

DETERMINATION OF SARA CONSTITUENTS OF SOUTHWESTERN NIGERIAN TARS SANDS AND THEIR PHYSICAL PROPERTIES

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ABSTRACT

Utilization potentials of Nigerian massive crude bitumen and associated heavy oil represent a promising source of security and economic benefits for the nation. However, production and processing technology of tar sands resources is often limited by the existence of and distribution of chemical family groups in the crude bitumen. Such a limitation is presently experienced in Canada and elsewhere. To avoid similar scenario in Nigeria, it is believed that the characterization of Nigerian crude bitumen beyond the standard assay analysis will provide a key to how it will respond to recovery, processing and conversion processes. To address this concern, an experimental study was conducted to assess quantity of Saturates, Aromatics, Resins and Asphaltenes components of Nigerian crude bitumen and study possible effects of these components on production process and the environment.

Results obtained from the chromatographic analysis of the raffinate and extract products revealed that Nigerian bitumen has high utilization potentials because of its high content of aromatics (29.80 wt. %). The results also indicate high content of asphaltenes (24.65 wt. %) indicating high implications on Nigerian bitumen production technology options. In addition, the implications of detected Vanadium, Nickel, Sulphur, and aromatics in the analyzed bitumen samples on the environment were equally discussed.

I. INTRODUCTION

The Nigerian tar sand proven reserve has been conservatively estimated to be more than 50 million tons. Based on average bitumen content of 15% by weight the Nigerian rich tar sand deposits constitute a potential reserve of over 40 billion barrel of bitumen [1], which is about 40% of Canada's deposit known to be one of world's richest deposits of tar sands [2].

In order to maintain Nigerian self – sufficiency of petroleum and petroleum products, commercial tar sands development must be planned to recover and upgrade the bitumen to syncrude and high market value products. The designing of this project require a full-scale physical and chemical characterization of the bitumen to aid in the development of suitable full scale production performance test schedule, identification of products of conversion processes, a priority list of the compounds of most concern and data to provide public awareness and/or support prior to construction of a full scale facility or test run at a full scale facility.

Bitumen/heavy oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of varying molecular weight and polarity. A common practice in the petroleum industry is to separate the heavy oil into four chemically distinct components: Saturates, Aromatics, Resins and Asphaltenes (SARA). The classic definition of asphaltenes is based on the solution properties of petroleum residuum in various solvents. Asphaltenes are, broadly speaking, n-heptane and n-pentane insoluble and aromatic soluble. They are asphalt compounds soluble in carbon disulfide but insoluble in paraffin naphtha.

Bitumen is a complex mixture of hydrocarbons which can be separated into two major fractions: extract and raffinate. Separating of extract and raffinate (maltene) fractions is done by diluting asphalt with straight chain, saturated hydrocarbons (n-alkanes) such as: n-pentane (C₅H₁₂) and n-heptane (C₇H₁₆). The maltenes remain in solution in the n-alkane solvent. Precipitation of asphaltenes from raw petroleum provides a huge problem for the petroleum industry. This problem includes progressive precipitation and accumulation of asphaltene at the sand face

and perforation, tubing, surface production lines and storage tanks thus limiting the production capacity of facilities. Depending on severity, asphaltene deposition may lead to loss of production, mechanical failure of tubular equipment, increased production downtime, increased handling costs and minimum profitability. Method of detection of asphaltene depends in the field include visual observation of produced fluids and unusual drop in production rate, wellhead pressure and temperature. In the laboratory, chromatographic methods can be used to determine the asphaltene content and molecular weight and infrared analysis can determine chemical composition [3].

In petroleum production it is important to take necessary steps to prevent the deposition problem caused by asphaltenes. If this is tackled by modification of the production practice, rather than chemical [4] or mechanical mean, the cost of production can be reduced appreciably. This can be achieved by proper laboratory tests, development of deposition production models and designing the oil production and transportation systems accordingly since asphaltenes are amorphous "non-crystalline" in nature and do not uniformly melt in the presence of heat, a better knowledge of the mechanisms that cause the deposition [5]. The heavy organics deposits resulting from asphaltenes flocculation are quite hard to deal with in petroleum production practices. Asphaltenes and resins are responsible for adding most of the colours to crude oils. "Black oils" usually contain the highest asphaltene content.

