Engineering and Chemical Characterisation of Natural Bitumen Resources from Nigeria

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Abstract

Engineering and chemical properties of bitumen in Agbabu were evaluated for their suitability in road pavement construction. Raw samples of natural bitumen were collected in Agbagbu, Mile 2 and Mulekangbo, Ondo State, Nigeria. The engineering properties analysis involves bitumen penetration, flash and fire points, water content, loss on heating and specific gravity. Chemical evaluation includes analysis of heavy metals by the use of Atomic Absorption Spectroscopy (AAS) and analysis of Poly Aromatic Hydrocarbons (PAHs) using Gas Chromatography/Mass Spectrometer (GCMS). Agbabu and Mulekangbo bitumen samples fall within 200/300 penetration grade, classified as temperature susceptible bitumen, while samples of Mile 2 fall within 100/150 penetration grade, classified as conventional paving bitumen. Thus, Agbabu and Mulekangbo bitumen can be used in temperate regions of the world, while Mile 2 bitumen can best be applied in tropics, after upgrading by modifiers. The results of AAS indicate a high concentration of iron in the samples in the decreasing order of Fe<Zn<Cu<Mn<Pb<Ni. For Agbabu bitumen sample, the concentration indicates Fe (509 mg/kg), Zn (16 mg/kg), Cu (14 mg/kg), Pb (1 mg/kg), Ni, Cd and Mn are negligible, Mile 2 bitumen sample indicates Fe (8605 mg/kg), Zn (36 mg/kg), Cu (35 mg/kg) Mn (27 mg/kg), Ni and Cd are negligible; for Mulekangbo bitumen sample: Fe (8905 mg/kg), Zn (48 mg/kg), Cu (39 mg/kg), Mn (37 mg/kg), Pb (7 mg/kg), Mn (37 mg/kg), Ni (1 mg/kg) and Cd is negligible. Metals like Pb, Ni, Cd, even though present in small concentration can cause environmental hazard. GCMS analysis revealed high percentage of PAHs such as Chrysene, Pyrene, Fluorene, Phenanthrene and Anthracene in Mulekangbo bitumen sample, while Agbabu and Mile 2 bitumen samples indicate low percentage of target PAHs. PAHs present in bitumen sample of Mulekangbo can be carcinogenic and mutagenic, thus, exposure to these compounds can pose health/environmental risks. This study recommends clean technology during refining process to remove hazardous PAHs from the bitumen to prevent human and environmental health challenges during utilization.

Keywords: *Natural bitumen, engineering properties, heavy metals, PAHs, pavement construction*

1. Introduction

Bitumen is a mixture of organic liquids that are highly viscous, black, sticky, composed primarily of highly condensed polycyclic aromatic hydrocarbons and metals such as nickel, iron and vanadium. In other words, bitumens contain a complex mixture of aliphatic compounds, cyclic alkanes, aromatic hydrocarbons, PAHs and heterocyclic compounds containing nitrogen, oxygen and sulfur atoms, and metals (e.g. iron, nickel, and vanadium). Elemental analyses indicate that most bitumens contain primarily hydrocarbons, i.e. carbon, 79–88%; hydrogen, 7–13%; sulphur, traces to 8%; oxygen, 2–8%; nitrogen, 3%; and the metals vanadium and nickel in parts per million (Speight, 2000). The exact chemical composition of bitumen varies depending on the chemical complexity of the original crude petroleum and the manufacturing processes. Consequently, no two bitumen products are chemically identical, and chemical analysis cannot be used to define the exact chemical structure or chemical composition of bitumens. It is soluble in carbon disulphide, chloroform, ether and acetone, partially soluble in aromatic organic solvents, and insoluble in water at 20°C (IPCS, 2004). The compositional value of its constituents influences the industrial applications of bitumen. The principal refinery process used for the manufacture of bitumen is a two-step distillation: atmospheric distillation followed by vacuum distillation. The distillation is designed to remove polycyclic aromatic hydrocarbons (PAHs) from bitumen. This results in very low concentrations of PAH in the final product bitumen. This is sometimes followed by air rectification (mild oxidation) and/or oxidation (severe oxidation) depending on the required final product properties (Eurobitume and Asphalt Institute, 2015). Bitumen originates with chemical and physical attributes as immature oil which has undergone little secondary migration. The greatest amount of natural bitumen results from the bacterial degradation under aerobic conditions of originally light crude oils at depths of about 1,524 m or less and temperature below 80°C. The biodegradation involves loss of most of the molecular weight volatile paraffins and naphthenes, resulting in a crude oil that is very dense, highly viscous, black or dark brown and asphaltic (Meyer et al., 2007).

