU, E. & SAM, Z. Asphaltene Extraction Capacity of Different Solvents. Proceedings of the 7th International Conference on Informatics, Environment, Energy and Applications, 2018. ACM, 114-118.

NALWAYA, V., TANTAYAKOM, V., PIUMSOMBOON, P. & FOGLER, S. 1999. Studies on asphaltenes through analysis of polar fractions. *Industrial & engineering chemistry research,* 38**,** 964-972.

NEČEMER, M., KUMP, P., RAJČEVIČ, M., JAČIMOVIĆ, R., BUDIČ, B. & PONIKVAR, M. 2003. Determination of sulfur and chlorine in fodder by X-ray fluorescence spectral analysis and comparison with other analytical methods. *Spectrochimica Acta Part B: Atomic Spectroscopy,* 58**,** 1367-1373.

NORDGÅRD, E. L., SØRLAND, G. & SJÖBLOM, J. 2009. Behavior of asphaltene model compounds at W/O interfaces. *Langmuir,* 26**,** 2352-2360.

ORR JR, F., YU, A. & LIEN, C. 1981. Phase behavior of CO_2 and crude oil in low-temperature reservoirs. *Society of Petroleum Engineers Journal,* 21**,** 480-492.

ORTIZ, D., BAYDAK, E. & YARRANTON, H. 2010. Effect of surfactants on interfacial films and stability of water-in-oil emulsions stabilized by asphaltenes. *Journal of colloid and interface science,* 351**,** 542-555.

PAN, H., FIROOZABADI, A. & FOTLAND, P. 1997. Pressure and composition effect on wax precipitation: experimental data and model results. *SPE Production & Facilities,* 12**,** 250-258.

PIERRE, C., BARRÉ, L., PINA, A. & MOAN, M. 2004. Composition and heavy oil rheology. *Oil & Gas Science and Technology,* 59**,** 489-501.

POWERS, D., SADEGHI, H., YARRANTON, H. & VAN DEN BERG, F. 2016. Regular solution based approach to modeling asphaltene precipitation from native and reacted oils: Part 1, molecular weight, density, and solubility parameter distributions of asphaltenes. *Fuel,* 178**,** 218-233.

RASHID, Z., WILFRED, C. D., GNANASUNDARAM, N., ARUNAGIRI, A. & MURUGESAN, T. 2019. A comprehensive review on the recent advances on the petroleum asphaltene aggregation. *Journal of Petroleum Science and Engineering*.

RILEY, B. J., LENNARD, C., FULLER, S. & SPIKMANS, V. 2018. Pyrolysis-GC-MS analysis of crude and heavy fuel oil asphaltenes for application in oil fingerprinting. *Environmental Forensics,* 19**,** 14-26.

RODRIGUEZ, D. L. G. 2008. Modeling of asphaltene precipitation and deposition using the PC-SAFT equation of state. *Doctor of Philosophy dissertation, Houston Texas*.

ROGEL, E., OVALLES, C., VIEN, J. & MOIR, M. 2016. Asphaltene characterization of paraffinic crude oils. *Fuel,* 178**,** 71-76.

ROGEL, E., ROYE, M., VIEN, J. & MIAO, T. 2015. Characterization of asphaltene fractions: distribution, chemical characteristics, and solubility behavior. *Energy & Fuels,* 29**,** 2143-2152.

SACHANEN, A. N. 1945. chemical constituents of petroleum.

SANTOS, R., LOH, W., BANNWART, A. & TREVISAN, O. 2014. An overview of heavy oil properties and its recovery and transportation methods. *Brazilian Journal of Chemical Engineering,* 31**,** 571-590.

SCHRAMM, L. L. 2000. *Surfactants: fundamentals and applications in the petroleum industry*, Cambridge University Press.

SEDGHI, M. & GOUAL, L. 2014. PC-SAFT modeling of asphaltene phase behavior in the presence of nonionic dispersants. *Fluid Phase Equilibria,* 369**,** 86-94.

SEIFRIED, C., HU, R., HEADEN, T., CRAWSHAW, J. & BOEK, E. Asphaltene Precipitation from a Heavy Crude Oil with CO2 and Solubility of Crude Oil/CO_2 Mixtures. IOR 2015-18th European Symposium on Improved Oil Recovery, 2015.

SHARMA, N., YASIN, F., SHAHRUDDIN, S., FADZIL, M., RAJANTEREH, Y., CHANDRAMALAR, A. & SAMSODIN, N. 2016. CHARACTERISATION OF MALAYSIAN WAXY CRUDE OILS. *Petroleum & Coal,* 58.

