بسم الله الرحمن الرحيم

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Properties for Different Types of Crude Oil: A Comparative Study

دراسة مقارنة لخواص أنواع مختلفة من الزيوت الخام

A Thesis Submitted for the Degree of M.Sc in Chemistry

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بسم الله الرحمن الرحيم

ين َ آم َ ن ُوا م ِ نك ُم ْ و َ الَّذ ِين َ أُوت ُوا الْع ِلْم َ د َر َ ج َات ٍ و َ اللَّه ُ ب ِم َ ا

ت َع ْم َ ل ُون َ خ َب ِير ٌ

صدق الله العظيم

سورة المجادلة الآيةرقْم 11

DEDICATION

Dedicated to:

The soul of my father,

My mother,

My wife, my brothers and my sister.

Acknowledgment

I would like to thank Allah, Almighty, for giving me the strength to complete this work.

Acknowledgment and thank **Dr. Abdulsalam Abdullah** for supervision and encouragement.

Special thanks go to my family for their continued support.

Finally I would like to thank and acknowledge my colleagues and co-workers in the Adar and Gummry field for the time and efforts offered.

Abstract

The objectives of the current study were to study the chemical composition of different types of crude oil in Sudan, the relationship between chemical composition and physical properties of crude oil and to study the emulsion stability of crude oil.

Twenty samples collected from four different fields in the South Sudan have been investigated by means of Brookfield viscometer, Anton paar and high-performance liquid chromatography (HPLC). Using HPLC the samples have been separated into four chemical group classes, namely saturates, aromatics, resins, and asphaltenes, the so-called SARA fractions. Using multivariate analysis techniques such as solvent extraction to measure asphaltene content and wax content after precipitation by controlling the temperature, also water cut, emulsion and poor point were measured according to ASTM.

The results show that out of the twenty samples studied, nineteen were confirmed waxy samples (Table 1) while one was non-waxy from the pour point and wax content measurements. The SARA analysis carried out on all of the samples. On the other hand, the sample showed a high percentage of saturates ranging from 40 wt% to 66 wt%. Sample 6 which was non-waxy crude oils even had saturates of 40%. Thus, SARA analysis data on its own might not be a tool to distinguish waxy crude oils from non-waxy crude oils. According to the results in chart 4 the API and SARA fractions were correlated in only 45% of the samples studied. On the other hand, in 55% of the studied samples the correlation between SARA and API was not clear. There is an increase of the emulsion stability as the viscosity increases. However, viscosity also correlates well with the SARA data of the crude oils, Pour point correlates fairly well to resins, aromatic and saturates,

مستخلص البحث:

الهدف من الدراسة الحالية هو دراسة التركيب الكيميائي لأنواع مختلفة من النفط الخام في السودان ، والعلاقة بين التركيب الكيميائي والخصائص الفيزيائية للنفط الخام ودراسة استقرار مستحلب النفط الخام.

تم فحص 20 عينة من أربعة حقول مختلفة في جنوب السودان. تم تحليل العينات عن طريق مقياس اللزوجة Brookfield، Anton paar لقياس الكثافه و (HPLC). بواسطة HPLC تم فصل العينات إلى أربع فئات مجموعة كيميائية ، وهي المشبعة ، والمركبات العطرية ، والراتنجات ، والأسفلت ، ما يسمى كسور SARA، باستخدام تقنيات التحليل متعدد المتغيرات مثل استخلاص المذيبات لقياس محتوى الأسفلت ومحتوى الشمع ودرجة الانسكاب بالتحكم في درجة الحرارة ، تم أيضًا قَسْر المياه ومستحلبها ونقطة ضعفها وفقًا لـ ASTM.

أظهرت النتائج أنه من بين العشرين عينة التي تمت دراستها ، تم تأكيد تسعة عشر عينة شمعية (الجدول 1) بينما كان واحدًا غير شمعي من قياسات درجة الانسكاب والشمع. أظهر تحليل SARA على جميع العينات أن العينات تحتوي على نسبة عالية من المركبات المشبعه تتراوح بين 40٪ إلى 66٪ بالوزن. العينة 6 التي كانت عبارة عن زيوت خام غير شمعية كانت نسبة المركبات المشبعه 40٪. وبالتالي ، قد لا تكون بيانات تحليل SARA من تلقاء نفسها أداة للتمييز بين النفط الخام الشمعي من الزيوت الخام غير الشمعية. ووفقًا للنتائج الواردة في الرسم البياني رقم 4 ، تم الربط بين API و SARA في 45٪ فقط من العينات التي تمت دراستها. من ناحية أخرى ، في 55 ٪ من العينات المدروسة ، لم يكن الارتباط بين SARA و API

واضحًا. هناك زيادة في استقرار المستحلب مع زيادة اللزوجة. ومع ذلك ، ترتبط اللزوجة أيضًا جيدًا مع بيانات SARA للزيوت الخام، ترتبط نقطة الانسكاب بشكل جيد مع الراتنجات والعطرية والشبع ،

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LIST OF ABBREVIATIONS:

API: American Petroleum Institute.

ASTM: American Society for Testing and Material

SARA: Saturated compounds Aromatic compounds Resins Asphaltine.

WAT: Wax Appearance Temperature.

CHAPTER ONE

INTRODUCTION

1-Introduction

Many types of crude oil are produced around the world. The market value of an individual crude stream reflects its quality characteristics. Crude oils that are light (higher degrees of API gravity, or lower density) and sweet (low sulfur content) are usually priced higher than heavy (U.S. Energy Information Administration. 2013) Most of the studies and reviews show that the amount of oil that can be extracted with primary drive mechanisms is about 20 – 30% and by secondary recovery can reach up to 40% but using modern enhanced oil recovery (EOR) techniques, recovery can reach up to 60 – 65%. These techniques of enhanced oil recovery (EOR) are essentially designed to recover oil commonly described as residual oil. The oil that cannot be extracted by primary recovery as well as secondary recovery techniques, this amount of recovery depends on the amount of oil produced from the primary recovery (Tariq Ahmed, 2001). According to the Department of Energy U.S.A, the amount of oil produced worldwide is only one third of the total oil available. So by using the EOR techniques we will be able to produce more oil as the demand increase while we have a shortage in the supply. (Saleem et al. 2011).

1.1. Key Challenges Facing the oil Industry in Sudan

The economy has been dependent on petroleum since the start of the oil boom in 1999 according to the Sudan country office; (2018). Fiscal and exchange rate policies were heavily influenced by the oil sector. The oil sector provided large budget revenues that allowed the government to maintain a low tax burden on the non-oil economy. It also provided the bulk of the country's foreign exchange earnings and allowed the maintenance of an overvalued exchange rate. Sudan faces some key challenges with the development of the petroleum sector during the 2015-

2030 periods. These uncertainties are related to the following: (i) The international supply and demand for oil and related price prospects in the near and longer-term; (ii) the prospects for oil and gas exploration and production in the decade ahead; (iii) the likely growth in domestic demand for oil and gas products; and institutional arrangements for the sector. (Sudan country office, 2018)

The quality of Sudan's oil varies substantially among fields, with a significant portion of production of relatively low quality. The exported crude oil is of two standard qualities: Nile Blend and Dar Blend. Nile Blend is a good quality crude oil that is readily saleable on international markets, but the Dar Blend has characteristics that include a high acid content that make it difficult to sell to most refineries. Most of the Dar Blend comes from fields that are located in the South. A third crude blend, Fula, is produced in fields located in Sudan. The quality of this oil is lower than the Dar Blend and is therefore sold only in the domestic market.

Cited in African development bank group Sudan country office. (2018), Sudan has two oil refineries with a total capacity of 121,700 bbl/d, and three topping plants, which are small-scale, less complex refineries with a total capacity of 22,000 bbl/d. The largest refinery, the Khartoum (or al-Jaili) refinery, is located just north of Khartoum and has a distillation capacity of 100,000 bbl/d. It became operational in 2000 with a capacity of 50,000 bbl/d to process the Nile Blend. The refinery's capacity was expanded in 2006 to also process Sudan's highly acidic Fula Blend. According to one of its operators, China's CNPC, the Khartoum Refinery was the world's first modern refinery with a delayed coking unit for high-acid and high-calcium crude oil. The country's other full conversion refinery is the Port Sudan refinery (21,700 bbl/d). The three small topping

plants are El Obeid (10,000 bbl/d), Shajirah (10,000 bbl/d), and Abu Gabra (2,000 bbl/d). The Malaysian company, Petronas, had planned to construct a 100,000 bbl/d refinery in Port Sudan, but no progress has been reported. There are no oil refineries in South Sudan.

1.2. Oil fields:

1.2.1. **Adar and Gummry oil field**

The Adar oilfield, also known as the Adar Yale, Adar Yeil or Adaril field, is an oilfield situated in the Melut Basin in South Sudan estimated to contain about 276 million of oil.

1.2.2. **Melut oil field**

The Melut Basin in South Sudan is shaping up to be one of the major sources of crude oil in Africa. The basin is located about 700 miles south of Khartoum east of the river Nile and despite the political difficulties in the area, the development has continued with a number of companies actively participating in the construction of marine export terminal facilities for the project, of 1380 km of export pipeline constructed in 4 segments (A1, A2, B1 and B2) or in the construction of the six pumping stations for the pipeline. At the moment, one of the latest projects include the design and construction of new field processing facilities for a supplementary oil field at Moleeta, which is expected to increase the Sudanese oil production by over 50,000 bpd. Most of the proven reserves of crude oil and natural gas of Sudan and South Sudan are located in the Muglad and Melut basins, which extend into both countries. According to the BP (2013) Statistical Review of World Energy, South Sudan has approximately 3.5 billion barrels of proven reserves, while those of Sudan are put at 1.5 billion barrels.

1.2.3. **Palogue oil field**

The Palogue oil field is an oil field located in Melut Basin. It was discovered in 2003 and developed by China National Petroleum Corporation. It began production in 2003 and produces oil. The total proven reserves of the Palogue oil field are around 2.9 billion barrels and production is centered around 22,000 barrels per day.

1.3. Chemical and Physical Properties of Crude Oils

Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, nonvolatile compounds. The hydrocarbon structures found in oil include saturates, aromatics, and polar compounds that include resins and asphaltenes. The resins and asphaltenes are largely recalcitrant in the environment. They evaporate, dissolve, and degrade poorly and thus may accumulate as residues after a spill. Fig.(1)

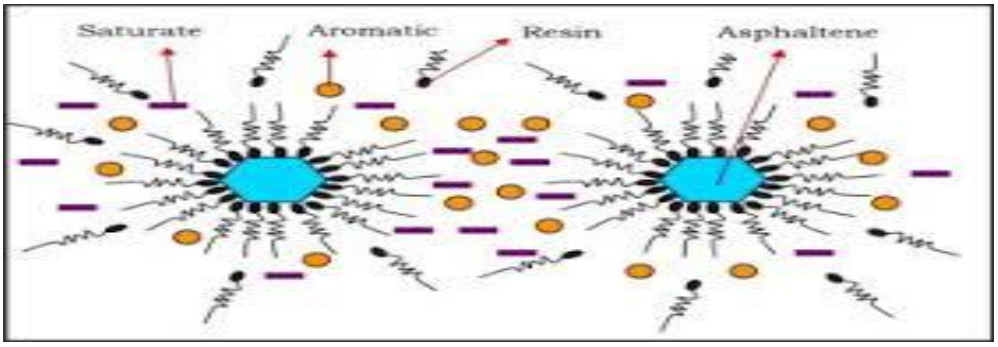


Fig.(1) SARA fractions

The distinct physical and chemical properties of diluted bitumen arise from two components: the bitumen provides the high-molecular-weight components that contribute most to density, viscosity, and adhesion; and the diluent contributes the low-molecular-weight compounds that confer volatility and flammability, and that determine the rate at which evaporation increases the density of the residual oil.

Because diluted bitumen has higher concentrations of resins and asphaltenes than most crude oils, spills of diluted bitumen products will produce relatively larger volumes of persistent residues. Such residues may be produced relatively rapidly when gas condensate has been used as the diluent, and these weathered residues display striking differences in behavior compared to other oils: exceptionally high levels of adhesion, density, and viscosity.(Hollebone, B, 2015)

Contrasts between diluted bitumen and other crude oils are strongly enhanced by weathering. Weathered heavy crude and especially weathered diluted bitumen are, for example, much more adhesive than the other oils. The densities of the oils also vary, with weathered heavy oils approaching the density of fresh water and weathered diluted bitumen possibly exceeding the density of fresh water.

Crude oil derives, by way of geological processing, from organic material initially buried in sediments at the bottom of ancient lakes and oceans. Crude oil formed at depth in a sedimentary basin migrates upward because of lower density. Many such migrations end with the oil collecting beneath a layer of impermeable rock, also referred to as a “trap,” and forming a reservoir that can be tapped by drilling.

If the oil approaches the surface, it cools and comes in contact with groundwater. At the oil-water interface, anaerobic microorganisms degrade the oil in the absence of oxygen. The progressive loss of metabolizable molecules from the oil leads to an increase in viscosity and eventually results in a tarry residue that clogs the pores of the strata through which the oil had been migrating. Over a long duration and with adequate sources of oil from below, enormous deposits of biodegraded oil residue

can accumulate. This sequence is how the Alberta oil sands (Adams, J.;et.al, 2013) and other oil-sand deposits were formed.

Bitumen is separated from the host rock or sand by heating, which reduces its viscosity so that it can flow to a collection point. Once collected, it is mixed with a diluent so that its viscosity is low enough to allow transport in a transmission pipeline. Such mixtures are called diluted bitumen.

