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Presented by:

LAOUNI FERIAL

MEHRI ICHRAK

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Jury Members:

President of Committee	Mr. Rouane Azzedine	MCB (UKM Ouargla)
Examiner	Mr. Achi Fethi	PR (UKM Ouargla)
Academic Supervisor	Mr. Tabchouche Ahmed	MCA (UKM Ouargla)

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DEDICATION

I dedicate this memoir to my dear parents **“Hamid and Saliha”,** for their unconditional love and to my sisters

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DEDICATION

To those who taught me to dream, to persevere, and to never give up...

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Ichrak Mehri

Abstract:

This thesis examines organic deposits, including asphaltenes and paraffins, in oil wells. These deposits, which affect production flow and increase costs, are studied using solubility tests, volume and mass kinetics, as well as thermal and spectroscopic analyses. The objective is to characterize these deposits and identify effective methods for their recovery. The results demonstrate the effectiveness of solvents such as toluene and hexane in the extraction of asphaltenes, and provide insights into their behavior and chemical composition. This work proposes strategies for the management and recovery of organic deposits in the petroleum industry.

Key words : Asphaltenes – Paraffins – Solubility – Oil wells – Recovery

Résumé :

Ce mémoire examine les dépôts organiques, notamment les asphaltenes et les paraffines, dans les puits pétroliers. Ces dépôts, qui affectent le flux de production et augmentent les coûts, sont étudiés par des tests de solubilité, des cinétiques de volume et de masse, ainsi que des analyses thermiques et spectroscopiques. L'objectif est de caractériser ces dépôts et d'identifier des méthodes efficaces pour leur valorisation. Les résultats montrent l'efficacité des solvants tels que le toluène et l'hexane dans l'extraction des asphaltenes, et fournissent des insights sur leur comportement et leur composition chimique. Ce travail propose des stratégies pour la gestion et la valorisation des dépôts organiques dans l'industrie pétrolière.

Mot Clés :

Asphalténes – Paraffines – Solubilité – puits de pétroles – Récuperation

ملخص :

تدرس هذه الأطروحة الرواسب العضوية، بما في ذلك الأسفلتينات والبارافينات، في آبار النفط. تُدرس هذه الرواسب، التي تؤثر على تدفق الإنتاج وتزيد التكاليف، باستخدام اختبارات الذوبانية، وحركية الحجم والكتلة، بالإضافة إلى التحليلات الحرارية والطيفية. الهدف هو توصيف هذه الرواسب وتحديد طرق فعالة لاستخلاصها. تُظهر النتائج فعالية مذيبات مثل التولوين والهكسان في استخلاص الأسفلتينات، وتُقدم رؤىً ثاقبة حول سلوكها وتركيبها الكيميائي. يقترح هذا العمل استراتيجيات لإدارة الرواسب العضوية واستخلاصها في صناعة النفط.

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List of Acronyms

EOR	Enhanced oil recovery
API	American Petroleum Institute gravity
AFNOR	Association Française de Normalisation
DIN	Germen institute “Deutsches Institut für Normung”
ASTM	American Society for Testing and Materials
GOST	“Russian institute” Gosudarstvennyy Standart
SARA	Saturates, Aromatics, Resins, and Asphaltenes
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
UV-Visible	Ultraviolet–Visible Spectroscopy
FTIR	infrared spectroscopy
GC-MS	Gas chromatography-mass spectrometry
EDTA	Ethylenediaminetetraacetic Acid
DTPA	Diethylenetriaminepentaacetic Acid
C	Carbon
Si	Silicon
SiO_2	Quartz
$CaCO_3$	Calcite
Fe_2O_3	Iron oxide
Al_2O_3	Aluminum oxide

CO_2	Carbon Dioxide
Ca	Calcium
Fe	Iron
Ca^{2+}	Calcium ion with a +2 charge
O	Oxygen
N	Nitrogen
Ni	Nickel
S	Sulfur
V	Vanadium
DCM	Dichloromethane
DSC	Differential Scanning Calorimetry
H/C	Hydrogen-to-Carbon Ratio
C_nH_{2n+2}	General Formula for Alkanes (Paraffins)
n	number of carbon atoms in the alkane chain
CH_2	Methylene Group
C_7H_8	Toluene
$C_6H_5CH_3$	Structural formula of Toluene
CH_3	Methyl group
C_6H_{14}	n-Hexane
C_{18}	alkane with 18 carbon atoms
C_{60}^+	alkane or hydrocarbon species with 60 or more carbon atoms
$\pi \rightarrow \pi^*$	Electron transition from a bonding to an antibonding π orbital under UV-Vis excitation
H_2S	Hydrogen Sulfide
mol	Mole

g	“gram” unit of mass
ρ	Unit of density
η	Unit of dynamic viscosity
mL	“mililiter” unit of volume
wt	Approximate Weight
cm^3	“Cubic Centimeter” unit of volume
°C	“Celsius” unit of temperature
°F	“Degrees Fahrenheit” unit of temperature
ppm	Parts Per Million
atm	Atmosphere
nm	“nanometer” unit of length
mPa.s	“Millipascal-second” unit of viscosity
Abs	Absorbance

General Introduction

General Introduction

Crude oil is one of the most vital natural resources in the global energy sector, serving as a primary feedstock for fuels, petrochemicals, and a wide array of industrial products. Composed of a complex mixture of hydrocarbons and heteroatomic compounds, crude oil exhibits significant variability in its physical and chemical properties depending on its geographic and geological origin. While its extraction and processing are essential to modern industry, the production of crude oil often encounters several operational challenges that can compromise efficiency and economic viability.[1]

Among the most critical problems faced during crude oil production is the formation and accumulation of various types of deposits within production equipment, pipelines, and reservoirs. These deposits can lead to partial or complete blockages, increased maintenance costs, reduced flow rates, and, ultimately, production losses. The deposits can be broadly classified into organic and inorganic categories. Organic deposits are primarily composed of high molecular weight hydrocarbon fractions such as asphaltenes, paraffins, and maltenes.[2]

The principal objective of this study is to characterize and valorize the deposits formed in crude oil production systems, with a specific focus on the separation and detailed analysis of the organic components, particularly asphaltenes. This research aims to :

- Separate the mixture deposit into **organic** and **inorganic** fractions using toluene.
- Extract **asphaltenes** from the organic deposit fraction using n-hexane precipitation.
- Valorize the extracted asphaltenes by calcination and solvent volume kinetics and solubility test.
- Characterize the extracted asphaltenes and organic fraction using advanced analytical techniques, including:
    - X-Ray Diffraction (XRD) for crystallinity and structural analysis.
    - Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS) for morphological and elemental composition.
    - Gas Chromatography-Mass Spectrometry (GC-MS) for detailed molecular profiling.
    - UV-Visible Spectroscopy (UV-Vis) for optical and electronic behavior.

- Fourier Transform Infrared Spectroscopy (FTIR) for functional group identification.
- Melting point analysis for thermal and rheological behavior.

In addition, a distillation, density and viscosity analysis of crude oil will be carried out to better understand the distribution of volatile and heavy components.

This thesis is structured around three chapters:

- ✐ **Chapter One**: A general overview of the types of deposits encountered in crude oil production, with a focus on their formation mechanisms, classification, and associated operational problems.
- ✐ **Chapter Two**: An experimental study detailing the methods employed for the separation and extraction of deposits. This chapter will also present the results of the various characterization and valorization techniques applied to the extracted asphaltenes.
- ✐ **Chapter Three**: A comprehensive discussion and interpretation of the experimental results, linking the observed properties of the deposits with their potential implications for production and refining processes.

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Chapter 01:

Organic Deposits Generality

1.1. Introduction

The Hassi Messaoud oil field, located in the Ouargla region in the heart of the Algerian Sahara, is the largest and most significant oil field in Algeria, and one of the most prominent in Africa. Discovered in 1956 by SN REPAL and CFPA, it began commercial production in 1960 and is currently operated by Sonatrach, Algeria's national oil company. The field covers an area of approximately 40 by 40 kilometers and is composed of Cambrian-Ordovician sandstone reservoirs situated at an average depth of about 3,337 meters.[1] These reservoirs exhibit favorable porosity and permeability, which have enabled sustainable long-term production. The proven reserves of the field are estimated at around 6.4 billion barrels of oil, with an average output of approximately 350,000 barrels per day. Hassi Messaoud serves as a major hub in Algeria's hydrocarbon infrastructure, linking several key pipelines that transport crude oil to coastal refineries and export terminals. It also acts as a central processing point for crude oil coming from other fields across the country. To maintain and enhance oil recovery rates, advanced secondary and tertiary recovery methods such as water and gas injection are routinely employed. Over the decades, thousands of wells have been drilled in the field, and as production continues, challenges such as the deposition of asphaltenes have become increasingly significant. These heavy organic compounds can precipitate and accumulate in reservoirs and production equipment, leading to flow assurance issues and reduced well productivity. As such, a detailed understanding of the physicochemical properties of asphaltene deposits and their formation mechanisms is crucial for improving production efficiency and extending the operational lifespan of the wells. Hassi Messaoud thus remains not only a cornerstone of Algeria's energy sector but also a focus of ongoing research and technological development in petroleum engineering.[2]

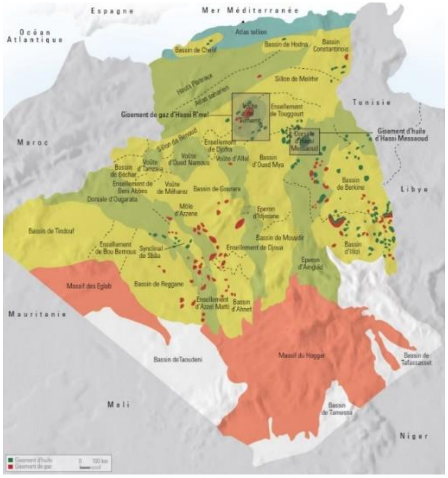


Figure 1: picture of geographical location of the Hassi Messaoud field.

1.2. Definition of crude oil

Crude oil is a naturally occurring, unrefined petroleum product composed primarily of hydrocarbons mainly alkanes, cycloalkanes, and aromatic hydrocarbons along with minor quantities of sulfur, nitrogen, oxygen, and trace metals. It is formed through the geological transformation of organic matter under high pressure and temperature conditions over millions of years, typically in sedimentary basins. Extracted through drilling techniques, crude oil must undergo a series of refining processes such as fractional distillation, cracking, and reforming to yield marketable products including fuels (gasoline, diesel, jet fuel), lubricants, asphalt, and chemical feedstocks for the petrochemical industry. Crude oil is typically classified by its API gravity (light, medium, or heavy) and sulfur content (sweet or sour), which influence its economic value and refining complexity. As a primary energy source, crude oil remains a cornerstone of global industrial activity, transportation infrastructure, and energy policy.[3]

Figure 2: picture of crude oil.

