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Characterization of Nigerian Bitumen Extract Fractions

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Research Article

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Abstract

A comparative study was carried out to determine the behavior of N-hexane, Diethyether and Methanol extracts of Nigerian bitumen obtained from Irele Community of Ondo State, Nigeria. Total sulphate, Nitrogen and Moisture content were determined for the three extracts. FTIR, XRF techniques were employed to characterize the raw bitumen while GCMS was used to analyse the extracts. Moisture and Nitrogen content determinations revealed that diethylether extract has higher moisture (1.3%) and Nitrogen (0.854%) ; N-hexane extract has 1.0% and 0.784% while methanol extract is not detected (ND) and 0.084 moisture and Nitrogen contents respectively. SO3 (13.74%), CaO (12.34%) and Fe2O3 (7.33%) are the dominant oxides shown by the XRF spectroscopy with trace quantities of many impurities amounting to 58.68%.

The total sulphate content of diethyether, n-hexane and methanol extracts was 0.70, 0.62 and 0.12% respectively. The Nigerian Bitumen compares favourably with other bitumen deposits, however, a lot of attention and resource is needed for its commercialization.

Keywords: Bitumen; Nitrogen Content; Moisture; Total Sulphate; Oxide Composition

Introduction

Bitumen is a sticky, black and highly viscous liquid or semiliquid form of petroleum. It may be found in natural deposits or may be refined product; it is a substance classed as a pitch [1,2]. Its viscosity ranges between 8 and 10 API degrees. Its density (kg/m3) lies between 1.0 and 1.18, insoluble in water, has a boiling point greater than 300°C with melting point ranging from 54-173°C and flash point greater than 200°C.

Bitumen manufactured from crude oil is obtained as the last residue in fractional distillation of crude petroleum. The heavy residue obtained from the fractional distillation process is further treated and blended to make different grades of paving grade bitumen [3,4]. Processed bitumen plays an important role in many everyday applications. It is one of the most used solid mineral resources said to be useful in roofing, environmental protection, pipe coating, land slip containment, walkways, sound-proofing, electrical insulation, cosmetics, medicine and textiles. Bitumen's waterproofing and adhesive properties, durability and resistance to heavy loads make it the ideal material for use in all-weather environments. It is also a prime material in applications where strength and weather proofing are essential requirements. Moreover, bitumen membranes are extensively used as sound-deny panels in the automobile markets. It is also used as bituminous paints and disinfectants on a number of different surfaces, bitumen-based lubricants, preservative to plastic, sealants, and as asphalt for road construction and maintenance [5-7].

Christina [8], and Guma, et al. [9], Nigeria has an estimated bitumen (and heavy oil) reserves of about 38 and 14.86 billion barrels and ranked 6th (in a list of top 10 countries) with bitumen and heavy oil reserves succeeded

by Madagascar,UK, China and Azerbaijan with Canada, Venezuela, Kazakhstan, Russia and USA taking the lead. Francis [10], reported that Nigeria has an extrapolated reserve of 42 billion barrels and ranked second largest country with bitumen reserves, after Venezuela. Bitumen can be converted to liquid and refined to produce commercial products like gasoline, fuel oil and asphalt.

Ondo State is the most noted area of bitumen activities in the belt and has offices of Nigerian Bitumen Development Project located at Akure and Ore. Generally, some distinct bitumen-impregnated hydrocarbon types of occurrence have been identified within the Nigerian bitumen belt from topsoil downwards and location to location as: Outcrop, rich sands, lean sands, shales and heavy crudes. The average bitumen content of Nigerian tar sand is about 20% by weight. Very rich natural bitumen deposits are found in Ondo State around the region of Idiobilayo, Foriku, Agbabu, Okitipupa, and Aiyibi. Generally, tar sands are composed of bitumen, water and some mineral impurities. Tar sands with 5–10% by weight bitumen content are designated as good or medium grade [9-11].