Diluted bitumen are engineered to resemble other crude oils that are transported via pipeline and processed in the same refineries. The composition of diluted bitumen is dependent on several factors, particularly the diluent or diluents chosen and the diluent-to-bitumen ratio. As a result, diluted bitumen has dimensions of variability significantly exceeding those of crude oil from a given source region. (Adams, J.; ,et.al, 2013)

1.3.1. Saturated Hydrocarbons

Under the anaerobic conditions prevailing during formation of the oil sands, the saturated hydrocarbons are mostly biodegradable, the aromatic hydrocarbons much less so, and the resins and asphaltenes not at all. A heavy crude, or the bitumen from an oil sand, is composed of the residue from a very protracted process whereby microbial action consumes most of the metabolizable saturates.

The saturated hydrocarbon fraction in diluted bitumen thus differs from that in other crude oils because the readily metabolizable molecules are missing. This is seen most dramatically in chemical analyses that reveal the distribution of individual compounds in the crude oil. The diluted bitumen, in contrast, is dominated by a hump representing the profusion of branched and cyclic hydrocarbons that are more resistant to biodegradation. These are so numerous and varied that their peaks overlap

and they cannot be resolved by this gas chromatographic analysis. The diluted bitumen has a small series of peaks indicating the presence of some straight-chain hydrocarbons that derive from the diluent.

1.3.2. Aromatic Hydrocarbons

Crude oils contain aromatic hydrocarbons possessing one or more aromatic rings. Those with more than one ring are commonly referred to as polycyclic aromatic hydrocarbons (PAHs). The one-ring compounds are most abundant and are referred to collectively as BTEX, an acronym based on the chemical names of benzene, toluene, ethyl benzene, and xylenes. The most common aromatic hydrocarbons with two rings are naphthalenes. Other commonly measured groups include the three-ring phenanthrenes, dibenzothiophenes, and fluorenes and also the four-ring chrysenes.

The napthalenes and the even larger phenanthrenes are progressively less volatile and soluble compared to BTEX. PAHs are present as unsubstituted or parent forms but the vast majority are alkyl substituted PAHs. The aromatic hydrocarbons are of interest because of their toxicity.

1.3.3. Resins and Asphaltenes

The resins and asphaltenes characteristic of heavy crudes and diluted bitumen can precipitate from the oil as black sludge and cause numerous problems: clogging well bores, pipelines, and apparatus. (Yang, C.; et al., 2014) Moreover, refining costs increase with the abundances of resins and asphaltenes. (Yang, C.; et al., 2014) For all of those reasons, light and medium crudes have been favored. With increasing pressure on supplies, and with continued improvements in refining processes, heavy crude oils have come into broader use, the content of resins and asphaltenes in light and medium crude oils is very much lower than that in heavy crude oils, and lower still than that in diluted bitumen.

The resins and asphaltenes have presented major challenges to chemical analysts. (Yang, C.; et al., 2014) The range of structures and the tendency of the molecules to cluster in larger, multimolecular aggregates make it difficult to determine even rudimentary properties like molecular weight. It has been shown only recently (McKenna, A. M; et al., 2013) that most individual molecules in the heavy residues have from 30 to 70 carbon atoms. They comprise a complex mixture of polycyclic molecular structures in that range. These molecules tend to stick together, not only in bulk (the property that makes asphalt an attractive paving material) but even at the low concentrations prevailing when samples are injected into analytical instruments. The resulting "nanoaggregates" have masses two to five times higher than those of the molecules of which they are composed. The apparent molecular weights are accordingly higher than the true molecular weights. Heteroatoms (mainly nitrogen, sulfur, and oxygen) and metals (mainly nickel, vanadium, and iron) are also present in higher relative abundances in the resin and asphaltene fractions than in the saturate fraction. As a result, the heteroatom content of bitumen is higher than that of other crude oils.

1.3.4. Chemical Composition of Diluents

The density and viscosity of raw bitumen are too great to allow transportation by transmission oil pipeline without heating or alteration of the material. To reduce the viscosity and density, a diluent must be added to bitumen to produce an engineered mixture with a density of less than 0.94 g/cm^3 and a viscosity of less than 350 cSt. Additional industry-standard specifications that are largely a function of the operating temperature of the pipeline vary seasonally. Diluents alone do not confer unique chemical or toxicological properties to diluted bitumen; all crude oils contain similar, light end components. The compositions of diluents,

however, can strongly affect the weathering behavior of diluted bitumen, chiefly because the evaporation of a highly volatile diluent will more readily produce a heavy residue.

The individual selection of diluents varies depending on the desired outcome, the current cost of acquiring and transporting the diluent to the bitumen source, and other internal considerations of pipeline operators. Specific information about the diluents used is typically not publicly available. In general, diluents used fall into two broad categories: naturally occurring mixtures of light hydrocarbons, synthetic crude oil, or both.

Synthetic crude oil is produced by upgrading bitumen to reduce its density and viscosity for transport by pipeline. When mixed with bitumen to obtain the required viscosity and density, synthetic crude oils yield a product that can be handled efficiently and economically by conventional heavy oil refineries. A drawback is that supplies of synthetic crudes are limited by the availability of upgraders at the source of extraction and that roughly a 50:50 mixture of bitumen with synthetic crude oil is required to obtain the desired density and viscosity.

The alternative, and more commonly used, diluents are naturally occurring mixtures of light hydrocarbons. These light hydrocarbons are acquired from two sources: ultralight crude oils and gas condensates. Gas condensates are produced by separating most of the C_3 and all of the C_4 and higher hydrocarbons from natural gas. Because the ultralight crudes and gas condensates are less dense and less viscous than synthetic crude oil, diluent-to-bitumen ratios are roughly 30:70. The particular mixture of light hydrocarbons in the diluent can be important in spill response. If the diluent is dominated by lighter compounds (C_4-C_8), it can evaporate more readily in the event of a spill, yielding a dense and viscous residue that must be accounted for in response.

1.4. What are asphaltenes in petroleum, oilsands, and heavy oil?

Definition

Asphaltenes are present in most petroleum materials, and in all heavy oils and bitumens from oilsands. This material is defined by solubility: the components that dissolve in toluene and precipitate in nalkane solvents are the asphaltenes. For analytical purposes, the concentration of asphaltene in a crude oil is defined by precipitation with either n-pentane (C5) or n-heptane (C7). (Mostowfi, F.; et al, 2009) The concentration of C7-asphaltene in a very low density crude oil may be only a fraction of 1%, while the concentration in a dense bitumen can be can be over 20% of the total mass. The low solubility of the asphaltene fraction makes it very important in production and processing of petroleum. In comparison to a whole petroleum or bitumen, the asphaltenes have lower hydrogen content (4.8-8%), and a higher content of sulfur, nitrogen, nickel, vanadium, and oxygen. The low concentration of hydrogen gives a high density of 1100-1200 kg/m3, compared to circa 1000 kg/m3 for bitumen and <1000 kg/m3 for heavy oil and other petroleums. Molecular composition The separation of asphaltenes by precipitation gives a complex mixture of components, enriched in the least soluble components of petroleum and the components that aggregate together the most strongly. Due to the aggregation of the asphaltenes, complete molecular analysis by methods such as mass spectrometry has not yet been achieved. Pyrolysis (thermal cracking in inert gas) of asphaltenes demonstrates a complex range of attached pendant groups, including 1-3 ring aromatics and cycloalkanes1-5. The asphaltenes are rich in ring groups, not straight chains, with a size of ring groups ranging from 1-7 rings in a single cluster. Bridges between

these clusters give larger molecules and extreme diversity of composition.(Liao, Z. W, 2009)

Representative asphaltene molecules

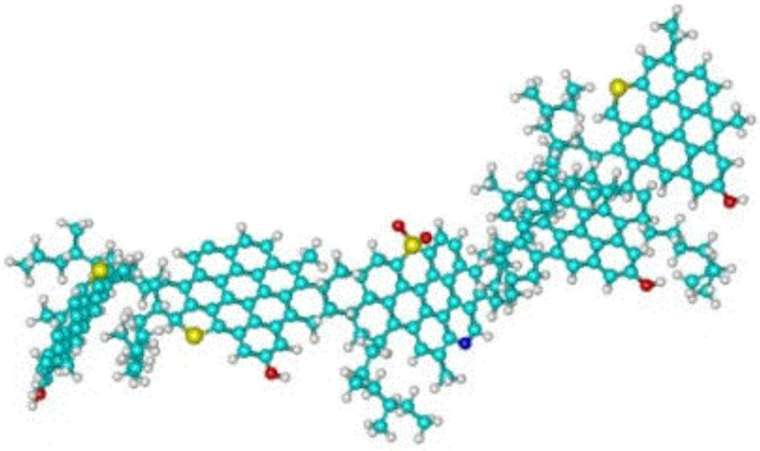


Fig. (2) Hypothetical Asphaltene

For any complex mixture we need to consider three aspects of this question; what is the largest size, what is the smallest size, and what is the average of the population? Depending on the method that we use to determine molecular size, or molecular weight, the data may be biased toward one end or the other of the distribution. Asphaltene components tend to associate with each other; therefore, these measurements can also be systematically biased too high. The maximum and minimum sizes are both constrained by solubility. (Payzant, J. D.; et al, 1991) The least soluble large aromatic clusters will give the smallest asphaltenes, with molar masses in the range of 400-500 Da (i.e. molecular weight). The largest possible molar mass will depend on the geological processes that form petroleum, and on solubility in the original petroleum liquid. Direct evidence is lacking, but many researchers believe that the upper bound is in the range of 2000-3000 Da. Due to molecular aggregation, all methods

of measuring the average molar mass suffer from undefined biases and errors. Aggregation of asphaltene components A variety of experimental measurements show that asphaltene components aggregate to form clusters or nanoparticles over a wide range of concentration and temperature, both in petroleum and in solvents such as toluene. (Karimi, A.; et al, 2011) Many of the aggregates dissociate as the concentration is decreased6, or as the temperature is increased7, but to date the complete de-aggregation of natural asphaltene has not been verified. A range of analytical techniques put the mean aggregate size in the range of 2–20 nm6, 8-12. Several molecular interactions can contribute to the formation of very stable aggregates or clusters of molecules:

I. Acid-base interactions
II. Hydrogen bonding
III. Coordination complexes of metals such as vanadium
IV. The association of apolar, cycloalkyl and alkyl groups in hydrophobic pockets
V. Aromatic or π-π stacking

Each of these interactions is relatively weak in isolation, but like Velcro, the combination of multiple weak links gives a strongly associated structures. (Dechaine, G. P.; Gray, M. R., 2011)

1.5. Wax in crude oil

Waxes present in crude oil are considered to be responsible for its poor flow properties. Bombay 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 Bombay high crude have been determined. The hard wax components present in the crude do not appear to significantly influence the low temperature rheology of the crude oil, but do contribute to sludge formation. (K.M.Agarwal;et al,1989)

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..(A. MajhiY. K., 2015)

Paraffin wax produced from crude oil consists primarily of long chain, saturated hydrocarbons (linear alkanes/ *n*-paraffins) with carbon chain lengths of C18 to C75+, having individual melting points from 40 to 70°C. This wax material is referred to as “macrocrystalline wax.” Naphthenic hydrocarbons (C18 to C36) also deposit wax, which is referred to as “microcrystalline wax.” Macrocrystalline waxes lead to paraffin problems in production and transport operations; microcrystalline waxes contribute the most to tank-bottom sludges. (Garcia, et al, 1998) **Fig 3** shows the generic molecular structures of n-paraffins, iso-paraffins, and naphthenes. The n-heptane structure is an example of a “normal” paraffin; 2-methyloctane is an “iso” paraffin and n-butylcyclopentane is a naphthene. These specific n-paraffins and naphthenes are too small to crystallize as wax deposits (i.e., outside the carbon-number range specified above). The drawings illustrate the type of structures involved.

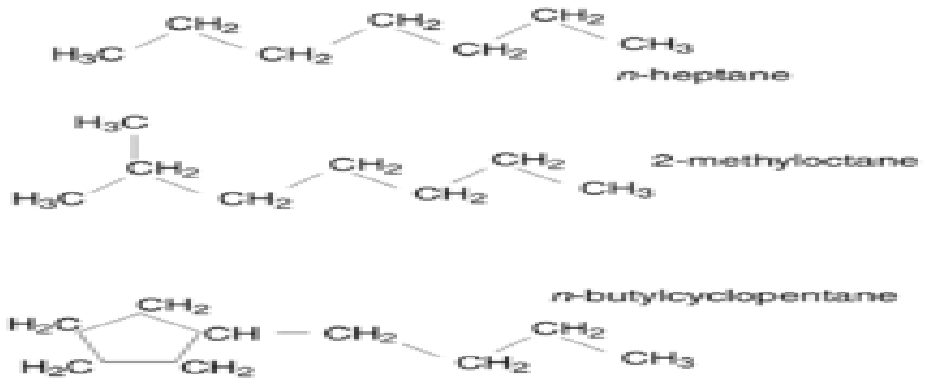


Fig. (3) Structures of hydrocarbon classes involved in wax deposition.

Waxes isolated from crudes can contain various amounts of all classes: n-paraffins, naphthenes, and iso-paraffins. For example, waxes derived from several Venezuelan crudes (Garcia, et al, 1998) showed n -paraffin/(cyclo + iso paraffin) ratios ranging from 1.28 to 0.23. The iso-paraffins of the 2-methyloctane type (**Fig. 3**) are more likely to be included in a wax deposit than the more highly branched alkanes.

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.

