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Investigating Non-Uniformity of Wax Appearance Temperature of Crude Oil in Nigeria

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ABSTRACT

A significant sample of crude oil found in Niger Delta have between moderate to high wax content which makes flow process sometimes difficult at low temperatures due to the formation of gel-like structure which increases viscosity of the fluid. Removal of wax from flowlines and reservoirs can account for significant additional operating costs. To evaluate these potential costs, the operating conditions that allow waxes to precipitate at any point in the production line be identified, and deposition rates must also be estimated to determine the implications associated with removal of wax deposits. This project investigates the non-uniformity in wax appearance temperature of crude oil in the Niger delta and the flow behavior of waxy crude oil under variation in the temperature of the external environment of the flow. The temperature at which the first wax crystals appear during cooling is known as the wax appearance temperature. once below the WAT, the crude oil can form the gel like structure. Breaking down this structure to restart and maintain the flow often require energy and cost intensive approach. This project focuses on characterizing different waxy crude oil samples using thermal and compositional analysis, specifically with measurement of WAT in the context of the field of flow assurance. The test is based on the experimental design technique, and the behavior of the fluids evaluated based on the variation generated by the flow. The carbon distribution of oil samples and their corresponding wax components were analyzed by high temperature gas Chromatography. The crude oil properties determined include wax content, Aromatics, asphaltene, saturates and resin content by HPLC, pour point, wax appearance temperature by optical microscopy and paraffin carbon number distribution of whole oil and wax precipitate by GC- FID. Asphaltene and resin content were found to influence the oil cloud point, while saturates content, paraffin carbon number of crystallizing waxes and wax content control its low temperature flow properties including the wax appearance temperature. This study shows that the seven Niger delta crude oil studied have wax content between 4.5 to 22.1 weight percent with WAT in the range of -19oC to 27.5oC the results showed that the aromatics and asphaltene interaction had a significant impact on the wax appearance temperature (WAT) and hence largely responsible for the variations on the WAT of crude oil samples.

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Abbreviations

1. API American Petroleum Institute
2. ASTM American Society for Testing and Materials
3. BF Bright Field
4. DSC Differential Scanning Calorimeter
5. GC Gas Chromatography
6. HPLC High Performance Liquid Chromatography
7. HTGC High-Temperature Gas Chromatography
8. NIR Near-Infrared Spectroscopy
9. NMR Nuclear Magnetic Resonance
10. NP non-paraffinic
11. P1–4 Paraffinic petroleum
12. PL Polarized Light
13. SAP Saturates, Aromatic and Polar
14. SARA Saturates, Aromatic, Resins and Asphaltenes
15. WAT Wax Appearance Temperature
16. WDT Wax Deposition Temperature
17. TLC-FID Thin Layer Chromatography with Flame Ionization Detection
18. UOP Universal Oil Products Collection
19. Q Total thermal effect of wax precipitation
20. CW Wax precipitated concentration Q constant thermal value of wax precipitation
21. TF Final DSC temperature
22. FTIR Fourier transform infrared spectroscopy

Introduction

Nigeria is believed to have a large deposit of paraffinic crude oils which has been proven to have good quality considering their API gravity and Sulphur content. It is also believed to contain moderate to high contents of paraffinic waxes. Characteristically, waxy crude oils have undesirably high pour points and are difficult to handle where the flowing and ambient temperatures are about or less than the pour-point. They exhibit non-Newtonian flow behavior at temperature below the cloud point due to wax crystallization. Consequently, the pipeline transportation of petroleum crude oil from the production wells to the refineries is threatened.

The Niger Delta crude oil, which is the mainstay of Nigerian economy, exhibits waxiness, with deposits in the range of 30-45 % (Adewusi 1997; Fasesan and Adewumi, 2003; Taiwo et al., 2009 and Oladiipo et al., 2009). In fact, pipelines have been known to wax up beyond recovery in Nigeria. Production tubing has also been known to wax up, necessitating frequent wax cutting, using scrapers conveyed by wireline, which is an expensive practice. Billions of dollars have been lost to its prevention and remediation (Oladipoet.al.,2015). The resultant effect on the petroleum industries includes among others, reduced or deferred production, well shut-in, pipeline replacements and/or Abandonment. For efficient operation of a pipeline system, steady and continuous flow. The difficulties in transportation are due to this complex nature of crude oil, which cause a variety of difficulties during the production, separation; transportation and refining of oil (Al-Becharah et al., 2014).

Paraffinization is one of the main problems in oil production and causes considerable losses to the oil industry. The wax precipitation phenomenon associated with paraffin deposition can result in unscheduled production shutdowns and promote operational risk conditions. Moreover, it can cause production losses and irreparable damage to equipment (Pauly et al., 2014). In the region, the produced crude oil exhibits a density of approximately 30° API, almost no sulfur and high concentrations of dissolved waxes. Although these properties are great for the manufacture of lubricant oils and yield high added value, the presence of wax adds many complications to production, transportation and storage by hindering the flow in pipes (Thomas, 2004; Novaes, 2009).

Temperature also influences the solubility of waxes in crude oil. When approximately 5% of the waxes crystallize because of oil cooling, a crystal lattice appears and traps some of the oil inside; this process is called “gelling” and hinders the fluid flow. Thus, the crude oil flow rate also interferes with wax solubility. The lower the oil flow rate, the longer it stays inside the piping, which favors heat exchange with the external environment (Vieira, 2008). Once production starts, the oil flows through the pipelines, losing heat to the external environment, with consequent temperature decreases and reduced soluble light oil fractions. Such production conditions cause the oil viscosity to increase, which leads to production problems due to the precipitation of waxes.

In addition, there has been a significant increase in both onshore and offshore deep water development activities in the Niger Delta region and as inland reserves continue to decline even as the country targets an increase in the oil and gas reserve to about 50 billion barrels by 2030. For offshore production, economic feasibility of the projects may depend on realistic estimates of flow problems and associated remedial/preventive techniques. The cost of designing and implementing additional flow assurance equipment can be substantial. Similarly, the cost of having to solve such problems where an insufficient program was initially setup can be tremendous. Flow assurance studies for such systems often require measurement of certain key crude oil properties. Wax Appearance Temperature (WAT), Asphaltenes Precipitation Onset, Pour Point and Gel Strength are amongst the properties of concern. In subsea completions, where flowlines may be on the ocean floor at about 1.5oC to 5.0oC, knowledge of WAT of the crude is essential as the fluid may flow some considerable distance from the reservoir to the surface through the cold seabed and tubing.
The crystal growth produces high molecular weight wax, which reaches a point where it precipitates out of the crude oil. In clear crudes the wax deposition gives the oil a cloudy appearance. This temperature is called the cloud point, or wax appearance temperature (WAT) Since paraffins and wax occur naturally in crude oil, there is a potential for wax deposition at every step from oil production to refining. The wax deposits reduce the internal diameter of tubular transportation pipelines, restrict or block valves, and impede other production equipment. Severe wax deposition can lead to a complete stop in production; which can translate into millions of lost dollars. There are many ways to remove or prevent wax deposition. For example, thermal methods include heating and insulating the pipeline or introducing hot fluids above the WAT to melt or prevent wax deposition.

Statement of the Problem

Wax deposition is one of the most challenging flow assurance issues in oil production processes. The related problems span from reservoirs to refineries, but their consequences can be particularly challenging when the affected area is difficult to reach, such as flow lines and producing wells. Wax deposition during crude oil production, transportation, and processing has been a major concern from inception of oil exploration, discovery and utilization. The effect of which mostly leads to low mobility ratios, blockage of production tubing/pipelines as well as fouling of surface and processing facilities, among others costing the industry; equipment, man power billions of dollars in losses. Having understood the composition of paraffinic crude oil and the implication of wax in crude oil samples, it is therefore pertinent to investigate the non-uniformity in the W.A.T of crude oil in comparison with non-wax content crude from several fields in Niger delta in an attempt to examine the causative factors and possible controls. Flow assurance issues resulting from wax precipitation and deposition are expected to increase significantly in the future because oil production from many regions is has shifted to the low temperature deep sea environment especially in onshore locations. Although a number of remedial measures exist to clean wax deposits in production and transport facilities such as mechanical, chemical and thermal techniques, they are very expensive and often times fail to achieve the desired results especially in offshore environments. Presently, there is no universally effective treatment for wax deposition problem because treatment methods are highly case – dependent. A more proactive approach to solving wax deposition problems would involve preventive measures, which is what this research also partially aims to achieve. In this study, the light organics composition of some Niger-Delta waxy crude oils is investigated by also considering the paraffin composition of crystallized waxes in relation to the oil in order to gain a better understanding of the reasons for the variations in their wax appearance temperature.

The aim of this study is to investigate the non-uniformity in the wax appearance temperature of crude oil samples in the Niger Delta.

Literature Review

A review of literature is presented on this chapter; this is to enhance the understanding of waxy crude oil and the characterization of petroleum fluids including heavy and light fractions required for the determination of variances in the wax appearance temperatures. Through this review of literature, a thorough understanding of previous studies which have been carried out in the area of WAT and related studies is achieved.