According to Christina [8], Adedinila [11]; as well as Adebiyi and Akhigbe [12], the natural bitumen deposits of Ondo State are found in two basic forms, namely; soft and low viscosity /plain bitumen and outcrops of bitumen-impregnated sands extracted either by small-scale surface mining, large-scale surface mining and in-situ extraction.

Experimental

Materials

Sample Procurement, Preparation and Pretreatment

N-hexane, Diethylether, Methanol were purchased from a scientific shop in Sokoto State and stored without further treatment. Raw bitumen sample was obtained from Irele Community of Ondo State, Nigeria and preserved in plastic container till further use.

Preparation of Bitumen Extracts

The Extraction method adopted was Solvent extraction method using N-hexane, Diethyl ether and Methanol solvents. Fifty (50g) of the bitumen sample was transferred into a thimble and placed in the Soxhlet extractor fixed with boiling flask, filled to three quarter (3/4) with N-hexane. The same was used for Diethyl ether and Methanol solvents. Continuous extraction was done until a 1h contact time was reached. The three (N-hexane, Diethyl ether and Methanol) extracts collected in separate glass containers.

Analyses of Extracts

Total sulphate content as determined by Spectrophotometry method (Turbidometric and Colorimetric Method) described by Subramanian M, AOAC [13] and Nitrogen content by Kjeldhal method [14].

Nitrogen Concentration (Kjeldhal Method)

The method described by Krebs RD [14] was adopted for the Nitrogen content determination. One gram (1g) of the sample was weighed into 250ml kjeldhal flask. One tablet of kjeldhal catalyst was added followed by 10ml of concentrated H_2SO_4. It was heated gently for 15 minutes and rapidly at high temperature of 35°C until a clear or light green or grey colour was observed. The solution was allowed to cool and diluted to 100ml with distilled water. 5ml of 2% boric acid was put into 100ml beaker. 2 to 3 drops of mixed indicator were added and put at the tip of the condenser which has been fixed with the Markham distiller. 5ml of the diluted digest was put into the Markham, followed by 10ml of 40% NaOH and the tap closed. It was steam distilled until 50ml of the distillate was recovered in the beaker at the tip of the condenser. The distillate was then titrated with 0.01M HCl until the colour changed to give the end point. The same process was carried out with the blank (distilled water used for dilution).

Total Sulphate Concentration (Turbidometric Method)

Turbidometric method described by Subramanian M, AOAC [13] was adopted to determine the total sulphate concentration. The sample was digested 2gm of it into a Kjeldahl flask. At pH 3.0, 5 ml of concentrated HNO_3 was added and evaporated. 10 ml of 70% $HClO_4$ was added with few boiling ships. It was heated strongly until a clear solution was observed. 6M NaOH was added to neutralize it. It was made up to 100ml with distilled water in volumetric flask. 5ml of conditioning reagent (50ml glycerol, 30ml concentrated HCl, 300ml distilled water, 100ml 95% ethanol and 75g NaCl) was added. On stirring, a spoonful of Barium chloride crystal was added and stirred constantly for one minute. It was poured into the absorbance cell and the absorbance of the turbidity produced was taken by UV Spectrophotometer at 425nm. Absorbance of the Blank and serial dilution of primary standard sulphates stock solution were obtained at the same temperature.

Characterization

The XRF spectrum was obtained using Xenemetrix X-Cite multi-element spectroscopic bench top analyzer The elemental composition was developed using Horizon MB® XRF software. GC-MS was carried out using a CE 5980 GC coupled to an HP Finnigan 8222 MS held at 80°C for three minutes and raised to 310°C at 3°C min-1, 1µl of the sample was punctured through the inlet using an automatic sampling device at final temperature for 20 minutes with hydrogen as the carrier gas with a flow rate of 1ml/min, pressure of 50 kPa. Representative peaks matching the available compounds

were generated by Agilent ChemStation software.

Results

Results of various determinations are presented in the Tables 1-5.