1.5.1. Solvent dewaxing:

Wax deposition is one of the chronic problems in the petroleum industry. The various crude oils present in the world contain wax contents of up to 32.5%. Paraffin waxes consist of straight chain saturated hydrocarbons with carbons atoms ranging from C18 to C36. Paraffin wax consists mostly with normal paraffin content (80–90%), while, the rest consists of branched paraffins (iso-paraffins) and cycloparaffins. The sources of higher molecular weight waxes in oils have not yet been proven and are under

exploration. Waxes may precipitate as the temperature decreases and a solid phase may arise due to their low solubility. For instance, paraffinic waxes can precipitate out when temperature decreases during oil production, transportation through pipelines, and oil storage. The process of solvent dewaxing is used to remove wax from either distillate or residual feedstocks at any stage in the refining process. The solvents used, methyl-ethyl ketone and toluene, can then be separated from dewaxed oil filtrate stream by membrane process and recycled back to be used again in solvent dewaxing process.(Mohamed rehan;et al, 2016)

1.5.2. Wax deposition

Wax deposition is one of the serious problem in oil industry. It has got a crucial attention to overcome this issue in more hostile environment in new oil fields exploration especially in deep water. Waxes, that are known as mostly heavy saturated paraffins, tend to precipitate when the temperature and pressure of oil fields drop during the production and transportation. Wax Appearance Temperature (WAT) determines the deposition of the wax on the reservoir or pipelines when the temperature of the reservoir or production line falls below the WAT. WAT is regularly used to measure the tendency of a crude oil to produce wax in relation with pressure and temperature reduction. In simple words, WAT is the temperature at which the first wax crystal appears. Wax deposition will be complex and costly. It will cause a lot of difficulties in blocking of transport equipments and pipelines. If not treated, well can eventually decrease or in worst condition block the flow in production line or even in well (Sanjay *et al.*, 1995; Merino-Garcia and Correra, 2008; Al-Yaari, 2011; Taraneh *et al.*, 2008; Alghanduri *et al.*, 2010; Zhu *et al.*, 2008; Elsharkawy *et al.*, 2000; Aiyejina *et al.*, 2011).

As the temperature of the crude drops below a critical level and/or as the low-molecular-weight hydrocarbons vaporize, the dissolved waxes begin to form insoluble crystals. The deposition process involves two distinct stages: nucleation and growth. Nucleation is the forming of paraffin clusters of a critical size ("nuclei") that are stable in the hydrocarbon fluid. This insoluble wax itself tends to disperse in the crude.

Wax deposition onto the production system ("growth") generally requires a "nucleating agent," such as asphaltenes and inorganic solids. The wax deposits vary in consistency from a soft mush to a hard, brittle material. Paraffin deposits will be harder, if longer-chain n-paraffins are present. Paraffin deposits can also contain: (Allen, et a,1982)

- Asphaltenes
- Resins
- Gums
- Fine sand
- Silt
- Clays
- Salt
- Water

High-molecular-weight waxes tend to deposit in the higher-temperature sections of a well, while lower-molecular-weight fractions tend to deposit in lower-temperature regions. Prior to solidification, the solid wax crystals in the liquid oil change the flow properties from a Newtonian low viscosity fluid to a very-complex-flow behavior gel with a yield stress. In order to overcome wax deposition problem, the better understanding of the physical characterization of crude oil is necessary. Viscosity, density and pour point are properties that ascertain handling characteristics of crude oils. In this

study, crude oils from Malaysian oil fields are studied to determine their wax formation tendency for flow assurance purposes. For this study, density, viscosity and pour point of all crude oils is measured by digital den-sity meter (DMA 4500 M), advanced AR-G2 rheometer and D-97 ASTM methods, respectively. Result showed that there is linear trend between density and temperature. In general, wax precipitation and deposition has direct relationship with wax content of crude oil. Moreover, the shear rate has considerable effect on viscosity reduction. Temperature reduction causes viscosity to increase. However, it is against shear rate that tends to lower it. (Andhy Arya Ekaputra; et al, 2014)

1.5.3. Coping with waxes

The primary chemical parameter to establish is the critical temperature at which these wax nuclei form—the wax appearance temperature (WAT). The WAT (or "cloud point") is highly specific to each crude. The WAT value is a function of. (Hammami, 1997)

- Oil composition
- Cooling rate during measurement
- Pressure
- Paraffin concentration
- Molecular mass of paraffin molecules
- Occurrence of nucleating materials such as asphaltenes, formation fines, and corrosion products
- Water/oil ratio
- Shear environment

A variety of experimental methods have been used to obtain this number. Among these are:

- Differential scanning calorimetry (DSC) - measures the heat released by wax crystallization
- Cross polarization microscopy (CPM) - exploits the fact that insoluble wax crystals rotate polarized light, but liquid hydrocarbons do not
- Filter plugging (FP) - measures the increase in differential pressure across a filter, which can be attributed to wax-crystal formation
- Fourier transform infrared energy scattering (FTIR) - detects the cloud point by measuring the increase in energy scattering associated with wax solidification

Each of these techniques has its advantages and disadvantages. A comparison/review of these methods is found in Monger-McClure, et al. (Monger-McClure, 1997) In testing, cloud points, measured by each of the four methods, agreed with the average value of all methods within 3 to 5°F.

Of more importance, is how well laboratory-measured cloud points anticipate WATs found in the field. Measured cloud-point data should only match field results for wells producing at low shear (high shear rates tend to delay the deposition of waxes). Another inherent problem is that the cloud-point measurement sees the precipitation of the most insoluble paraffin, not the mass of lower-molecular-weight paraffins that might contribute the major amount of wax deposit. Nevertheless, CPM measurements have been found to correlate well with the temperature at field deposition, more so than optical techniques that required a greater mass of wax to register a signal.[3] A major problem in correlating these measurements and simulations with field experience is the acquisition of good field data. (Monger-McClure, 1997) Illustrative of the state of the art in interpreting these measurements is that closer agreement is found

between stock-tank oil measurements and field experience, even though it is live oil that is being produced.

An alternative to the measurement of cloud point is its prediction from compositional data by thermodynamic models. These models can predict cloud point as the temperature at which the first infinitesimal amount of wax appears, as well as predicting that mass of wax precipitating out of solution that, from experience, corresponds to field deposition. (Calang, et al, 1997) Models that use detailed n-paraffin composition input data, as obtained from high-pressure gas chromatography, generally outperform models based on less specific information like compositions to C7+ [the numbers are more generally available in the routine pressure/volume/temperature (PVT) reports].

1.5.4. Paraffin deposition models

Given the cloud point, what is the propensity for wax precipitation during the production and, in particular, the pipelining and processing of the crude? This is the regime of "paraffin deposition models." These are engineering simulators used to predict wax buildup in flowing systems, (Brill, J. 1997) taking into account such parameters as:

- Heat transfer
- Phase behavior of the crude
- Flow regime
- Wax deposition kinetics
- Shear rate
- Diffusivity
- Wall conditions (roughness, coatings, scale)
- Produced-water/oil ratio

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.*, 2004).

In the Bahian Recôncavo 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).

Paraffins are both linear (n-paraffins) and branched (iso-paraffins) chain alkanes, and they have low reactivity with most compounds. Their chains can have a high carbon number, which implies a higher wax appearance temperature. The low-molecular-weight paraffins are the main components of natural gas, and the medium- and high-molecular-weight ones are found in crude oil (Farayola *et al.*, 2010; Gao, 2008; Jamaluddin *et al.*, 2001).

Paraffins are in equilibrium with other crude oil components, and any change in pressure, temperature and even composition can affect the equilibrium, thereby influencing the formation of precipitate. According to Santos (1994), the greater the crude oil wax content, the greater the precipitation rate and, therefore, the amount of precipitated wax. The light oil components keep the waxes soluble. The high pressure of the reservoirs maintains the light compounds solubilized in the crude oil, which favors the solubilization of waxes in the fluid (Tinsley; Prud'Homme, 2010). This

condition ensures low viscosity and Newtonian behavior of the crude oil (Azevedo, 2003).

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 (Venkatesan *et al*., 2005; Gao, 2008).

According to Vieira (2008), the first paraffin crystals start to form at a specific temperature, which is called the wax appearance temperature (WAT) and varies depending on the origin of the crude oil. Crystallization occurs in three steps:

- Nucleation - formation of small particles of crystallized material from which the first paraffin crystals will grow.
- Growth - mass transport of the solution towards the nuclei formed during the nucleation stage.
- Agglomeration - when the growing crystals are joined together, thereby yielding larger crystals.

With the nuclei already formed, there is incorporation of new paraffin molecules at the growth sites, and additional molecules of other species are

grouped at these sites and become part of the structure. The nuclei form an ordered lamellar-structure arrangement.

After crystallization starts in a medium that contains water as an emulsion, the crystal lattice formation phenomenon occurs in a different manner. When the emulsion is of the water-in-oil type, the oil is waxy and the fluid temperature is below the WAT, the precipitated waxes are deposited onto the surface of the water drops, thereby contributing to the growth of the formed precipitate (Oliveira *et al.*, 2010). When a large crystal lattice is in the vicinity of the water drops, a structure is formed; this structure percolates the drops into the lattice and captures them. According to Visitin (2008), this structure also provides mechanical resistance to the flow, thereby resulting in an increase in the viscosity and pour point of the oil.

1.5.5. Prevention/inhibition

As with other solids-depositing problems, prevention can be more cost effective than removal. One key to wax-deposition prevention is heat. Electric heaters can be employed to raise the crude oil temperature as it enters the wellbore. The limitations are the maintenance costs of the heating system and the availability of electrical power. As with hydrates, maintaining a sufficiently high production level may also keep the upper-wellbore temperature above the WAT. In addition, high flow rates tend to minimize wax adherence to metal surfaces because of the shearing action of the flowing fluid. Insulated pipelines are also an alternative to minimize, if not eliminate, the problem, but the cost can be prohibitive for long pipelines.

Wax deposition can be prevented, delayed, or minimized by the use of dispersants or crystal modifiers. As with asphaltenes, paraffin-wax

characteristics vary from well to well. Chemicals that are effective in one system are not always successful in others, even for wells within the same reservoir. “For this reason it is of fundamental importance to establish a good correlation between oil composition and paraffin inhibitors efficiency, leading to an adequate product selection for each particular case, avoiding extremely expensive and inefficient ‘trial-and-error’ procedures.” (Garcia, et al,1998)

1.5.6. Crystal modifiers

Paraffin-crystal modifiers are chemicals that interact with the growing crude-oil waxes by cocrystallizing with the native paraffin waxes in the crude oil that is being treated. These interactions result in the deformation of the crystal morphology of the crude-oil wax. Once deformed, these crystals cannot undergo the normal series of aggregation steps. Types of paraffin-crystal modifiers include:

- Maleic acid esters
- Polymeric acrylate and methacrylate esters
- Ethylene vinyl acetate polymers and copolymers

1.5.7. Dispersants

Dispersants act to keep the wax nuclei from agglomerating. Dispersants are generally surfactants and may also keep the pipe surface water wet, minimizing the tendency of the wax to adhere. Some water production is required, of course. High levels of water alone may maintain the system in a water-wet state. As with scale prevention, a smooth surface tends to decrease wax adherence. However, the operational problem is to maintain such a surface for an extended period of time. Various forms of erosion are highly detrimental.

Obviously, these inhibitors must be delivered into the crude oil at temperatures above the WAT. This need not cause a problem for surface equipment, but it could cause a problem for wellbore treatment, if the bottomhole temperatures are low.

1.5.8. Removal of deposits

Removal of wax deposits within a wellbore is accomplished by:

- Cutting
- Drilling
- Chemical dissolution
- Melting—the use of hot oil, hot water, or steam

Of these, the use of hot oil has been the most popular, normally pumped down the casing and up the tubular. It is intended that the high temperature of the liquid phase heat and melt the wax, which then dissolves in the oil phase. Using the bottom-up delivery approach, hot oil first reaches those waxes most difficult to melt. The higher in the tubular the hot oil proceeds, the lower its temperature becomes, thereby reducing its wax-carrying capacity. Hot oiling can cause permeability damage, if the fluid containing the melted wax enters the formation. (Allen, et al, 1982)

Hot water, hot-water/surfactant combinations, and steam are alternatives to hot oiling. Plain hot-water treatments do not provide the solvency required to remove the wax, hence the use of surfactants to disperse the wax. The advantage of water is its greater heat capacity.

Chemical generation of heat has also been proposed as a method of melting wax deposits. One field-tested scheme uses the thermo-chemical process of reacting two specific nitrogen salt solutions, acidic ammonium chloride

and sodium nitrite (Khalil, et al, 1997) an orgainc solvent is included to keep the wax in solution after the system has cooled.

Various aromatic solvents can be used to dissolve the wax. These are generally not heated, relying solely on the solvency properties of the fluid. As with asphaltene dissolution, o-xylene has been one of the more effective solvents for waxes. Kerosene and diesel tend to be poor solvents. However, as with asphaltenes dissolution, one solvent does not necessarily work equally well on all wax deposits; an example of solvent screening procedures is given in Ferworn, et al.(1997)

Pigging is the primary mechanical method of removing wax buildup from the internal walls of pipelines. The pig cuts the wax from the pipe walls; a bypass can be set with a variable-flow pass, allowing the pig to prevent wax buildup in front. Pig sizing can vary, and multiple pig runs with pigs of increasing size can be used. For subsea pigging, a looped flow-line is required or a subsea pig launcher for a single flow-line. The major uncertainty in this operation is the wax hardness as it is formed in the pipeline.

Coiled tubing with the appropriate cutters at the end also can be used for wax removal—the drawback for pipeline cleaning being the limited reach of the coiled tubing. For wellbore cleaning this is obviously less of a problem.

