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Evaluation of the Chemical Composition of Tar Sands of Southwestern Nigeria

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Abstract: Tar sand samples obtained from different locations in Olowo/Irele, Iwopin, Agbabu and Ofosu/Oshosu in Ondo State, Nigeria were pyrolysed at three different temperatures: 100, 150 and 200°C. A detailed analysis was conducted on the pyrolysed samples after an exhaustive soxhlet extraction with benzene as solvent. The percentage of the oil obtained at different temperatures increases as the temperature increases. Column chromatographic method was used to elute five different fractions comprising: saturates, monoaromatics, diaromatics, polyaromatics and polars/resins. These results indicate that tar sands can be potential sources of feedstock for the petrochemical industry in the country.

Key words: Tar sands, hydrocarbons, feed stocks, petrochemicals

INTRODUCTION

Nigeria is richly endowed with abundance of natural resources such as crude oil, tar sands and natural gas. Crude petroleum is found in abundance in Southern parts of the country. Crude petroleum constitutes the largest foreign exchange earner for the country. This has prompted effective and intensive exploration for hydrocarbons by oil companies in the oil sands and heavy oil deposits of Southwestern Nigeria[1].

Tar sands are impregnated sands that yield mixtures of liquid hydrocarbons, which require further processing other than mechanical blending before becoming finished petroleum products.

Until recently, the Nigeria bitumen deposits were known as tar sands, but are now called oil sands. Oil sands are deposits of bitumen; viscous oil that must be vigorously treated in order to convert it into an upgraded crude oil before it can be used in refineries to produce gasoline, kerosene and other fuels.

Bitumen is about 20% of the actual oil sands found in Nigeria. The remaining 76% is mineral matter including clay and sands and around 4% of water. The conventional crude oil is either pumped from the ground or flow naturally. Oil sands must be mined or recovered *In situ*. Oil sands recovery process includes extraction and separation systems to remove the bitumen from the sand and water.

Crude oil is a liquid, which comprises of mixtures of various substances, the separation of which is sometimes difficult[2]. They are principally compounds comprising of carbon and hydrogen also called hydrocarbons. Sulphur, oxygen and nitrogen are also present in crude oil[2]. Nigeria's crude oil contains an insignificant proportion of sulphur[2].

Nigeria's crude oil is formed from decomposition of aquatic substances, such as marine animals and plants, which have been buried under various layers of mud and silt. Over the years, the sediments exert great pressure and high temperature occurs, as less oxygen is present at the depths. The buried organisms are transformed into crude oil and gas.

The Niger Delta Basin contains vast quantities of sedimentary rock and crude oil is mainly found around such rocks[2]. Bitumen or tar sands exist in a belt stretching from east of Ijebu-ode in Ogun state to east of Ore in Ondo state. Field exploration has given an indicated reserve of about 30 billion barrels of heavy crude equivalent reserves of bitumen in Ondo, Ogun, Ekiti and Edo states of Nigeria. Apart from being a major source of heavy crude oil and petroleum derivatives, the tar sands are also potential sources of heavy mineral sands like limonite, Zircon and Sulphur which are all vital industrial raw materials.

The bitumen in these tar sands has chemical properties similar to petroleum and therefore constitutes an attractive source of hydrocarbons[3]. The bitumen was found to consist of predominantly aromatic and naphthanic components with high boiling points[3].

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There are enormous deposits of tar sands in Ogun, Ondo, Ekiti and Edo states of Nigeria[3,4]. In spite of this abundance of tar sands deposit in the country, Nigeria imports their raw materials for the production of hydrocarbons used in the country. It has been suggested that if the tar sands deposits are mined and processed for hydrocarbons, the life of the petroleum industry in Nigeria would be extended by more than 40 years assuming the current production rate of about 2 million barrels of crude oil per day is maintained[3,4].

In Nigeria, research has not been intensively conducted, for the improvement and upgrading the quality of the bitumen in the tar sands into high grade oils that can be harnessed for petrochemicals. In this case, the bitumen of high boiling point will be converted to lower boiling hydrocarbons generating gas oil products such as gasoline, kerosene or naphtha[3].

The present study reports on the constituents of the bitumen tar sands of Southwestern Nigeria. The aim is to generate and provide alternative feed stock for synthetic petroleum and petrochemicals in the country.

MATERIALS AND METHODS

Sample collection: Samples of tar sands were collected from Olewe/Irele, Iwopin, Agbabu and Oshosu/Ofosu villages from the Nigeria, Bitumen (Tar sands) Project, Akure, Ondo state of Nigeria on 20th January 2000.

Sample treatment and analysis: 20 g of tar sand from Olowo/Irele were weighed into a reactor of known weight. The sample was repeated with two more reactions and labeled as IB, IRB, IKB, IC, IRC and IKC where A, B, C represents varying temperatures: 100, 150 and 200°C, respectively. For the other sets of samples from Iwopin, Agbabu and Ofosu/Oshosu were obtained three sets of samples for the different temperatures.