Bitumen either in natural form or obtained from petroleum consists of four fractions namely: saturates, aromatics, resins and asphaltenes. PAHs often play a key role in the hazard evaluations of materials with respect to their impact on health and the environment. Recently, PAHs have played an important role in the outcome of the cancer hazard assessment of occupational exposure to bitumen and its emissions. Crude oils contain low parts of PAH/PAC and as such low (ppm) levels may be present in bitumen. The PAHs are mainly released during the burning of petroleum and its derivatives (USEPA, 2007). Hydrocarbon having benzene properties are called aromatic, and in the presence of two or more fused benzene rings, they become known as PAHs. According to Lopes (2008), the acute symptoms in pavers involve: eye irritation, nose and throat irritation, headache, dryness and skin irritation. Hein et al. (2013) estimated that global bitumen and heavy oil resources are around 5.6 trillion barrels, with most of these located in the Western Hemisphere. The high viscosity of bitumen prevents it from flowing to a wellbore under in-situ reservoir conditions. Natural bitumens are naturally occurring deposits of asphalt-like material, these deposits have physical properties that are similar to those of petroleum derived asphalt, but the composition is different. They exist in two main forms; either as pare bitumen accumulated down-deep below the earth surface or outcrops as oil impregnated sand, which is generally known as tar sand or oil sand. In Nigeria, natural bitumen has been found in Ondo, Ogun, Lagos, Edo and Enugu States with a combined proven reserve of about 14.86 billion barrels with a quality estimated to be second largest in the world but yet to be explored for economic purposes.

The major applications of bitumen are in paving for roads and airfields, hydraulic uses (such as dams, water reservoirs and sea-defence works), roofing, flooring and protection of metals against corrosion. More than 80% of bitumens are used in many different forms of road construction and maintenance. It is also the basic feedstock for petroleum production from tar sands. The extracts from bitumen are very rich in aromatics, which makes it a suitable feedstock for petrochemical industries (Lurgi, 1987). The chemical composition of bitumen is a great determinant of its grade or quality. Bitumen derived from different sources, or produced with different manufacturing processes and/or crudes can have wide variations in chemical compositions and other physicochemical properties with different levels of service benefits. Any bitumen whose chemical composition and other physicochemical properties deviates significantly from compositions of bitumen of standard grades or known acceptable qualities can be unreliable in service for most engineering applications or cause unpredictable problems in its service usage (UNEP and ILO, 2004).

This investigation of the engineering material is conducted due to the large reserves of natural bitumen resources and potentials for sustained production in large quantity in Nigeria, high demand for better strength of road elements, lesser road maintenance, increase in traffic, poor construction materials and continuous road failure caused by rutting, cracking and moisture damage. Thus, this study is necessitated to provide basic information of the quality and performance grade of the bitumen for the implementation of good resistance roads of high performance traffic loading, high bearing capacity and to ensure the health and safety of workers during the execution process of highway works.

2. Description of the study area

Bitumen samples were collected from four different locations, Agbabu, Mile 2 (Samples A and B) and Mulekangbo sites, where bitumen outcrops occur in Odigbo and Okitipupa Local Government Areas of Ondo State, called bitumen belt of Southwestern Nigeria. It lies between latitudes 6° 31’ N and 6° 38’ N and longitudes 4° 46’ E and 4° 52’ E (Figure 1). The location falls within the eastern Dahomey Basin and runs through Edo, Ondo and Ogun States (Adegoke et al., 1980). It is an area of lowlands with few ridges about the lowlands, the hills are very high which are characteristic of the tropical rainforest of southwestern Nigeria. The temperature is relatively high during the dry season with the temperature reaching about 30°C. The area is well drained by NE-SW trending rivers like Oluwa, Ufara, Omilala, Opeki, Shasha, Oba and Ogun. The rivers dominate the drainage system of the study area and it's mainly dendritic. Some of the sample locations can be assessed by roads and footpaths while, other locations can only be assessed by footpaths.

3. Geology of the study area

Geologically, the main bitumen belt in Nigeria occurs on the eastern margin of a costal sedimentary basin known as the Benin Basin. The eastern ward limit of the Benin basin is marked by the Okitipupa High while, the basin extends westwards into Togo and the Volta Delta (Ghana). The crystalline basement rocks form the foundation of the whole area (FMSMD, 2006). The study area falls within the sedimentary terrain in the Dahomey basin of Southwestern, Nigeria. The sedimentary terrain of Agbabu falls within the eastern portion of the Dahomey Basin. The geologic sequence is composed of the Nkporo Shale, upper Coal measures, Imo shale group, coastal plain sands (Benin formation) and quaternary coastal alluviumin (Figure 2). The Nkporo Shale is made up of shale, sandy clay and lenses of sand. The Imo shale group is composed off shale while the Coastal Plain Sands has alternations of clay/sandy clay and clayey sand/sand. The Quaternary Coastal Alluvium is composed of an alternating sequence of sand and silt/clay (Jones & Hockey, 1964). The aquifer units are sand, sandstones, clayey sand and dissolved/ fractured limestone which are unconfined and confined in nature. The study areas belong to the Afowo Formation of the Cretaceous Abeokuta Group, uncomfortably overlying the basement. The Afowo Formation is composed of coarse to medium grained sandstone with variable but thick interbedded shale, siltstone and claystone. The sandy facies are tar bearing while the shale are organic rich.

The Dahomey basin is an Atlantic margin basin containing Mesozoic-Cenozoic sedimentary succession reaching a thickness of over 3000 m. it extends from southeastern Ghana to the western flank of the Niger Delta. Its stratigraphy is classified into Abeokuta Group, Imo Group, Oshosun Formation, Ilaro Formation and Coastal Plain sands and Alluvium (Jones & Hockey, 1964). Omatsola & Adegoke (1981) recognized three formations belonging to the Abeokuta Group. These are: Ise Formation (Neocomian-Albian) consisting essentially of continental sands, grits and siltstones, overlying the basement complex. Overlying the Ise Formation is the Afowo Formation (Turonian-Maastrichtian) consisting of coarse to medium grained sandstones with interbeds of shale, siltstones and clay. The Araromi Formation (Maastrichtian-Paleocene) conformably overlies the Afowo Formation and consists of sands, overlain by dark-grey shales with interbeds of limestones and marl.