1.2.1. Crude oil classification

Crude oils are classified according to their API gravity (American Petroleum Institute gravity), which is a function of their density relative to water. This classification provides an indication of the oil's quality and its ease of processing in refineries. Based on API values, crude oils are categorized as follows: bitumen (< 8° API), extra-heavy crude oils (8–10° API), heavy crude oils (10–20° API), medium crude oils (20–30° API), light crude oils (30–40° API), and condensates (> 40° API), which are very light hydrocarbons typically associated with natural gas production.[4]

- The relationship between API gravity and the density at 15°C is given by the following formula:

$$^{\circ}\mathrm{API} = \frac{141.5}{d(15^{\circ}C)} - 131.5$$

1.2.2. Crude oil production

Crude oil production refers to the entire set of operations involved in extracting oil from underground reservoirs and bringing it to the surface for processing. The process begins with geological exploration to identify potential oil reserves, followed by the drilling of production wells. Once a reservoir is accessed, crude oil may flow naturally due to reservoir pressure, or enhanced oil recovery (EOR) techniques such as water, gas, or steam injection may be employed to maintain pressure and increase extraction efficiency. After reaching the surface, crude oil undergoes primary treatment to separate it from impurities like water, natural gas, and sediments. The treated crude is then stored or transported to refineries for conversion into usable products. The volume and efficiency of crude oil production depend on several factors, including reservoir characteristics, extraction technology, reservoir depth, and economic or geopolitical conditions.[5]

1.2.3. Crude oil production problems

Crude oil production faces several technical, environmental, and economic challenges. One of the primary issues is reservoir depletion, where the natural pressure declines over time, leading to a decrease in production rates. This often requires costly enhanced oil recovery (EOR) techniques to maintain output. Another major problem is formation damage, such as clogging of the reservoir pores due to fines migration, scaling, or wax and asphaltene deposits, which reduce permeability and hinder oil flow. Environmental concerns are also critical, including the risk of oil spills, greenhouse gas emissions, and contamination of groundwater during drilling and production operations. Additionally, economic volatility, such as fluctuating oil prices and high production costs especially in deepwater or unconventional reservoirs can impact the profitability and feasibility of projects. In politically unstable regions, geopolitical risks further complicate operations, while stricter regulatory frameworks demand more advanced technologies and safety standards, increasing operational complexity.[6]

1.3. The mechanism formation of deposit

The formation of deposits in oil wells is a complex phenomenon that occurs due to various physicochemical changes during oil production. These deposits can broadly be categorized into organic and inorganic types, each arising from distinct mechanisms and influencing the well's performance in different ways. As oil travels from the reservoir to the surface, it experiences significant changes in pressure, temperature, and composition, all of which can contribute to the precipitation of certain components that were originally stable under reservoir conditions.[7]

Figure 3: Picture of deposit formation in well.

1.4. Deposit flocculation

The phenomenon of deposit flocculation in oil production dates back to the early 20th century, when engineers observed that heavy components like asphaltenes and waxes could destabilize and form solid deposits under varying production conditions. Initially misunderstood and attributed to impurities, it became clear with time that pressure, temperature, and fluid composition changes could trigger the aggregation of these heavy molecules a process now known as flocculation. In the 1940s–50s, improved analytical tools allowed researchers to better understand asphaltenes, showing they remain stable under reservoir conditions but flocculate when pressure drops or light hydrocarbons are introduced. The role of colloidal stability and solvent polarity in this process became evident. By the 1970s–80s, thermodynamic models and molecular theories such as Yen’s model advanced the understanding of asphaltene behavior, emphasizing their polar cores and resin-mediated stabilization. Today, flocculation is a key focus in flow assurance, with advanced lab techniques and predictive models used to manage and mitigate deposition risks in oil production and transport.[8]

1.5. Generality of deposit :

A deposit generally refers to a collection or accumulation of material that settles or forms in a particular location over time. This material can be organic or inorganic and can result from various natural processes such as sedimentation, precipitation, or chemical reactions. In a broader sense, a deposit forms when substances like minerals, chemicals, or organic matter accumulate in a way that leads to their concentration in specific areas. In the context of geology, deposits can refer to layers of sediment or mineral resources that are left behind by water, wind, or other environmental factors. In industrial and natural systems, deposits can also refer to the buildup of substances like scale, wax, or corrosion products that occur in pipes, wells, or equipment, often leading to blockages or inefficiencies.[9]

1.5.1. Deposit Types :

Deposits encountered in oil production systems can be broadly classified into two main types organic and inorganic:

- **Organic deposits** primarily include paraffins (or waxes) and asphaltenes, which are naturally present in crude oil. Paraffins tend to precipitate when the temperature of the produced fluid drops below the wax appearance temperature, forming solid crystals that accumulate in tubing and pipelines. Asphaltenes, on the other hand, are heavier, more complex molecules that become unstable due to pressure drops or changes in oil composition, leading to their deposition near the wellbore or in surface facilities.
- **Inorganic deposits** are typically composed of scales and corrosion products. Scale forms when dissolved minerals such as calcium carbonate or barium sulfate precipitate out of water due to shifts in temperature, pressure, or the mixing of incompatible waters. Corrosion products, like iron sulfides or oxides, result from chemical reactions between well fluids (such as CO_2 or H_2S) and metal surfaces in the production system. Both types of deposits can significantly impair production efficiency by reducing flow rates, damaging equipment, and increasing the need for intervention and maintenance.[10]

1.5.2. Definition of organic deposit :

An organic deposit in chemical terms refers to the accumulation of high molecular weight, carbon-based compounds primarily paraffins, asphaltenes, and resins that precipitate out of crude oil due to changes in temperature, pressure, or fluid composition during production. Paraffins are long-chain saturated hydrocarbons (alkanes) that crystallize when the temperature drops below their wax appearance temperature, while asphaltenes are complex, polyaromatic molecules containing heteroatoms like nitrogen, sulfur, and oxygen, which become insoluble when pressure drops or composition changes. These compounds are originally stable under reservoir conditions but lose solubility as oil flows to the surface, leading to their deposition in tubing, pipelines, and surface equipment, where they can restrict flow and cause operational challenges.[11]


ASPHALTENE

PARAFFIN

Figure 4: Picture of asphaltene and paraffin deposit.

1.5.3. Organic deposit types :

Organic deposits in oil production are primarily composed of heavy hydrocarbon compounds that become unstable and precipitate from crude oil under certain conditions. The main types of organic deposits include :

1. **Paraffins:** These are long-chain alkanes (typically C_{18} to C_{60}^{+}). that crystallize when the fluid temperature drops below the wax appearance temperature (WAT). They form solid waxy layers inside production tubing, flowlines, or surface equipment, especially in colder environments.
2. **Asphaltenes:** These are complex, high-molecular-weight polyaromatic compounds containing heteroatoms such as nitrogen, sulfur, and oxygen. Asphaltenes are soluble

in aromatic solvents like toluene but insoluble in light alkanes like n-heptane. They precipitate due to pressure reduction, compositional changes (e.g., gas injection), or temperature variations.

3. **Resins:** Resins are amphiphilic molecules with both polar and nonpolar components. While they do not usually precipitate on their own, they interact with asphaltenes and help stabilize or destabilize them in solution, playing a key role in asphaltene aggregation and deposition.

4. **Naphthenates:** These are salts formed from the reaction of naphthenic acids (naturally occurring in some crude oils) with divalent metal ions like calcium or sodium. Under certain conditions, they can precipitate and form soap-like organic deposits, especially at water–oil interfaces.[12]

Figure 5: Picture of paraffins and resins.

1.5.4. The chemical composition of organic deposit

Here's a concise table summarizing the important chemical composition of the main types of organic deposits:

Table 1: chemical composition of organic deposit.

Type	Main component	Chemical features	Solubility behavior
Paraffins	Long-chain alkanes (C_{18}–C_{60}^{+})	Saturated hydrocarbons, nonpolar (C_nH_{2n+2})	Precipitate when temperature < Wax Appearance Temp
Asphaltenes	Polycyclic aromatics, N, S, O, metals	High molecular weight, polar groups, aromatic rings	Insoluble in n-heptane, soluble in toluene
Resins	Aromatic rings, alkyl chains, polar groups	Amphiphilic, lower MW than asphaltenes	Soluble in oil, stabilize or destabilize asphaltenes
Naphthenates	Naphthenic acids + metal ions (e.g., Ca^{2+})	Metal-organic salts, soap-like structure	Precipitate at oil–water interfaces

1.5.5. Organic deposit advantages

Organic deposits in oil production are generally considered problematic, but under certain conditions, they can offer some advantages or be repurposed for beneficial uses. Here are a few potential advantages of organic deposits, especially when viewed from a broader industrial or research perspective:[13]

- **Indicator of Reservoir Behavior:** The presence of organic deposits such as asphaltenes can provide valuable information about changes in reservoir pressure, temperature, or fluid composition, serving as an early warning for flow assurance issues.
- **Source of Valuable Hydrocarbons:** Organic deposits like paraffins and asphaltenes contain significant hydrocarbon content that, if recovered and processed, can be used as feedstock for fuel, bitumen, or chemical production.

- **Stimulation Strategy Design:** Understanding the composition of organic deposits helps in customizing stimulation and chemical treatment programs, improving the efficiency of well interventions and extending equipment life.
- **Material Science and Nanotechnology Applications:** Asphaltenes, due to their complex molecular structures, are being explored for use in carbon-based materials, such as adsorbents, nanocomposites, and even in energy storage technologies.
- **Environmental Remediation and Research**: Studying organic deposits helps in environmental monitoring and provides insight into natural hydrocarbon degradation, aiding in spill response strategies and bioremediation research.

1.6. Paraffin deposit

1.6.1. Definition of paraffin

Paraffins are high-molecular-weight hydrocarbons that tend to accumulate in production equipment, including tubing, surface facilities (such as wellheads and pipelines), and other storage systems. The term "paraffin" is derived from the Latin "parum affinis," meaning "little affinity," which is fitting, given that paraffin deposits are insoluble in most crude oils and resist attacks from acids, bases, and oxidizing agents.

Paraffin deposits are typically solid, light yellow in color, and brittle in texture. They are odorless and tasteless and commonly form during the production and transportation of crude oil in the oil and gas industry. These deposits can cause significant challenges, particularly in pipeline flow assurance and storage systems, where they can obstruct flow and reduce efficiency.[14]

Figure 6: Parafin deposit.

1.6.2. Composition and structure of paraffins

Paraffins, more commonly referred to as "alkanes", are the chemical family of saturated hydrocarbons resulting in straight or branched chain, which do not contain molecules of Carbon (C) and Hydrogen (H), This means that the carbon chains do not contain double or triple bonds in the carbon skeleton and that each carbon atom is attached to two or three hydrogen atoms.

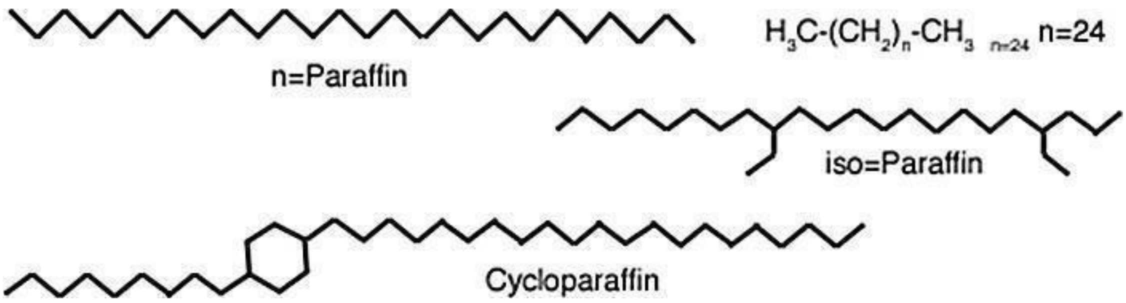


Figure 7: Chemical structure of paraffins.