Classification of Crude Oil

Crude oil, a highly complex mixture of paraffinic, naphthenic and aromatic hydrocarbons can be classified on the basis of chemical composition according to the proportion of hydrocarbon constituents. The paraffinic crude oils are rich in straight chain and branched paraffinic hydrocarbons. It may also be classified by geological source, as arising from productive sands, sandstones and limestones. A light crude oil generally has an API (American Petroleum Institute) gravity greater than 40 (specific gravity, <0.82), a medium crude oil between 15 and 40 (specific gravity, 0.82–0.97) and a heavy crude oil less than 15 (specific gravity, >0.97). Crude oils are designated in industry according to their suitability for use in various products. Thus, a crude oil may be referred to as a ‘gasoline crude’, a ‘wax crude’, a ‘lube crude’, an ‘asphalt crude’, and so forth Several literatures have been written on waxy and non-waxy crude oil. In this section, I shall be examining in an attempt to review some of the notable works of prominent scholars on this topic. Petroleum crude oil is referred to generically as a fossil energy resource and is further classified as a hydrocarbon resource, coal and oil. Shale kerogen has also been included in this classification. However, the petroleum crude is classified based by the raw crude by the in other words oil is classified with geographic region. The classification of petroleum crude oil is derived from the density of the raw petroleum (API gravity) and its various non- hydrocarbon components (especially Sulphur), is then added to the geographic designation. End result of all this classification that helps to determine the price of a specific barrel of crude as well as how much demand there is for that particular oil. Also, the crude oil is classified on the basis of these three: density, compound type, and content of saturates, Asphaltenes, Resins, Paraffins, Naphthene.

Physio-Chemical Characterization of Crude Oil

Physicochemical characterization seeks to define the physical and chemical properties, composition, identification, quality, purity, and stability of the crude. The most common physical properties used to describe petroleum are density, viscosity, and boiling point ranges. The density of crude oils is usually expressed as API (American Petroleum Institute) gravity, which is inversely related to specific density.

Viscosity

Viscosity is an empirical parameter that describes the resistance of a fluid to flow. It can be also determined by ASTM-D7042 on a viscometer or by rheological tests. Viscosity of crude oil samples is influenced by wax precipitation. The onset of wax precipitation is signaled by sudden increase in viscosity causing a deviation from Newtonian to non- Newtonian behavior. The viscosity and yield point of crude oil are affected by wax composition. Studies have shown that by increasing the wax composition, the viscosity and yield point also increases and that when the wax composition decreases, the viscosity and yield point also decrease. The ingredients of the crude oil determine its viscosity. Especially tar or asphaltene, increase the thickness of crude. The higher the viscosity, the more difficult it is to transport through a pipe. Pumping highly viscous liquids can be very energy-intensive and wearing for machines and pipes.

The second major factor influencing viscosity is the temperature. There is a direct relationship between temperature and viscosity of waxy crude oil. The higher the temperature the lower the viscosity. The heat has to be high enough to ensure that the crude at the end of the pipe is still pumpable. As longer the crude is in the pipe as more the temperature decrease.

Light and Heavy Crude Oils

Generally, light crude oil contains of lower characteristic compare to heavy crude oils. Most of crude oils in Malaysia is light or slightly intermediate crude oils and it can be recognized through the physical properties. The table below shows the physical properties of crude oils.

Table 1: Comparison of Physical Properties of Heavy and Light Crude Oils

Physical properties	Type of crude oils	
	Heavy crude oils	Light crude oils
oAPI	10< oAPI< 20	oAPI>40
Yield of Gasoline	High	Low
Viscosity	High	Low
Pour point	Low	High
Density	High	Low
Specific Gravity	High	Low

Waxes in Crude Oil

In the works of siljuberg, (2012), he described Wax also known as paraffin wax in crude oil, as one of the notorious pipe blockers, with asphaltene as the second molecules. He examined the solubility of wax crystals as a function of temperature. He posited that pressure hardly influences the solubility Below its melting point, the crystalline wax structure is formed either from their distinct compounds or from the combination of one another. His work was limited on the basis of his assumption that pressure have a little implication on the solubility of wax, hence his works centered mostly on temperature effects on wax solubility.

Effect of Temperature on the Physical Properties of Wax

Temperature plays a major role in the phase behavior of hydrocarbon fluids. Effects of temperature on some pertinent physical properties of waxy crude oil including density, sheer stress and viscosity were studied in a bid to gain better understanding of the behavior of waxy crude oil. The discussion in this section is primarily informed by the intention to understand, specifically, the effect of temperature on certain properties of interest, viz., the viscosity, density, and surface tension. This can also provide further clues on the prospects of the proposed wax precipitation and deposition point.

Significance of Waxy Crude Oil

Wax deposition brings severe challenges to the production, transportation, and storage of crude oils. Accumulation of wax can block the pipeline, lead to equipment failure, and lose production. Waxes present in crude oil are considered to be responsible for its poor flow properties. Some Niger delta high crude is very waxy and has a pour point of + 30 °C. The influence of nature and concentration of waxes on some of the flow properties, namely pour point, plastic viscosity and yield stress, of dewaxed Nigerian high crude have been determined. Many crudes contain dissolved waxes that can precipitate and deposit under the appropriate environmental conditions. These can build up in production equipment and pipelines, potentially restricting flow (reducing volume produced) and creating other problems. Precipitated wax has pronounced effect on kinematic viscosity and pour point of crude oils. (Majhi. et al, 2015)

A “clean waxy crude” is defined as a crude oil that consists of only hydrocarbons and wax as the heavy organic constituents. “Regular waxy crudes” contain other heavy organics in addition to the waxes (e.g., asphaltenes and resins). These heavy organics have interactions with the crude, which can either prevent wax-crystal formation or enhance it.

Characterization of the Wax Precipitation in Crude Oil Based on Wax Appearance Temperature

Waxy crude oil characterization can simply be described as the process of determining the physical and chemical properties of the crude oil which defines its behavior, particularly at low temperatures where wax crystallization occurs. This includes assessing its rheological properties (viscosity, yield stress, and thixotropy), wax appearance temperature (WAT), and the nature of the wax crystals themselves. Crude oils are not analyzed routinely for their content of various classes of hydrocarbons and nonhydrocarbons; rather, they are usually characterized by their physical properties (specific gravity or density, viscosity) and their sulfur content. Wax precipitates usually have low solubility in aromatic and naphthenic solvents and other organic solvents; due to the gelation of precipitates, the deposition of wax is undesirable. In the case of wax deposition, methods such as pigging and heating can be used to eliminate deposits that lower efficiency (Guo et al., 2004). Usually, to prevent wax precipitation, materials called "inhibitors" are added to the oil. The interaction of inhibitor molecules with wax molecules reduces the WAT. This use of inhibitors requires the accurate study of wax compounds (Guo et al., 2004).

Degree of Waxiness

Degree of waxiness has been described as an empirical relationship that gives an insight of the extent of the waxiness of a crude oil and could be used to determine the type and or extent of remedial measures to be applied to specific wells with wax problems. The degree of waxiness is a more qualitative term that describes the tendency of a crude oil to form wax crystals and deposit wax as the temperature decreases. The degree of waxiness relates to the potential for wax deposition problems in pipelines and other equipment.

Relationship Between Wat, Waxiness Degree and N-Paraffin Distribution

n-paraffin distribution refers to the relative amounts of different straight-chain alkanes (n-paraffins) present in a crude oil or petroleum fraction. These n-paraffins are characterized by their number of carbon atoms, and their distribution can be determined using techniques like high-temperature gas chromatography. It has been established that n- paraffins are predominantly responsible for wax deposition problems (Misra, 1995). The understanding of the n- paraffin distribution of a crude oil can help evaluate the components affecting the properties of waxy crude oil. The n- paraffin distribution Can be determined with the Agilent 7890 A series high resolution gas chromatography (HRGC) Equipped with a flame ionization detector (FID)

Wax Appearance Temperature

Wax appearance temperature also known as cloud point is the temperature above which a slight decrease in temperature will result in wax formation in waxy crude. When a high-temperature waxy crude loses heat to a temperature lower than the WAT, the paraffin molecules would form clusters of aligned chains. Once these nuclei reach a critical size and establish a stability, more attachment of molecules would contribute to the growth of the crystal. The formation of these nuclei causes the fluid to take on a cloudy appearance, hence the name cloud point. This also is referred to as the wax crystallization temperature or WAT (Mystra, 2019).

WAT depends on the concentration and molecular weight of waxes and the chemical characterization of hydrocarbon matrix.

The wax appearance temperature is an important characteristic to evaluate the possible wax precipitation of a given fluid. The techniques used to determine the WAT are visual, cold finger, cross-polarized microscopy, light transmittance and ultrasonic methods. Another method for WAT determination is using differential scanning calorimetry (DSC).

Differences in Wax Appearance Temperature (WAT) between crude oil samples are primarily due to variations in their chemical composition, specifically the presence and concentration of waxes, and the cooling rate during the measurement. Waxes are long-chain hydrocarbons that tend to precipitate out of the crude oil as solid crystals when the temperature drops below the WAT. Literatures have established that the higher the wax content in a crude oil sample, the higher its WAT will be. Waxes are the main cause of wax precipitation, and a higher concentration will lead to wax formation at a higher temperature. Depending on the types of wax, Different types of waxes (e.g., paraffin waxes, microcrystalline waxes) have varying melting points, which can influence the WAT. For example, microcrystalline waxes, known for their lower melting points, can lead to a lower WAT compared to paraffin waxes.