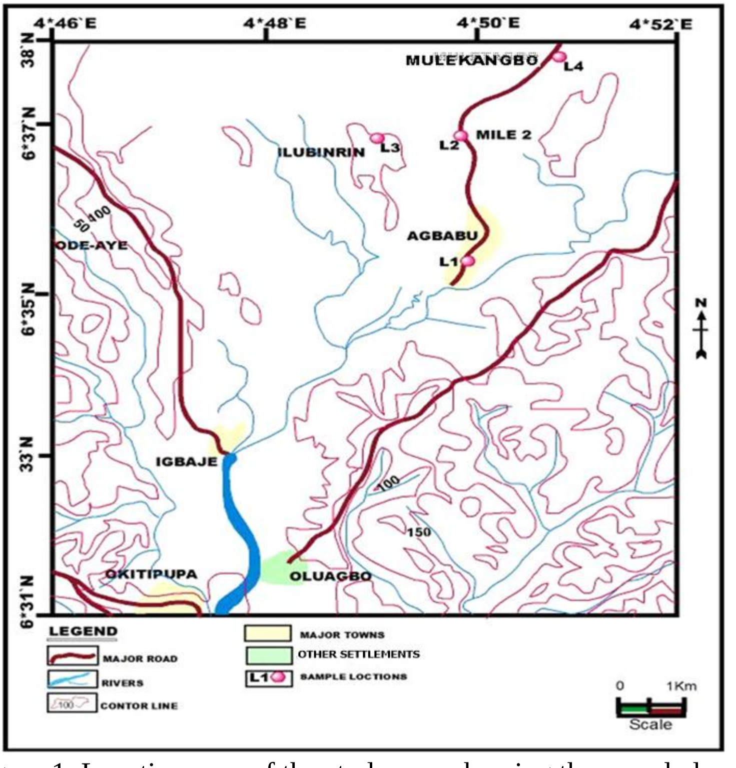

Figure 1. Location map of the study area showing the sample locations

4. Material and Method

4.1. Sample collection

Four natural bitumen samples were collected at four different locations within the richest bitumen spots at Agbabu, Mile 2 (Samples A and B) and Mulekangbo. One sample was collected from a standard extraction hole drilled with metal casing by early explorers of bitumen in Agbabu. Two bitumen samples were collected from the deposits within a water logged area, some kilometers away from Agbabu community and the last bitumen sample was collected at the well drilled by the early explorers of Mulekangbo community in a cocoa plantation site. The sample collection involved the use of dip stick, hand trowel, sterilized plastic containers, marker, GPS (each sample location was plotted using a global positioning system) and paper tape. The samples were collected and properly kept in a well labeled plastic containers and were later taken to the laboratory for the required analysis.

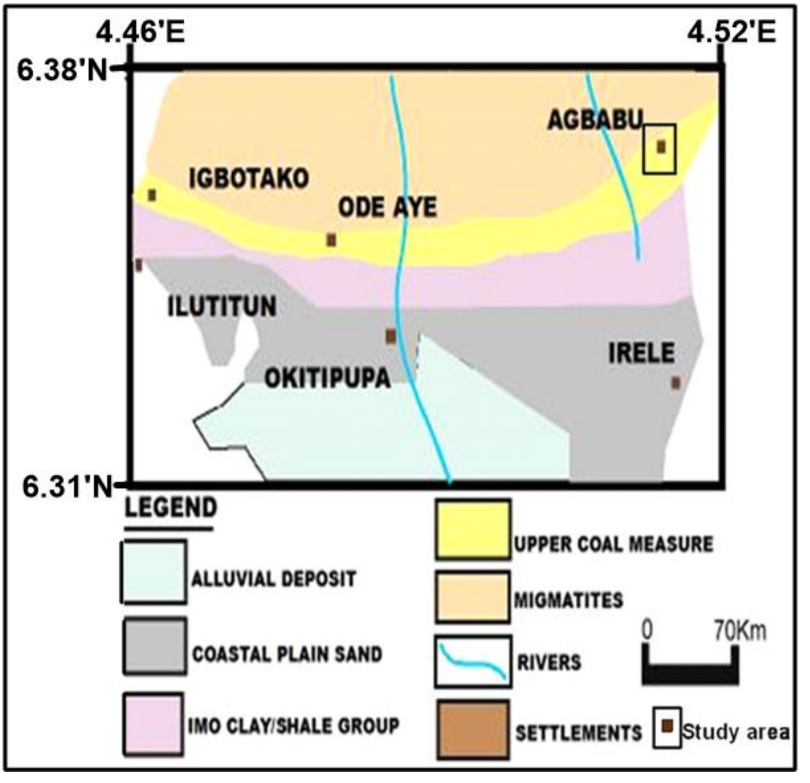

Figure 2. Geological map of the study area

4.2. Determination of flash and fire points

The flash point tells the critical temperature above which suitable precautions are required to be taken to eliminate the danger of fire during heating. The flash-point is the temperature at which bitumen fume may flash, or spark. This temperature is usually 230°C or higher for common paving bitumen. The flash-point provides an indication of fire hazard and the test is frequently used to indicate whether a given product has been contaminated with materials of lower flash-point (ASTM D92-01 (2001)).