A distinction is made between paraffins made up of linear alkanes (n-alkanes) and those made up of branched alkanes (iso-alkanes), namely:

- ✓ Liquid or fluid paraffins (paraffinum perliquidum), (n = 8 to 19) with a viscosity of 25 to 80 mPa.s;
- ✓ Oily or pasty paraffins (paraffinum subliquidum), with a viscosity of 110 to 230 mPa.s;
- ✓ Solid paraffins (paraffinum solidum), waxes (n = 20 to 46) with a solidification temperature between 50 and 62°C.

Linear alkanes (n-alkanes) are the dominant elements in solid paraffins, while branched alkanes (iso-alkanes) predominate in micro-waxes. White, fairly transparent, and odorless, paraffin melts between 40 and 71°C. [15]

1.7. Asphaltene deposit

1.7.1. Definition of asphaltene

Asphaltenes are solid, black-brown, brittle materials first named by French chemist Boussingault in 1837 during bitumen distillation. In modern terms, they are high molecular weight, aromatic-rich hydrocarbons that are insoluble in paraffinic solvents (like n-heptane or n-pentane) but soluble in aromatic solvents such as toluene or benzene. In crude oil, asphaltenes exist as colloidal particles stabilized by resins and lighter hydrocarbons, forming micelle-like structures. When asphaltenes deposit in reservoir pores, they can block pore spaces, reducing permeability and eventually halting oil flow. Continued deposition leads to asphaltene adsorption on rock grains, making the formation oil-wet and further decreasing oil recovery efficiency.[16]

Figure 8 : Asphaltene deposit.

1.7.2. Chemical Composition of Asphaltenes

Asphaltenes, which originate from the breakdown of organic matter, are primarily made up of carbon and hydrogen. On average, they contain about 81% ± 3.5% carbon and 7.8% ± 1% hydrogen by weight. This corresponds to an H/C atomic ratio of approximately 1.15 ± 0.15, similar to that of condensed polyaromatic structures.

In addition to these major elements, asphaltenes also include significant amounts of nitrogen, Sulfur, and oxygen:

- Nitrogen (N) : 0.5% to 3.3%

- Sulfur (S) : 0.3% to 10.3%
- Oxygen (O) : 0.3% to 4.9%

Asphaltenes are known to concentrate most of the metals found in crude oil, accounting for up to 80% of the total metal content. The most common metals are nickel and vanadium, with some crude oils containing up to 6000 ppm of vanadium. These metals are mostly associated with porphyrinic structures, although non-porphyrinic metal complexes can also be present.[17]

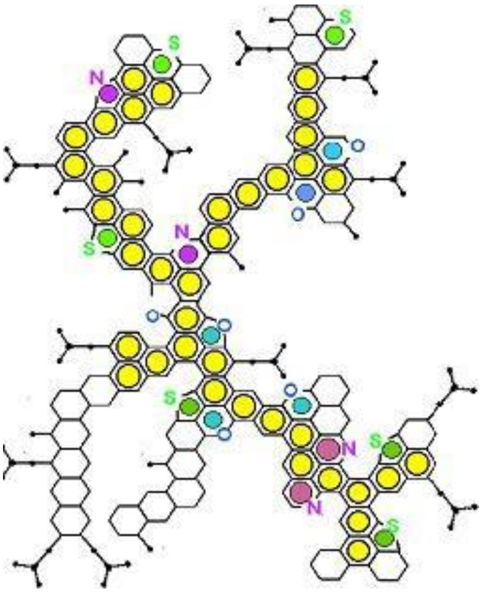


Figure 9:Composition of asphaltene.

1.8. Properties of Asphaltene

This table highlights the main characteristics that influence asphaltene behavior in crude oil production systems:

Table 2: Properties of asphaltene in crude oil.

Property	**Description**
Chemical Composition	High-molecular-weight polycyclic aromatic hydrocarbons containing heteroatoms (S, N, O) and trace metals (Ni, V).
Carbon Content	80-85%
Hydrogene Content	7-10%
Oxygen Content	1-4%
Sulfur Content	0.3-10%
Nitrogen Content	0.5-3%
Trace Metals (Ni, V)	0.001-1%
Solubility	Insoluble in light alkanes (e.g., pentane, heptane), soluble in aromatic solvents (e.g., toluene, xylene).
Appearance	Dark, solid or semi-solid (powdery or crystalline).
Molecular Weight	Typically >1,000 g/mol.
Density	1.1 - 1.5 g/cm³

1.9. Origin of asphaltenes

The origin of asphaltenes is closely linked to that of kerogens, which are products formed through various chemical and biochemical transformations of organic matter accumulated and deposited within the source rock. During burial, the increase in temperature causes the thermal degradation of kerogens, contributing to the formation of smaller structures known as asphaltenes and resins.[18]

Figure 10: Sample of asphaltenes.

1.9.1. Maltenes

Maltenes are the soluble fraction of crude oil or bitumen that remain after the removal of asphaltenes, which are insoluble in lighter solvents like toluene or benzene. This fraction consists of a complex mixture of hydrocarbons, including saturates (alkanes), aromatics (benzene ring compounds), resins (more polar compounds that help stabilize asphaltene structures), and non-polar hydrocarbons. Maltenes are essential in determining the viscosity, flow properties, and overall stability of crude oils, particularly those rich in asphaltenes, such as heavy oils and bitumens. Their interaction with asphaltenes can influence the oil's behavior during extraction and refining, making them critical in improving the efficiency of these processes. In short, maltenes are the lighter, soluble components of crude oil that significantly impact both its physical properties and its processing in refineries.[19]

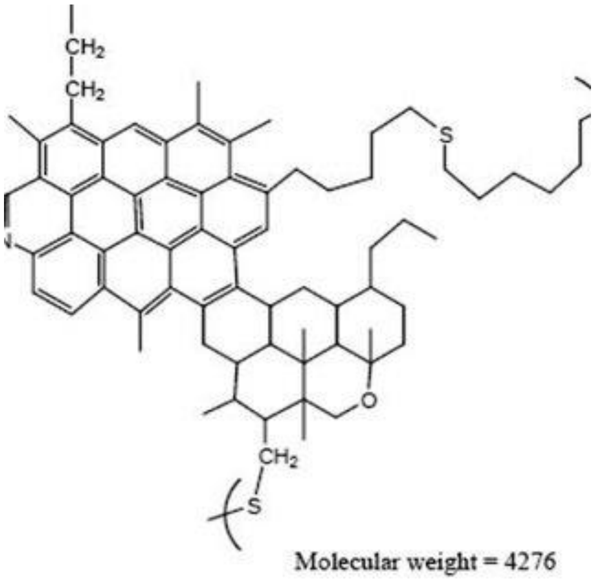


Figure 11: Various maltenes constituents.

1.9.2. Element composition of maltenes:

Table 3: Element composition of maltenes.

Element	Approx wt%
Carbon (C)	80-88%
Hydrogene (H)	10-13%
Sulfur (S)	0.5-5%
Nitrogen (N)	0.1_1%
Oxygen (O)	0.1-2%
Metals (NI, V)	<100ppm

1.9.3. Fractionation

The petroleum industry operates upstream in exploration and drilling, and downstream in refining crude oil through a process called SARA fractionation, which separates components into Saturates, Aromatics, Resins, and Asphaltenes. Refining begins with atmospheric distillation to obtain light products (e.g., gases, gasoline, kerosene), followed by vacuum distillation of the residue to isolate heavier components. Saturates are non-polar aliphatic hydrocarbons, while aromatics are benzene-based compounds. Resins are polar aromatics containing heteroatoms (N, O, S), soluble in solvents like heptane and pyridine but not in propane. Asphaltenes are the heaviest and most polar fraction, with high molecular weight and aromaticity, and are defined by their insolubility in paraffinic solvents but solubility in aromatic solvents. The vacuum residue is typically separated into SARA components based on solubility and polarity through precipitation or chromatography.[20]

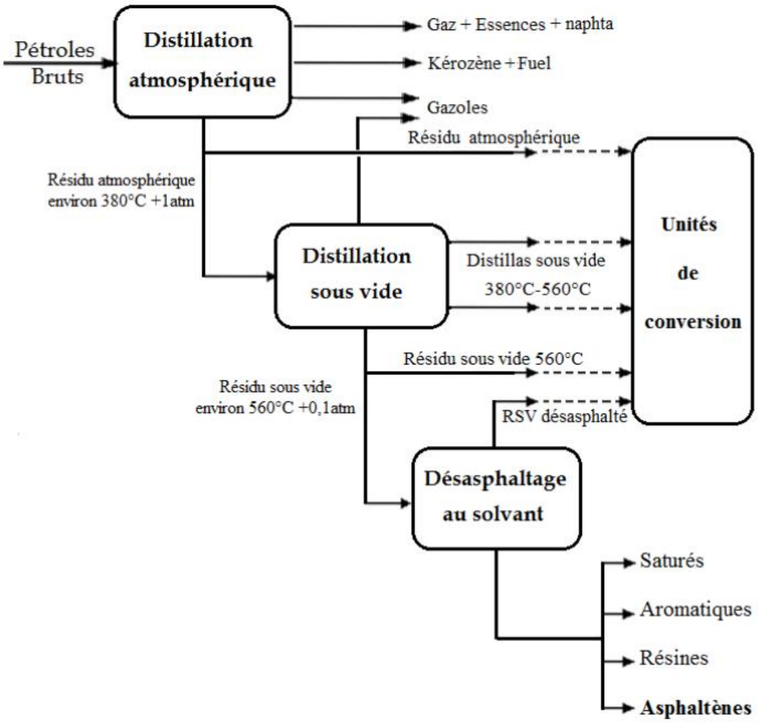


Figure 12 : Schematic representation of petroleum fractionation.

1.10. Influence of different parameters on the stability of asphaltenes

1.10.1. Influence of Temperature and Pressure on Asphaltene Stability

Numerous studies have examined how temperature and pressure affect asphaltene precipitation. Alves et al. and Andersen & Birdi proposed that increasing temperature enhances crude oil stability by disrupting asphaltene aggregation and reducing aggregate size. Chandio et al. found that asphaltene solubility generally increases with temperature, although some studies (e.g., Speight and Alves) reported increased precipitation at higher temperatures. Contradictory results also exist, such as Anderson’s findings showing decreased precipitation with rising temperature for n-alkanes with more than five carbon atoms. Neilson et al. confirmed that particle size decreases with temperature when asphaltenes are diluted in light alkanes.