1.6. **Oil emulsions**

Crude oils are typically water in crude oil (w/o) emulsions, which are often very stable. Among the indigenous natural surfactants contained in the crude oils, asphaltenes and resins are known to play an important role in the formation and stability of w/o emulsions. Asphaltenes are defined as

the fraction of the crude oil precipitating in pentane, hexane, or heptane, but soluble in toluene or benzene.(Manar, 2012) The presence of emulsions in the crude oil will reduce the quality of the crude itself, increase the operating cost due to emulsions separation as well as cause of corrosion to the transport system and will contaminate catalyst used for the refining process. Since emulsions bring numerous disadvantages to the oil and gas industry, it is important to review on the formation of emulsions. (S.F.Wong; et al, 2015).

Crude oil is seldom produced alone because it generally is commingled with water. The water creates several problems and usually increases the unit cost of oil production. The produced water must be:

- Separated from the oil
- Treated
- Disposed of properly

All these steps increase costs. Furthermore, crude oil must comply with certain product specifications for sale, including the amount of basic sediment and water (BS&W) and salt, which means that the produced water must be separated from the oil to meet crude specifications.

Produced water may be produced as "free" water (i.e., water that will settle out fairly rapidly), and it may be produced in the form of an emulsion. A regular oilfield emulsion is a dispersion of water droplets in oil. Emulsions can be difficult to treat and may cause several operational problems in wet-crude handling facilities and gas/oil separating plants. Emulsions can create high-pressure drops in flow lines, lead to an increase in demulsifier use, and sometimes cause trips or upsets in wet-crude handling facilities. The problem is usually at its worst during the winter because of lower

surface temperatures. These emulsions must be treated to remove the dispersed water and associated inorganic salts to meet crude specifications for transportation, storage, and export and to reduce corrosion and catalyst poisoning in downstream processing facilities.

Emulsions occur in almost all phases of oil production and processing: inside reservoirs, wellbores, and wellheads; at wet-crude handling facilities and gas/oil separation plants; and during transportation through pipelines, crude storage, and petroleum processing.

Crude oils vary considerably in emulsifying tendency. Some form very stable emulsions that are difficult to separate. Others do not emulsify or form loose emulsions that separate quickly. In an untreated emulsion, the density difference between the oil and the water will cause a certain amount of water to separate from the oil by natural coalescence and settling; however, unless some form of treatment is used to accomplish complete separation, a small percentage of water probably will remain in the oil, even after extended settling. The remaining water will be in minute droplets that have extremely low settling velocities. These droplets also will be widely dispersed, so that they have little chance to collide, coalesce into larger droplets, and settle.

The amount of water that emulsifies with crude oil in most production systems can vary widely, ranging from < 1 to > 60 vol% (in rare cases). The most common range of emulsified water in light crude oils (i.e., above 20°API) is from 5 to 20 vol%, and in crude oils that are heavier than 20°API is from 10 to 35 vol%.

1.6.1. Types of emulsions

Produced oilfield emulsions can be classified into three broad groups:

- Water-in-oil
- Oil-in-water
- Multiple or complex emulsions

Water-in-oil emulsions consist of water droplets in a continuous oil phase, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. **Figs. 4 and 5** show the two basic (water-in-oil and oil-in-water) types of emulsions. In the oil industry, water-in-oil emulsions are more common (most produced oilfield emulsions are of this kind); therefore, the oil-in-water emulsions are sometimes referred to as "reverse" emulsions.

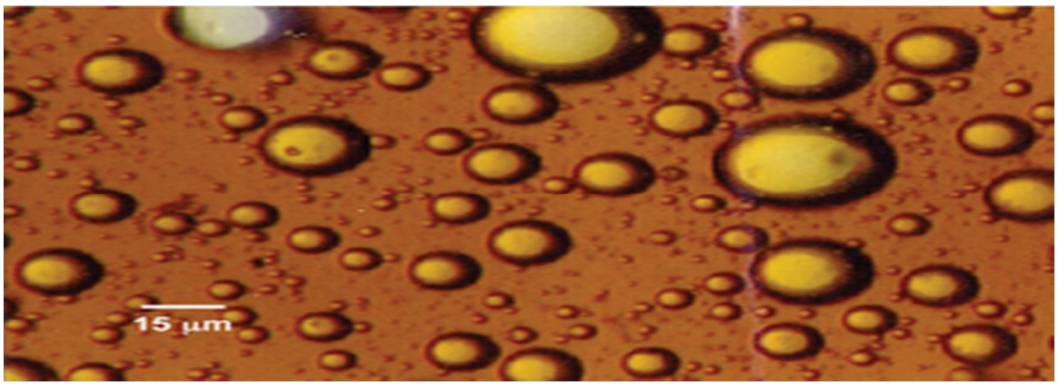
- 

Fig. (4) Photomicrograph of a water-in-oil emulsion.

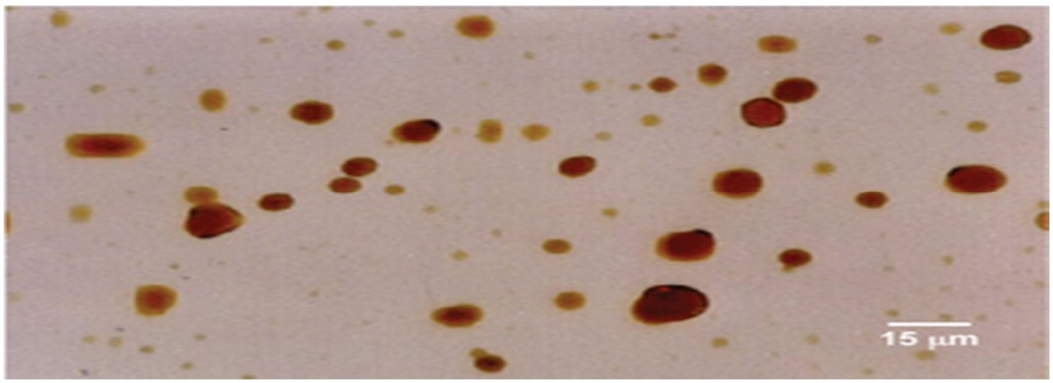
- 

Fig. (5) Photomicrograph of an oil-in-water emulsion.

Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water emulsion consists of water droplets suspended in larger oil droplets that, in turn, are suspended in a continuous water phase. **Fig. 5** shows an example of a multiple emulsion.

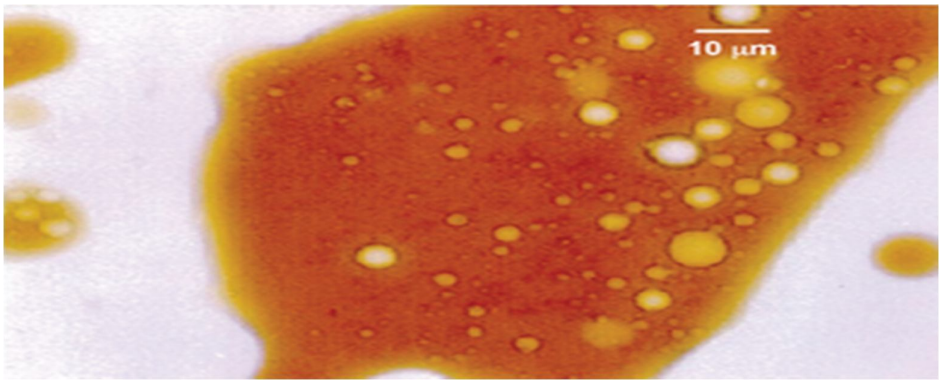


Fig. (6) Photomicrograph of a water-in-oil-in-water emulsion.

Given the oil and water phases, the type of emulsion formed depends on several factors. As a rule of thumb, when the volume fraction of one phase is very small compared with the other, the phase that has the smaller fraction is the dispersed phase and the other is the continuous phase. When the volume-phase ratio is close to 1 (a 50:50 ratio), then other factors determine the type of emulsion formed.

Emulsions are also classified by the size of the droplets in the continuous phase. When the dispersed droplets are larger than 0.1 μm, the emulsion is a macroemulsion.(Manning, 1994) and (Becher;P, 1966) Emulsions of this kind are normally thermodynamically unstable (i.e., the two phases will separate over time because of a tendency for the emulsion to reduce its interfacial energy by coalescence and separation). However, droplet coalescence can be reduced or even eliminated through a stabilization mechanism. Most oilfield emulsions belong in this category. In contrast to

macroemulsions, there is a second class of emulsions known as microemulsions. These emulsions form spontaneously when two immiscible phases are brought together because of their extremely low interfacial energy. Microemulsions have very small droplet sizes, less than 10 nm, and are considered thermodynamically stable. Microemulsions are fundamentally different from macroemulsions in their formation and stability.

1.6.2. Emulsion characteristics

In a true emulsion, either the drop size must be small enough that forces from thermal collisions with molecules of the continuous phase produce Brownian motion that prevents settling, or the characteristics of the interfacial surfaces must be modified by surfactants, suspended solids, or another semisoluble material that renders the surface free energy low enough to preclude its acting as a driving force for coalescence.

An emulsion's characteristics change continually from the time of formation to the instant of complete resolution. Accordingly, aged emulsions can exhibit very different characteristics from those that fresh samples do. This is because any given oil contains many types of adsorbable materials and because the adsorption rate of the emulsifier and its persistence at the interface can vary. The emulsion characteristics also change when the liquid is subjected to changes in the following:

- Temperature
- Pressure
- Degree of agitation

1.6.3. Formation of emulsions

Crude oil emulsions form when oil and water (brine) come into contact with each other, when there is sufficient mixing, and when an emulsifying agent or emulsifier is present. The amount of mixing and the presence of emulsifier are critical for the formation of an emulsion. During crude oil production, there are several sources of mixing, often referred to as the amount of shear, including:

- Flow through reservoir rock
- Bottomhole perforations/pump
- Flow through tubing, flow lines, and production headers
- Valves, fittings, and chokes
- Surface equipment
- Gas bubbles released because of phase change

The amount of mixing depends on several factors and is difficult to avoid. In general, the greater the mixing, the smaller the droplets of water dispersed in the oil and the tighter the emulsion. Emulsion studies have shown that the water droplets can vary in size from less than 1 μm to more than 1000 μm.

The second factor important in emulsion formation is the presence of an emulsifier. The presence, amount, and nature of the emulsifier determines, to a large extent, the type and "tightness" of an emulsion. The natural emulsifiers in a crude are resident in the heavy fraction. Because there are different types of crudes and because these crudes have different amounts of heavy components, the emulsifying tendencies vary widely. Crude with a small amount of emulsifier forms a less stable emulsion and separates

relatively easily. Other crudes contain the right type and amount of emulsifier, which lead to very stable or tight emulsions.

1.6.4. Emulsifying agents

Produced oilfield water-in-oil emulsions contain oil, water, and an emulsifying agent. Emulsifiers stabilize emulsions and include surface-active agents and finely divided solids.

1.6.4.1. Surface-active agents

Surface-active agents (surfactants) are compounds that are partly soluble in both water and oil. They have a hydrophobic part that has an affinity for oil and a hydrophilic part that has an affinity for water. Because of this molecular structure, surfactants tend to concentrate at the oil/water interface, where they form interfacial films. This generally leads to a lowering of the interfacial tension (IFT) and promotes dispersion and emulsification of the droplets. Naturally occurring emulsifiers in the crude oil include higher boiling fractions, such as:

- Asphaltenes and resins
- Organic acids
- Bases

These compounds have been shown to be the main constituents of interfacial films that form around water droplets in many oilfield emulsions. The stabilizing effects of asphaltenes are discussed in Oil emulsions stability. Other surfactants that may be present are from the chemicals injected into the formation or wellbores, e.g.:

- Drilling fluids
- Stimulation chemicals

- Corrosion inhibitors
- Scale inhibitors
- Wax
- Asphaltene control agents

1.6.4.2. Finely divided solids

Fine solids can act as mechanical stabilizers. These particles, which must be much smaller than emulsion droplets (usually submicron), collect at the oil/water interface and are wetted by both oil and water. The effectiveness of these solids in stabilizing emulsions depends on factors such as (Schubert, H. and Armbroster, H. 1992):

- Particle size
- Interparticle interactions
- Wettability of the particles

Finely divided solids found in oil production include:

- Clay particles
- Sand
- Silt
- Asphaltenes and waxes
- Corrosion products
- Shale particles
- Mineral scales that collect at the oil/water interface
- Drilling muds

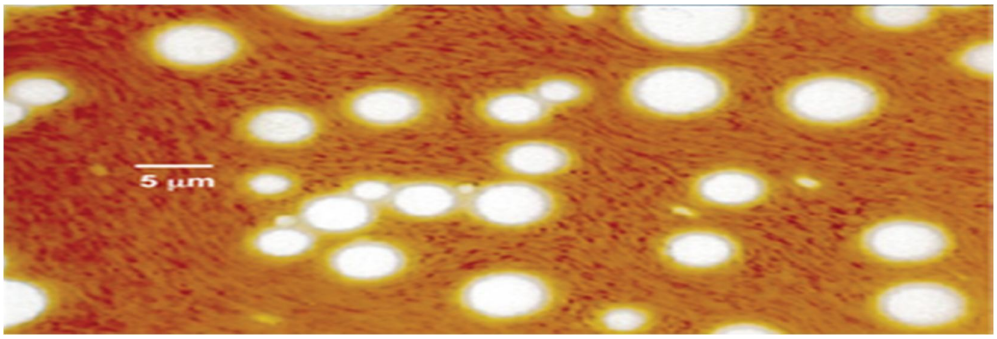
- 

Fig. (7) Photomicrograph of an emulsion showing the presence of solids.