Chemical treatment techniques include addition of dispersants, anti-foulants, and aromatic solvent which may be used to control asphaltene deposition. Aromatic solvents for asphaltene deposits need to have a high aromaticity to be effective, and antifoulants have proven effective in condensate stabilization units in gas plants. In order to investigate about asphaltene solubility or precipitation a number of investigators [4] have tested several inhibitors. Their results indicate that the activity of inhibitors is not only dependent on the acidic head, but also of the aliphatic or aromatic tail of the inhibitor. Particularly, for the sulphonic acids, when the chain-length of the aliphatic group increased from 13 to 24 carbon atoms, the inhibitor activity increased 5 fold. Substitutions of the hydrocarbon within C18-sulphonic acids by aromatics like benzene, toluene, ortho-or para xylene gave approximately the same activity.

Deposition of the asphaltene present in heavy oil could be due to various causes depending on their molecular nature. For instance, by examining each heavy organic compound separately one may argue that mercaptans and organometallics cause deposition due to dissociation or solubility effects. Diamonds and paraffin/wax may cause deposition due to lowery of the crude oil temperature and formation of crystalline solids. The reason for the asphaltene deposition can be many factors including variations of temperature juncture, composition, flow regime and wall and electrokinetic effect. When various heavy organic compounds are present in a petroleum fluid their interactive effects must also be considered in order to understand the mechanism of their collective deposition or lack of it. This is especially important when one of the interacting heavy organics components is asphaltene. Arterial blockage in the petroleum industry is mostly due to the deposition of heavy organics from petroleum fluids. Heavy organics such as paraffin, resin, asphaltene, diamodoid, mercaptans and organometallic compounds may exist in crude oil in various quantities and forms. Such compounds could precipitate out of the crude oil solution due to various forces causing blockage in the oil reservoir, in the well, in the pipelines and in the oil production and processing facilities [5]. Solid particles suspended in the crude oil may stick to the walls of the conduits and reservoirs. The toughness of the precipitate has a lot to do whether there is asphaltene present in the crude oil even in minute quantities. Asphaltenes which is a highly polar compound could act as glue and mortar in hardening the deposits and as a result, causes a barrier to the flow of oil.

In general, solids in crude oil fall into two classes "basic sediment" and "filterable solids". These particles have an economic impact on the petroleum industry. When carried along in the oil, they can cause fouling, foaming, erosion, coagulants (molecular weight 10, 000), might provide an indirect aid in solids removal [4]. Coagulants are molecules with strong polar charge which act to disrupt charges on the surface of the oil droplet that would otherwise prevent coalescence. Flocculants act to coalesce oil droplets, because they are very soluble in oil, but in some cases they can have drastically reduced solids removal, meaning that solids never die, they just move around.

Flocculation of asphaltene in paraffin crude oils is known to be irreversible. This is the major cause of irreparable arterial blockage damage to the flow of petroleum fluids. Due to their large size and their absorption activity to solid surfaces, flocculated asphaltene can cause irreversible deposition which may not wash away by current remediation

techniques. Asphaltene and its flocculates are known to be surface-active agents. It is known that as gas is rejected into a reservoir the likelihood of asphaltene flocculation is increased.

Experimental evidence [4] suggests that for an oil mixture there is a critical concentration of resins below which the asphaltene flocculate may precipitate and above which they cannot precipitate regardless of how much the oil mixture is agitated, heated or pressurized, sort of changing its composition. The onset of steric colloidal formation of asphaltene in a crude oil can be accurately detected using viscometer techniques as demonstrated [6]. While the mechanisms of asphaltene flocculation and steric colloid formation is well understood and modeled [5], the phase behaviour of asphaltene micelle formation is not well characterized and in many cases in recent years it is confused with the asphaltene steric colloids. Despite the experimental evidence in the micellization of asphaltenes, little or no theoretical and modeling research has been performed to explain and quantify this phenomenon. Nevertheless, the theories of micelles solutions of oil/surfactants/water are well known. These theories may be used to explain the micellization of asphaltenes in aromatic solvents if it is assumed that the properties of these systems are similar to that of oil/surfactant/water systems.

The impetus for this laboratory evaluation is to be able to establish and quantify saturate, aromatic, resin and asphaltene components and physical characterization data for bitumen extracted from Nigerian tar sands. This seems to be a basic building block in scientific quest to find a solution to many irreversible heavy organic deposition problems. It would assist to estimate relative products spectrum and yields from these resources and provide adequate information that would guide in environmental management. Laboratory scale test apparatus was designed to rapidly and accurately evaluate the physical and chemical properties of Nigerian crude bitumen.