Regarding pressure and resin influence, studies show that resins significantly raise the precipitation threshold of asphaltenes when present in high concentrations. Resins stabilize asphaltenes by forming steric colloids or by adsorbing at the interface between aggregates and crude oil. While some researchers argue that asphaltene precipitation is irreversible and resins are essential for stability, others suggest it is reversible and that resins are not always necessary.[21]

1.10.2. Influence of time, nature and quantity of flocculant

The precipitation of asphaltenes is significantly influenced by the flocculant's type, quantity, and contact time. A high flocculant-to-oil ratio is required, and the amount of asphaltenes precipitated depends on the flocculant's carbon chain length. Studies have shown that shorter-chain n-alkanes (e.g., n-pentane, n-hexane, n-heptane) precipitate more asphaltenes, particularly those rich in resins and aromatics, while longer chains ($n > 5$) have a lesser effect. The polarity of the flocculant also plays a key role: more polar solvents like acetone yield less polar asphaltenes. Fractionation using solvents of varying polarity (e.g., toluene, dichloromethane, tetrahydrofuran) demonstrates structural and chemical differences among asphaltene fractions. Additionally, a minimum contact time of 8 hours is recommended to allow proper diffusion and complete precipitation.[22]

1.11. International Standards for Asphaltene Extraction

Several methods are used to extract asphaltenes from crude oil or petroleum residues. The most commonly accepted definition of asphaltenes follows the AFNOR petroleum standard 115-60, which defines asphaltenes as the fraction of crude oil that is insoluble in n-heptane but soluble in hot benzene at its boiling point. This standard is equivalent to the British IP-143/84 and German DIN 51-595 standards, although these use n-hexane as the precipitating solvent. The American ASTM893-69 standard instead uses n-pentane, while the Soviet GOST 11858-56 standard uses petroleum ether.[23]

The generally recommended conditions for asphaltene separation are as follows:[24]

- n-Heptane is used as the flocculating agent because it more effectively removes maltenes (a mixture of aromatics, saturates, and resins) compared to other alkanes.

- The typical mass ratio of crude oil or petroleum residue to solvent is 1 g of sample to 40 mL of solvent.
- The contact time between the oil and the solvent should be 24 hours, under agitation and protected from light to avoid parasitic reactions induced by exposure to light.

Moreover, both the nature and the proportion of asphaltenes in crude oil ranging from 0.1% to 20% for heavy crudes vary significantly from one reservoir to another.

1.12. Remediation Strategies

1. Chemical Removal : [25]

- Use solvents like xylene or toluene to dissolve asphaltenes and heavy organic deposits.
- Inject hot diesel or light hydrocarbons to remove wax buildup in tubing and flowlines.
- Apply acid treatments (e.g., hydrochloric acid, acetic acid) to dissolve carbonate or iron-based scale.
- Use chelating agents (e.g., EDTA, DTPA) to remove barium, strontium, or iron sulfide scales without forming solids.
- Apply dispersants or emulsifiers to break down and flush away complex deposits.

2. Mechanical Removal : [26]

- Run coiled tubing with high-pressure jetting tools to clean tubing walls and perforations.
- Deploy wireline tools like scrapers, brushes, or bailers to mechanically remove deposits from the wellbore.
- Use downhole rotating brushes or milling tools for hard or stubborn deposits like cement, scale, or solidified wax.

3. Thermal Stimulation : [27]

- Inject hot oil, hot water, or steam to melt and mobilize waxy or hydrate plugs.
- Apply electrical or chemical heaters to raise temperature locally and assist in breaking up deposits.

Chapter 02:

Characterization and Valorization analysis

2.1. Introduction

In oil and gas production, the accumulation of deposits such as asphaltenes, waxes, and scale within wells, pipelines, and production equipment presents a significant operational challenge. These deposits can obstruct fluid flow, reduce production efficiency, and lead to costly maintenance and downtime. To mitigate these issues, solvent-based treatments have become a widely adopted method for the removal and prevention of such blockages. Solvents, which can be either aromatic or aliphatic in nature, work by chemically interacting with the deposits, disrupting their solid structure and facilitating their dissolution into the surrounding fluid. [28] For example, aromatic solvents like toluene and xylene are highly effective in dispersing asphaltene aggregates, while aliphatic solvents such as diesel and kerosene are commonly used to dissolve paraffin waxes. The efficiency of solvent treatments is largely dependent on factors such as temperature, solvent composition, and the specific nature of the deposit. This chapter delves into the fundamental mechanisms behind solvent interactions with deposits, the types of solvents used, and the practical considerations for applying solvent-based remediation techniques in oil and gas operations. Through these methods, operators can enhance flow assurance, minimize production downtime, and reduce the need for costly mechanical interventions.[29]

Figure 13: Wax deposit before and after remediation.

2.2. Preliminary Characterization and valorization Methods for Organic Deposits

In the context of organic deposit characterization, several simple and cost-effective analytical methods were selected for their suitability in a standard laboratory setting. These include solubility tests, calcination, thin-layer chromatography (TLC), infrared spectroscopy (FTIR), and optical microscopy. These techniques are advantageous due to their accessibility, ease of implementation, and ability to provide valuable preliminary insights into the chemical and structural nature of the deposits. They enable the differentiation of major compound families, the assessment of organic versus inorganic content, and the detection of key functional groups. The combined application of these methods offers an efficient and rational approach for guiding further in-depth analyses or potential valorization strategies.[30]

2.2.1. Solvent solubility

Solvent solubility is a key factor in managing organic deposits in petroleum production, as it determines how well a solvent can dissolve or precipitate compounds like asphaltenes and paraffins. Based on the principle of "like dissolves like," solvent effectiveness depends on molecular compatibility with the deposit. Toluene, an aromatic solvent, is highly effective in dissolving asphaltenes due to its aromatic ring structure, which enables strong π–π interactions with the aromatic cores of asphaltene molecules. These interactions break apart asphaltene aggregates, allowing them to dissolve. In contrast, n-hexane, a non-polar aliphatic solvent, lacks this aromatic character and instead promotes asphaltene precipitation by reducing their solubility. This selective solubility is used both in laboratory tests (like asphaltene precipitation index) and in the field for treatment operations. Thus, understanding solvent behavior is essential for developing effective strategies to dissolve or control problematic organic solids in oilfield systems. [31]

2.2.2. Toluene solvent

Toluene is an aromatic hydrocarbon solvent commonly used in the petroleum and chemical industries. It is a clear, colorless liquid with a characteristic sweet odor and the chemical formula C_7H_8. Toluene consists of a benzene ring bonded to a methyl group (CH_3), making it a highly effective non-polar solvent for dissolving organic substances such as asphaltenes, resins, oils, and greases.[32]

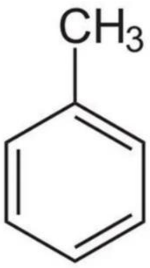


Figure 14: Chemical composition of toluene solvent.

- **Properties of Toluene solvent**

Table 4: Properties of Toluene solvent

Property	**Value/Description**
Chemical formula	$C_6H_5CH_3$ (Methylbenzene)
Molecular Weight	92.14 g/mol
Appearance	Clear, colorless liquid
Boiling point	~110.6°C (231.1°F)
Melting point	-95°C (-139°F)
Density	~0.867 g/cm³ at 20°C
Polarity	Non-polar (aromatic hydrocarbon)

2.2.3. n-hexane solvent

n-Hexane is a straight-chain aliphatic hydrocarbon with the chemical formula C_6H_{14}. It is a colorless, volatile, and non-polar solvent, commonly used in industrial and laboratory settings. In the petroleum industry, n-hexane is often used to dissolve or extract paraffinic (wax) compounds, thanks to its high solvency for long-chain alkanes.[33]

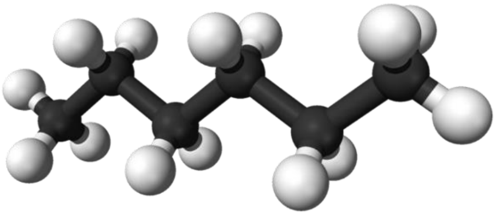


Figure 15: Chemical composition of n-Hexane solvent.

- **Properties of n-hexane solvent**

Table 5: n-hexane properties

Property	**Value / Description**
Chemical formula	C_6H_{14}
Molecular Weight	86.18 g/mol
Appearance	Clear, colorless liquid
Boiling point	~68.7°C
Melting point	-95°C
Density	~0.66 g/cm³ at 20°C
Polarity	Nonpolar

2.3. Separation of Organic and Inorganic Compounds from Deposits and Asphaltene Precipitation

2.3.1. Experiment part

❖ **Materials and Reagents:**

- **Required Equipment:**
  1. Glass beakers (100–250 mL)
  2. Trough
  3. Spatula
  4. Precision balance (±0.001 g)
  5. Magnetic stirrer or glass rod
  6. Erlenmeyer flask, funnel and filter paper

7. Oven for drying

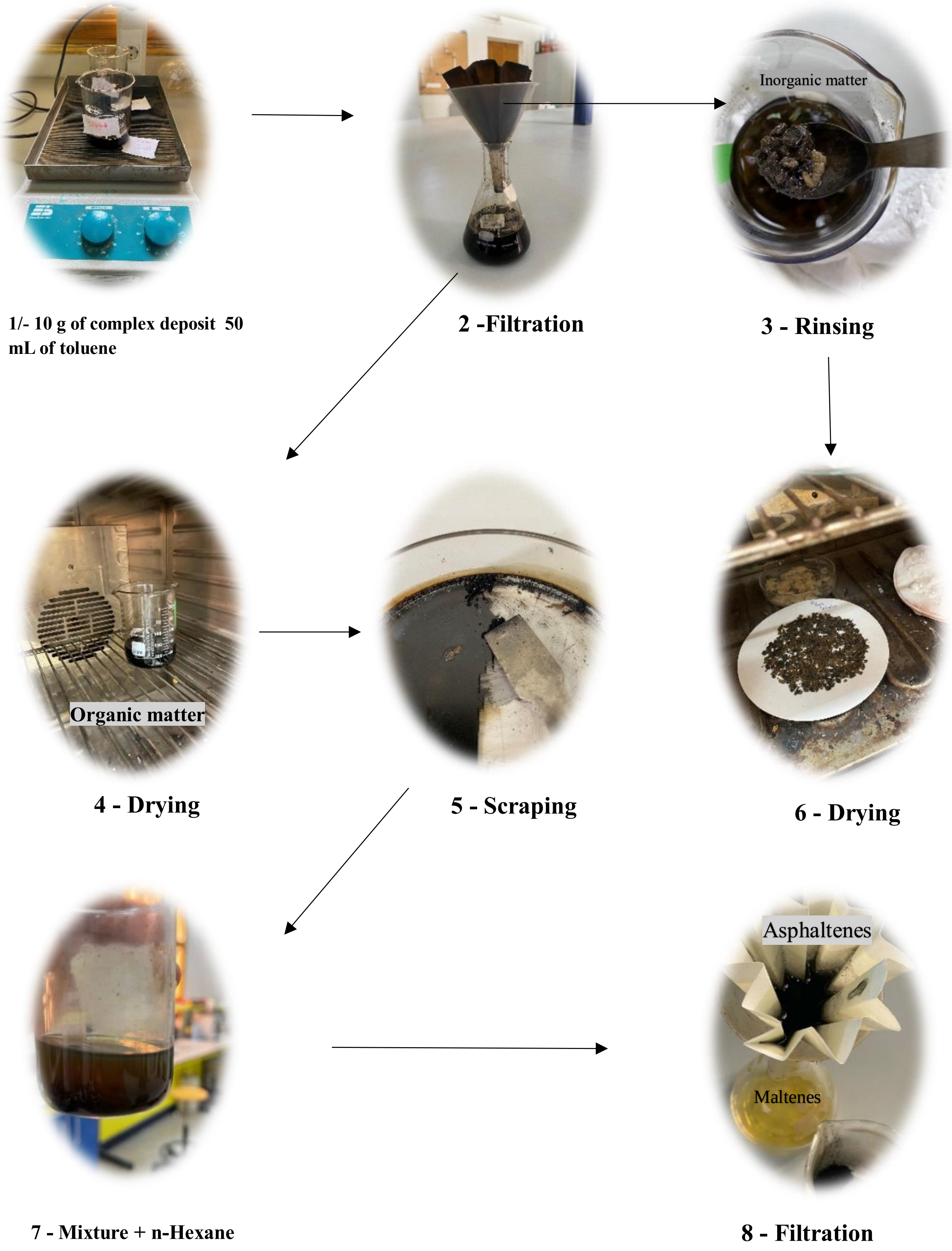
- **Required Chemicals :**
  - Complex Deposit (collected from Hassi Messaoud field)
  - n-Hexane (or n-heptane) – for asphaltene precipitation.
  - Toluene (or benzene) – optional, for organic/inorganic separation from complex deposit.