The presence and proportions of other hydrocarbon fractions in the crude oil, such as lighter hydrocarbons, can also affect the WAT. Lighter hydrocarbons can act as diluents, increasing the solubility of waxes and raising the WAT. In summary, the WAT of a crude oil sample is a reflection of its specific chemical composition, particularly the type and concentration of waxes, and the conditions under which the WAT is measured.

Crude Oil Waxing Characteristics

Crude oil waxing characteristics refer to the tendency of some crude oils to solidify or congeal at relatively low temperatures due to the presence of wax-forming compounds, primarily long-chain saturated hydrocarbons. This phenomenon is also known as wax appearance temperature (WAT). The wax crystals precipitate out of the oil as the temperature drops, leading to a decrease in flow ability and potentially causing blockages in pipelines. The waxing deposition characteristics of crude oil is of great significance to the exploitation and transportation of high waxy crude oil. In the works of Meirong yang et al 2018 three series of simulated crude oils were prepared on the basis of composition analysis and composition remixing of crude oil. The carbon distribution of oil samples and their corresponding wax components were analyzed by high temperature gas chromatography. The variation of waxing point, peak temperature and average exothermic enthalpy of these simulated crude oils were measured by Differential Scanning Calorimetry (DSC). The results showed that the increase of resin and asphaltene content had little effect on the waxing appearance temperature (WAT) and Wax precipitation peak temperature (WAPT). The increase of aromatics contents significantly decreased them, while some asphaltene may precipitate. The increase of wax content will greatly increase these two temperatures, which is detrimental to the wax removal by heating method.

Pour Point

When waxy crude is flowing through a pipeline, and as a result of the continuous cooling of the crude below the WAT caused by the transfer of heat towards the surrounding, crystals of wax form and grow in sizes to form partial to total blockage of the pipe cross-sectional area. The pour point temperature can be seen to be the lowest temperature at which the waxy crude is mobile. This can be identified as the stock tank oil gelation temperature. Crude oils and gas condensate contain waxy components that called as paraffin where the concentration, structure and molecular weight vary from one hydrocarbon source to another (Farah, 2013). Both of them present may be constituents of the heavier polar fraction of oil known as asphaltenes. Paraffin has only limited solubility in the crude unless the temperature of the oil above the cloud point or wax appearance temperature (WAT).

Aromatics and Relationship with Wat

Aromatic hydrocarbons are a group of unsaturated hydrocarbons bounded with the general formular of CnH2n-6. hydrocarbon compounds are characterized with a ring structure, rather than the chain structure typically seen in olefins. Aromatics occur naturally in crude oil. In fact, they are a significant component of crude oil waxy or non-waxy along with paraffins and naphthene's are created using reforming and come from crude oil or, more rarely, coal processing. As earlier stated, Aromatics occur naturally in crude oil. However, in respect to the subject under review, WAT of waxy crude oil, Aromatics decrease the wax appearance temperature (WAT) by improving the solubilization of wax crystals. This happens because aromatics can act as solvent for asphaltenes and other heavy components, reducing the interaction between wax and asphaltene molecules, which would otherwise increase WAT. When aromatics are present, they can help to solubilize asphaltene and resin molecules, which would otherwise tend to interact with wax and increase the temperature at which the wax starts to solidify. By reducing the interaction between wax and asphaltene/resin, the overall tendency for wax to precipitate at higher temperatures (i.e., increased WAT) is lessened. The presence of aromatics can also affect the size and shape of wax crystals. In essence, aromatics act as a "diluent" for the wax and asphaltene/resin mixture, preventing the formation of larger, less soluble wax crystals that would otherwise increase WAT. In the works of (Meirong Yang et al., 2018) on the study of the effect of crude oil composition on waxing characteristics of waxy crude oil. The result reveals the effect of aromatic hydrocarbons on WAT though was limited to general hydrocarbon with no specific details on the waxy crude oil. The result reveals that the increase of aromatics content, WAT decreases from 46.6℃ to 39.6 ℃, WAPT decreases from 20.1℃ to 10.8℃ and the average exothermic enthalpy increases first and then decreases. The increase of aromatics effectively improves the solubility of high carbon alkanes and makes it difficult to precipitate. The increase of aromatics also effectively prevented the precipitation of C16~C25 in crude oil. Aromatics can increase resin solubility in crude oil and thus decreases resin adsorption on asphaltene surface.

Sara Analysis

This is a technique employed in the Separation of crude oil into hydrocarbon fractions such as saturate, aromatic, resin and asphaltene (SARA) fractions in order to obtain the concentration of each group. It provides information about the different components of the oil, which can be helpful in understanding its properties and behavior, including its wax content and tendency to precipitate wax This chemical analysis of crude oil is necessary for upstream, midstream and downstream operations; as it yields information such as crude oil stability (asphaltenes' stability), fouling propensity and the blending compatibility of the crude oil. Since SARA analysis can give information on asphaltenic stability, there is need to investigate the use of this analysis for wax precipitation tendency or wax instability.

Relationship between Wax Appearance Temperature and Sara Analysis

In the works of Jaber Taheri Shakib et al., 2020 where they examined the effect of wax–asphaltene molecular interactions on wax appearance temperature (WAT), he posited that The WAT point in crude oil depends on the interaction of wax and asphaltene molecules. The molecular features that enhance their interaction increase the WAT. Three modes will enhance this interaction. The first condition occurs when the wax and asphaltene molecules are compatible with the molecular scale. The second happens when the carbon number of alkane chains is wax is low in which the aromaticity and length of substituted alkyl chains of asphaltene molecules improve the interaction. The third condition occurs if wax has paraffinic-aromatic compounds.

SARA analysis can be applied qualitatively together with oil paraffin distribution to predict the relative waxiness and variations in their wax appearance temperature impacting the flow behavior of waxy crude oil and their potential for wax problems in the oilfield.

Materials and Methods

All waxy crude oil samples used in this study was gotten from seven wells from five different Niger Delta Oil field in Nigeria. seven different types of crude oil are to be studied in this work. These are labeled as below based on the geographical source. Physical properties measurements, the crude samples were shaken vigorously for one hour to homogenize and presents good representation of samples.

Standard methods were employed in determination of the physical properties.

The materials used are: Test tubes, measuring cylinders, refrigerator, gas chromatogram, thermometer, water bath and automated cloud and pour point analyzer (ASTM D2500).

Test Procedure

Sample collection and analysis of oil sample was carried out in line with recommended procedures of the American Society of Testing and Materials-ASTM. The steps below outline the procedures followed to obtain the results.

1. During sampling all glassware is rinsed properly with water and properly air- dried.
2. The wares are later rinsed with the crude oil to be sampled before the sample for analysis were collected.
3. Basic sediment and water were carried out using the centrifugation process to separate the water from the oil sample as the GC Chromatography to be used was water sensitive.
4. All the chemical reagents used in this study are of analytical reagent grade.

Compositional Analysis

The compositional analysis was carried out to achieve two specific objectives relating to the purpose of this research:

Paraffin carbon number distribution: This was determined by gas chromatography (GC) (ASTMD3328) analysis using an Agilent 7890 A gas chromatograph equipped with a flame ionization detector (FID). This gas chromatography (GC) is preferred to some other methods because it allows for compositional identification of the hydrocarbon definitions and represents a reliable method for defining hydrocarbon wax content.

1 micro-liter of crude oil sample was injected at 250oC and 18.54psi. The column was 50 meters long, 0.5micrometers thick with an internal diameter of 0.2mm. Helium was used as carrier gas at a rate of 15cm/sec. The maximum column temperature was about 300oC. The experimental procedure is outlined:

First, the sample is introduced into the gas chromatography machine through what's called an injection port or a sample port. In most modern devices, the sample ports are heated to inject and vaporize the analyte simultaneously. The injection port includes components such as a micro syringe, a rubber septum, and a vaporization chamber. The chamber is typically heated around 50° Celsius above the boiling point of the sample and then combined with the carrier gas.

This Gas chromatography technique is employed to characterize the carbon number distribution of petroleum waxes and the normal and non-normal hydrocarbons. It is oriented by ASTM D5442-17. In this work the GC evaluated the carbon distribution up to C36. Table 1 to 8 presents some physicochemical characterization of the six paraffinic oils used. All crude oils have relatively similar values of density

i. The Wax content was determined by precipitation method. The wax content was determined using the GC it separates the saturate fraction using and the analyses them using GC with flame ionizing detector. It involves, separating saturates from other polar components through chromatography and then further separating waxes from the saturate fraction. The wax content is then calculated by analyzing the area of specific wax peaks in the chromatogram its percentage in the various sample calculated.

Figure 1: Analog Water Bath for Cooing

A water bath is a piece of scientific equipment used to maintain a steady temperature for a prolonged time when incubating samples. The water bath is preferred over an open flame when heating flammable substances. It is employed to enable some chemical reactions at high temperatures. The sensor converts the temperature of the water into a resistance value, which is then amplified and compared by an integrated amplifier. This produces the control signal, which effectively regulates the average heating power of the electric heating tube and keeps the water at a constant temperature.

The Wax Appearance Temperature (Wat)

Automated cloud point tester designed for ASTM D2500 specification was used. The optical microscopy method was deployed to determine the wax appearance temperature.