Test cup, a thermometer and a bunsen burner were used for the fire point experiment. The test cup used was filled with the bitumen sample to the standard level; thermometer was inserted into the cup and heated at the rate of 5°C/min. The test flame was lighted and adjusted to a diameter of 3.8 to 5.4 mm. The test flame was applied when the temperature read on the thermometer has reached each successive 2°C mark. A lighted flame was passed across the sample at interval of 15 seconds. The flash point was considered as the lowest liquid temperature at which application of the test flame caused the vapors of the sample to flash, while the fire point was considered as the temperature at which the test flame causes the sample to ignite and remain burning for at least 5 seconds.

4.3. Determination of loss on heating

Bitumen sample was scooped into the test cup and weighed to an accuracy of 0.01 gm at room temperature. Then it was place in an oven and was heated for five hours at 163°C. After that, the sample from the oven was brought out and cooled to room temperature and the weight was taken at an accuracy of 0.01 gm, with the value noted and recorded.

Calculation

i) Loss on heating = Weight of bitumen before heating – weight of bitumen after heating.

ii) Percentage of loss on heating = Loss on heating / Weight of bitumen before heating * 100.

4.4. Determination of Water Content (water-in-bitumen)

100 g of bitumen sample was measured and transferred to a cylindrical container. Sufficient trichloroethylene free from water was added to permit refluxing to take place and then bolt on the cover with a dry gasket in position and fixed the receiver and condenser in place. Adequate flow of water through the condenser and heat to give a steady reflux action was ensured. Continuous heating was ensured until the volume of water in the receiver remained constant. Then the volume of water was then measured and its mass was recorded. Then, the water content was calculated as a percentage by mass of original sample to the nearest 0.1%.

4.5. Determination of specific gravity

Bitumen sample was heated in oven to melt. 100 g of the heated sample was weighed into a gravity bottle of a known weight and volume. The weights of the bottle plus the sample was taken and recorded. The sample was allowed to cool for about 30 minutes and the solvent (trichloroethylene) was added to the sample in the bottle to the standard mark. It was ensured that the bottle was shaken while adding the solvent to allow for outright dissolution of the sample. The bottle was then put in the water bath at 25°C for about one hour and refilled to the mark due to a little decrease in the level of the solvent in the bottle and weighed.

The specific gravity of the bitumen sample was calculated as:

Specific gravity = *density of natural bitumen/density of water at 4°C following standard procedure*.

4.6. Determination of penetration

The penetrometer used for the conduction of this test was made up of a needle assembly with a total weight of 100 g and a device for releasing and locking in any position. The bitumen samples from each location was scooped in a test cup and heated until pouring temperature, and then cooled to room temperature. The sample container was then placed in the transfer dish with water at the required temperature of 25°C, from the constant temperature bath, the sample being completely covered with water at all times. The needle was then released for 5 secs and relocked immediately at the end of the period and the penetration value was obtained from its digital indicator. Care was taken not to disturb or jolt the apparatus when releasing the needle. This was repeated for all the samples.

4.7. Determination of Chemical Composition

The chemical composition includes the heavy metals and PAHs analysis. The heavy metal is determined majorly by the use of Atomic Absorption Spectrophotometer. The Polycyclic Aromatic Hydrocarbons were determined by the use of the GCMS. The materials used for this analysis include; measuring cylinder, beaker, conical flask, funnel, filter paper, hot plate, fume cupboard, AAS, and the reagent used are: Aqua regia (HCl + HNO_3) and perchloric acid.

Procedure: 0.5 gm of samples was weighed into a digesting flask and digestion was carried out with 10ml of mixture of conc. HNO_3 and HCl (aqua regia) with few drops of perchloric acid added. The mixture were heated on digesting block until the fume of the acid ceased and made up with distilled water into a 500 ml standard flask. Analysis was carried out with AAS VGP 210 following the standard procedure as described by the operation manual of the equipment.

4.8. PAH Analysis

The bitumen sample was extracted using Methanol and the extracts was transferred to 100 ml pear-shaped flasks and evaporated to nearly dryness under reduced pressure of 150 mbar at 35°C using a rotary evaporator fitted with thermostated heating bath). An additional 10 ml n-hexane was added to the concentrated extracts and evaporated to a small volume (about 1 ml). Then the sample was transferred to 1.5 ml chromatographic vial for gas chromatography analysis. The PAHs were quantified by internal calibration performed with a GCMS (Agilent GC6890/5973MSD). For PAHs analysis, a HP-5 MS column (Aglient, length 30 m, i.e. 0.25 mm, film thickness of 0.25 mm) was employed with the following temperature program: 60–280°C at 6°C min^{-1}, isothermal holding at 280°C for 20 min using helium as the carrier gas. The instrument was operated with an initial flow of 1.2 ml min^{-1}, head pressure 0.03 Mpa, and injection mode as follows: splitless (1 ml), temperature of injector: 280°C. The Mass Spectrometer (MS) was operated using the electron impact (EI) ionization mode at 70 eV (electron volt), scanning from 50 to 550 mass units at 0.82 s $scan^{-1}$. All PAHs were determined by selective ion monitoring.