❖ Process steps:

To begin the separation process, weigh 10 grams of the complex deposit and transfer it into a beaker. Add 50 mL of toluene to the beaker to dissolve the organic components, then place the beaker on a magnetic stirrer and stir the mixture continuously for 24 hours at room temperature. Once the stirring is complete, filter the mixture using filter paper, a funnel, and an Erlenmeyer flask. At this stage, the inorganic matter is retained on the filter paper, while the organic matter dissolved in toluene passes through and is collected in the flask. To ensure thorough separation, rinse the inorganic residue retained on the filter paper with toluene approximately six times. Next, transfer the organic solution (toluene extract) into an evaporation dish and place it in an oven set at 110 °C for 2 hours to evaporate the toluene and recover the organic residue. After drying, use a spatula to scrape the black powder representing the organic matter from the dish and transfer it into a clean beaker. Add 40 mL of n-hexane to the beaker, stir gently, and then allow the mixture to stand undisturbed for 24 hours to facilitate the precipitation of asphaltenes. After this period, filter the mixture again using filter paper, a funnel, and an Erlenmeyer flask. The asphaltenes will remain on the filter paper, while the maltenes will be collected in the filtrate.

Figure 16: Picture of required chemicals.

Process schematic:



2.4. Solubility test for Asphaltenes in various solvents

To evaluate the solubility of our isolated asphaltenes in selected solvents of different polarity toluene, distilled water, acetone, ethanol, dichloromethane, and n-hexane in order to characterize their polarity-dependent solubility behavior.

- **Materials and Equipment :**

  - Dried asphaltene sample
  - Solvents :
    1. Toluene (aromatic, nonpolar)
    2. Distilled water (highly polar)
    3. Acetone (polar aprotic)
    4. Ethanol (polar protic)
    5. Dichloromethane (moderately polar)
    6. n-Hexane (nonpolar aliphatic)
  - 6clean, dry test tubes or glass vials (labeled)
  - Analytical balance
  - Magnetic stirrer or vortex mixer
  - Spatula or glass rod

- **Procedures :**

1. Weigh about 0.05 g of dried asphaltene into each of the six labeled test tubes, one for each solvent.
2. Add 5 mL of each solvent to the corresponding tube:

   - Tube 1 : n-Hexane
   - Tube 2 : Ethanol
   - Tube 3 : Acetone
   - Tube 4 : Dicloromethane (DCM)
   - Tube 5 : Distilled water
   - Tube 6 : Toluene

3. Place the tubes on a magnetic stirrer or shake manually for 15 minutes.

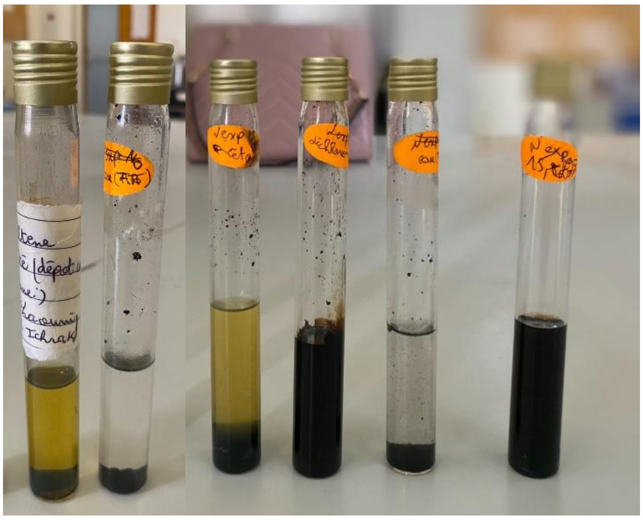


Figure 17 : Picture of tubes results of solubility test.

2.5. Volume Kinetics by toluene with deposit

Determine the minimum volume of toluene required to dissolve 1 gram of organic deposit by testing solvent volumes from **1 mL to 10 mL** and to confirm the ratio we used in the organic/inorganic separation **(1g/5mL).**

- **Procedures :**

  - Prepare 10 clean tubes, label them from 1 mL to 10 mL
  - Add 1.00 g of the same organic deposit into each tube.
  - Add 1 mL, 2 mL, ..., up to 10 mL of toluene to each respective tube.
  - Place on magnetic stirrer or shake for a fixed time (e.g. 4 hours) at room temperature or 50 °C.
  - Observe whether the deposit is fully, partially, or not dissolved.
  - Optionally, filter and weigh any undissolved material to calculate % solubility.

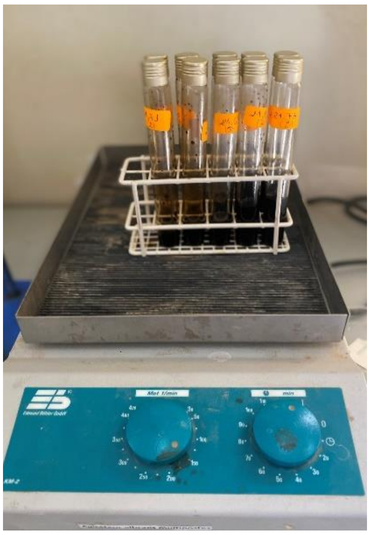


Figure 18: Picture of tubes of volume kinetic.

2.6. Experimental results

Table 6: Separation of Deposit Fractions at Varying Toluene Volumes.

Toluene volume (mL) in tubes (with 1g of deposit)	**Inorganic matter (g)**	**Organic matter (g)**	**Asphaltene/Maltenes mixture (g)**
1	1.28	0.58	0.03
2	1.44	1.28	0.04
3	1.43	2.11	0.04
4	1.4	2.26	0.04
5	1.43	3.08	0.05
6	1.28	4.4	0.02
7	1.43	5.52	0.03
8	1.3	6.51	0.04
9	1.4	7.65	0.02
10	1.32	8.24	0.04

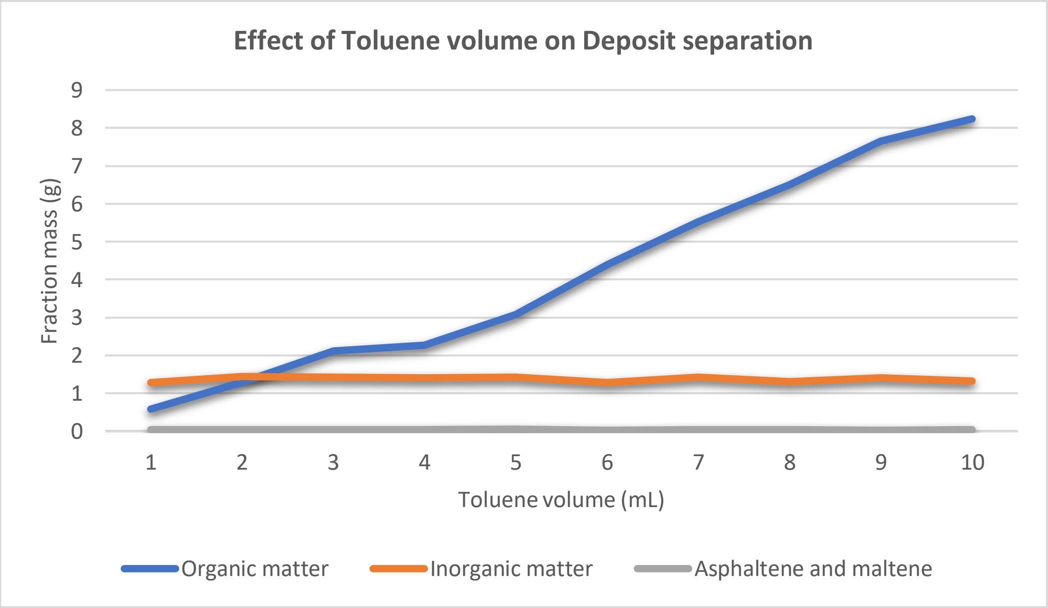


Figure 19: Diagram of Toluene volume effect on deposit separation.

2.7. Volume and mass kinetics by Toluene with deposit

To evaluate the effect of increasing deposit mass and solvent volume on dissolution kinetics in toluene.

❖ **Protocol :**

1. **Labelling :**
    - Label each of the 10 tubes from Tube 1 to Tube 10.
2. **Weighing :**
    - Using an analytical balance, weigh the required mass of deposit for each tube (1 g to 10 g, increasing by 1 g per tube).
    - Transfer each weighed deposit into its corresponding labeled tube.
3. **Solvent Addition :**
    - Using a volumetric pipette or graduated cylinder, add the corresponding volume of toluene to each tube (5 mL to 50 mL, increasing by 5 mL per tube).
4. **Mixing:**
    - Place on magnetic stirrer or shake for a fixed time.

Figure 20: Picture of tubes mass and volume kinetic.

❖ Experimental Design :

Table 7: experimental design table.