SHEN, Z. & SHENG, J. J. Experimental Study of Asphaltene Aggregation during CO_2 and CH_4 Injection in Shale Oil Reservoirs. SPE Improved Oil Recovery Conference, 2016. Society of Petroleum Engineers.

SHEN, Z. & SHENG, J. J. 2018. Experimental and numerical study of permeability reduction caused by asphaltene precipitation and deposition during CO_2 huff and puff injection in Eagle Ford shale. *Fuel,* 211**,** 432-445.

SHENG, J. 2013. *Enhanced oil recovery field case studies*, Gulf Professional Publishing.

SHIBULAL, B., AL-BAHRY, S. N., AL-WAHAIBI, Y. M., ELSHAFIE, A. E., AL-BEMANI, A. S. & JOSHI, S. J. 2017. The potential of indigenous Paenibacillus ehimensis BS1 for recovering heavy crude oil by biotransformation to light fractions. *PloS one,* 12**,** e0171432.

SHKALIKOV, N., VASIL'EV, S. & SKIRDA, V. 2010. Peculiarities of asphaltene precipitation in n-alkane-oil systems. *Colloid journal,* 72**,** 133-140.

SHUKLA, A. 2018. *Analytical Characterization Methods for Crude Oil and Related Products*, John Wiley & Sons.

SIMANZHENKOV, V. & IDEM, R. 2003. *Crude oil chemistry*, CRC Press.

SNOWDON, L. R., VOLKMAN, J. K., ZHANG, Z., TAO, G. & LIU, P. 2016. The organic geochemistry of asphaltenes and occluded biomarkers. *Organic Geochemistry,* 91**,** 3-15.

SORRELL, S., SPEIRS, J., BENTLEY, R., BRANDT, A. & MILLER, R. 2010. Global oil depletion: A review of the evidence. *Energy Policy,* 38**,** 5290-5295.

SPEIGHT, J. G. 1994. Chemical and physical studies of petroleum asphaltenes. *Developments in petroleum science,* 40**,** 7-65.

SPEIGHT, J. G. 1999. The chemical and physical structure of petroleum: effects on recovery operations. *Journal of Petroleum Science and Engineering,* 22**,** 3-15.

SPEIGHT, J. G. 2014. *The chemistry and technology of petroleum*, CRC press.

STEWART, R. J., JOHNSON, G., HEINEMANN, N., WILKINSON, M. & HASZELDINE, R. S. 2018. Low carbon oil production: Enhanced oil recovery with CO_2 from North Sea residual oil zones. *International Journal of Greenhouse Gas Control,* 75**,** 235-242.

STRAUSZ, O. P., MOJELSKY, T. W. & LOWN, E. M. 1992. The molecular structure of asphaltene: an unfolding story. *Fuel,* 71**,** 1355-1363.

TAREK, A. 2007. Equations of state and PVT analysis. *Gulf publishing company, Houston, Texas***,** 32.

TISSOT, B. & WELTE, D. 2012. *Petroleum formation and occurrence: a new approach to oil and gas exploration*, Springer Science & Business Media.

TREJO, F., CENTENO, G. & ANCHEYTA, J. 2004. Precipitation, fractionation and characterization of asphaltenes from heavy and light crude oils. *Fuel,* 83**,** 2169-2175.

VAFAIE-SEFTI, M. & MOUSAVI-DEHGHANI, S. 2006. Application of association theory to the prediction of asphaltene deposition: Deposition due to natural depletion and miscible gas injection processes in petroleum reservoirs. *fluid phase equilibria,* 247**,** 182-189.

VANANTON, H. W. 1997. Asphaltene Solubility and Asphaltene Stabilized Water-in-Oil Emulsions.

VARGAS, F. M., GONZALEZ, D. L., HIRASAKI, G. J. & CHAPMAN, W. G. 2009. Modeling asphaltene phase behavior in crude oil systems using the perturbed chain form of the statistical associating fluid theory (PC-SAFT) equation of state. *Energy & Fuels,* 23**,** 1140-1146.

VERMA, M. K. 2015. *Fundamentals of carbon dioxide-enhanced oil recovery (CO_2-EOR): A supporting document of the assessment methodology for hydrocarbon recovery using CO_2-EOR associated with carbon sequestration*, US Department of the Interior, US Geological Survey.

VILLARD, Y., FAJARDO, F. & MILNE, A. Enhanced Oil Recovery Using Innovative Asphaltene Inhibitors in East Venezuela. SPE International Conference and Exhibition on Formation Damage Control, 2016. Society of Petroleum Engineers.