1.7. Characteristics and physical properties

Oilfield emulsions are characterized by several properties including:

- Appearance and color
- BS&W
- Droplet size
- Bulk and interfacial viscosities

1.7.1. Appearance and color

Color and appearance is an easy way to characterize an emulsion. The characterization becomes somewhat easy if the emulsion is transferred into a conical glass centrifuge tube. The color of the emulsion can vary widely depending on:

- Oil/water content
- Characteristics of the oil and water

The common colors of emulsions are dark reddish brown, gray, or blackish brown; however, any color can occur depending on the type of oil and water at a particular facility. Emulsion brightness is sometimes used to

characterize an emulsion. An emulsion generally looks murky and opaque because of light scattering at the oil/water interface. When an emulsion has small diameter droplets (large surface area), it has a light color. When an emulsion has large diameter droplets (low total interfacial surface area), it generally looks dark and less bright. Understanding the characteristics of an emulsion by visual observation is an art that improves with experience.

1.7.2. Basic sediment and water

Basic sediment and water (BS&W) is the solids and aqueous portion of an emulsion. It is also referred to as BSW, bottom settlings and water, or bottom solids and water. Several methods are available to determine the amount of water and solids in emulsions. Standard methods have been proposed by several organizations including the (Becher,P.1966):

- Institute of Petroleum
- American Petroleum Institute
- American Society for Testing Materials

The most common technique for the determination of oil, water, and solids consists of:

1. Adding a slight overdose of a demulsifier to an emulsion
2. Centrifuging it
3. Allowing it to stand

The amount of solids and water separated is measured directly from specially designed centrifuge tubes. When only the water content is desired, Karl-Fischer titration can also be used. It is very accurate at low contents of water (<2%) but can also be used for determining higher

content (>10%). Other, less common methods are based on (Becher,P.1966):

- Electrical properties (conductance and dielectric constants)
- Gamma-ray attenuation
- Microwave-based meters

1.7.3. Droplet size and droplet-size distribution

Produced oilfield emulsions generally have droplet diameters that exceed 0.1 μm and may be larger than 100 μm. Emulsions normally have a droplet size range that can be represented by a distribution function. **Fig. 8** shows the drop-size distributions of typical petroleum emulsions. The droplet-size distribution in an emulsion depends on several factors including the:

- Interfacial tension (IFT)
- Shear
- Nature and amount of emulsifying agents
- Presence of solids
- Bulk properties of oil and water

Droplet-size distribution in an emulsion determines, to a certain extent, the stability of the emulsion and should be taken into consideration in the selection of optimum treatment protocols. As a rule of thumb, the smaller the average size of the dispersed water droplets, the tighter the emulsion and, therefore, the longer the residence time required in a separator, which implies larger separating plant equipment sizes. The photomicrographs in **Figs. 1** through **4** show the droplet-size distribution for several emulsions.

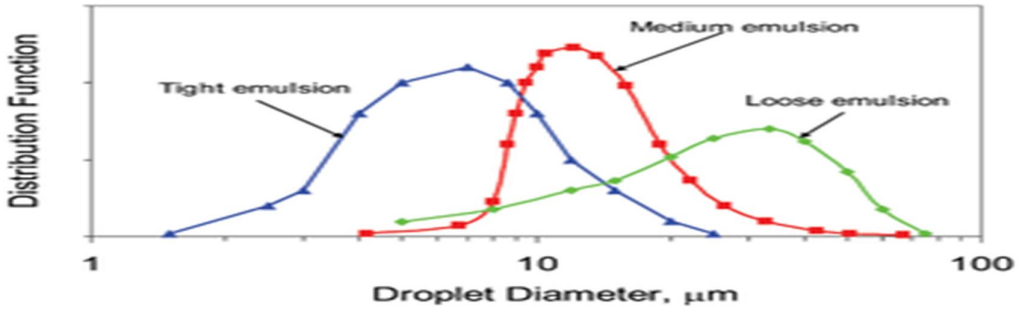


Fig. (8) Droplet-size distribution of petroleum emulsions.

The droplet-size distribution for oilfield emulsions is determined by the following methods.(Becher,P. 1966)

- Microscopy and image analysis. For example, the emulsion photomicrographs in **Figs. 1** through **4** can be digitized and the number of different-sized particles measured with image analysis software.
- By the use of electrical properties such as conductivity and dielectric constants.
- By the use of scattering techniques such as light scattering, neutron scattering, and X-ray scattering. These techniques cover droplet sizes from 0.4 nm to more than 100 µm.
- Physical separation including chromatographic techniques, sedimentation techniques, and field-flow fractionation.

1.7.4. Rheology

Viscosity of emulsions

Emulsion viscosity can be substantially greater than the viscosity of either the oil or the water because emulsions show non-Newtonian behavior. This behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate. At a certain volume fraction of the water phase (water cut), oilfield emulsions

behave as shear-thinning or pseudoplastic fluids (i.e., as shear rate increases, viscosity decreases).

Stabilization of the emulsion

There are many factors that usually favour emulsion stability such as low interfacial tension, high viscosity of the bulk phase and relatively small volumes of dispersed phase. A narrow droplet distribution of droplets with small sizes is also advantageous, since polydisperse dispersions will result in a growth of large droplets on the expense of smaller ones. The potent stabilization of the emulsion is achieved by stabilization of the interface (25- 27).

Interfacial viscosity

The previous discussion on viscosity was limited to bulk emulsion viscosity. A closely related and very important property, especially for demulsification, is the interfacial viscosity, or the viscosity of the fluid at the oil/water interface. As mentioned previously, water-in-oil emulsions form rigid interfacial films encapsulating the water droplets. These interfacial films stabilize an emulsion by lowering IFT and increasing interfacial viscosity. These films retard the rate of oil-film drainage during the coalescence of water droplets, thereby greatly reducing the rate of emulsion breakdown. The oil-drainage rate depends on the interfacial shear viscosity. High interfacial viscosities significantly slow the liquid drainage rate and thus have a stabilizing effect on the emulsion. Emulsion interfacial viscosity plays a very important role in demulsification. (I.B. Ivanov ed. 1988)(Mohamed,R.A; et al, 1994)

1.7.5. WEATHERING AND ITS EFFECTS ON PHYSICAL PROPERTIES

The behavior of a crude oil or diluted bitumen released into the environment is shaped not only by its chemical composition but also by its physical properties. Those of particular interest are density, viscosity, flash point, and adhesion. Oil spilled into the environment undergoes a series of physical and chemical changes that in combination are termed weathering. Weathering processes occur at different rates, but they begin as soon as oil is spilled and usually proceed most rapidly immediately after the spill. Most weathering processes are highly temperature dependent and will slow to insignificant rates as temperatures approach freezing.

The most important weathering process is evaporation, (National Research Council, 2003) which accounts for the greatest losses of material. Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of bitumen evaporates. Importantly, properties of the residual oil change as the light components of the oil are removed.

1.7.6. Density

Given that the density of fresh water is 1.00 g/cm^3 at environmental temperatures and the densities of crude oils commonly range from 0.7 to 0.99 g/cm^3 (see Table 2-3), most oils will float on freshwater. Because the density of seawater is 1.03 g/cm^3, even the heaviest oils will usually float on seawater. But evaporative losses of light components can lead to significant increases in density of the residual oil. The densities of some weathered, diluted bitumen and of undiluted bitumen can approach and possibly exceed that of freshwater. Accordingly, those materials can submerge and may sink to the bottom. In this respect, diluted bitumen

differs not only from light and medium crude oils, but even from most conventional heavy crude oils.

Importantly, as the density of a weathering oil approaches that of water, contact with even small amounts of sand, clay, or other suspended sediment can trigger submergence. For this reason, the density of the oil residue itself (i.e., not including any associated natural particulate matter) does not need to exceed that of water for the residue to sink from the surface.

1.7.7. Viscosity

Viscosity is defined as the resistance to flow of a liquid: the lower the viscosity, the more readily a liquid flows. For example, water has a low viscosity and flows readily, whereas honey, with a high viscosity, flows poorly. The viscosity of oil is largely determined by its content of large, polar molecules, namely resins and asphaltenes. The greater the percentage of light components such as saturates and the lower the amount of asphaltenes, the lower the viscosity. Temperature also affects viscosity, with a lower temperature resulting in a higher viscosity. The variations with temperature are commonly large. Oil that flows readily at 40ºC can become a slow-moving, viscous mass at 10ºC. Evaporative losses selectively remove lighter components and, consequently, increase the viscosity of the residual oil.

In a study by Karen Schou et al (1984) series of experimental viscosity data for seven different North Sea oils is presented. A new corresponding states method for prediction of the viscosity of both gaseous and liquid hydrocarbon fluids has been developed. The required input is critical constants and the molecular weight of each component. Very accurate results were obtained for the crude oils using the C_{7+}-characterization

procedure of Pedersen *et al*. The viscosity correlation is also shown to give satisfactory results for pure hydrocarbons and binary mixtures. In a study by Andhy Arya Ekaputra (2014), density and viscosity for 3 different Malaysian crude oils in the different conditions have been measured. Experimental results show that there is linear trend between density and temperature. Also, wax precipitation and deposition has direct relationship with wax content of crude oil. The shear rate has considerable effect on viscosity reduction. Temperature reduction caused viscosity to increase. However, it is against shear rate that tends to lower it.

CHAPTER TWO

MATERIALS AND METHODS

2- Materials and Methods

2.1- Objectives of the study:

To study the chemical composition of some types of crude oil in Sudan.

To study the relationship between chemical composition and physical properties of crude oil.

To study the emulsion stability of crude oil.

Attempt to optimize oil productivity and to reduce the production cost accordingly.

2.2. Study Subjects

A crude oil samples were taken from four different fields from Upper Nile state:

Adar oil field

Palogue oil field

Gummry oil field

Melut oil field

2.3. Methods:

Four different petroleum fields were included in the study. This study was carried out using different types of crude oil, analysis for these samples were conducted to determine the viscosity, density, API, pour point, base sediment, water cut, wax content, asphaltene content and SARA test. HPLC and GC-MS were used to study the light constituents of the crude oil. According to ASTM (AMERICAN SOCIETY FOR TESTING AND

MATERIALS) the pour point, water cut & base sediment, density & API, viscosity, wax content, asphaltene content of the samples were measured.

2.3.1. Standard Test Method for Determination of SARA Fractions ASTM D893-69 & D2549-75

For crude oils, deasphalting of the sample was done by a standard asphaltene precipitation by alkanes like pentane, hexane or heptane. The remaining SAR fractions were then separated by HPLC using silica or bonded phase columns, and an alkane as the mobile phase. The complexity of the material in a crude oil, and the lack of an aromatic/resin selective column makes it impossible to draw a clear distinction between aromatics and resins. Therefore, a method specific definition of aromatics and resins was employed.

Separation of saturates and aromatics, with backflushing of the resins, had been obtained on amino columns, cyano columns and aminocyano columns. However, two coupled columns such as cyano/aminocyano or silica/cyano were employed.

The purpose of the first column was to retain the resins, while the second retains the aromatics. The saturate fraction has no retention on such columns, and was therefore eluted directly through the columns. The resins and aromatics were eluted from their respective columns with appropriate solvents.

2.3.2. Standard Test Method for Determination of Asphaltene ASTM D 6560

A test portion of sample is mixed with n-heptane, and the mixture heated under reflux, and the precipitated Asphaltene`s, waxy substances and inorganic materials collected in the filter paper. The waxy substances were removed by washing with hot heptane in extractor, and then the Asphaltene`s is separated from inorganic materials by dissolution in hot

toluene. Then extracted solvent is evaporated and the asphaltene was weighed.

2.3.3. Standard Test Method for Determination of Wax ASTM

UOP 46-85 The sample is dissolved in methyl ethyl ketone, the solution cooled to –32°C to precipitate the wax, and filtered. The oil content of the filtrate was determined by evaporating the methyl ethyl ketone and weighing the residue.

2.3.4. Standard Test Method for Determination of Pour point ASTM D 97

After preliminary heating, the sample was cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen was observed was recorded as the pour point.

2.3.5. Standard Test Method for Determination of Base Sediment & Water Cut ASTM D4007

Known volumes of crude oil and solvent (water saturated if required) were placed in a centrifuge tube and heated to 60°C 63°C). After centrifugation, the volume of the sediment-and-water layer at the bottom of the tube was read

2.3.6. Standard Test Method for Determination of API

The sample was injected by syringe in the injection point at the density meter; the digital results of density and API were recorded.

2.3.7. Standard Test Method for Determination of Viscosity ASTM D2983

The programmable brook field 111D ultra was used to measure the viscosity of crude oil, firstly the instrument and the water bath were putted

on and adjusted, secondly known volumes of crude oil was placed into a cell, the cell was placed into a cell holder in the brook field viscometer, finally the program was started and the results were recorded.

2.4. Materials:

The chemicals and methods used in this study are chosen based on suitability and economic feasibility.

2.4.1. Instruments:

I. Centrifuge.
II. Anton paar density meter.
III. Brookfield DV 111 Ultra viscometer.
IV. HPLC.

2.4.2. Apparatus:

I. Cone tubes.
II. Refluxer.
III. Evaporating vessel (borosilicate glass).

2.4.3. Chemicals:

I. Varsol.
II. Demulsifier.
III. Methyl ethyl ketone.
IV. N-heptane.
V. Methyl benzene (toluene).
VI. Trichloro-methane.
VII. Xylene.
VIII. Propane-2-ol.
IX. Acetic acid.