5. Result and Discussion

5.1. Engineering Properties of bitumen samples

The values obtained for flash and fire points of the natural bitumen samples of the study area are as shown in Table 1. The values ranged from180°C - 241°C and 220°C - 288°C for flash and fire points respectively. Mulekangbo bitumen sample has the lowest flash and fire point values, while Mile 2 (Sample B) bitumen has the highest values. This result is similar with that of previous study by Guma et al (2012) for two tested natural bitumen samples.

The values of loss on heating ranged from 1.15% - 2.52%. The result indicates that Mile 2 (Sample A) bitumen has the lowest value of percentage loss of water during heating, while Agbabu bitumen sample has the highest value of percentage loss of water on heating. Based on this result, only Mile 2 (Sample A) bitumen of all tested bitumen samples meets the requirement of 1% loss on heating (ASTM 1998) bitumen grading.

The percentage of water present in the bitumen samples of Mulekangbo and Mile 2 (Sample A) is 3.9% (Table 1). Agbabu bitumen sample has the lowest percentage of water of 1.9%. The high value obtained for Mulekangbo and Mile 2A samples may be due to their presence in waterlogged area. This high value in moisture in bitumen requires modification/upgrading of the bitumen in the study area to prevent reduction in adhesiveness of bitumen to aggregate during compaction in pavement construction. The specific gravity (Gs) of the bitumen samples ranged from 0.68 – 0.84. The specific gravity of each sample compares favourably with that for asphalt standard of 1 maximum as given by ASTM D5-97 (1998).

The penetration of bituminous material is a measure of the consistency of bitumen at a given temperature. This property in-turn indicates the quality and grade of bitumen. As can be observed from Table 1, the values of penetration of bitumen fall in the range of 100 – 300 dmm. The penetration value of Mile 2 (Samples A and B) bitumen fall in the range of 100/150 for bitumen of acceptable grades commonly used to manufacture asphalt mixes, cut-back bitumen, bitumen emulsions and modified bitumen. An increase in penetration value of bitumen implies hardening of the material. This hardening of bitumen has a negative effect on the quality of bitumen. Hardening of bitumen has been emphasized to be responsible for distresses such as breakdown and rupture in the pavement which led to premature failure of road (Nassar et al, 2012). Based on the bitumen grade summarized in Table 2, two of the four bitumen samples collected (Mile 2 bitumen (Samples A and B)) fall within the grade 100/120 and 120/150 respectively, classified as conventional paving bitumen can be applied on road construction in the tropic regions like Nigeria, when appropriately upgraded or modified in order to provide a variety of properties such as good resistance to aging, durability, high performance traffic loading and high bearing capacity. Abgabu (Sample C) and Mulekangbo (Sample D) bitumen flow at room temperature classified as temperature susceptible bitumen and can be best applied for road pavement in temperate regions of the world.

Table 1. Summary of the engineering properties of bitumen samples

Sample Location	Water-in-bitumen (%)	Penetration at 25 °C (dmm)	Gs	Loss on heating (%)	Flash Point (°C)	Fire Point (°C)
Sample A (Mile 2A)	3.9	110	0.84	1.15	196	240
Sample B (Mile 2B)	2.2	150	0.68	2.35	241	288
Sample C (Agbabu)	1.9	206	0.68	2.52	238	277
Sample D (Mulekangbo)	3.9	226	0.82	2.25	180	220

Table 2. The grade of bitumen

Bitumen location	Grade	Best possible use
Mile 2A (Sample A)	100/120	Conventional paving bitumen
Mile 2B (Sample B)	120/150	Conventional paving bitumen
Agbabu (Sample C)	200/300	Temperature susceptible bitumen
Mulekangbo (Sample D)	200/300	Temperature susceptible bitumen

5.2. Trace metals in bitumen samples

The concentration of trace metals in bitumen samples are shown in Table 3. Trace metals have been employed in the natural bitumen characterization. Iron (Fe) concentrations range from 509 to 8905 mg/kg. High level of Iron (Fe) in sample collected from Mile 2 (8905 mg/kg) and Mulekangbo (8605 mg/kg), in contrast to the sample collected from Agbabu (509 mg/kg). The concentration of the elements for all the samples in decreasing order is as follow: Fe > Zn > Cu >Mn>Pb. The concentration of iron is the highest (8905 mg/kg) while Pb is the lowest (1.00 mg/kg). The concentration of heavy metals in the samples shows slight similarities with the work obtained by Bakare et al. (2015). The exceptional high concentration of iron for sample collected from Mile 2 (Sample A) may be as a result of the presence of the sample in waterlogged area. The regular occurrences of the high rainfall and flooding have contributed to the leaching of most trace elements and this has contributed to the increased level of these metals. The relatively high levels of Fe, Pb and Ni observed in the result of some of the samples may be associated with the bitumen sample obtained from the marine environment. The presence of Manganese (Mn) and Lead (Pb) in sample from Mile 2 and Mulekangbo, may pose environmental hazard and catalytic poisons during the refining of the bitumen.

The differences that occur with other studies may be due to the fact that previous studies of Ipinmoroti and Aiyesanmi (2001) and Adebiyi and Omole (2007) were conducted on bituminous sand while the present study used flow bitumen obtained from observatory wells. During the process of extraction of bitumen from bituminous sand, some of the metal contents might have been leached out from the sample, hence, the relatively lower concentrations of some metals reported. It is observed that work has not been carried on Mulekangbo observatory well. The result of Mulekangbo bitumen sample indicates high concentration of Fe, Mn, Pb, and Zn. These heavy metals when present in high quantity cause environmental hazards. The exceptionally high concentration of heavy metals may be due to contaminations during collection of the sample, because the sample was found in contact with biogenic materials and with water emanated from the well beneath.