Few grams of the different samples of crude were weighed into a test tube, centrifuged, heated in a water bath to 40˚C and inserted into the sample jar of the automated cloud point tester. The jar was cooled and monitored at 3˚C intervals for cloudy appearance. Studies have shown that The rate at which the crude oil is cooled during the WAT measurement can influence the measured WAT. Faster cooling rates can lead to supercooling (where the oil cools below the WAT without wax formation) or superheating, which can shift the measured WAT. In other to obtain a more accurate WAT, which represents the temperature at which wax crystals first appear under equilibrium conditions, slower cooling rates was used. The temperature at which the sample showed haziness of cloud was noted as the WAT The procedure was repeated about three times and the average was eventually recorded as the final mean of the WAT.

Figure 2: Automated Cloud and pour point analyzer (ASTM D250

Sara Analysis

The SARA Analysis Involves Three Main Stages

i. System cleans up and preparation: This procedure was carried out on almost all the equipment used for the analysis. However, here after extensive troubleshooting trials, two simple cleaning and flushing steps are established to ensure correct device operation. Generally, prior to start any experiment, the whole system (including the columns, lines, valves, and sample loop) is flushed with toluene for approximately 20–30 min to achieve a stable baseline in the HPLC UV–vis detector. When ensuring the system is completely clean, the carrier phase is switched to n-pentane and injected through the system for another 30–40 min. This step is crucial to flush out toluene from the system and fill all the columns with n-pentane. Upon attaining a stable baseline in the refractive index detector (RID), the system is primed to introduce the prepared oil sample and commence the automated process
ii. The sample preparation stage: Here, A very small amount of sample is required in this stage therefore about 40 mg of the oil sample was diluted to a 10 ml volume of toluene to provide a 4 mg/ml solution. The sample is ready to be inject through the system to separate its SARA fractions without leaving overnight as required in conventional methods.
iii. The SARA Separating procedure: the sample is loaded via a syringe in a 50 μL sample loop and subsequently displaced from the sample loop to the columns using n-pentane as the carrier phase, since the injected sample is diluted in toluene, asphaltene particles do not deposit or precipitate in the in-line filter. Consequently, the asphaltene content is filtered and precipitated within the guard and PTFE-packed columns in excess of n-pentane, simultaneously resins (polar) and aromatics (polarizable) remain on the columns, respectively. The nonpolar fraction (i.e., saturate) is not retained and adsorbed by these columns and is then directed towards the refractive index detector (RID) for quantification.

Results and Discussion

The result explained in this study are presented in this chapter, the results were discussed to have an understanding on the causes of the variations on the wax appearance temperatures of the different samples.

Results of the Compositional Analysis

Table 2 to 8 below shows the experimental result of the compositional analysis, the distribution of the components in the oil and the carbon number distribution of crude, the results indicate that the crude oils are rich in light end paraffin's. The low average n-paraffin carbon number of crude oil sample SBR and OZR correspond to its low wax content, indicating that the oil is relatively richer in non-crystallizable low molecular weight alkanes which also provide solvency for the higher molecular weight crystallizable alkanes. Below are the tables of the compositional analysis data for respective crude oils.

Table 2: compositional Analysis Data for ELE Sample

Table 1: ELE Sample Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.02
3	C3	0.21
4	i-C4	0.30
5	n-C4	0.75
6	i-C5	1.35
7	n-C5	1.46
8	C6	4.81
9	C7	11.19
10	C8	15.88
11	C9	10.34
12	C10	7.83
13	C11	5.67
14	C12	4.71
15	C13	4.32
16	C14	4.22
17	C15	4.56
18	C16	3.44
19	C17	2.72
20	C18	2.88
21	C19	2.09
22	C20	1.92
23	C21	1.42
24	C22	1.28
25	C23	1.14
26	C24	1.01
27	C25	0.89
28	C26	0.74
29	C27	0.65
30	C28	0.58
31	C29	0.52
32	C30+	1.10
	Total	100.00
	Sample Properties:	
	MW [g/mol]	165.66
	Density [g/cm3]	*0.8196[g/cm3]
	MW C20+ [g/mol]	359.15
	Mol % C20+	11.27

Table 3: Compositional Analysis Data for OBGE Sample

Table 2: OBGE Sample Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.00
3	C3	0.00
4	i-C4	0.01
5	n-C4	0.01
6	i-C5	0.04
7	n-C5	0.06
8	C6	0.56
9	C7	3.94
10	C8	8.83
11	C9	8.80
12	C10	6.89
13	C11	9.17
14	C12	8.48
15	C13	5.62
16	C14	5.01
17	C15	5.51
18	C16	4.58
19	C17	3.51
20	C18	3.61
21	C19	2.94
22	C20	2.82
23	C21	1.98
24	C22	1.84
25	C23	1.71
26	C24	1.62
27	C25	1.51
28	C26	1.41
29	C27	1.34
30	C28	1.23
31	C29	1.14
32	C30+	5.83
	Total	100.00
	Sample Properties:	
	MW [g/mol]	222.87
	Density [g/cm3]	*0.8887[g/cm3]
	MW C_{20}+ [g/mol]	432.62
	Mol % C_{20}+	22.45

Table 4: Compositional Analysis Data for SBR Sample

Sample SBR Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.16
3	C3	0.15
4	i-C4	0.17
5	n-C4	0.14
6	i-C5	0.19
7	n-C5	0.08

8	C6	0.27
9	C7	0.93
10	C8	0.76
11	C9	0.52
12	C10	0.68
13	C11	1.73
14	C12	3.37
15	C13	5.10
16	C14	7.20
17	C15	6.51
18	C16	5.41
19	C17	5.24
20	C18	5.06
21	C19	5.01
22	C20	5.54
23	C21	4.69
24	C22	4.34
25	C23	3.74
26	C24	3.39
27	C25	2.90
28	C26	2.60
29	C27	2.31
30	C28	1.88
31	C29	1.57
32	C30+	18.36
	Total	100.00
	Sample Properties:	
	MW [g/mol]	340.73
	Density [g/cm3]	*0.9377[g/cm3]
	MW C_{20}+ [g/mol]	472.41
	Mol % C_{20}+	51.33

Table 5: Compositional Analysis Data for EGB Sample

Table 4: Sample EGB Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.14
3	C3	0.89
4	i-C4	0.62
5	n-C4	1.83
6	i-C5	1.58
7	n-C5	1.90
8	C6	3.65
9	C7	9.58
10	C8	11.72
11	C9	7.63
12	C10	7.03
13	C11	5.31
14	C12	4.78
15	C13	5.03
16	C14	4.85
17	C15	5.27
18	C16	4.33
19	C17	3.25
20	C18	3.41
21	C19	2.67
22	C20	2.27
23	C21	1.97
24	C22	1.81
25	C23	1.53
26	C24	1.27
27	C25	1.11
28	C26	0.97
29	C27	0.77
30	C28	0.64
31	C29	0.52
32	C30+	1.67
	Total	100.00
	Sample Properties:	
	MW [g/mol]	178.21
	Density [g/cm3]	*0.8448[g/cm3]
	MW C_{20}+ [g/mol]	365.48
	Mol % C_{20}+	14.54

Table 6: Compositional Analysis Data for OMR Sample

Table 5: Sample OMR Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.06
3	C3	0.31
4	i-C4	0.27
5	n-C4	0.74
6	i-C5	0.93
7	n-C5	1.10
8	C6	3.00
9	C7	8.03
10	C8	11.66
11	C9	9.49
12	C10	5.94
13	C11	4.84
14	C12	4.44
15	C13	5.13
16	C14	4.79
17	C15	4.91
18	C16	4.16
19	C17	3.54
20	C18	3.70
21	C19	3.08

22	C20	2.66
23	C21	2.35
24	C22	2.12
25	C23	1.79
26	C24	1.50
27	C25	1.35
28	C26	1.16
29	C27	0.94
30	C28	0.71
31	C29	0.51
32	C30+	4.79
	Total	100.00
	Sample Properties:	
	MW [g/mol]	205.33
	Density [g/cm3]	*0.8783[g/cm3]
	MW C_{20}+ [g/mol]	205.33
	Mol % C_{20}+	19.90

Table 7: Compositional analysis Data for ORD Sample

Table 6: Sample ORD Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.12
3	C3	1.41
4	i-C4	0.95
5	n-C4	2.62
6	i-C5	1.91
7	n-C5	2.36
8	C6	4.14
9	C7	9.60
10	C8	13.25
11	C9	8.53
12	C10	5.75
13	C11	4.07
14	C12	3.71
15	C13	3.13
16	C14	3.39
17	C15	4.07
18	C16	3.47
19	C17	3.07
20	C18	3.13
21	C19	2.82
22	C20	2.53
23	C21	2.30
24	C22	2.07
25	C23	1.93
26	C24	1.77
27	C25	1.51
28	C26	1.37
29	C27	1.26
30	C28	1.13
31	C29	0.97
32	C30+	1.63
	Total	100.00
	Sample Properties:	
	MW [g/mol]	179.44
	Density [g/cm3]	* 0.8494[g/cm3]
	MW C_{20}+ [g/mol]	358.21
	Mol % C_{20}+	18.48