2.5. Statistical analysis

After all tests being done and data were collected, all data had been entered into computer for data analysis by utilizing Microsoft Excel program. Descriptive statistical analysis was used to determine frequency distribution for variables with representation of results by figures.

CHAPTER THREE

RESULTS AND DISCUSION

3- Results and Discussion

3.1. SARA distribution Vs Wax content:

Separation of crude oil into hydrocarbon fractions such as saturate, aromatic, resin and asphaltene (SARA) fractions is needed in order to obtain the concentration of each group. This chemical analysis of crude oil is necessary for upstream, midstream and downstream operations; as it yields information such as crude oil stability (asphaltenic 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. In this work twenty samples collected from four different fields in the South Sudan were studied. The modified ASTM D2549–02 was employed to separate the crude oil samples into their various chemical species. Pour point and wax content were measured on the samples to determine whether they are waxy crude oils or non-waxy crude oils.Out of the twenty samples studied, nineteen were confirmed as waxy samples (Table 1) while one was non-waxy from the pour point and wax content measurements. The SARA analysis was carried out on all the samples it showed the samples had a high percentage of saturates ranging from 40 wt% to 66 wt%. Sample 6 which was non-waxy crude oils even had saturates of 40%. Thus, SARA analysis data on its own might not be a tool to distinguish waxy crude oils from non-waxy crude oils. This goes in consistency with the study of (Bella Mmata et.al. (2017)) who researched thirteen samples collected from three different fields in the Niger Delta region.

Table 1: SARA distribution and Wax content

Sample	*Saturates*	Aromatic	Resins	*Asphaltene content*	*Wax content*
1	**48**	**34**	**16.2**	**1.8**	**29.17**
2	**43**	**33**	**22**	**3**	**20.24**
3	**62**	**32**	**5.9**	**0.1**	**41.4**
4	**66**	**27**	**6.84**	**0.16**	**41.6**
5	**56**	**30**	**12.9**	**1.1**	**37.24**
6	**40**	**38**	**17**	**5**	**12.6**
7	**44**	**42**	**13.1**	**0.9**	**30.9**
8	**55**	**35**	**9.8**	**0.2**	**41.8**
9	**58**	**34**	**7.8**	**0.2**	**43.07**
10	**45**	**41**	**13.7**	**0.3**	**18.9**
11	**60**	**32**	**7.7**	**0.3**	**41.78**
12	**45**	**39**	**15.8**	**0.2**	**36.4**
13	**65**	**30**	**4.4**	**0.6**	**41.34**
14	**44**	**36**	**19**	**1**	**23.3**
15	**51**	**33**	**15.7**	**0.3**	**38.23**
16	**57**	**37**	**5.4**	**0.6**	**41.34**
17	**49**	**35**	**13.8**	**2.2**	**24.9**
18	**48**	**37**	**13.4**	**1.6**	**22.4**
19	**40**	**44**	**14**	**2**	**22.1**
20	**65**	**25**	**9.7**	**0.3**	**44.59**

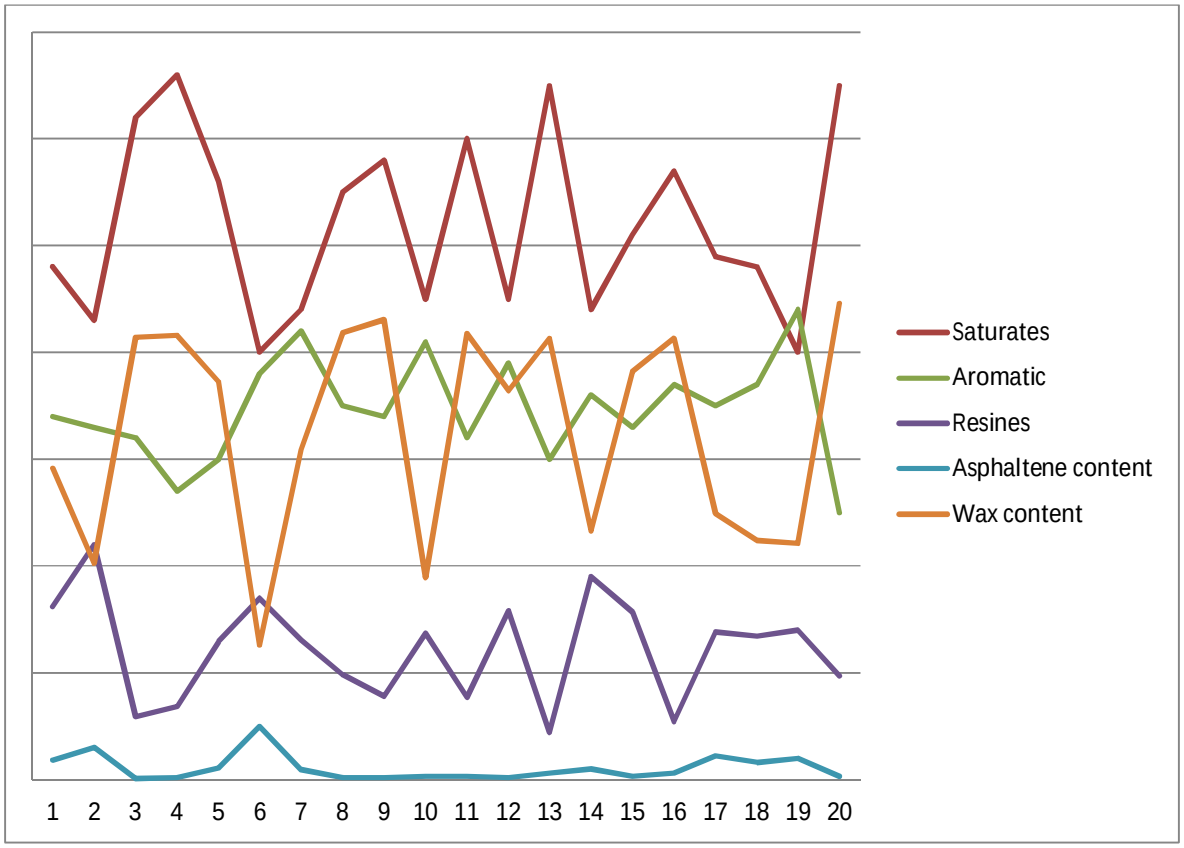


Fig (9): SARA disribution and Wax content

3.2. **SARA distribution and Emulsion:**

There are many different asphaltenes some of which make much more stable emulsions than others. Recent work has shown that there are hundreds of asphaltene components varying very much in composition and molecular size (Fingas 2011). The percent of asphaltenes (or resins) certainly does not tell the whole story about the sions-stabilizers.

Several scientists reviewed emulsions and concluded that the asphaltene content is the most important factor in the formation of emulsions (Gu et al. 2002, Yarranton et al. 2000, Kilpatrick and Spiecker 2001). Even in the absence of any other possibly-synergistic compounds such as resins, asphaltenes were found to be capable of forming rigid, elastic films which are the primary agents in stabilizing water-in-crude oil emulsions. The exact conformations by which asphaltenes organize at oil-water interfaces and the corresponding intermolecular interactions have not been elucidated. Workers studying only crude oil emulsions concluded that water-in-oil emulsions are exclusively stabilized by asphaltenes, although the specific stability was not measured (Kilpatrick and Spiecker 2001). Even though the emulsions contain inorganic solids, waxes and other organic solids, the main stabilization comes from asphaltenes. Other workers have noted that solid particles, such as clays, when present, can stabilize or enhance the stability of emulsions (Sztukowski and Yarranton 2004). According to (Table2) we can find good relationship between asphaltene and emulsion stability see chart3.

Table 2: SARA distribution and Emulsion

Sample	*Saturates*	Aromatic	Resins	*Asphaltene content*	Emulsion	Emulsion 2
1	**48**	**34**	**16.2**	**1.8**	**3.5**	**1**
2	**43**	**33**	**22**	**3**	**4**	**2**
3	**62**	**32**	**5.9**	**0.1**	**2**	**0**
4	**66**	**27**	**6.84**	**0.16**	**2**	**0**
5	**56**	**30**	**12.9**	**1.1**	**1.5**	**0.1**
6	**40**	**38**	**17**	**5**	**3**	**1**
7	**44**	**42**	**13.1**	**0.9**	**1**	**0**
8	**55**	**35**	**9.8**	**0.2**	**1**	**0**
9	**58**	**34**	**7.8**	**0.2**	**0.1**	**0**
10	**45**	**41**	**13.7**	**0.3**	**6**	**1**
11	**60**	**32**	**7.7**	**0.3**	**5**	**1.5**
12	**45**	**39**	**15.8**	**0.2**	**5**	**2**
13	**65**	**30**	**4.4**	**0.6**	**4**	**1**
14	**44**	**36**	**19**	**1**	**2**	**0.8**
15	**51**	**33**	**15.7**	**0.3**	**1**	**0**
16	**57**	**37**	**5.4**	**0.6**	**2**	**0**
17	**49**	**35**	**13.8**	**2.2**	**6**	**2**
18	**48**	**37**	**13.4**	**1.6**	**2**	**1**
19	**40**	**44**	**14**	**2**	**6**	**3**
20	**65**	**25**	**9.7**	**0.3**	**8**	**4**

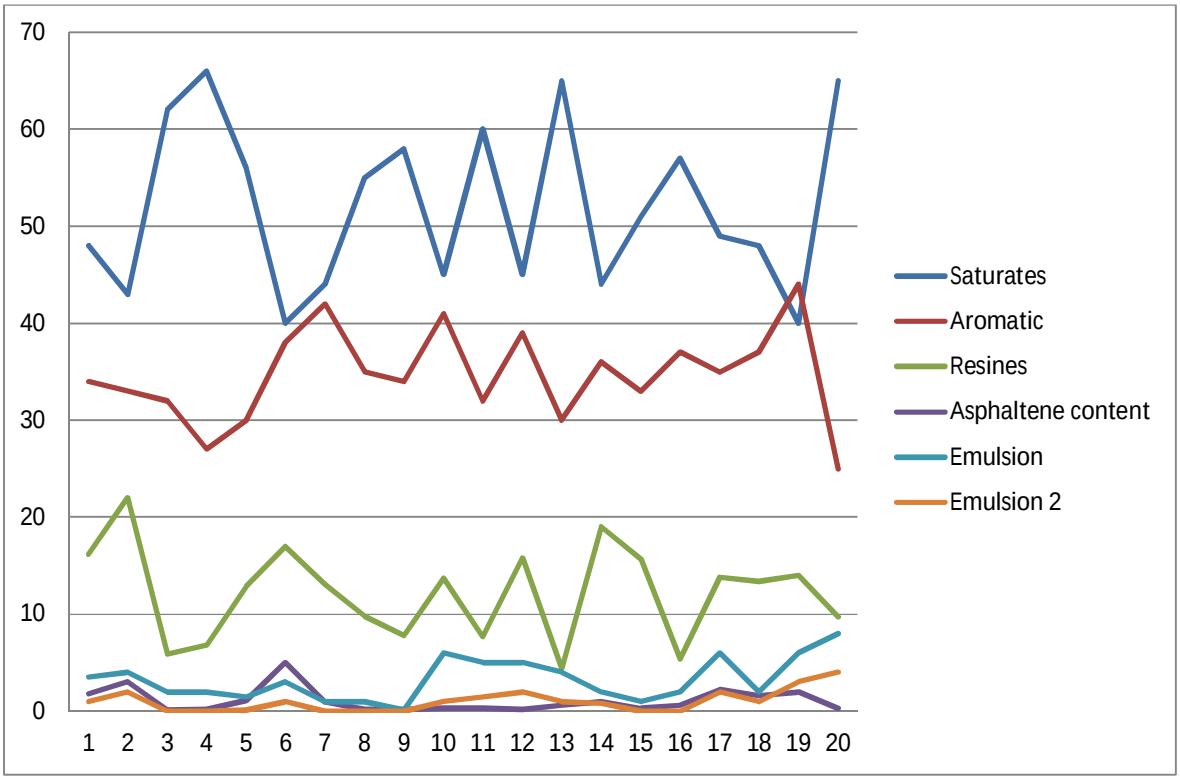


Fig (10): SARA disribution and Emulsion

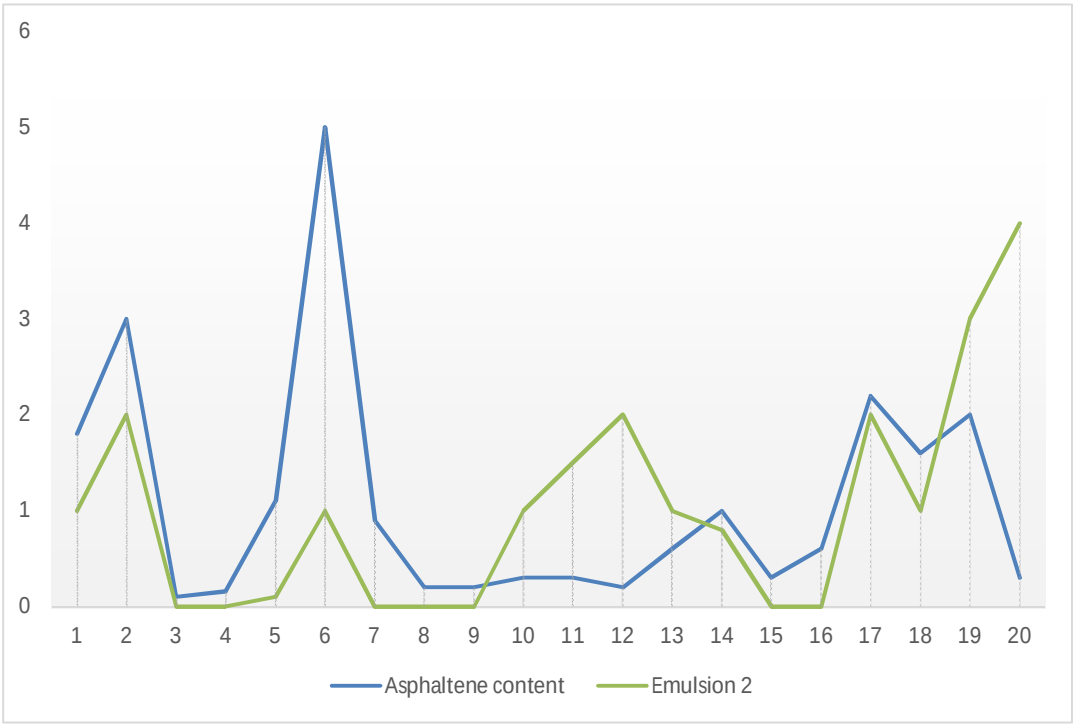


Fig. (11): Asphaltene and Emulsion stability

3.3. SARA distribution Vs API

As shown in Table 3 API ranging from 19.21 to 35.39, were one sample below 20 which considered as a heavy crude oil, and nine samples between 20 - 30 known as a medium crude oil, and the rest ten samples above 30 and these are light crude