0.2 g of glass wool was introduced into the reactor, not beyond the constriction to prevent the tar sands from escaping while evacuating. The reactor was evacuated using a pressure pump for 30 min and sealed immediately. The reactor was weighed again and the new weight noted.

Pyrolysis: The furnace used for the pyrolysis was oven type U40 memmert 854 schevabach. The oven was set at the operating temperature and allowed to run for 10 min before the reactor was introduced into it. The duration of pyrolysis was 2 hrs in each case. The operating temperatures were 100, 150 and 200°C.

To terminate a run, the reactor was removed from the oven and allowed to cool to room temperature, after which it was stored in the freezer over night. The alteration of temperature was necessary for us to study the effect of temperature on the composition of tar sand.

Air buoyancy factor: The weight of air in the reactor was calculated to give the air buoyancy factor. 20 g of the sample were transferred into a reweighed reactor, which was similar to the ones used, earlier on. The glass wool was fixed in place and the reactor sealed after it had been evacuated. The reactor was weighed and then stored in the freezer over night. It was removed from the freezer, the seal removed and the reactor weighed immediately while it was still cold.

Soxhlet extraction: The reactor was cut open and the sample tied in a white cloth, which we discovered was more efficient than a thimble and dropping inside the soxhlet extractor for extraction using benzene as solvent. To ensure exhaustive extraction, the process lasted for 72 h. At completion, the benzene was recovered from the oil by distillation. The oil was kept in a hot air oven at 68°C for 24 hrs until constant weight was obtained. It was then transferred to the desiccators to cool. The sand was air dried for 48 hrs and then weighed. The percentage oil in the sand was calculated.

Precipitation of asphaltenes: 1 g of oil were placed in a beaker dissolved in 2 mL of benzene. This was transferred to 250 mL sample bottle and 80 mL of hexane was added to the bottle. The bottle was shaken after which it was placed in a deep freezer for 24 hrs.

The maltene fraction was decanted into a conical flask and the precipitate of asphaltene was washed into a 100 mL beaker with benzene. The Hexane was recovered from the maltene fraction by distillation. The maltene and asphaltene fractions were kept in a hot air oven for two hours and then transferred to a desiccator to cool to a constant weight. The percentage of asphaltene and maltene in the tar sand were then calculated.

Determination of volatile matter: 1 g of oil were placed in an evaporation basin kept in a hot air oven of 105±1°C for 24 hrs. The evaporation basin was removed and kept in a desiccator to cool to constant weight. The percentage volatile matter of the oil was then calculated.

Determination of ash content: The oil after determination of the volatile matter was placed in muffle furnace and the temperature of the furnace gradually raised to 600°C and maintained for 6 hrs after which the oil sample was transferred to the desiccators to cool to constant weight. The percentage ash was calculated and the ash preserved in 8% HCl solution.

Determination of sulphur content: The flask containing the oil was weighed. A piece of sodium metal was cut with a spatula and placed in fusion tube. The tube was heated mildly until the sodium melted and its vapor rose in the tube. 1-2 drops of the oil were dropped into the molten

Table I: The constituents of bitumen and tar sand (%) at 100 and 150°C

	Bitumen		Tar sand	
Location	100°C	150°C	100°C	150°C
Olowo/Irele	20.7±0.1	22.6±0.1	79.3±0.1	77.4±0.1
Iwopin	19.5±0.1	21.2±0.1	80.5±0.1	78.8±0.1
Agbabu	99.5±0.1	99.7±0.1	1.0±0.1	0.3±0.1
Oshosu/Ofosu	12.6±0.1	13.4±0.1	82.4±0.6	86.6±0.1

Data are means of triplicate determination ± standard deviations

Table 2: The constituents of asphaltene and maltene (%) in the tar sand at 100 and 150˚C

	Asphaltene		Maltene	
Location	100°C	150°C	100°C	150°C
Olowo/Irele	5.49±0.01	5.88±0.01	15.21±0.01	16.72±0.01
Iwopin	5.05±0.01	5.26±0.01	14.44±0.01	15.94±0.01
Agbabu	27.03±0.01	26.52±0.01	71.97±0.01	73.18±0.01
Oshosu/Ofosu	3.68±0.01	3.79±0.01	8.92±0.01	9.60±0.01

Data are means of triplicate determinations ± standard deviations

sodium. The tube was removed from the champs and heated first mildly and then strongly until the tube became red hot. It was held at this temperature for 2-3 min and the tube was plunged into an evaporation basin containing 10 mL of distilled water and the basin covered immediately with a white tile. After the reaction of the un-reacted sodium was completed, the white tile was removed and the content of the basin heated and brought to boil then filtered and washed several times with distilled water. The filtrate was acidified with 2.0 mL dilute acetic acid.