Result of Moisture Content Determination

The result of moisture content determination for the 3 bitumen extracts is presented in the Table 1.

Extract/Solvent	Moisture content (%)
Diethyl ether (DEE)	1.3
N-Hexane	1.0
Methanol	ND

Table 1: Result of Moisture Content.
KEY: **ND;** Not Detected

Result of Nitrogen Content

The result of nitrogen content for the 3 bitumen extracts is presented in the Table 2.

Extract/Solvent	Nitrogen content (%)
Diethyl ether	0.854
N-Hexane	0.784
Methanol	0.084

Table 2: Result of Nitrogen Content

Result of the Total Sulphate Analysis

The result of total sulphate concentration in the 3 bitumen extractions is presented in Table 3.

Extract/Solvent	Sulphate content (%)
Diethyl ether	0.70
N-Hexane	0.62
Methanol	0.12

Table 3: Result of Total Sulphate Analysis.

Result of XRF Analysis

The result of X-ray florescence spectroscopy (XRF) Analysis of the Nitrogen Bitumen Extraction is presented in Table 4.

S/N	Oxide/Element	IUPAC Name	% Composition
1	Fe_2O_3	Iron (III) oxide	7.33
2	Al_2O_3	Aluminum oxide	1.23
3	SiO_2	Silicon dioxide	3.73
4	SO_3	Sulfur trioxide	13.74
5	CaO	Oxo calcium	12.34
6	TiO_2	Titanium dioxide	1.14
7	SrO	Strontium oxide	1.81
8	Other Oxides (Trace) Including L.O.I		58.68

KEY: **L.O.I;** Loss on Ignition
Table 4: Result of XRF Analysis.

Result of GC-MS Analysis

The GC-MS result is presented in Table 5.

S/N	Dominant Compound		Area (%)			Quality (%)	
		NH	DEE	ME	NH	DEE	ME
1	9,12-Octadecadienoic acid	61.28	62.78	2.82	99	97	98
2	n-Hexadecanoic acid	7.44	6.47	6.33	98	98	99
3	Linoelaidic acid	-	-	64.18			90
4	Octadecanoic acid	11.29	11.21	10.64	99	96	98
5	Methyl 9,12-heptadecadienoate	2.77	3.40	2.75	93	86	93
6	Butyl 9,12-octadecadienoate	6.85	5.19	6.50	95	95	95
7	9,17-Octadecadienoicacid	4.22	4.65	3.82	97	95	96

KEY: **NH;** N-hexane, **DEE;** Diethyl-ether, **ME;** Methanol
Table 5: Result of GC-MS Analysis of the Various Bitumen Extracts.

Discussion

The result of the moisture content determined for the 3 bitumen extracts is presented in Table 1. The result showed that highest moisture content (1.3%) was obtained in the DEE extract followed by N-Hexane (1.0%) while no moisture content detected in the Methanol extract. The result of the high moisture content in bitumen reported by Read J, Singh PS South African bitumen, (11.06 ± 0.11%) was less than that of Edo state Nigeria (16.77 ± 1.47%). The low value of moisture content showed that the Nigerian bitumen is of good quality and can withstand long storage without decomposing. Accordingly, the least value of moisture obtained in the methanol extract justifies that the methanol was good drying agent and as expected, showed less moisture than the other two extracts. Similar opinions were reported by Speight [15], Spirov and coworkers [16], Liu, et al. [17], Abramov, et al. [18], Odebunmi and George [19] as well as Ohenhen, I [20].

The nitrogen content determination for the 3 bitumen extracts presented in the Table 2 while the total sulphate analysis in Table 3. DEE extract had 0.854 and 0.70% Nitrogen and total sulphate respectively. N-Hexane extract had 0.784 and 0.62% Nitrogen and total sulphate respectively, while Methanol recorded 0.084 and 0.12 Nitrogen and total sulphate composition respectively. Similar result obtained by Carrington S, Akande JM [21,22] reported 0.81±1.65% and 0.77 ±1.47% for nitrogen and total sulphate concentrations respectively.