Table 3: SARA distribution and API

Sample	*Saturates*	Aromatic	Resins	*Asphaltene content*	API
1	**48**	**34**	**16.2**	**1.8**	**24.91**
2	**43**	**33**	**22**	**3**	**19.21**
3	**62**	**32**	**5.9**	**0.1**	**32.97**
4	**66**	**27**	**6.84**	**0.16**	**30.83**
5	**56**	**30**	**12.9**	**1.1**	**24.13**
6	**40**	**38**	**17**	**5**	**20.96**
7	**44**	**42**	**13.1**	**0.9**	**32.76**
8	**55**	**35**	**9.8**	**0.2**	**35.39**
9	**58**	**34**	**7.8**	**0.2**	**31.9**
10	**45**	**41**	**13.7**	**0.3**	**30.18**
11	**60**	**32**	**7.7**	**0.3**	**32.2**
12	**45**	**39**	**15.8**	**0.2**	**30.86**
13	**65**	**30**	**4.4**	**0.6**	**31.94**
14	**44**	**36**	**19**	**1**	**29.72**
15	**51**	**33**	**15.7**	**0.3**	**29.92**
16	**57**	**37**	**5.4**	**0.6**	**30.12**
17	**49**	**35**	**13.8**	**2.2**	**27.67**
18	**48**	**37**	**13.4**	**1.6**	**29.27**
19	**40**	**44**	**14**	**2**	**27.66**
20	**65**	**25**	**9.7**	**0.3**	**27.65**

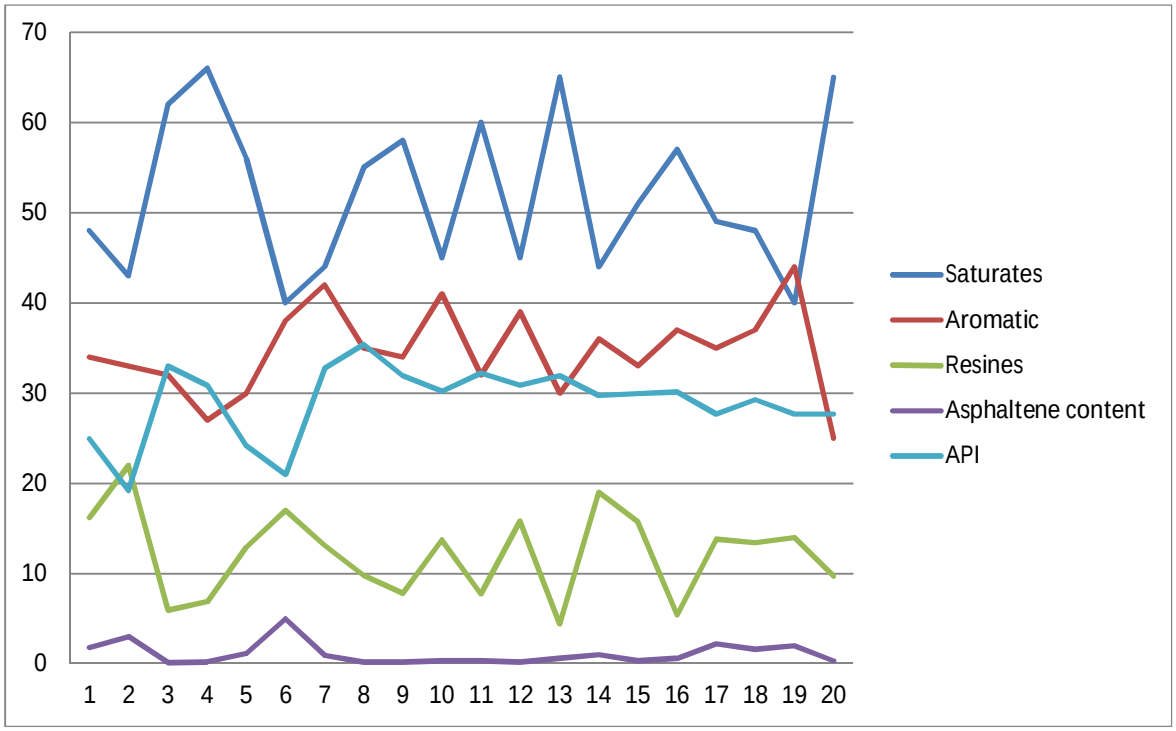


Fig. (12): SARA disribution and API

According to the results in chart 4 the API and SARA fractions was correlated in good percentage of the samples studied. On the other hand, there are some of the studied samples the correlation between SARA and API was not clear. The major inaccuracy lies with the unstable types because of the fact that there are four different fields from where the study samples collected, each very different, as well as the possible presence of emulsion breakers or asphaltene suspenders in the oils. See chart 5 and chart 6



Fig. (13): Resins and API

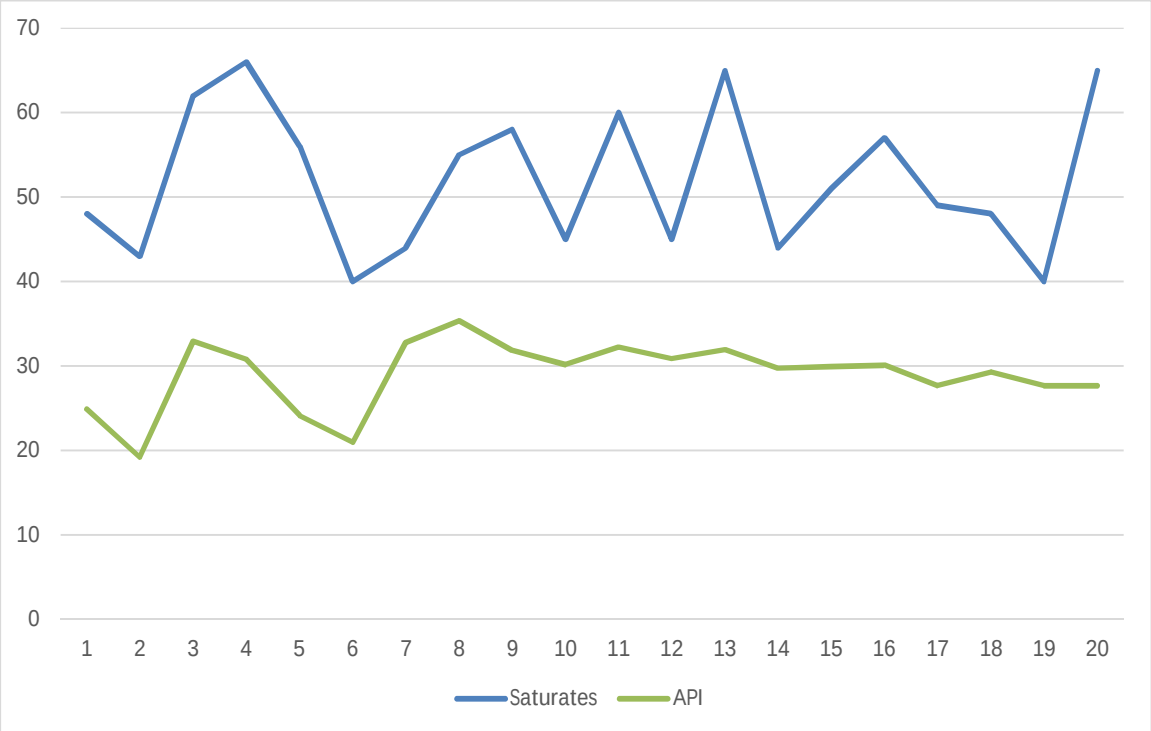


Fig. (14): Saturates and API

3.4. SARA distribution Vs Viscosity:

Twenty crude oils of different fields have been systematically analyzed with regard osity and SARA (saturates, aromatics, resins, asphaltenes) fractionation. Viscosity asured for the complete crude oil matrix (20 crude oils), and in general there is an in ne emulsion stability as the viscosity increases. However, viscosity also correlates wel SARA data of the crude oils. On the other hand, study cited by (Pål V. Hemmings 2007) using critical electric field technique (E-critical) shows a temperature depen ording to the Arrhenius law.

osity does not correlate simply with hydrocarbon groups. A reasonably good (rl= elation can be obtained between the common logarithm of viscosity and the su altenes, resins, and waxes (GC).

e is a good correlation between viscosity and density at the same temperature, but is study viscosity was measured at 50℃ and the density at 15℃ to calculate the density.

perature affects both density and viscosity, see table 6 and chart 10 for viscosity le.

Table 4: SARA distribution and Viscosity

Sample	*Saturates*	Aromatic	Resins	*Asphaltene content*	Viscosity @50
1	**48**	**34**	**16.2**	**0.1**	**20**
2	**43**	**33**	**22**	**0.16**	**35**
3	**62**	**32**	**5.9**	**0.2**	**16**
4	**66**	**27**	**6.84**	**0.2**	**45**
5	**56**	**30**	**12.9**	**0.2**	**88**
6	**40**	**38**	**17**	**0.3**	**38**
7	**44**	**42**	**13.1**	**0.3**	**24**
8	**55**	**35**	**9.8**	**0.3**	**80**
9	**58**	**34**	**7.8**	**0.3**	**158**
10	**45**	**41**	**13.7**	**0.6**	**23**
11	**60**	**32**	**7.7**	**0.6**	**35**
12	**45**	**39**	**15.8**	**0.9**	**26**
13	**65**	**30**	**4.4**	**1**	**52**
14	**44**	**36**	**19**	**1.1**	**184**
15	**51**	**33**	**15.7**	**1.6**	**77**
16	**57**	**37**	**5.4**	**1.8**	**146**
17	**49**	**35**	**13.8**	**2**	**150**
18	**48**	**37**	**13.4**	**2.2**	**133**
19	**40**	**44**	**14**	**3**	**889**
20	**65**	**25**	**9.7**	**5**	**450**