Table 3: Concentrations of trace metals (ppm) in bitumen samples

	Sample locations		
Heavy metals (mg/kg)	Agbabu	Mile 2	Mulekangbo
Zn	16.00	48.00	36.00
Cu	14.00	39.00	35.00
Pb	1.00	7.00	5.00
Ni	ND	1.01	ND
Cd	ND	ND	ND
Mn	ND	37.00	27.00
Fe	509.00	8905.00	8605.00

ND: not detected

5.3. Polycyclic Aromatic Hydrocarbons

The asphalt binders (or bitumen) release fumes which have PAHs. The PAHs belong to a class of complex chemical compound whose structure is in the form of linked benzene rings, and is widely distributed in the atmosphere. However, some PAHs are considered to have carcinogenic and/or mutagenic potential. Bitumen emissions, generated upon heating, may contain two-ring to seven-ring PAHs, several of which are mutagenic and carcinogenic (IARC, 2011). In mammalian cells, exposure to bitumen emissions or their condensates produced mutagenic intermediates and DNA adducts.

Analysis of the sample from Mile 2 contains wide spectrum of PAHs (Figure 3). In the sample, 37 PAHs have been found, with Hexadecane showing a higher percentage of 6.56%, others like Phenanthrene, Naphthalene and its derivatives show lower percentage. The United States Environmental Protection Agency (USEPA, 2000), ranked sixteen PAHs as priority in relation to health and the environment: Naphthalene (Na), Acenaphthalene (Ac), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Ph), Anthracene (An), Pyrene (Py), Chrysene (Ch), Fluoranthene (FL), Benzo [a] anthracene (BaA), Benzo [b] fluoranthene (BbF), Benzo [k] fluoranthene (BKF), Benzo [a] pyrene (BaP), Dibenzo [a, h] anthracene (DA), Benzo [g, h, i] perylene (BPE) and Indeno [1,2,3-c, d] pyrene (IP). Possible long-term damage caused by chronic health hazard has diverted more attention to PAHs.

According to WHO (1998), apart from PAHs, several other substances potentially harmful to health are asphaltenes, straight and branched aliphatic hydrocarbons, naphthene aromatics and resins. From the analysis of Agbabu bitumen sample, Duodecane, ethyl ester shows a wide spectrum (Fig. 4) and the presence of benzene (target) ranged from 1.16 to 2.57%. Spectrum of PAHs values of bitumen sample collected at Mulekangbo is shown in Fig. 5. The result of PAHs from bitumen sample collected at Mulekangbo indicates higher amount of Pyrene, and a considerable high amount of the entire target PAHs like Chrysene, Fluorene, Anthracene, Phenanthrene, Triphenylene and Fluoranthrene, but Triphenylene, Benz [a] anthracene, and Cyclohexane are negligible. The effects of PAHs present in Mulekangbo bitumen sample are considered to have carcinogenic and/or mutagenic potential. Exposure to these compounds through inhalation or even absorption through the skin during application to streets and roads can cause skin cancer (Gasthauer et al., 2007). The emissions generated during the production and application of the bitumen from this location would pose health and environmental risk to those involved. Also, these PAHs can leach into the environment through the degradation of the road surface and contaminate water bodies. When bitumen is applied during mixing in asphalt binders, it is usually handled at elevated temperatures, so trace amounts of PAHs may occur in the hot bitumen fume and cause cancers risk to the workers handling the mixing.

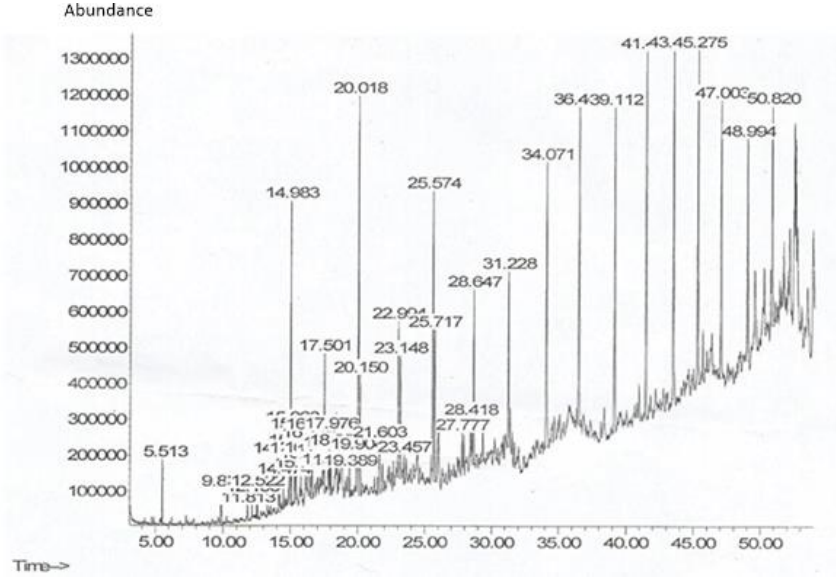

Figure 3. Spectrum of PAHs values of bitumen sample collected at Mile 2.