WANG, X.-B., CHI, C.-Q., NIE, Y., TANG, Y.-Q., TAN, Y., WU, G. & WU, X.-L. 2011. Degradation of petroleum hydrocarbons (C_6–C_{40}) and crude oil by a novel Dietzia strain. *Bioresource technology,* 102**,** 7755-7761.

WANG, X. & GU, Y. 2011. Oil recovery and permeability reduction of a tight sandstone reservoir in immiscible and miscible CO_2 flooding processes. *Industrial & Engineering Chemistry Research,* 50**,** 2388-2399.

WANG, Y., LIU, L., DIAO, X. & WU, C. 2015. Forecasting the real prices of crude oil under economic and statistical constraints. *Energy Economics,* 51**,** 599-608.

WANG, Y., SHEN, C., WANG, C., ZHOU, Y., GAO, D. & ZUO, Z. 2018. Maternal and embryonic exposure to the water soluble fraction of crude oil or lead induces behavioral abnormalities in zebrafish (Danio rerio), and the mechanisms involved. *Chemosphere,* 191**,** 7-16.

WAUQUIER, J.-P. 1995. *Petroleum Refining: Crude oil, petroleum products, process flowsheets*, Editions Technip.

WU, J., PRAUSNITZ, J. M. & FIROOZABADI, A. 1998. Molecular-thermodynamic framework for asphaltene-oil equilibria. *AIChE Journal,* 44**,** 1188-1199.

YARRANTON, H., POWERS, D., OKAFOR, J. & VAN DEN BERG, F. 2018. Regular solution based approach to modeling asphaltene precipitation from native and reacted oils: Part 2, molecular weight, density, and solubility parameter of saturates, aromatics, and resins. *Fuel,* 215**,** 766-777.

YASIN, G., BHANGER, M. I., ANSARI, T. M., NAQVI, S. M. S. R., ASHRAF, M., AHMAD, K. & TALPUR, F. N. 2013. Quality and chemistry of crude oils. *Journal of Petroleum Technology and Alternative Fuels,* 4**,** 53-63.

YEN, T. F. & CHILINGARIAN, G. V. 2000. *Asphaltenes and asphalts, 2*, Elsevier.

YIN, Y. & YEN, A. Asphaltene deposition and chemical control in CO_2 floods. SPE/DOE Improved Oil Recovery Symposium, 2000. Society of Petroleum Engineers.

YOUNG, C. G., AMAIS, R. S., SCHIAVO, D., GARCIA, E. E., NOBREGA, J. A. & JONES, B. T. 2011. Determination of sulfur in biodiesel microemulsions using the summation of the intensities of multiple emission lines. *Talanta,* 84**,** 995-999.

YUAN, M., MOSLEY, J. & HYER, N. Mineral scale control in a CO_2 flooded oilfield. SPE International Symposium on Oilfield Chemistry, 2001. Society of Petroleum Engineers.

ZANGANEH, P., DASHTI, H. & AYATOLLAHI, S. 2018. Comparing the effects of CH_4, CO_2, and N_2 injection on asphaltene precipitation and deposition at reservoir condition: A visual and modeling study. *Fuel,* 217**,** 633-641.

ZHANG, D., JI, Q. & KUTAN, A. M. 2019. Dynamic transmission mechanisms in global crude oil prices: Estimation and implications. *Energy,* 175**,** 1181-1193.

ZHANG, Y.-J. & WEI, Y.-M. 2010. The crude oil market and the gold market: Evidence for cointegration, causality and price discovery. *Resources Policy,* 35**,** 168-177.

ZHENG, S., LI, H. & YANG, D. 2013. Pressure maintenance and improving oil recovery with immiscible CO_2 injection in thin heavy oil reservoirs. *Journal of Petroleum Science and Engineering,* 112**,** 139-152.

ZHONG, Z., LI, G., ZHU, B., LUO, Z., HUANG, L. & WU, X. 2012. A rapid distillation method coupled with ion chromatography for the determination of total sulphur dioxide in foods. *Food chemistry,* 131**,** 1044-1050.

ZORZENÃO, P. C., MARIATH, R. M., PINTO, F. E., TOSE, L. V., ROMÃO, W., SANTOS, A. F., SCHEER, A. P., SIMON, S., SJÖBLOM, J. & YAMAMOTO, C. I. 2018. Asphaltenes subfractions extracted from Brazilian vacuum residue: Chemical characterization and stabilization of model water-in-oil (W/O) emulsions. *Journal of Petroleum Science and Engineering,* 160**,** 1-11.