This paper describes the apparatus used in the study and also discusses the result of various test performed on samples. Preliminary conclusions are drawn as to the technical and environmental implications of Nigerian crude bitumen development and the requirements for future research.

II. EXPERIMENTAL

1. Materials studied

Investigations were carried out on bitumen samples obtained from tar sands collected from two different locations namely: Agbabu and Olowo-Irele sites of the bitumen deposits in Ondo State, Nigeria. Agbabu is located in latitude 60 351.448N and longitude 40 491.883E while Olowo-Irele is located in latitude 60 391.169N and longitude 40 531.409E. Both in the southwestern part of Nigeria (Figure 1). The samples were collected by scooping the viscous tar sands into airtight container and conveyed immediately to laboratory for analysis.

The Experimental aspects of the present study consist essentially of (1) extraction of bitumen from tar sands (2) deasphalting the extracted bitumen with n-pentane followed by (3) chromatographic analysis and detailed characterization of the solvent-free extract and raffinate samples obtained from the deasphalting experiments [7].

2. Separation of SARA Components

The experiment was carried out in 10 liter flat bottom Pyrex flask at a constant temperature of 45^oC by heating the flask with a thermostated heating mantle. Deasphalting was accomplished using an n-pentane solvent system for a period of 2 hours and 100 grams of the extracted bitumen was used while the solvent-bitumen ratio was varied. For the first hour, the system was agitated with air and was then allowed to progress to equilibrium condition without agitation. Two distinct phases – a liquid phase at the top (raffinate) and a solid phase at the bottom (extract) – were observed at the end of the deasphalting process. These phases were carefully separated and weighed. Solvent removal from each was then accomplished by vaporization until constant-weight raffinate and extract products were obtained. In practice, the removal of the high boiling extraction solvent and its subsequent recovery will require a system of flash tower and vacuum steam stripper, which will reduce the solvent content in the finished raffinate and extract to 0.0, to 0.02 wt.%.

A dual-packed adsorption (silica-alumina gel) column (DAC) was used in the analyses to separate raffinate sample into saturate, aromatic and resin components. The column was a 61.0cm long by 1.6cm inner diameter,

100ml burette with a small pluck of glass wool immediately above the stop cock. The bottom half of the column was tightly packed with 88.0grams of fully activated Brockman, activity 11 alumina gel and the top half was equally tightly packed with 62.0grams of fully activated 60-120 mesh (250-125mm) silica gel. An electric vibrator was used for obtaining the packing. A 500 ml eluant reservoir was fitted at the top of the column. The detailed experimental procedure followed the ASTM method (D-2007) as published [8]. The SARA analysis is out-lined schematically in Figure 2.

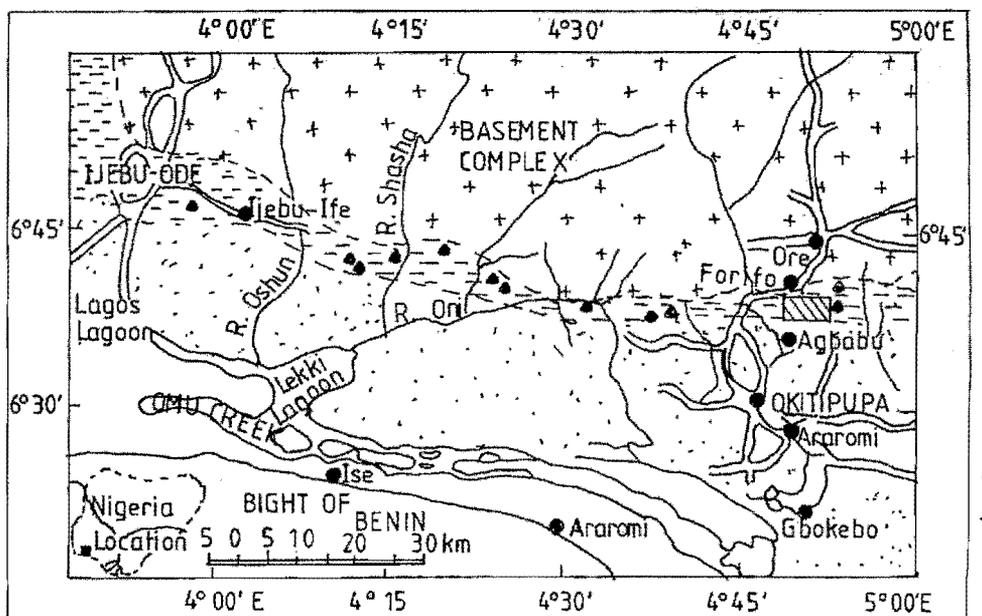


Figure 1: Geological Map of Southwestern Nigeria Showing Location of Tar Sand Deposits