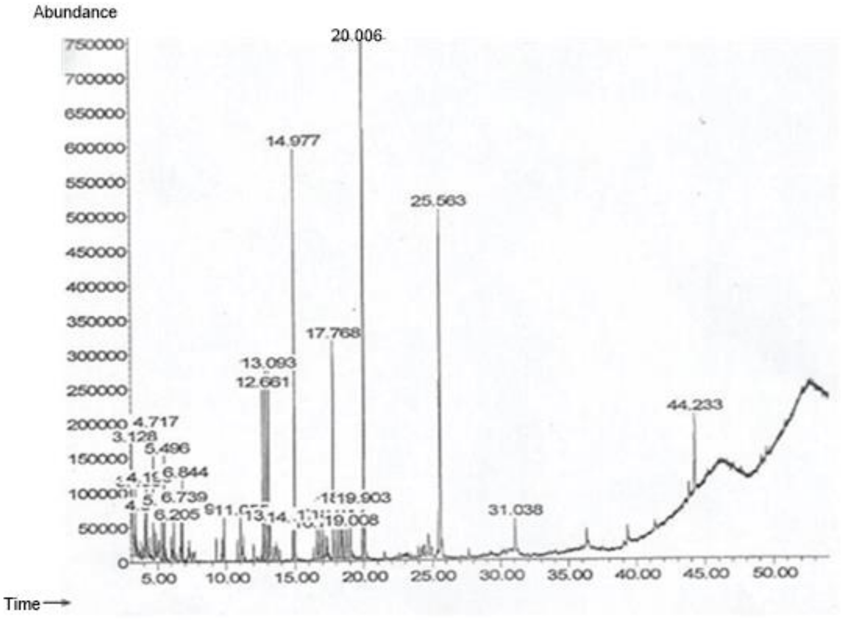

Figure 4. Spectrum of PAHs values of bitumen sample collected at Agbabu.

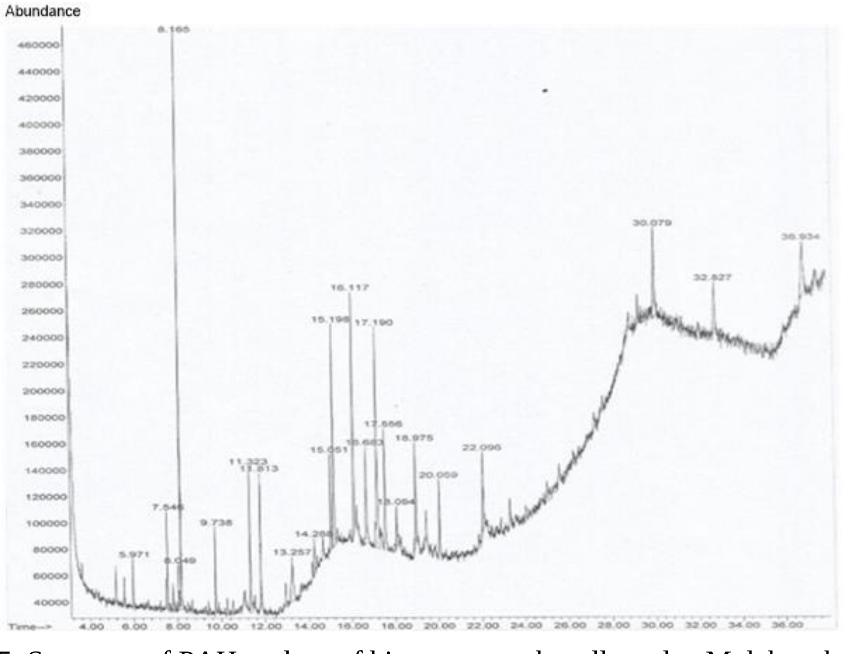

Figure 5. Spectrum of PAHs values of bitumen sample collected at Mulekangbo

6. Conclusion

The engineering and chemical properties of natural bitumen samples collected from Agbabu and its environs have been determined using standard methods. The water content of bitumen and loss on heating of the samples in the locations are greater than the recommended values of 0.2% and 1 max respectively. The specific gravity of the samples is below the standard value of 1.01 for bitumen of good grade. From the penetration values, the bitumen are classified into two grades. Agbabu and Mulekangbo bitumen samples are classified as temperature susceptible bitumen while, Mile 2 (sample A and B) are classified as conventional paving bitumen. Mile 2 bitumen can be applied successfully in road construction in the tropics, but this can only be achieved after they must have been upgraded.

The AAS test carried out showed that Agbabu, Mile 2 and Mulekangbo have a low concentration of heavy metals except for the high concentration of iron. However, low concentrations of lead and nickel in all the samples may pose environmental hazard and catalytic poisons during the refining of the bitumen. The GCMS revealed high percentage of PAHs in the bitumen sample collected from Mulekangbo and the targets PAHs like Pyrene, Anthracene, Fluorene, etc. are carcinogenic and mutagenic in nature. Exposure to these target PAHs during application to streets and roads through inhalation and absorption through the skin tend to pose health hazards. Therefore, exploitation of Mulekangbo bitumen must undergo the primary bitumen refining process "distillation" in order to remove the PAHs from the bitumen. The percentage of targets PAHs like Naphthalene in the samples collected from Agbabu and Mile 2 are low with no Pyrene, Anthracene and Fluorene. Thus, Agbabu and Mile 2 bitumen would have no impact on health and the environment during exploitation and utilization. This study recommends standard exploration and clean technology (distillation) during refining process to remove hazardous PAHs from the bitumen.