The result of the X-Ray Fluorescence (XRF) analysis of the nitrogen bitumen extraction is presented in Table 4. The results showed the presence of eight major oxide/elements. Trace (Other impurities) had the highest percentage (%) composition of 58.68%, followed by Sulfur trioxide (SO_3) with 13.74%, Oxo calcium (CaO) with 12.34%, Iron (III) oxide (Fe_2O_3) with 7.33%, Silicon dioxide (SiO_2) with 3.73%, Strontium oxide (SrO) with 1.81%, Aluminium oxide (Al_2O_3) with 1.23% and lastly, Titanium dioxide (TiO_2) had the least with 1.14%. Litrature by Lancaster IM, Souraki Y, Onojake MC, Adebiyi FM, Energy L [23-27] which stated in their study that asbestos rock contains 37.86% asphalt, 43.28% carbonate solids, and 18.86% other impurities. Other impurities could have been solid SiO_2, $CaSO_4$, CaS, and others.

According to Onoh JK, Adegoke OS, Adedimila AS, Read J, Singh PS, Adegoke OS, Vancleave J [28-35] these solids have very low solubility in water and acid when compared with carbonate solids. This cause other impurities still remain in the asphalt. In the previous study, asbuton rock from Lawele was previously found to contain mineral and asphalt. Asphalt from asbuton rock has high viscocity because the asphaltene content is high. On the average, asbuton rock contains 30.08% asphalt and 9.92% mineral. However, The CaO content decreases with the increase of other oxides present in the limestones. This may be attributed to the leaching of calcium by the solution and subsequent reprecipitation. Change of environment is indicated by the increase of SiO_2 content with the influx of terrigenous material [29]. The presence of Fe_2O_3 and high Ca indicates reducing environment and deposition in closed basin. The presence of little amount of phosphate and manganese in the limestone indicates a warm and humid climate during the deposition of carbonate sediments Adedimila AS [30] Fe_2O_3 correlates positively with S and authigenic minerals (pyrite, marcasite, calcite, gypsum).

The use of chemical agents to react with the minerals was found to be much more expensive and difficult to control the product, since certain chemical agents reacted to a particular mineral only, while usually, about 15 – 20% of the minerals were not limestone. Besides, some acid compounds chosen were also reactive to the metal equipment used in the process [31-35].

Table 5 presents the GC-MS results of the three extracts in the work. The dominant compounds obtained in all the 3 solvents were about six viz; 9,12-octadecanoic acid, n-Hexadecanoic acid, octadecanoic acid, methyl-9,12-heptadecadienoate, butyl-9,12-octadecadienoate as well as 9,17-octadecadienoic acid. Organic compounds, as reported by Ademoroti CMA, AOAC, Yasin G, Adebiyi FM [36-39] are the dominant compounds in the Nigerian bitumen extracts.

Linoelaidic acid appeared only in the ME extract, it is clear that the quality of the compounds is excellent and there is observable relation between the total area percentage of the compounds in the extracts.

The value for 9, 12-octadecadienoic acid is 61.28 and 62.78% in the NH and DEE extracts respectively, while insignificant amount (2.82%) is obtained in the ME extract.

Accordingly, the appearance of almost all the compounds gave best quality in the NH followed by ME and DEE. However, methyl9,12-heptadecadienoate ester showed the best appearance (3.40) in the DEE extract while butyl9,12-octadecadienoate ester showed best appearance (6.85) in the NH extract.

Conclusion

Extracts of Nigerian bitumen were used to test-run hypothesis by the ASTM 2007 that the quality of bitumen extracts is not significantly affected by the method of extraction and was observed to be true. The components of Nigerian Bitumen are mixtures, reach in different classes of hydrocarbons hence; the bitumen is a potential tool that can be utilised for energy production.

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