Table 8: Compositional Analysis Data for OZR Sample

Sample OZR Stock Tank Oil Composition		
No.	**Component**	**Composition**
		[mol %]
1	C1	0.00
2	C2	0.03
3	C3	0.02
4	i-C4	0.01
5	n-C4	0.05
6	i-C5	0.01
7	n-C5	0.01
8	C6	0.04
9	C7	0.05
10	C8	0.14
11	C9	0.64
12	C10	3.13
13	C11	4.53
14	C12	6.02
15	C13	7.00
16	C14	7.40
17	C15	7.05
18	C16	5.52
19	C17	6.22
20	C18	5.20
21	C19	5.69
22	C20	5.30
23	C21	3.85
24	C22	3.65
25	C23	3.23
26	C24	2.88
27	C25	2.53
28	C26	2.12
29	C27	1.90
30	C28	1.59
31	C29	1.40
32	C30+	12.79
	Total	100.00
	Sample Properties:	
	MW [g/mol]	303.46

	Density [g/cm3]	*0.9257[g/cm3]
	MW C_{20}+ [g/mol]	451.14
	Mol % C_{20}+	41.23

Table 9: Physiochemical Properties of the Crude Samples

Sample name	Wax contents (wt%)	Pour Point (OC)	Cloud point/ WAT (OC)
ELE	22.10	17.00	27.50
OBGE	11.70	-19.50	22.50
SBR	4.80	-38.70	15.00
EGB	11.07	16.00	14.00
OMR	8.70	8.00	24.20
ORD	22.05	36.50	25.00
OZR	4.50	-65.00	-19.00

Table 10: SARA Composition of Selected Crude Oil Samples

Sample name	Saturates	Aromatics	Resins	Asphaltenes
ELE	49.70	34.50	14.00	4.65
OBGE	40.00	28.22	17.00	5.25
SBR	38.00	42.30	4.80	2.24
EGB	49.70	40.91	1.33	4.34
OMR	38.00	30.40	13.00	4.80
ORD	49.56	38.53	1.42	7.45
OZR	35.33	54.20	3.78	4.77

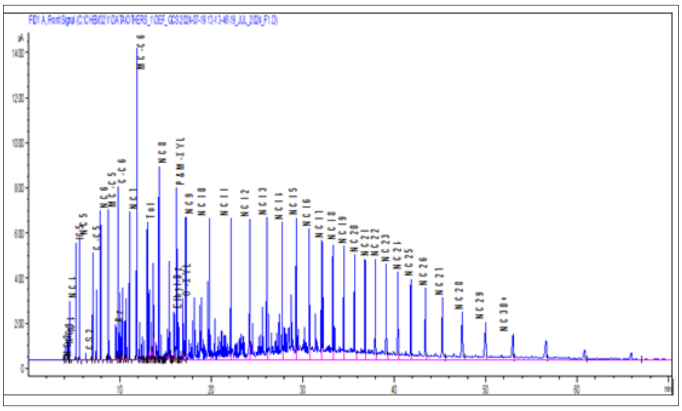

Figure 3: ELE Oil Sample HRGC FID Chromatogram

Figure 4 shows the GCMS analysis of the hydrocarbon number distribution of the paraffinic composition of the ELE samples. From the GCMS, the experimental measurement is shown in the form of chromatogram where the peaks represent the types of component present in the compound. This sample shows a high concentration of paraffins of C5 to C15 with the longest peak tilting towards the C8. The results showed the lighter components are more towards the left of the chromatogram while the heavier components are more towards the right of the chromatogram. The longer peaks represent the n paraffins while the short ones represent the iso. The waxes present nearly normal distributions, with chain sizes from C8 to 30 carbon atoms, with some differences between them.

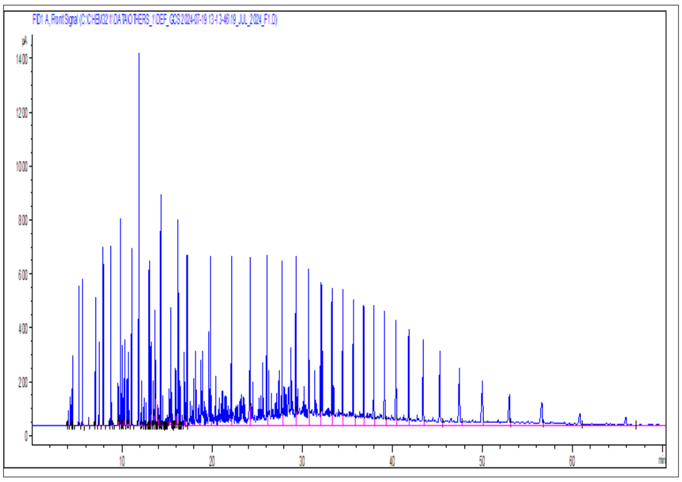

Figure 4: OBGE Oil Sample HRGC FID Chromatogram

As shown in Figures 5, the carbon number distribution of precipitated solid wax crystals at different temperatures has peak values. The carbon number distribution of the OBGE sample map of paraffin wax shows that the content of C11 in paraffin wax was the highest.

However, the peak appears lower than C11, with higher temperatures, the carbon number at the peak is decreased, gradually moving closer to C30+, as shown in the Figure 5. The wax precipitation characteristics at different temperatures are affected by many factors, including the temperature of the oil, the carbon number distribution of the paraffin in the waxy oil and the sensitivity of alkane crystallization to temperature. The higher the carbon number, the easier alkanes are to precipitate at high temperatures. Though the content of paraffin was low, it was more likely to precipitate than alkanes with lower carbon numbers, and its concentration increased in the precipitated wax crystals as witnessed with this sample. The peak value moves towards the alkanes of low carbon number as the temperature decreases. This suggests that wax precipitation is sensitive to temperature and the carbon number distribution of alkanes in paraffin plays a major role. A strong indicator of the wax appearance temperature variations.

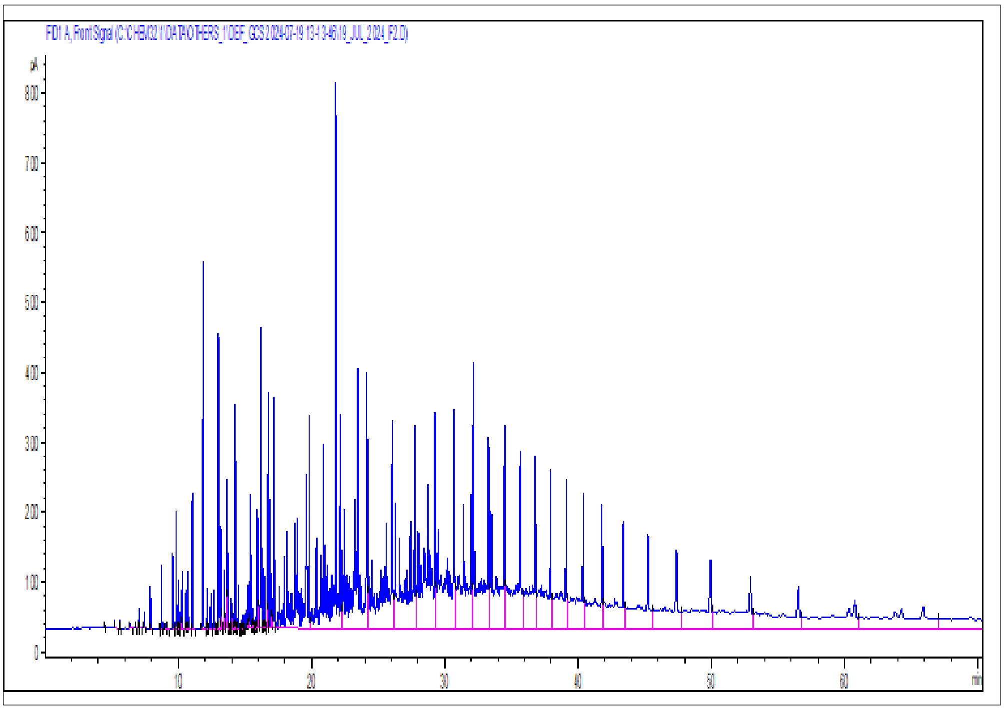

Figure 5: SBR Oil Sample HRGC FID Chromatogram

Figure 6 shows the chromatographic analysis of the hydrocarbon number distribution of the paraffinic composition of the SBR samples. In this waxy crude oil, just as with others, waxes primarily consist of n-alkanes, which are straight-chain hydrocarbons with varying carbon numbers. The HTGC separates these n-alkanes based on their boiling points, resulting in distinct peaks as shown above. As earlier indicated, the carbon number range of the n-alkanes in the wax fraction is a key indicator of wax content. For this analysis, waxes in crude oil typically have carbon numbers ranging from C13 to C30+. It differs slightly from the previous analysis in the sense that the wax forming carbon are relatively higher, accounting for over 78% of the total wax. The areas of the peaks corresponding to the n-alkanes in the wax range are integrated to determine the amount of each component. The total wax content can be determined by summing the areas of all the wax component peaks and expressing it as a percentage of the total sample area or weight.