Tube No	Deposit mass (g)	Toluene volume (mL)
1	1	5
2	2	10
3	3	15

4	4	20
5	5	25
6	6	30
7	7	35
8	8	40
9	9	45
10	10	50

❖ Experimental results:

Table 8: Separation of Deposit Fractions at Varying Toluene Volumes and deposit mass

Tube No	Inorganic matter (g)	Organic matter (g)	Asphaltene/Maltenes mixture (g)
1	1.34	1.57	0.05
2	2.7	5.76	0.04
3	3.72	9.94	0.05
4	5.34	13.45	0.06
5	6.47	16.17	0.06
6	6.95	14.63	0.17
7	8.28	19.46	0.09
8	9.47	28.08	0.25
9	10.64	34.93	0.18
10	11.57	29.81	0.33

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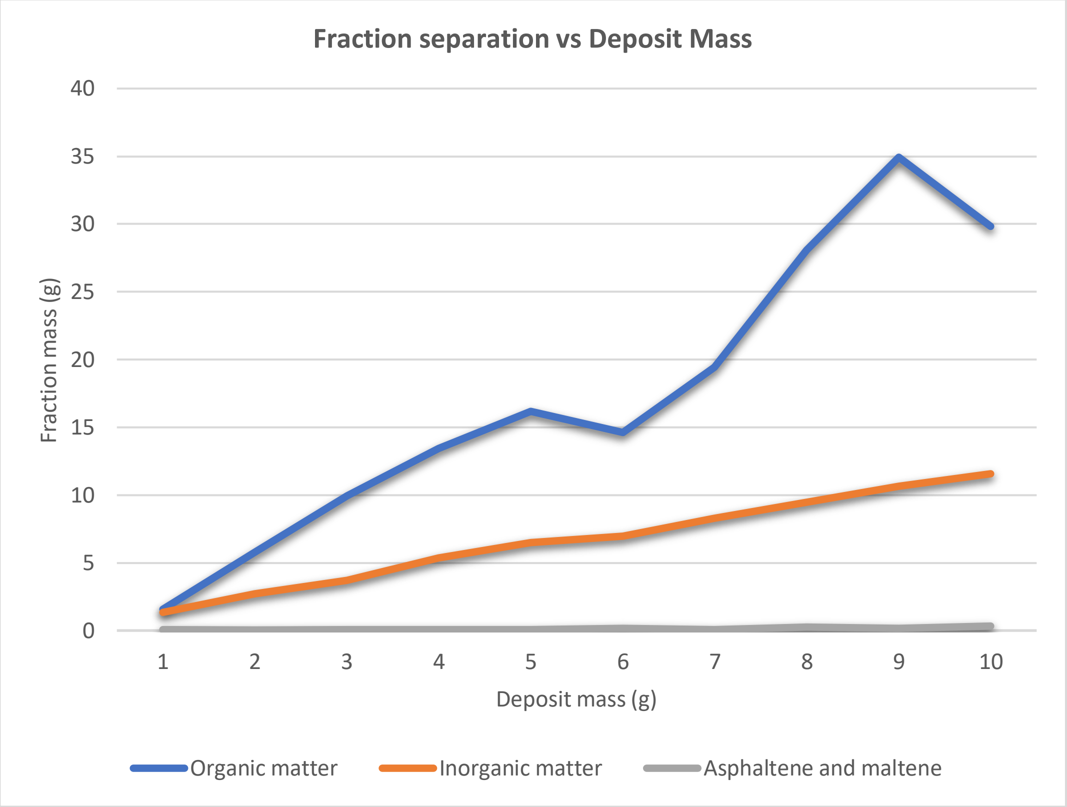

Figure 21: Effect of Deposit Mass and Toluene Volume on the Mass Fraction

2.8. Method of Analysis of Organic Matter by Calcination

To determine the asphaltene content of an organic material by calcination at 600 °C.

❖ **Stepwise Calcination :**

- Place the crucible containing the sample into a muffle furnace.
- Heat the sample in stages depending on the targeted components:
  - **250 °C for 1 hour** to remove light organic matter.
  - **500 °C for 1 hour** to burn off paraffins.
  - **600 °C or higher for 1 hour** to eliminate asphaltenes.

1. Begin by choosing a clean porcelain crucible and accurately measuring its initial mass using an analytical balance.

Figure 22 : Empty porcelain crucible.

2. Place the dried organic material in a porcelain crucible and weigh it.

Figure 23: Filled porcelain crucible.

3. Place the organic material in the oven for about an hour at 600°C for eliminate asphaltenes.

Figure 24: Picture of oven.

4. After the material has been calcined in the oven, its mass is measured using an analytical balance.

Figure 25: Filled porcelain crucible after calcination.

2.9 Crystalline Phase Identification of deposits by X-ray Diffraction (XRD) Analysis:

X-ray Diffraction (XRD) analysis of deposits is used to identify the crystalline phases and mineralogical composition present in solid deposits found in petroleum systems. The objective of XRD is to determine whether deposits contain crystalline inorganic components such as salts, sulfates, carbonates, or crystalline silica, as well as to detect any ordered structures within organic deposits. By analyzing the diffraction patterns generated when X-rays interact with the sample's crystal lattice, XRD provides fingerprint information on the types of minerals or crystalline compounds present. This helps differentiate between purely organic materials (typically amorphous and non-crystalline) and those mixed or coated with inorganic crystals, which can influence the deposits' mechanical properties and their impact on oil production. Understanding the crystalline composition through XRD supports the development of targeted strategies for deposit prevention, removal, and managing scaling issues in oilfield operations. [34]

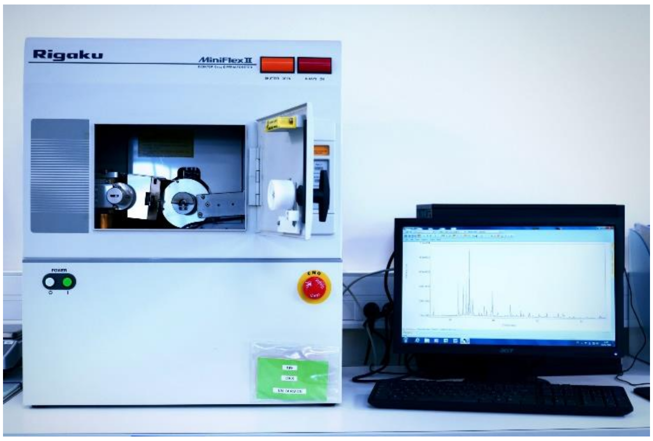

Figure 26: XRD analys.

2.10. Morphology and Elemental Composition of Organic Deposit by SEM/EDS Analysis:

The SEM/EDS analysis was conducted to characterize the nature and composition of organic deposits found in the petroleum system, with the objective of understanding their origin, structure, and potential impact on production. Scanning Electron Microscopy (SEM) revealed an amorphous, compact, and heterogeneous texture, typical of organic materials such as asphaltenes. The Energy Dispersive X-ray Spectroscopy (EDS) analysis showed a high carbon (C) content, confirming the organic nature of the deposit, along with the presence of sulfur (S), oxygen (O), and occasionally nitrogen (N), indicating the existence of polar compounds like resins. In addition, inorganic elements such as silicon (Si), calcium (Ca), iron (Fe), and nickel (Ni) were detected, suggesting possible interactions with mineral particles, inorganic precipitates, or corrosion-related residues. This combined analysis provides insight into the chemical complexity and formation mechanisms of the deposits, supporting the development of appropriate strategies for their prevention or removal in oilfield operations. [35]

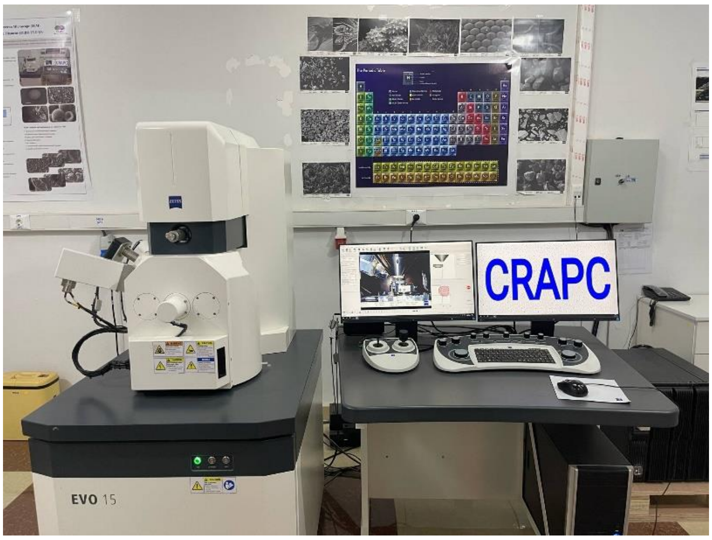

Figure 27: MEB/EDS Analysis.

2.11. Gas chromatography-mass spectrometry (GC-MS) of crude oil:

GC-MS analysis of crude oil is used to separate and identify its complex mixture of hydrocarbons, providing detailed information on saturates (n-alkanes), aromatics, and biomarker compounds. By injecting a diluted sample into the gas chromatograph, individual components are separated based on volatility, then detected and characterized by their mass spectra. This technique reveals key molecular markers such as n-alkanes, isoprenoids (pristane and phytane), and polycyclic aromatic hydrocarbons, which help determine the oil’s source, thermal maturity, and biodegradation level. Additionally, biomarkers like steranes and hopanes provide insights into the biological origin and depositional environment of the crude. GC-MS is thus essential for oil-source correlation, environmental forensics, and evaluating crude oil quality and history. [36]

Figure 28: Gas chromatography-mass spectrometry (GC-MS).

2.12. The density of crude oil:

The density of crude oil was determined using a glass pycnometer with a known volume (25.138 mL) following a gravimetric method. After cleaning and drying, the pycnometer was weighed empty, then filled with crude oil and weighed again after thermal stabilization at 20 °C. The density was calculated by dividing the mass difference by the pycnometer volume.

The density of crude oil was calculated using the following equation:

$$\rho = \frac{m_1 - m_0}{V}$$

Where :

- ρ is the density of the crude oil (in g/cm^3),
- m1 is the mass of the filled pycnometer (in g),
- m0 is the mass of the empty pycnometer (in g),
- Vis the volume of the pycnometer (in mL).

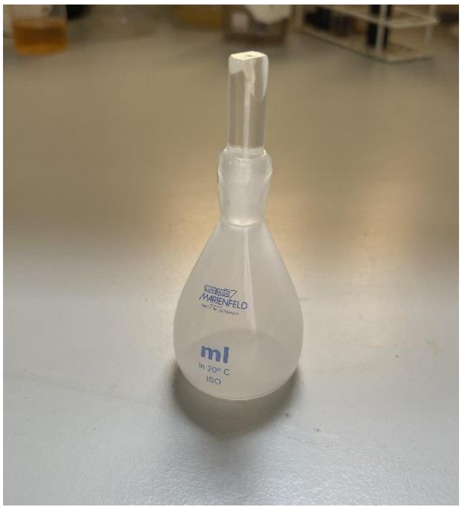

Figure 29: Pycnometer.

2.13. The dynamic viscosity of crude oil:

The dynamic viscosity of crude oil was determined by measuring the flow time of the fluid through a capillary viscometer under controlled temperature. This method ensures accurate results through repeated measurements. we used this formula to calculate dynamic viscosity from the flow time measured with a capillary viscometer is:

$$\boldsymbol{\eta = C \cdot t}$$

Where :

- η is the dynamic viscosity (in mPa.s or cP),
- C is a constant determined by the calibration of the viscometer (in mPa.s/s),
- t is the measured flow time (in seconds).

Figure 30: Capillary viscometer.

2.14. Distillation of crude oil:

The distillation of 100 mL of crude oil involves gradually heating the sample in a distillation flask up to a maximum temperature of 300 °C in order to separate its different fractions based on their boiling points. The setup includes a round-bottom flask heated with a heating mantle, a distillation column topped with a thermometer to monitor vapor temperature, a water-cooled condenser to condense the vapors, and a graduated cylinder to collect the liquid fractions. Each fraction is collected within a specific temperature range, allowing the identification of light, intermediate, and heavy components of the crude oil.

Figure 31**:** Distillation process.

- The distillation residue of crude oil is soluble in 10 mL of toluene, indicating that it is predominantly organic in nature.