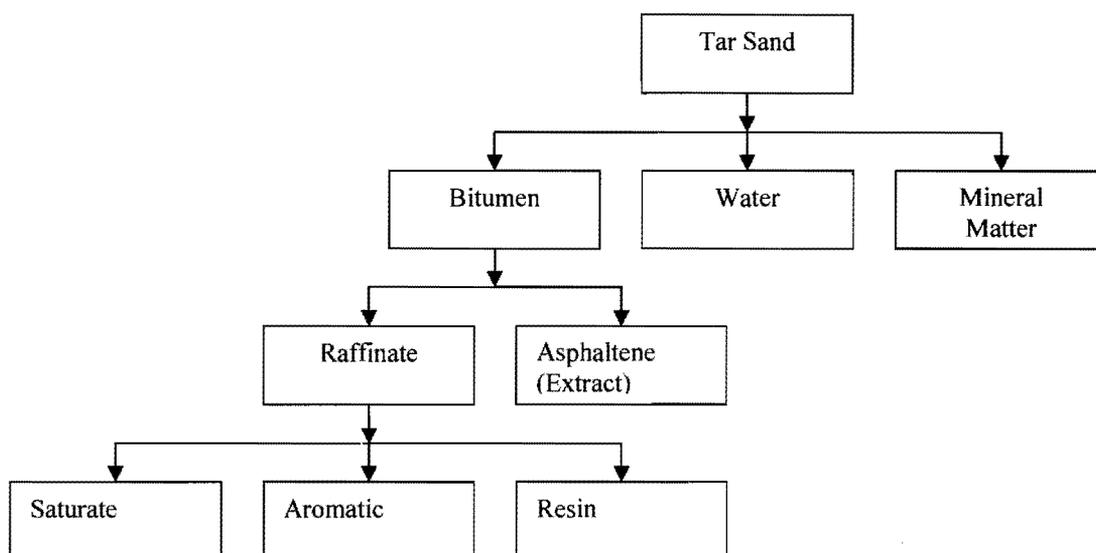


Figure 2: Tar Sand Fraction Separations Flow Chart

3. Physical Characterization

The solvent-free extract (asphaltic) and raffinate (deasphalted) components and the extracted bitumen were analyzed using high temperature programmed dual-packed absorption-elution chromatography (DAC) and gel-permeation chromatography (GPC). The GPC analysis employed a model chromatograph supplied by Waters Associates [9] to obtain the molecular weight and molecular size distribution for each sample analyzed. The GPC equipment consists essentially of a solvent reservoir, pump and injector, a column, a refractive index (RI) detector and a waste collection reservoir. For each analysis, a 10ml hypodermic syringe was used to inject 2ml of 4.5 ml% sample (an analytical reagent grade toluene) into the column, and the procedure was repeated three to four times for each sample to check for reproducibility of results.

4. Metals Content

Duplication of 1.00g samples each of the extract and raffinate samples contained in crucibles with lids were placed in a Gallenham muffle furnace maintained at 550°C for 5 hours for ashing. After ashing and cooling, 0.30g of the ash was leached with 5ml of 2M hydrochloric acid in an acid-cleaned polyethylene bottle at 85°C for 2 hours, filtered and the metals content in the leachate determined by Flame Atomic Absorption (AA) spectroscopy (Buck model A Atomic Absorption Spectrophotometer).

III. RESULTS AND DISCUSSION

Table 1 shows the relative concentration of bitumen in the two tar sand samples used. Average results of chemical and physical properties of the used bitumen samples Agbabu and Olowo-Irele are presented in Table 2. The average results of the characterization data measured for the bitumen samples investigated are shown in Table 3. The extract and the raffinate yields from the n-pentane extraction process of the bitumen are given in form of relative percentages of the two distinct phases in the samples. Table 3 also gives the average yield and product properties of Nigerian crude bitumen.

The raffinate was further analyzed to obtain more information on the saturates, aromatics and resins by means of the dual packed absorption-elution chromatographic technique. The average results are presented in Table 4. The influence of SARA concentrations on the system studied under different temperatures is presented in Table 5. It is observed that the viscosity increases with molecular weight. The deasphalted fractions have the lowest viscosity and hence the highest viscosity index. Similarly, the asphaltic fractions also have the highest viscosity and hence the lowest viscosity index.