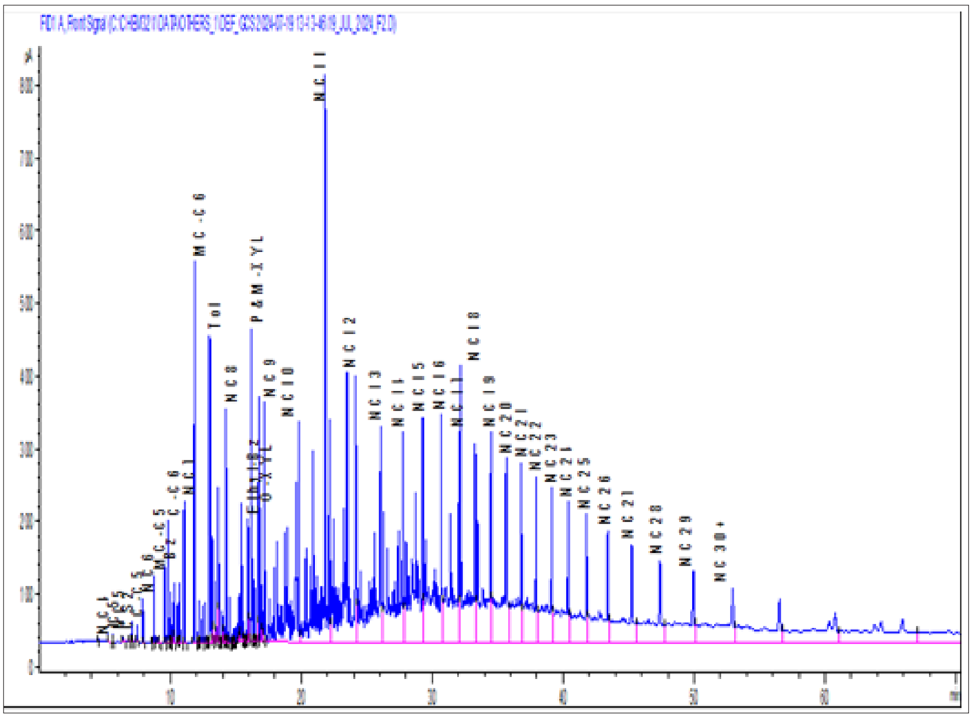

Figure 6: ORD Oil Sample HRGC FID Chromatogram

Gas Chromatography Mass Spectrometry

The significance of the GCMS is to analyze the hydrocarbon number distribution of the paraffinic composition in the crude samples. From the GCMS, the experimental measurement is shown in the form of chromatogram where the peaks represent the types of component present in the compound. The vertical axis of the chromatogram represents the abundance while the horizontal -axis represents the retention time. The lighter components are more towards the left of the chromatogram while the heavier components are more towards the right of the chromatogram. The longer peaks represent the n paraffins while the short ones represent the iso. The chromatograms are shown in Figure 4, 5, 6 and 7 for ELE, OBGE, OMR and OZR respectively. From table 2 to 8 and the chromatogram, in Figure 4 to 7, the waxes present nearly normal distributions, with chain sizes from C8 to C30 carbon atoms, with some differences between them. The ELE and ORD waxes have a greater abundance of paraffins in the range of C8 to C20, than wax EGB. But, in the range of C18 to C21, the wax ORD presents the highest content of lighter paraffins. However, the GC technique used to get the carbon number distribution of the crude oil waxes does not allow the identification of cyclo-paraffinic compounds which has been reported can also influence the wax crystallization phenomena.

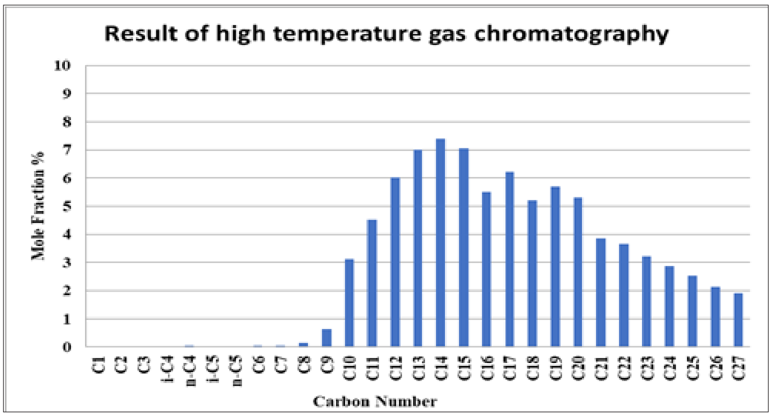

Figure 7: Average Carbon Number Distribution of Waxy Crude Oil

The summary of the average carbon number distribution of all the waxy crude oil components analyzed by high temperature gas chromatography were shown in Figure 8.

From the Figure, it can be seen that the main component of wax precipitation is the hydrocarbon of C10~C23, about 70% of the total wax content. The content of C24~C30 is about 25%, and hydrocarbons with higher carbon number than 30, C30+ only account for 7% of the total wax content. The composition of C6~C10 is 3%, and the alkanes or cycloalkanes in this carbon number range are mostly liquid in the standard state, and they may be adsorbed in the network of precipitated wax. The implication is that waxiness is not exclusively a function of high caron number and hence higher WAT as can be see that light ends can also precipitate wax and impact WAT as those of higher carbon number.

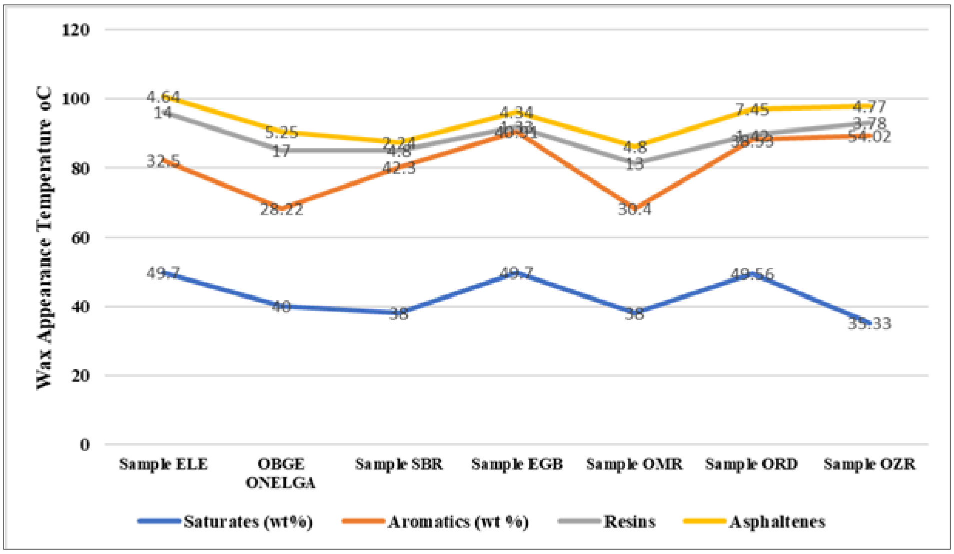

Figure 8: Sara and Wat Profile for Samples

SARA analysis breaks down the crude oil into four main components. The result in Fig.9 shows that each fraction has distinct chemical and physical properties influencing the behavior of the waxy crude oil with respect to the WAT. As earlier defined, this temperature at which the first wax crystals appear during cooling was determined to be the wax appearance temperature. The WAT and wax content of the deposits obtained where characterized using the HLGC. It was observed as profiled in the Fig. 9 that the dispersed asphaltenes amount varies in almost all cases with an increased WAT and wax deposit. Table 10 presents the results of the WAT and wax content of the deposits when the deposit with dispersed asphaltenes. the WAT and wax content of the deposits continuously increases with the increase of the dispersed asphaltenes. The effect of asphaltene on wax content of crude oil is shown in Figure 4.63. the figure shows that with the increase of asphaltene content, WAT decreases slowly from 27°C to 13.5°C. usually dispersed in crude oil in colloidal state. They are suitable to adsorb high carbon alkanes, which make the WAT decrease slowly, but this decrease is limited. which indicates that the increase of resin and asphaltene had little effect on the crystallization of C8 – C22. However, asphaltene may affect the wax deposition amount to some extent. It can therefore be inferred from the result and graphical illustration that the dissolved asphaltene in the waxy crude moderately impacts the WAT and partly responsible for the variations in the wax appearance temperatures of waxy crude oil samples analyzed. similarly, the saturates trend shows a true reflection of the nature of the crudes analyzed, the trend shows a linear increase with the WAT as expected Saturates, which include paraffins (alkanes), are a major component of wax in crude oil. High wax content in crude oil is directly linked to a high concentration of saturates but not independently sufficient to be responsible for the variations in WAT. However, aromatics content on WAT as shown in Figure 9. From the Figure, with the increase of aromatics content, WAT decreases from 27.5°C to -19°C, and the trend is more consistent with Aromatics. Continuing the analysis of fig 10, it is noted that OZR sample was characterized by the lower WAT values with a significantly high Aromatics and ELE shows the higher (Table 10), which may be evidence that the OZR is composed of fewer Aromatics and ELE has the highest. However, OZR has the smallest saturates, as highlighted above, being smaller than the others. with respect to the OZR, higher WAT value, large crystals were expected, one can infer from the observation that the increase of aromatics effectively improves the solubility of high carbon alkanes and makes it difficult to precipitate. The increase of aromatics also effectively prevented the precipitation of C16~C25 in crude oil. Studies have shown that aromatics can increase resin solubility in crude oil and thus decreases resin adsorption on asphaltene surface. This phenomenon promotes asphaltene to precipitate easily with the wax crystal until it was completely precipitated. Therefore. It can therefore be inferred from the result and graphical illustration that differences in the Aromatic content in the waxy crude are responsible for the variations in the wax appearance temperatures of waxy crude oil samples analyzed. As it has been established from the signatory plot that a consistent proportionate relationship exists between the wax appearance temperature and the Aromatic content of the waxy crude samples making the Aromatics to impact more on the WAT than other components.