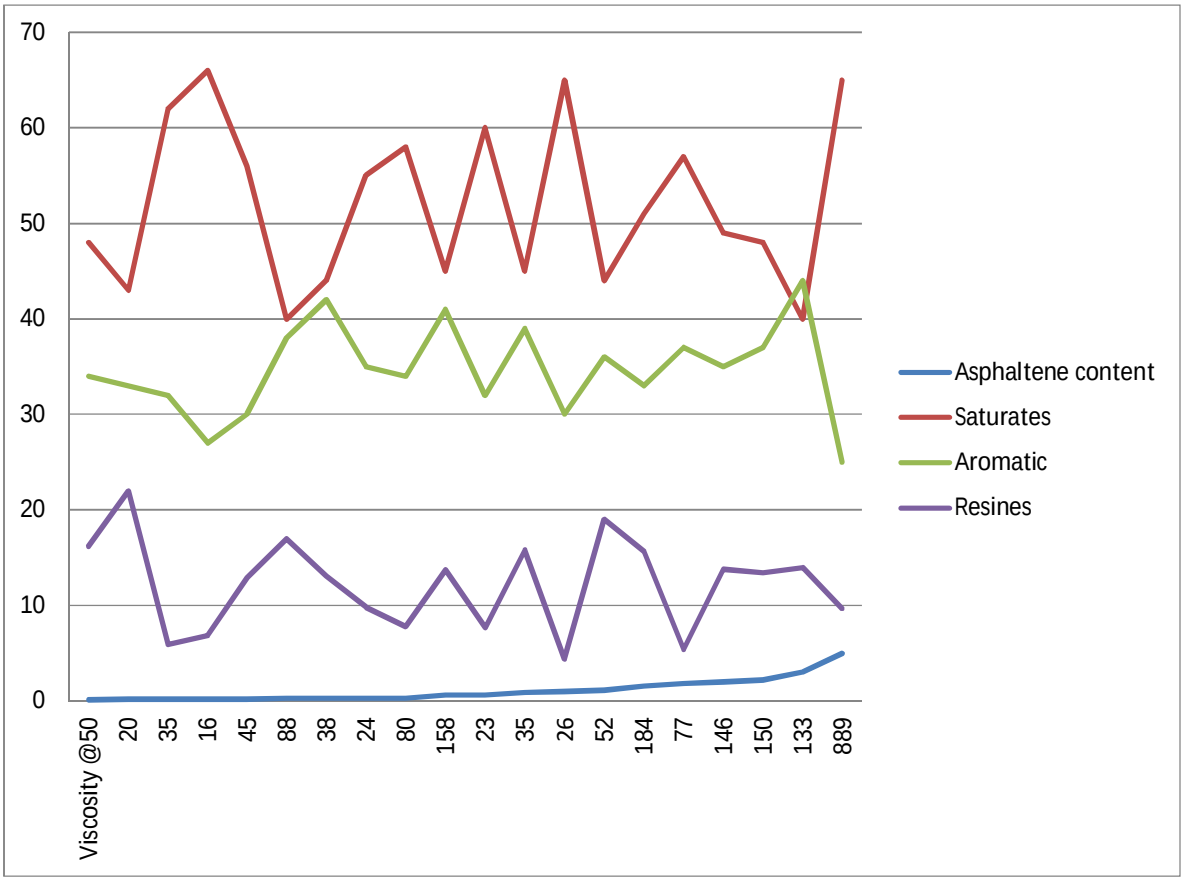


Fig. (15): SARA Distribution Vs Viscosity

3.5. SARA distribution Vs Pour Point

Table 5: SARA distribution and Pour Point

Sample	*Saturates*	Aromatic	Resins	*Asphaltene content*	Pour point
1	**48**	**34**	**16.2**	**1.8**	**33**
2	**43**	**33**	**22**	**3**	**36**
3	**62**	**32**	**5.9**	**0.1**	**39**
4	**66**	**27**	**6.84**	**0.16**	**39**
5	**56**	**30**	**12.9**	**1.1**	**36**
6	**40**	**38**	**17**	**5**	**12**
7	**44**	**42**	**13.1**	**0.9**	**33**
8	**55**	**35**	**9.8**	**0.2**	**45**
9	**58**	**34**	**7.8**	**0.2**	**42**
10	**45**	**41**	**13.7**	**0.3**	**39**
11	**60**	**32**	**7.7**	**0.3**	**42**
12	**45**	**39**	**15.8**	**0.2**	**42**
13	**65**	**30**	**4.4**	**0.6**	**42**
14	**44**	**36**	**19**	**1**	**39**
15	**51**	**33**	**15.7**	**0.3**	**42**
16	**57**	**37**	**5.4**	**0.6**	**42**
17	**49**	**35**	**13.8**	**2.2**	**33**
18	**48**	**37**	**13.4**	**1.6**	**33**
19	**40**	**44**	**14**	**2**	**30**
20	**65**	**25**	**9.7**	**0.3**	**48**

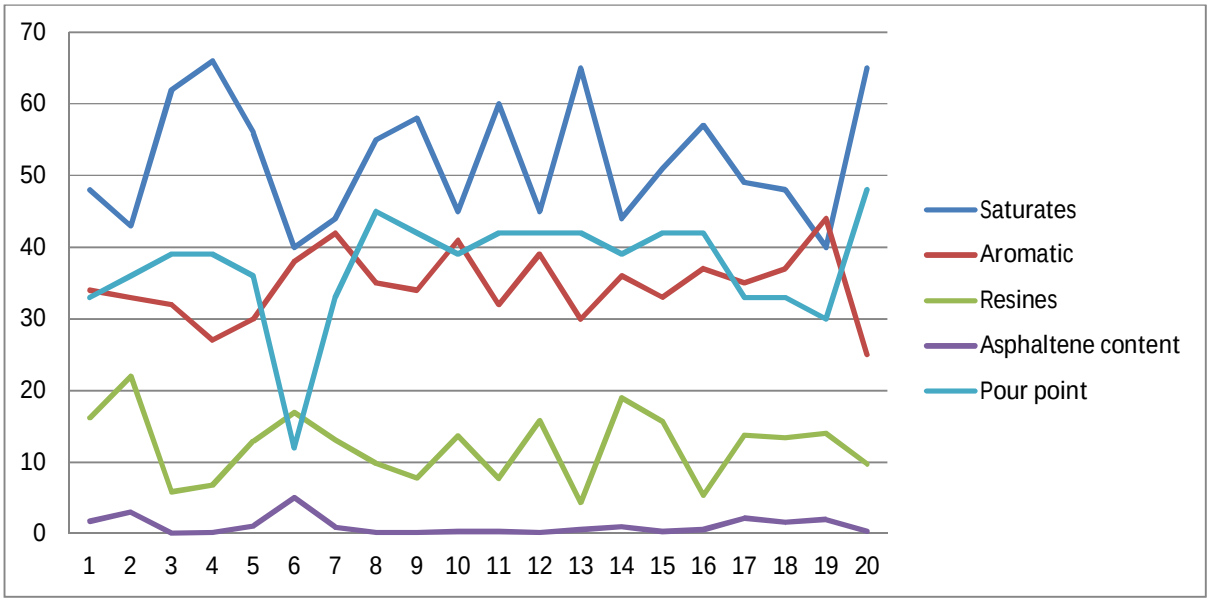


Fig. (16): SARA distribution and Pour Point

As shown in chart 9 above, pour point correlates fairly well to saturates, aromatics and resins but we can find better correlation between wax content and pour point as shown in chart 10

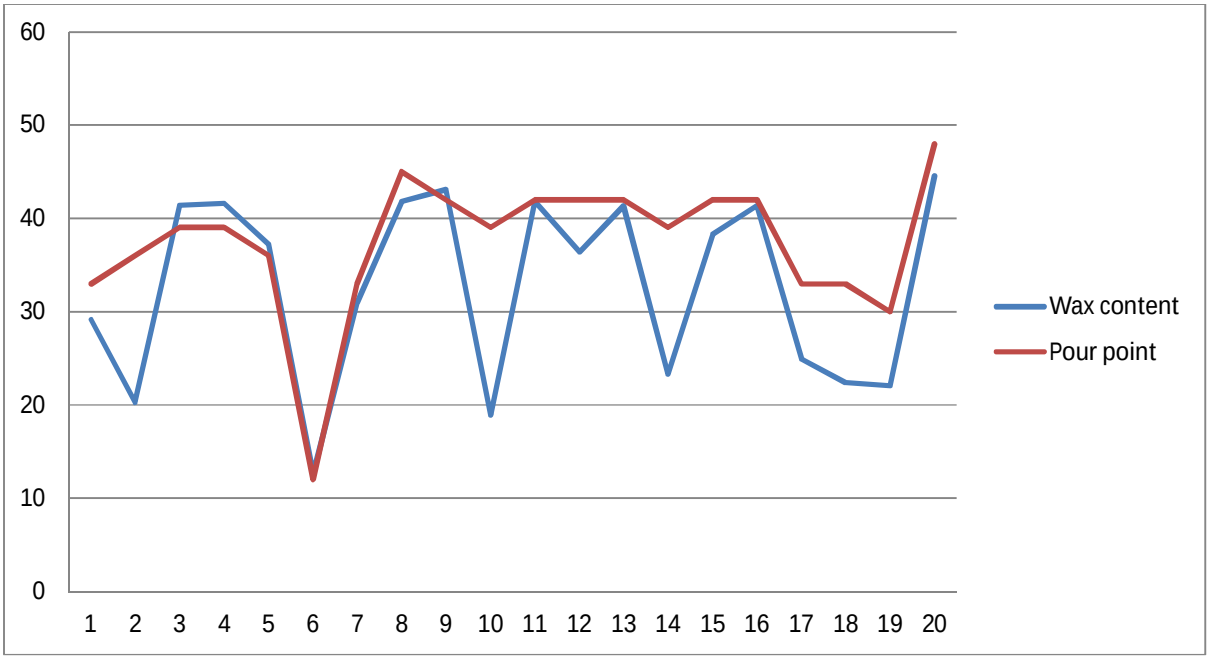


Fig. (17): Wax Content and Pour Point

Table 6: Viscosity Profile

Temperature	Sample-4	Sample-1	Sample-3
52	142	33	18
51	144	35	20
50	146	35	20
49	149	38	20
48	153	38	20
47	158	39	21
46	162	40	22
45	167	42	24
44	174	43	24
43	180	46	27
42	190	47	28
41	197	50	31
40	206	53	35
39	220	57	39
38	236	63	45
37	258	68	53
36	283	78	68
35	319	89	95
34	367	107	138
33	427	134	222
32	525	177	375
31	741	259	748
		384	
		635	
		1049	

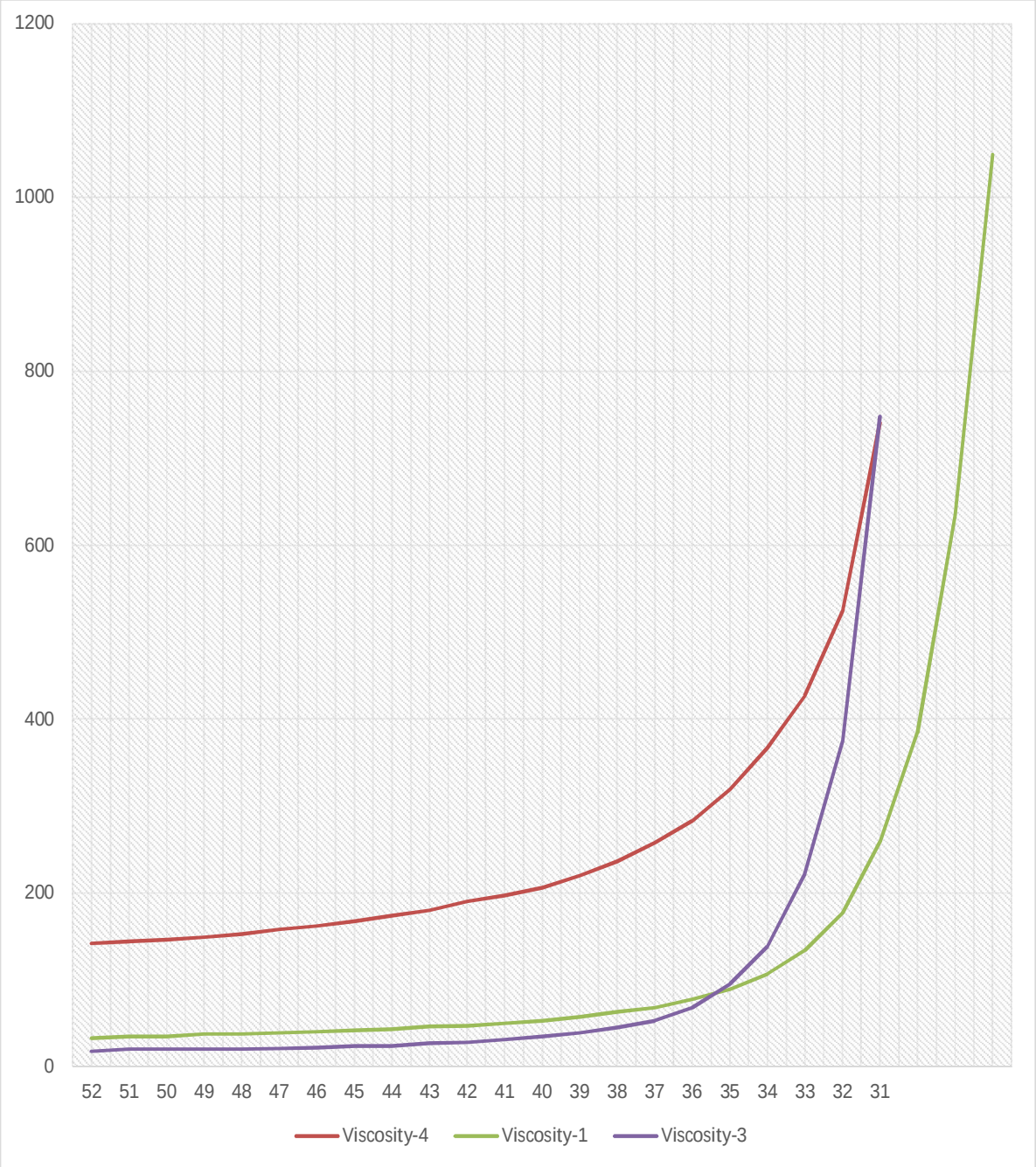


Fig. (18): Viscosity Profile

CONCLUSION AND RECOMENDATIONS

Conclusion:

In this study twenty samples collected from four different fields in the South Sudan were studied. The modified ASTM D2549–02 was employed to separate the crude oil samples into their various chemical species. Pour point and wax content were measured on the samples as well to determine whether they were waxy crude oils or non-waxy crude oils.

Based on the results of the present study it can be concluded that out of the twenty samples studied, nineteen were confirmed waxy samples (Table 1) while one was non-waxy from the pour point and wax content measurements. The SARA analysis carried out on all of the samples showed the samples had a high percentage of saturates ranging from 40 wt% to 66 wt%. Sample 6 which was non-waxy crude oils even had saturates of 40%. Thus, SARA analysis data on its own might not be a tool to distinguish waxy crude oils from non-waxy crude oils. According to the results in chart 4 the API and SARA fractions were correlated in only 45% of the samples studied. On the other hand, in 55% of the studied samples the correlation between SARA and API was not clear.

There is an increase of the emulsion stability as the viscosity increases. However, viscosity also correlates well with the SARA data of the crude oils.

Pour point correlates fairly well to resins, aromatic and saturates,

Recommendations:

Most types of crude oil were waxy oil in these fields, so the main problem will be the wax precipitation, wax inhibitors or pour point depressants should be injected to many wells. The determination of SARA fraction in crude oils can contribute greatly to our understanding of both physical and chemical oil properties. Many experiments remain to be carried out, both to fill in data gaps, and to confirm (or deny) untested hypotheses, such as carbon number distribution using the Gas chromatography.

Does asphaltene precipitation remove some waxes from the oil? Can better results be obtained with the GC determination of wax content? Exactly how do the individual SARA fraction contribute to oil viscosity? These are some of the questions that future research will attempt to answer.

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