2.15. UV-Visible Spectroscopy of Asphaltenes and Maltenes:

UV-Visible spectroscopy is a technique used to analyze the optical properties of substances by measuring their absorbance in the ultraviolet (200–400 nm) and visible (400–800 nm) ranges. It is particularly useful for characterizing petroleum fractions like asphaltenes and maltenes, which contain varying degrees of aromaticity. Asphaltenes typically exhibit strong absorbance peaks between 320–380 nm due to the presence of polycyclic aromatic hydrocarbons (PAHs) and conjugated π-systems, along with high absorbance in the UV region caused by their dense aromatic and heteroatom content. In contrast, maltenes, which consist of lighter aromatics, resins, and saturates, generally show broader absorbance with λmax around 400–420 nm, reflecting the presence of less condensed aromatic structures and more polar functional groups. [37]

Figure 32: UV-Visible Spectroscopy analysis.

2.16. FTIR Spectrum of Asphaltenes:

FTIR spectroscopy of asphaltenes reveals key functional groups and structural features. Strong absorption bands at 2920 and 2850 cm^{-1} indicate the presence of aliphatic CH_2 and CH_3 groups, while a band around 1600 cm^{-1} confirms aromatic C=C structures. A weak band between 3500–3100 cm^{-1} suggests low levels of OH and NH groups. Broad absorptions from 1700 to 1000 cm^{-1} point to various functional groups, including esters, ethers, and aromatic amines, with a notable carbonyl vibration at 1260 cm^{-1}. A sulfoxide band near 1030 cm^{-1} also appears, supporting the presence of sulfur-containing compounds as confirmed by elemental analysis. [38]

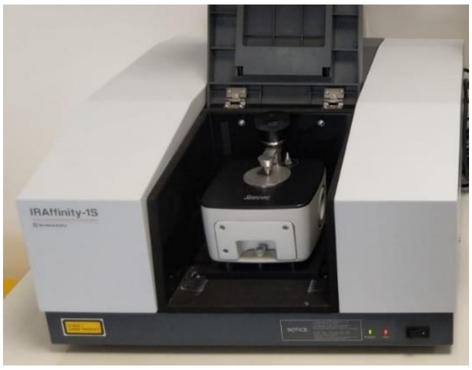

Figure 33: FTIR Analysis.

2.17. Melting Point Analysis of Asphaltenes:

The determination of a precise melting point for asphaltenes is not feasible due to their complex, heterogeneous nature. Asphaltenes are composed of a wide range of high molecular weight polyaromatic compounds with various heteroatoms (N, O, S, and trace metals), which do not melt in a classical sense but instead undergo thermal decomposition. Thermal analysis techniques such as Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are typically employed to assess their thermal behavior. These analyses show that asphaltenes begin to decompose at temperatures ranging from **300 °C to 400 °C (573–673 K)**, releasing volatile organic compounds, gases, and leaving behind a carbon-rich residue. This decomposition is attributed to the breaking of aromatic and aliphatic bonds within the molecular structure. The absence of a sharp endothermic peak in DSC further confirms that asphaltenes do not have a defined melting point but degrade over a broad temperature range. Understanding this thermal behavior is essential for designing heat-based treatment processes in petroleum production and refining systems. [39]

Figure 34: Melting point analysis.

Chapter 03: Results Discussion of The Experimental Study

3.1. Introduction

In the petroleum industry, the formation of organic deposits particularly those rich in asphaltenes poses significant challenges in terms of production, transportation, and equipment maintenance. These deposits can lead to wellbore blockages, fouling of surface facilities, and overall operational inefficiencies. Understanding their composition and behavior in the presence of solvents is therefore essential for designing effective mitigation and removal strategies.[40]

This chapter presents the experimental results obtained from various techniques used to separate and characterize the components of organic deposits. The methods employed include selective dissolution (notably with toluene), gravimetric quantification, and the identification of organic (asphaltenes and maltenes) and inorganic fractions. The experiments were designed to evaluate how solvent volume affects extraction efficiency and the relative distribution of deposit constituents.

The results are accompanied by technical commentary highlighting the observed trends, extraction yields, and the limitations of each analytical approach. These discussions provide insight into the underlying physicochemical mechanisms and their relevance to industrial applications particularly in formulating appropriate solvents or optimizing well cleaning protocols.

3.2. Observations and Results of solubility test

After adding 5 mL of each solvent to the asphaltene samples and stirring/shaking for 15 minutes, the solubility behavior was assessed visually based on the extent of dispersion, dissolution, or sedimentation. The following results were observed :

Table 9: Solubility test observation.

Tube	**Observation**
1	Asphaltenes remained completely undissolved, forming clumps and the yellowish tint, indicating the possible presence of maltenes.
2	Partial swelling of asphaltenes; some remained undissolved.
3	Similar to ethanol; slight dispersion but no complete dissolution.
4	Moderate dispersion observed, but not fully dissolved.
5	Asphaltenes floated or sank, no dissolution.
6	Asphaltenes fully dissolved; a homogeneous dark solution formed.

Table 10: results of solubility test.

Tube	Solvent	Polarity	Solubility
1	n-Hexane	Nonpolar (aliphatic)	Insoluble
2	Ethanol	Polar protic	Slightly soluble
3	Acetone	Polar aprotic	Slightly soluble
4	Dichloromethane	Moderately polar	Partially soluble
5	Distilled water	Highly polar	Insoluble
6	Toluene	Aromatic weakly polar	Completely soluble

3.3. Observation and results of Volume kinetics

While the toluene volume used across the 10 tubes varies slightly (from 1mL to 10mL), its effect on the separation of inorganic matter, organic matter, and asphaltene/maltenes reveals some trends:

As the volume of toluene increased from 1 mL to 10 mL:

- The inorganic matter recovered increased progressively from 1.28 g to 1.32 g, with minor fluctuations.
- The organic matter increased significantly, from 0.58 g (at 1 mL) to 8.24 g (at 10 mL).
- The asphaltene/maltenes mixture remained low and fairly stable, varying between 0.02 g and 0.05 g, with a slight peak at 5 mL of toluene (0.05 g).

❖ **Results:**

The solubility and separation test of deposit fractions using varying volumes of toluene revealed that the ratio of 1 g of deposit to 5 mL of toluene provides the highest yield of asphaltenes/maltenes among the tested conditions. Despite minor fluctuations in toluene volume across the samples, the tube corresponding to this 1:5 ratio demonstrated the greatest recovery of asphaltene/maltene mixture (0.05 g), indicating an optimal solvent-to-deposit balance for dissolving the polar aromatic fractions without excessive dilution.

This result confirms that a 1:5 (w/v) ratio ensures efficient solubilization of asphaltenes while maintaining practicality in solvent use. Therefore, this ratio was selected as the standard for subsequent extractions and analyses to maximize yield and analytical consistency.

3.4. Observation and results of volume and mass kinetics

The experiment was conducted using increasing deposit masses (1 g to 10 g) and corresponding toluene volumes (5 mL to 50 mL). The goal was to evaluate how varying both parameters affects the separation of the deposit into three fractions: inorganic matter, organic matter, and asphaltene/maltenes mixture.

Key trends observed :

- Inorganic matter increased progressively with the increase in both deposit mass and toluene volume, rising from 1.34 g (tube 1) to 11.57 g (tube 10).
- Organic matter also rose significantly with increasing deposit mass, from 1.57 g to a peak of 34.93 g (tube 9), with a slight drop to 29.81 g in tube 10.
- The asphaltene/maltenes mixture showed more variability. While it generally increased, especially from tube 6 onward, there was a notable jump from 0.09 g (tube 7) to 0.25 g (tube 8), and a peak of 0.33 g (tube 10).
- The total recovered mass (sum of all three fractions) always exceeded the initial deposit mass. This could be due to residual toluene, moisture, or other non-removed substances retained during analysis.

❖ **Results**

- Recovery of all components increases with larger deposit masses and toluene volumes, confirming a direct relationship between input material and extractable yield.
- The organic matter is the dominant fraction, accounting for the majority of the recovered mass in all tubes, and showing the highest sensitivity to both deposit and solvent volume.
- Inorganic matter shows consistent growth, proportional to the increase in deposit mass, but remains lower than organic content in most cases.
- Asphaltene/maltenes content, although a small fraction, increases more notably in tubes 6 to 10, indicating that higher toluene volumes may favor partial dissolution or release of heavier fractions at higher deposit loads.
- The highest asphaltene/maltene yield (0.33 g) was recorded at the maximum deposit and solvent volume (tube 10).
- Tube 9 shows the highest organic recovery (34.93 g), suggesting optimal solvent-to-solid ratio may exist before diminishing returns or saturation effects appear.

3.5. Observation and result of Calcination

❖ Observation (Calcination at 600 °C)

- A 0.50 g sample of organic deposit was heated to 600 °C.
- After calcination, the remaining weight was 0.15 g.
- All asphaltenes were eliminated at this temperature.

❖ Results

- Mass loss : 0.35 g
- Residue (inorganic content): 0.15 g → 30% of original mass
- Volatilized organic content (including asphaltenes): 0.35 g → 70%

This confirms that asphaltenes are thermally unstable at 600 °C and are part of the organic matter, not the inorganic ash.

❖ Discussion

The results show that 70% of the deposit mass is organic, including both maltenes and asphaltenes, while 30% is inorganic residue that remains after high-temperature treatment. The fact that asphaltenes decompose at 600 °C is consistent with known behavior, as they are complex polyaromatic hydrocarbons that combust or decompose at high temperatures.

3.6. Observation and results of X-ray Diffraction (XRD) Analysis on deposits:

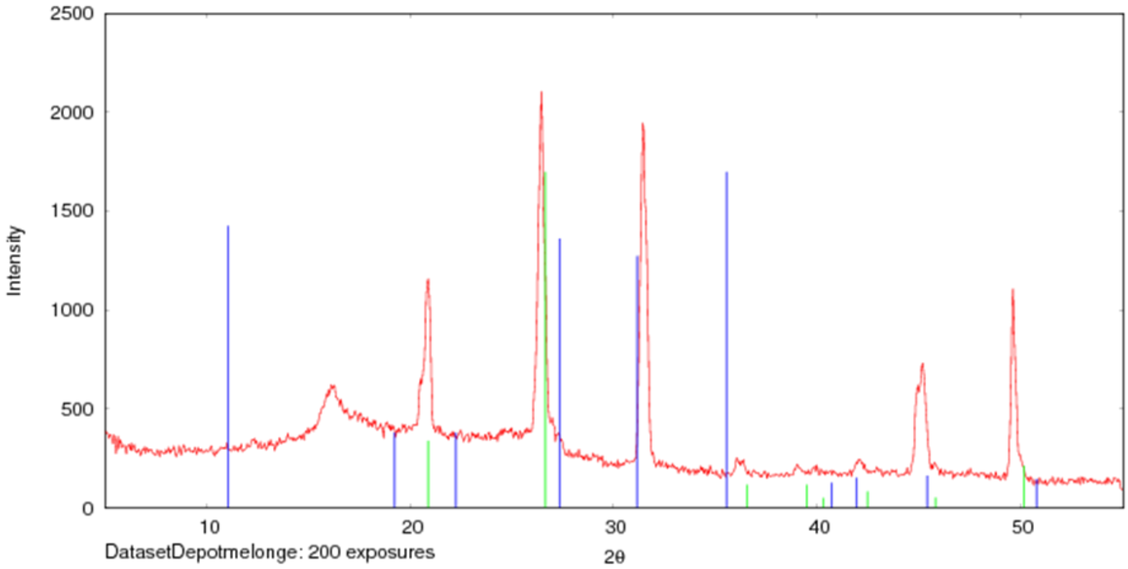

Figure 35 : Mixture Deposit Sample

Observation and result:

The XRD pattern shows sharp peaks, indicating a crystalline structure. Major peaks around 27°, 28°, 40°, and 50° suggest the presence of inorganic minerals such as quartz (SiO_2), calcite ($CaCO_3$), and possibly metal oxides (e.g., Fe_2O_3 or Al_2O_3) The absence of broad humps confirms low amorphous content, highlighting that the deposit contains both organic and significant inorganic crystalline phases.