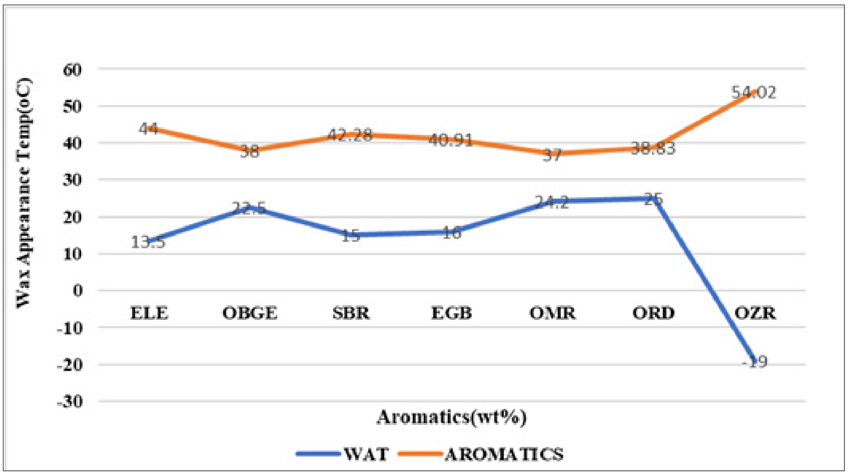

Figure 9: WAT and Aromatics Profile for Waxy Crude Samples

The effect of aromatics content on WAT is shown in Figure 4.61, from the plot, it can be observed that with the increase of aromatics content, WAT decreases from 27.5°C to -19.0°C. The increase of aromatics effectively improves the solubility of high carbon alkanes and will make it difficult to precipitate. ELE and OZR with a relatively high Aromatics content of values between 44 and 54.2 weight percent manifests low WAT of between -19oC and 13.5oC Generally, increased aromatic content can destabilize asphaltenes, causing them to precipitate and potentially impacting WAT. However, aromatics can also interact with wax molecules, and their specific effect on WAT depends on the aromatic structure and the composition of the wax. The Aromatic content of the waxy crude sample impacts more consistently and exhibit more variations with the WAT.

Effect of Aromatics on Wat

The effect of aromatics content on WAT is shown in Figure 10, from the plot, it can be observed that with the increase of aromatics content, WAT decreases from 27.5°C to -19.0°C. The increase of aromatics effectively improves the solubility of high carbon alkanes and will make it difficult to precipitate. ELE and OZR with a relatively high Aromatics content of values between 44 and 54.2 weight percent manifests low WAT of between -19oC and 13.5oC Generally, increased aromatic content can destabilize asphaltenes, causing them to precipitate and potentially impacting WAT. However, aromatics can also interact with wax molecules, and their specific effect on WAT depends on the aromatic structure and the composition of the wax. The Aromatic content of the waxy crude sample impacts more consistently and exhibit more variations with the WAT.

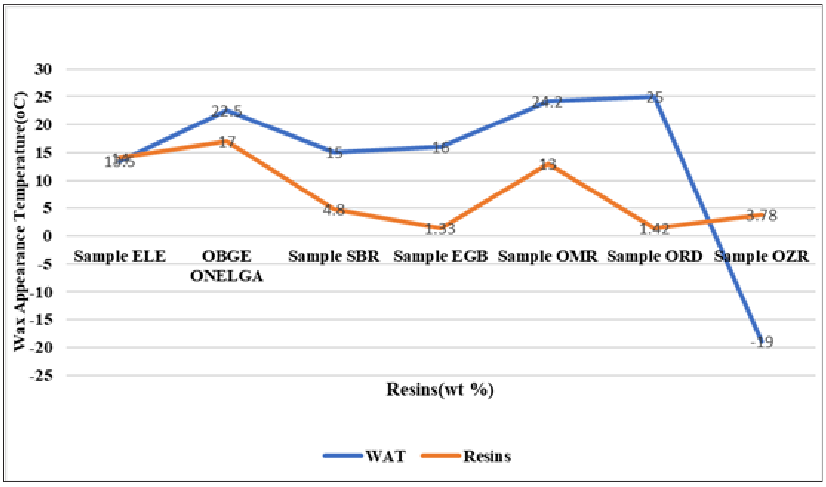

Figure 10: WAT and Resin Profile for Waxy Crude Samples

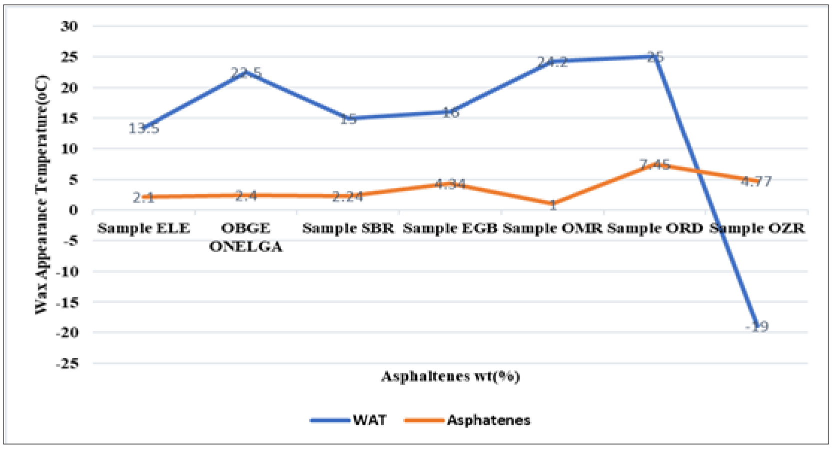

Figure 11: WAT and Asphaltene Profile for Waxy Crude Samples

Figures 11 and 12 shows similar response to the wax appearance temperature. The figures show that with the increase of resin and asphaltene content, WAT decreases slowly from 25°C to -19.0°C. this decline is not consistent as can be seen in the case of ELE and OMR with asphaltene weight percent of 2.1 and 1.0, shows a decrease and an increase between the WAT values of 13.5oC and 24.2oC respectively. This trend is also noticed in the resin, The weight percent of ELE, OBGE and ORD varied between 11.4, 1.3 and 1.42 with the WAT showing inconsistency values with 27.5oC, 22.5oC and 25.0oC respectively. This trend with others shows a partial correlation with WAT variations but not consistent. Resin and asphaltene are fused aromatic hydrocarbon compounds, usually dispersed in crude oil in colloidal state. They are suitable to adsorb high carbon alkanes, which make the WAT decrease slowly, but this decrease is limited. they have little effect on the WAT. Therefore, the effect of resin and asphaltene on prediction of WAT variations need not be considered in the thermodynamic method, but also, they may affect the wax deposition amount to some extent.

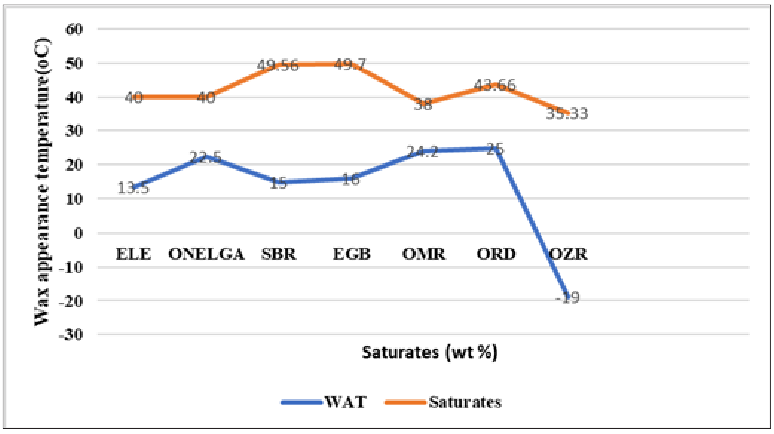

Figure 12: WAT and Saturates Profile for Waxy Crude Samples

The effect of saturates on WAT is shown in Figure 13. It highlights the relationship between the wax appearance temperature and the saturates content of the waxy crude sample. The trend shows a linear proportion with the WAT. For instance, OZR sample with the lowest saturates has the lowest wax WAT and ORD with a relatively high saturates have a high wax appearance temperature with slight variations with respect to SBR and EGB samples. This variation is an indication that saturates content though partially impacts on the WAT is not independently responsible for the WAT variations. Though no singular universally cited scholar has made these propositions, but the relationship is well-established in petroleum science that Higher saturate content, specifically the paraffinic hydrocarbons within the saturate fraction, is strongly correlated with increased WAT. This is because these saturated hydrocarbons can precipitate out of solution as waxes at lower temperatures, leading to a higher WAT as expected Saturates, which include paraffins (alkanes), are a major component of wax in crude oil. High wax content in crude oil is directly linked to a high concentration of saturates which is exactly what this plot represents.