In general, these observations for the basic parameters of the bitumen samples indicate that the extracted bitumen from Nigerian tar sands possesses good quality indices as portrayed by the physical and chemical parameters. Even though, the degree of asphaltenes of the bitumen samples used was high (24.65wt. %), this is possibly because it was derived from biodegraded crude oil. However, the aromatics, resins and paraffinicity (measured as saturates content) are given as 29.80, 30.75 and 14.80 wt. % respectively. This means that crude bitumen of high asphaltene concentration is expected to have more tendencies to suffer from the problem of asphaltene flocculation and deposition. This has been proved by many investigators [5, 10-13].

For pollution control, information on the sources is one of the basic requirements [14]. WHO [15] stressed the importance of this for potential health gains as demonstrated by USDOT [16]. These results from the analyzed samples could have a far-reaching impact on environmental management of the tar sands and end users' areas just as it would help in the protection of health of the workers if given deserved attention by concerned authorities in the country.

The bitumen yields of tested samples were in the range of 45 – 83 % (Table 2) and this call for proper handling for environmental pollution prevention. The presence of trace heavy metals (Vanadium and Nickel) at detectable level (Tables 2 – 4) also means the same environmentally because during production and processing activities of these tar sands, the metals could find their ways into the environment. Their environmental contamination could be via air, water, or soil. Through air, this could be in form of fumes. Nucleation, coagulation, and condensation of vapours of the metals could result in particulate formation [17]. Their presence in the raffinate part (Table 4)

confirms the possibility of the release as fumes into the environment and this could pose great dangers to lives around, as they may not be easily removed.

Nickel is not removed at a rate that would significantly reduce public exposure thus exposing the people living around to its ambient concentration. It is a carcinogen [18] and this confirms the danger in its inhalation from a contaminated environment. If present in particulate form it can easily be removed from the atmosphere through rain washout and deposition. Rain washout of soluble form of nickel [19] could lead to water contamination while atmospheric deposition of the insoluble form could result in soil and vegetation contamination. The presence of sulphur in the analyzed samples is a strong indication that both the soluble salts of nickel (sulphate) and the insoluble compounds (sulphite) could be released into the environment from the tar sands. Both forms of nickel were identified as influencing DNA repair inhibition in human [20].

Like nickel, environmental contamination of vanadium through the air could lead to DNA damage [21] and the release of super oxide anions [22] which are dangerous substances, in human body. The detection of its compound in water [23] confirms that rain washout effect of particulates removal from air polluted atmosphere earlier mentioned could result in water contamination by vanadium in a vanadium contaminated environment.

In addition to the sulphite and sulphide forms of nickel which could be induced by the presence of sulphur in the tar sands is the possibility of gaseous SO₂ formation which can contaminate the environment together with mercaptans. Health impacts of SO₂ as showed by DOH [24] make this detection a useful information. It is an indication that acid rain could be experienced in the tar sands deposit area.

Aromatics (which are mostly volatile organic compounds) detected from these samples (Table 4) are also of environmental concern. Akeredolu and Sonibare [25] once detected some of these compounds (Benzene, Toluene, and Xylene) in a Nigerian petroleum refinery's environment. They are volatile and their potential impact when released into an environment could be felt several kilometers away from source. Some are carcinogens thus the handling of these tar sands at any level calls for a protection against the compounds.

Implications of the above as revealed by various levels of the compounds classified by the Federal Ministry of Environment in Nigeria as hazardous [26] are the need for adequate control measure in the tar sands development. There is a need for environmental control to prevent mental retardation due to intoxication from heavy metals [27]. During the production and processing of the tar sands, workers should put on respirators preferably those with correct sorbent materials as demonstrated by Lee and Wu [28]. Apart from site and factory workers, the immediate and distant environment of the tar sands areas could be at risk if any of the identified pollutants could be allowed into the environment because pollution level of an area could increase if it receives air masses that pass directly over a contaminated area [29].