Reference

Adebiyi, F.M., Omole, A.A., (2007). Organic, chemical and elemental characterization of components of Nigerian bituminous sands bitumen. Energy Sources. *Part A: Recovery, Utilization and Environmental Effects, 29(8)*, 669-676.

Adegoke, O.S., Ako, B.D., Enu, E.I., (1980). *Geotechnical Investigation of the Ondo State bituminous sands*. Geology and Reserves Estimate. Geological Consultancy Unit, Department of Geology, Obafemi Awolowo University, Ile-Ife. 1: 56.

ASTM D5-97 (1998). *Standard Test Method for Penetration of Bituminous Materials*. Annual Book of ASTM Standards, Volume 04.03, American Society for Testing and Materials, Philadelphia 19103-1187.

ASTM D92-01 (2001). *Standard Test Method for Flash and Fire Points by Cleveland Open Cup*, ASTM, International, West Conshohocken, PA, www.astm.org

Bakare, H.O., Esan, A.O., Olabemiwo, O.M., (2015). Characterisation of Agbabu natural bitumen and its fractions using Fourier transform infrared spectrometry. *Journal of Chemistry and Materials Research, 7(8)*, 1-11.

Eurobitumen and Asphalt Institute, (2015). *The Bitumen Industry – a Global Perspective*, 3rd edition, Eurobitumen and Asphalt Institute, ISBN 978-1-934154-73-1.

Federal Ministry of Solid Minerals Development (FMSMD), (2006). *Technical Overview in Nigeria's Bitumen Belt and Development Potential. Report*: Federal Ministry of Solid Minerals Development, Abuja, Nigeria, 1-14.

Gasthauer, E., Maze, M., Marchand, J.P., Amouroux, J., (2007). Characterization of asphalt fumes composition by GC/MS and effect of temperature. *Fuel, 87*, 1428-1434.

Guma, T.N., Madakson, P.B., Yawas, D.S., Aku, S.Y., (2012). Assessment of physicochemical properties of some bitumen from Nigerian Resources. *Nigerian Journal of Basic and Applied Science, 20(2)*, 177-181.

Hein, F.J., Leckie, D., Larter, S.R., Suter, J.R., (2013). Heavy oil and bitumen petroleum systems in Alberta and beyond: The future is non-conventional and the future is now. *AAPG Studies in Geology, 64*, 1-21.

International Agency for Research on Cancer (IARC) (2011). Monographs on bitumen and bitumen emissions and some heterocyclic polycyclic aromatic hydrocarbons, 12.

International Programme on Chemical Safety (IPCS) (2004). *Concise International Chemical Assessment Document 59: Asphalt (Bitumen)*. Geneva, Switzerland: World Health Organization.

Ipinmoroti, K.O., Aiyesanmi, A.F., (2001). Trace metals in the bituminous sands of Ondo State, Nigeria. *Nigerian Journal of Science, 35*, 63-68.

Jones, H.A., Hockey, R.D., (1964). The Geology of Part of Southwestern Nigeria. *Geological Survey of Nigeria (GSN) Bulletin, 31*: 101.

Lopes, J.L., (2008). Riscos para a saude de trabalhadores de pavimentacao com asfalto. Revista de Gestao Integrada em Saude do Trabalho e Meio Ambiente. Sao Paulo.

Lurgi, R., (1987). *Distillation test on tar sand from Ondo State, Nigeria*. Essen, 1-8.

Meyer, R.F., Attanasi, E.D., Freeman, P.A., (2007). Heavy oil and natural bitumen resources in geological basins of the world: *U.S. Geological Survey Open-File Report 2007-1084. http://www.pubs.usgs.gov/of/2007/1084.*

Nassar, I.M., Kabel, K.I., Ibrahim, I.M., (2012). Evaluation of the effect of waste polystyrene on performance of asphalt binder. *ARPN Journal of Science and Technology, 2(10)*, 927-935.

Omatsola, M.A., Adegoke, O.S., (1981). Tectonic Evolution and Cretaceous Stratigraphy of the Dahomey Basin. *Journal of Mining and Geology, 18(1)*, 130-137.

Read, J., Whiteoak, D., (2003). *The Shell bitumen handbook,* fifth edition; Hunter, R. N., Ed., Thomas Telford: London.

Speight, J.G., (2000). *Asphalt. In: Kirk-Othmer encyclopedia of chemical technology*. New York, USA: John Wiley and Sons, Inc., 1-33.

UNEP and ILO, (2004). *Concise International Chemical Assessment Document 59*, Published Under the Joint Sponsorship of the United Nations Environment Programme, the International Labour Organization and World Health Organization, Geneva, Switzerland.

United State Environmental Protection Agency (2000). *Hot mix asphalt plants – Emission assessment report*, 454/R-00-019.

United State Environmental Protection Agency, (2007). Integrated Risk Information System (IRIS) on Polycyclic Organic Matter. *http://www.epa.gov/iris*.

World Health Organization (WHO) (1998). *Selected non-heterocyclic Polycyclic Aromatic Hydrocarbons. International Programme on Chemical Safety*, Environmental Health Criteria 202, Geneva.