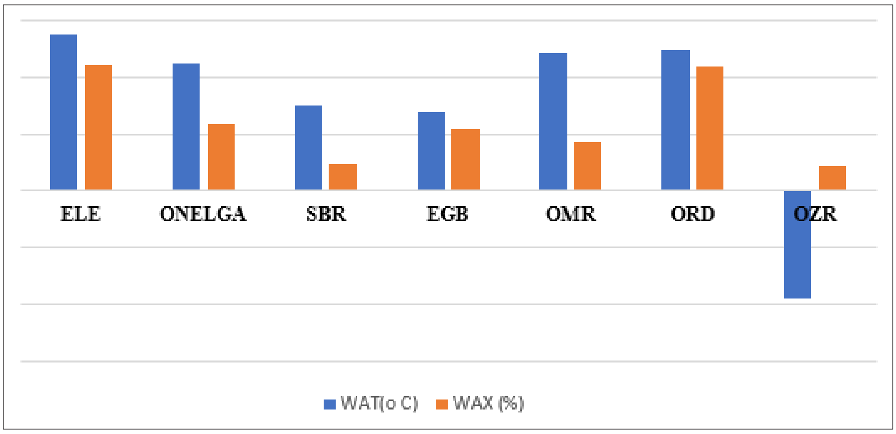

Figure 13: Wax Against WAT Profile for Waxy Crude Samples

The plot wax and wax appearance temperature measured by the GC and ASTM D2500 are shown in Figure 14. However, for OZR crude oil, there is a significant depression in the width plot, this is due to the low content of wax in the crude oil sample. Table 9 shows the wax content for each crude oil sample. ELE crude oil has the highest total weight percent followed by ORD, to OBGE, EGB, OMR, SBR and OZR. By comparing the results obtained from crude oil samples, we can see a relationship between paraffinic composition, wax appearance temperature and wax content. ELE crude oil with highest content of paraffinic composition seems to have higher wax appearance temperature and wax content while OZR with lowest content of paraffinic composition seems to have lower wax appearance temperature and wax content. This correlates with the submission of (Meirong Yanet et al., 2018) which posited that WAT and WAPT increases significantly with increasing wax content. This relationship is important for development of wax deposition prediction model.

Table 11: Summary of Results of Experiments Carried out on Samples

Sample Name	Cloud Point/ WAT(˚C)	Pour Point(˚C)	Wax content (wt %)	Saturates (wt%)	Aromatics (wt %)	Resins (wt.%)	Asphaltenes (wt %)	C_{20}+ Molecular weight (g/mol)	C_{20}+ Mole fraction (mol %)
ELE	27.50	17.00	22.1	49.70	32.50	14.00	4.64	359.15	11.27
OBGE	22.50	-19.50	11.7	40.00	28.22	17.00	5.25	432.62	22.45
SBR	15.00	-38.67	4.80	38.00	42.30	4.80	2.24	472.41	51.33
EGB	14.00	16.00	11.07	49.70	40.91	1.33	4.34	365.48	14.54
OMR	24.20	3.00	8.70	38.0	30.40	13.00	4.80	205.33	19.90
ORD	25.00	26.50	22.05	49.56	38.53	1.42	7.45	358.21	18.48
OZR	-19.00	-65.00	4.50	35.33	54.02	3.78	4.77	451.14	41.23

Relationship Between Carbon Number and Mole Fraction of Wax Precipitated in Crude Oil

The Physicochemical characterization is employed to characterize the carbon number distribution. In this work, the high temperature Gas Chromatography (HTGC) evaluated the carbon distribution up to C30+. The sample was analyzed to get the wax content and carbon number distribution. Fig 8 shows the carbon number distribution of waxy crude oil. As it is known, wax refers to the n-paraffin, so all the carbon number distributions in this study are the n-paraffin carbon number distribution, which was obvious from the result of the HTGC and the summary plot. The average carbon number distribution of crude oils and wax fraction (Table 11) indicate that the crude oils are rich in light end paraffins (< C -10).

The results of the crude oil components analyzed by high temperature gas chromatography were shown in Figure 4 to 7. It can be deduced that the main component of wax precipitation is the hydrocarbon of C8 – C20, which constitutes about 65% of the total wax content. This is an indication of the prevalence of micro-crystalline wax in the samples analyzed which studies reveals the larger the carbon chain size, the higher the crystallization temperature and correlates with the submission of (Roehner et al., 2002) on the relationship between carbon number and wax content which suggest a proportionate relationship between carbon number and wax content and that the larger the carbon chain size, the higher the crystallization temperature Also, the content of C20 - C30+ is about 30%, and hydrocarbons with higher carbon number than 40 only accounts for less than 10% of the total wax content. Also, Fig 10 clearly shows the relationship between the wax content and the wax appearance temperature. Moreover, the first peak of OZR is barely evident which can be a sign of less wax content. SBR has a second peak evident from Table 11 that is, this oil may contain the higher wax content as shown which invariably impacts the WAT. The plot shows a high degree of consistency with the wax content-wax appearance temperature. The higher the amount of wax present in a waxy crude, the higher the likelihood of the wax appearance temperature and by extension the higher the gelation point (the point at which the waxy crude oil transits from a liquid to a semi-solid or gel-like state due to the crystallization and agglomeration of wax molecules).

SARA Effect on WAT

SARA analysis breaks down the crude oil into four main components. The result shows that each fraction has distinct chemical and physical properties influencing the behavior of the waxy crude oil with respect to the WAT. As earlier defined, this temperature at which the first wax crystals appear during cooling was determined to be the wax appearance temperature. The WAT and wax content of the deposits obtained where characterized using the HLGC. It was observed as profiled in the Fig. 12 that the dispersed asphaltenes amount varies in almost all cases with an increased WAT and wax deposit. Table 9 presents the results of the WAT and wax content of the deposits when the deposit with dispersed asphaltenes. the WAT and wax content of the deposits continuously increases with the increase of the dispersed asphaltenes. The effect of asphaltene on wax content of crude oil is shown in Figure 12. the figure shows that with the increase of asphaltene content, WAT decreases slowly from 27°C to 13.5°C. usually dispersed in crude oil in colloidal state. They are suitable to adsorb high carbon alkanes, which make the WAT decrease slowly, but this decrease is limited. which indicates that the increase of resin and asphaltene had little effect on the crystallization of C8 – C22. However, asphaltene may affect the wax deposition amount to some extent. It can therefore be inferred from the result and graphical illustration that the dissolved asphaltene in the waxy crude moderately impacts the WAT and partly responsible for the variations in the wax appearance temperatures of waxy crude oil samples analyzed. similarly, the saturates trend shows a true reflection of the nature of the crudes analyzed. The trend shows a linear increase with the WAT as expected Saturates, which include paraffins (alkanes), are a major component of wax in crude oil. High wax content in crude oil is directly linked to a high concentration of saturates. However, aromatics content on WAT as shown in Fig. 10. From the Figure, with the increase of aromatics content, WAT decreases from 27.5°C to -19°C, and the trend is more consistent with Aromatics. Continuing the analysis of Fig 11, it is noted that OZR sample was characterized by the lower WAT values with a significantly high Aromatics and ELE shows the higher (Table 11), which may be evidence that the OZR is composed of fewer Aromatics and ELE has the highest. However, OZR has the smallest saturates, as highlighted above, being smaller than the others. with respect to the OZR, higher WAT value, large crystals were expected, one can infer from the observation that the increase of aromatics effectively improves the solubility of high carbon alkanes and makes it difficult to precipitate. The increase of aromatics also effectively prevented the precipitation of C16~C25 in crude oil. Studies have shown that aromatics can increase resin solubility in crude oil and thus decreases resin adsorption on asphaltene surface. This phenomenon promotes asphaltene to precipitate easily with the wax crystal until it was completely precipitated. Therefore. It can therefore be inferred from the result and graphical illustration that differences in the Aromatic content in the waxy crude are responsible for the variations in the wax appearance temperatures of waxy crude oil samples analyzed. As it has been established from the signatory plot that a consistent proportionate relationship exists between the wax appearance temperature and the Aromatic content of the waxy crude samples making the Aromatics to impact more on the WAT than other components.

Conclusion

Waxy crude oil characterization is necessary to proffer suitable solutions to wax precipitation and deposition problems. The information would help to make informed decision on the crude. The Seven (7) Niger Delta crude oil samples characterized exhibited wax deposition potential and variations in their wax appearance temperature (WAT). Results have shown that waxing tendency is not restricted to heavy crude oil samples. The light crudes are also susceptible to wax problems.

The wax appearance temperatures as measured by the high temperature gas chromatography showed some high values of WAT. Samples with WAT as high as 35.0oC is a cause for concern that wax precipitation could start early in some wells in the Niger Delta.

The signatory plot of Fig. 9 Shows that the saturates, resins, asphaltenes all impact on the wax and wax appearance temperature, However, Aromatics impact more significantly than the rest of them and therefore principally responsible for the variations on the wax appearance temperature.

So, in making a choice of crude oil for transportation and processing with minimal wax problems, beyond the wax content, consideration should be given to the Aromatics content as this could significantly impact on the WAT.

Obviously, SARA analysis can be applied qualitatively together with oil paraffin distribution to predict the relative waxiness and variations in their wax appearance temperature impacting the flow behavior of waxy crude oil and their potential for wax problems in the oilfield.

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