Several control measures are considered good enough to put these identified pollutants to check. For instance during exploration or refining of tar sands, NiO formation can be prevented by encouraging crystallizing and particle formation [30] which can be easily controlled. Electrostatic precipitator, gas scrubbers, etc are some of the control equipment that can assist in this environmental protection. For buildings located around the tar sands areas, sub-slab depressurization system can be used. Rydolk and Skaret [31] once reported positive results when indoor air quality of buildings located around voc (aromatics) – contaminated ground and fitted with the sub-slab depressurization system was monitored. As earlier pointed out by Bello et al [2], development and implementation of environmental guidelines for tar sands development in Nigeria is the best option for the control of these identified potential pollutants. Fatta et al [32] also agrees with this while reporting that developed guidelines for application of best available technologies are the best measure for pollution control.

Table 1: Bitumen, Water and Mineral Matter Content in Tar Sand Used ^a

| Sample | Bitumen (%) | Water (%) | Mineral Matter (%) |
|--------------|----------------|----------------|--------------------|
| Agbabu | 83.417 ± 0.052 | 15.143 ± 0.033 | 1.440 ± 0.035 |
| Olowo-Irele | 45.753 ± 0.023 | 33.48 ± 0.05 | 20.759 ± 0.041 |
| Mean (wt. %) | 64.585 ± 0.075 | 24.311 ± 0.083 | 11.099 ± 0.076 |

^a Expressed as Mean ± SD (% wt.)

Table 2: Average Results Physical and Chemical Properties of Nigerian Crude Bitumen Used

| Physical Properties | Value |
|--|--------|
| Gravity, API | 10.060 |
| Viscosity, cs (mm ² /s) at 100 ^o C | 4.8298 |
| Sulphur, wt. % | 0.40 |
| Conradson Carbon residue, wt. % | 17.30 |
| Pour Point, ^o C | 44.70 |
| Viscosity Index | 141.0 |
| Viscosity gravity Content | 0.8765 |
| Vanadium, ppm | 32.50 |
| Nickel, ppm | 35.30 |

Table 3: Average Yields and Product Properties of Nigerian Crude Bitumen Separation

| Sample | Value |
|---|-------|
| Deasphalted Oil (DAO) yield, wt % | 78.35 |
| Deasphalted Oil (DAO) Properties | |
| Degree API gravity | 12.20 |
| Viscosity, cS at 40 ^o C | 1.24 |
| Viscosity, cS at 100 ^o C | 0.20 |
| Pour Point, ^o C | 46.23 |
| n-Heptane Insoluble, UOP, wt % | <0.01 |
| Refractive Index | 1.54 |
| Metals (ppm) | |
| Nickel | 25.41 |
| Vanadium | 28.35 |
| Asphaltic Oil (AO) Yield, wt. % | 21.65 |
| Asphaltic Oil Properties | |
| Specific Gravity, 60/60 ^o F | 1.117 |
| Softening Point, R \$ B, ^o C | 42 |

Table 4: Average Results of the Characterization of Raffinate Components

| Parameter | Saturates | Aromatics | Resins |
|---------------------------|-----------|-----------|--------|
| Yield, wt. % | 14.80 | 29.80 | 30.75 |
| Gravity, ^o API | 13.65 | 13.02 | 12.42 |
| Viscosity | 0.43 | 0.62 | 0.20 |
| Surface Tension | 0.0350 | 0.0372 | 0.0386 |
| Pour Point | 27.07 | 30.45 | 43.18 |

| | | | |
|------------------|-------|-------|-------|
| Refractive Index | 1.45 | 1.54 | 1.62 |
| Metals | | | |
| Vanadium, ppm | 16.20 | 18.30 | 24.90 |
| Nickel, ppm | 11.10 | 16.40 | 27.30 |

Table 5: Kinematic Viscosity of SARA Components

| Family Group | Kinematic Viscosity (mm ² /s) (cS) | |
|--------------|---|--------------------|
| | 40 ^o C | 100 ^o C |
| Saturates | 0.20 | 0.08 |
| Aromatics | 0.43 | 0.19 |
| Resins | 0.62 | 0.37 |
| Asphaltenes | 1.21 | 0.86 |

IV. CONCLUSION

Based upon the conducted measurements, the following conclusions are drawn:

1. SARA components of the Nigerian crude bitumen were quantified and presented on the basis of physical and chemical characteristics.
2. The implications of the estimated SARA components on the Nigerian crude bitumen production technology options are also discussed.
3. Establishing the SARA components crude bitumen seems to be a basic building block in the scientific quest to find solutions to asphaltene crude oils production problems.
4. Vanadium, nickel, sulphur, and aromatics present in the analyzed samples calls for the development of adequate environmental guidelines for tar sands development in Nigeria for environmental protection against the potential degradation.

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