Organic deposit sample:

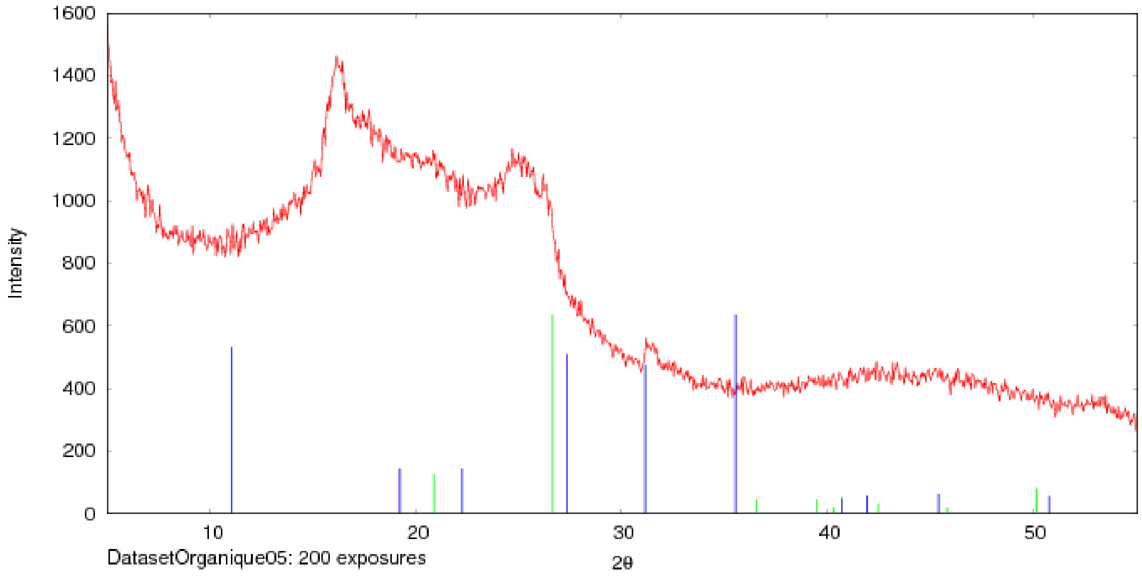

Figure 36: Diagram of XRD Analysis results on organic deposit sample.

Observation:

1. **Broad Hump (Amorphous Halo):**
    - The broad features between 10° and 30° (2θ) suggest a predominantly amorphous structure, typical of organic deposits like asphaltenes.
    - This confirms low crystallinity.
2. **Sharp Peaks (Crystalline Phases):**
    - Several sharp peaks, especially in blue and green, superimposed on the broad background, indicate the presence of minor crystalline inorganic phases.
    - These could correspond to minerals such as silica (SiO_2), calcium carbonate ($CaCO_3$), iron oxides, or nickel-based compounds commonly found in oilfield scale or corrosion products.
3. **Most Intense Peak :**
    - The highest peak around $2\theta \approx 17°$ may indicate a degree of structural ordering possibly from stacked aromatic rings in asphaltenes.

Results Interpretation :

- The deposit sample is mainly amorphous (likely organic) in nature.
- The minor crystalline peaks suggest inorganic impurities or interactions, possibly from:
    - Mineral fines
    - Scale formation (e.g., Ca, Si, Fe-based compounds)

- Corrosion residues

3.7. Observation and results of SEM/EDS Analysis on Organic deposit:

The results are not out yet.

3.8. Observation and results of (GC-MS) Analysis of crude oil:

The results are not out yet.

3.9. Results of Density Test of crude oil:

Calculation :

- Mass of empty container (M_0): 23.80 g
- Mass of container with sample (M_1): 44.15 g
- Volume of sample (V) : 25.138 mL
- Mass of sample ($M = M_1 - M_0$): 20.35 g
- Density ($\rho = M / V$): 0.809 g/mL

Result:

The measured density of 0.809 g/mL indicates that the crude oil is relatively light. This lower density may reduce the settling rate of heavier deposits, potentially delaying or limiting solid phase separation under static conditions.

3.10. Results of dynamic viscosity Test of crude oil:

Calculation :

$$\eta = C \times t = 5.6 \times 0.002 = 0.0112 \text{ Pa·s}$$

Result:

The dynamic viscosity of 0.0112 Pa·s indicates moderate flow resistance. Higher viscosity can slow down the settling of solid or heavy deposits, potentially reducing the efficiency of separation processes.

3.11. Observation and results of UV-Visible Spectroscopy on Asphaltenes and maltenes samples:

Asphaltene sample:

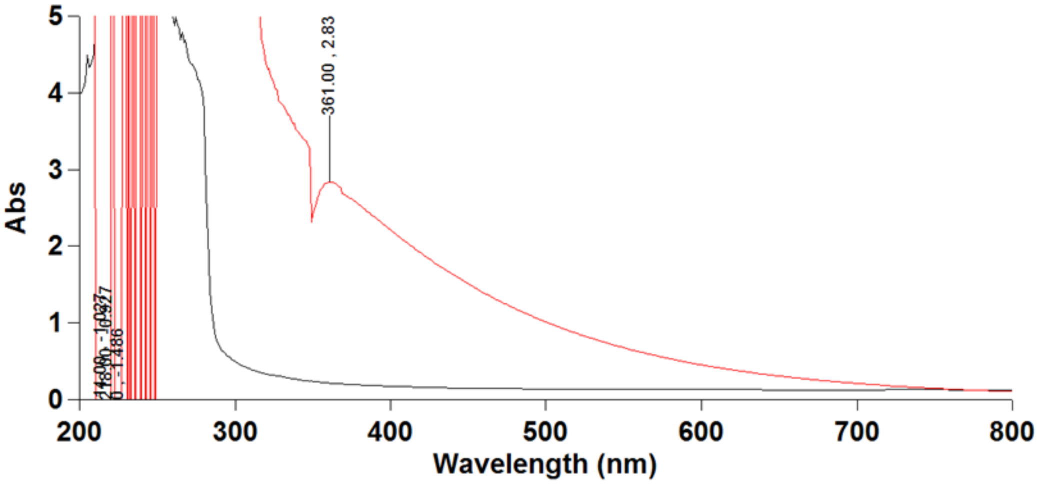

Figure 37: Diagram of UV-Visible result on Asphaltene sample.

Observation:

The UV-Vis spectrum shows a main absorbance peak at 361 nm, typical of polycyclic aromatic hydrocarbons (PAHs) and highly conjugated π-systems. Asphaltenes contain condensed aromatic ring systems and heteroatoms, which are responsible for this characteristic absorption. The intense and broad absorption in the UV region (especially below 300 nm) also supports the presence of complex aromatic and heteroatom-containing structures, contributing to their optical activity and tendency to aggregate.

Result:

- Peak at 361 nm indicates polycyclic aromatic hydrocarbons.
- The literature diagram, shows a characteristic peak around 300 nm, which is close to my observed peak at 361 nm, and this proximity further confirms the presence of asphaltenes in the sample [41].
- High UV absorbance confirms presence of aromatic structures and heteroatoms.
- Spectrum matches known behavior of asphaltenes.

Maltene sample:

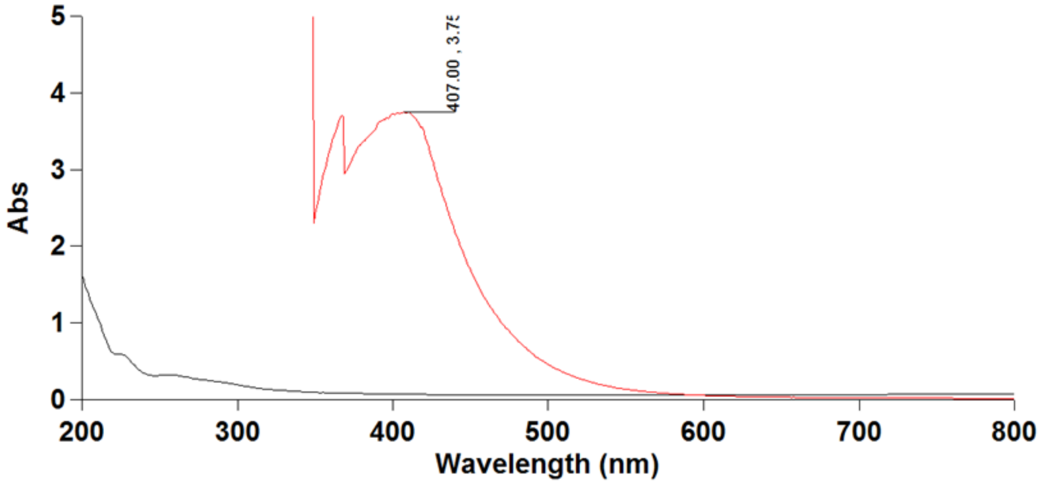

Figure 38: Diagram of UV-Visible Analysis on maltene.

Observation:

The UV-Vis spectrum of maltenes shows a strong peak at 407 nm, indicating the presence of aromatic compounds and conjugated systems. The broad absorption suggests a mixture of polar aromatics, resins, and unsaturated hydrocarbons typical of the n-Hexane soluble fraction.

Results:

- Main absorbance peak (λmax): 407.00 nm
- Absorbance at λmax: 3.72 a.u**.**
- The 407 nm peak indicates conjugated aromatics and polar resins, key maltene components.

- **Melting point analysis result:**

- The melting point of the extracted asphaltenes was found to exceed 250 °C.

Conclusion

Conclusion

This study focused on the extraction and characterization of organic deposits obtained from complex mixtures using toluene, followed by the extraction of asphaltenes from these organic deposits via n-hexane precipitation. A comprehensive suite of analytical techniques was employed to evaluate the physicochemical and structural properties of the extracted materials. X-ray diffraction (XRD) revealed the semi-crystalline nature of the deposits, while UV-Visible spectroscopy confirmed the presence of conjugated aromatic systems and polar functional groups. Scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS) provided insights into surface morphology and elemental composition.

Thermal and physical properties such as melting point, density, and dynamic viscosity were determined, highlighting the complex and heavy nature of the organic material. Distillation of crude oil and GC-MS analysis further clarified the chemical profile of the extracted fractions. Additionally, the valorization of the residues was demonstrated through calcination and the study of toluene extraction kinetics, underscoring the potential for material reuse and process optimization.

Overall, the successful extraction of asphaltenes from the organic deposit using n-hexane and their consistent characterization across all techniques validate both the extraction method and the integrity of the obtained asphaltenes. These findings contribute valuable knowledge to the understanding and potential valorization of organic deposits in petroleum systems.

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