Approximately, twice the volume of filtrate of lead acetate solution was added and left over night. The solution was filtered and the precipitated lead sulphide was washed several times with distilled water and dried. The percentage of sulphur in the oil was calculated after determining the weight of oil used by re-weighing the flask of oil.

Oil separation and elution: 5. g of silica gel and 10 g of alumina were activated in a hot oven at 105°C for eight hours. 0.2 g of glass wool was introduced into the column with the aid of a glass rod and then the alumina and silica gel in this sequence were packed into a column in the ratio 2:1.

The acidified sand was introduced into the column and 35 mL of hexane was used to wash the column. The sample of the oil was dissolved in 2 mL of hexane since the ratio of oil to silica gel and alumina is 1:70:140, respectively and it was introduced on the surface of the sand in the column. The first fraction, the saturates was eluted with 30 mL of hexane. The second fraction, the monoaromatics were eluted with 30 mL mixture of benzene and hexane in the ratio 1:19 volume/volume. The third fraction, the diaromatics were eluted with 30 mL of benzene and hexane in the ratio 3:17 volume/volume. The fourth fraction, the poly-aromatics were eluted with 30 mL mixture of benzene, diethylether and methanol in the ratio of 1:1:3 volume/volume. The fifth fraction, polars and resin were eluted with 30 mL of methanol.

All the fractions were collected and kept in a hot air for 24 hrs to evaporate the solvents to dryness. The flask were then removed and kept in a desiccator to cool to constant weight. The percentage saturates, monoaromatics, diaromatics, polyaromatics, the polars and resins were calculated.

RESULTS AND DISCUSSION

Table 1 gives the percentage weight of bitumen and residual sand (recovered sand after the extraction of bitumen by benzene). After the separation of the bitumen, from tar sand, by various methods, an initial upgrading of the bitumen is achieved by coking process. The organic materials thermally decomposed during coking. All chemical transformations leading to the conversion of the heavy oil to lighter products involve organic-organic interactions. The direct coking of sand involves the thermal decomposition of bitumen in the presence of an inorganic matrix[6]. The inorganic matrix of tar sand may play important role in the composition and yield of the product. More bitumen (13.4-99.7%) was recovered at the temperature of 150°C while lower content of bitumen (12.6-99%) were derived at the temperature of 100°C.

Enormous quantity of oil was obtained at 150°C than 100°C because thermal cracking is necessary to attain more oil recovery[5,6]. The Agbabu tar sand is richer in bitumen content (99-99.7%), followed by Olowo/Irele tar sand, which generated 20.7-22.6% of bitumen. The lowest quantity of bitumen was recovered from Oshosu/Ofosu tar sand, which contained (12.6-13.4%) of bitumen. The Agbabu tar sand contains heavy oil, thereby producing high yield of bitumen (99-97%).

Furthermore, the Agbabu tar sand have high maltene content (71.97-73.18%), followed by Olowo/Irele tar sand which contained 15.21-16.72% of maltene. The Iwopin tar

Table 3: The constituent of volatile matter, organic matter and ash content of tar sand (%) at 100 and 150°C

	Volatile matter		Organic matter		Ash	
Location	100°C	150°C	100°C	150°C	100°C	150°C
Olowo/Irele	1.87±0.01	1.94±0.01	99.75±0.01	99.65±0.01	0.25±0.01	0.36±0.01
Iwopin	1.69±0.01	2.05±0.01	99.70±0.01	99.53±0.01	0.30±0.01	0.47±0.01
Agbabu	1.81±0.01	2.12±0.01	99.82±0.01	99.74±0.01	0.18±0.01	0.26±0.01
Oshosu/Ofosu	2.14±0.01	2.21±0.01	99.58±0.01	99.50±0.01	0.42±0.01	0.50±0.01

Data are means of triplicate determination ± standard deviations

Table 4: Sulphur content of tar sand at 100 and 150°C

Location	100°C	150°C
Olowo/Irele	0.63±0.01	0.58±0.01
Iwopin	0.81±0.01	0.64±0.01
Agbabu	0.35±0.01	0.26±0.01
Oshosu/Ofosu	1.47±0.01	1.26±0.01

Data are means of triplicate determinations ± standard deviations

sand contains (14.44-15.94%) of maltene while the lowest content of maltene (8.92-9.60%) was recovered from the Oshosu/Ofosu tar sand (Table 2). The maltenes refers to the saturated hydrocarbon fractions available in the sample. The content of maltene increases as the temperature increased. The content of the asphaltene are generally low in the samples compared to the maltenes. More deposit of asphaltene was derived from the Agbabu tar sand, which contains (26.52-27.03%) of asphaltene. The asphaltenes are considerably more difficult to process than the maltene. This is because they contain higher concentration of metals, which however poison the catalyst used in the upgrading process[3,7]. The asphaltenes contains most of the heteroatoms comprising sulphur, oxygen and nitrogen available in the bitumen[3].

Table 3 showed the volatile matter, organic matter and ash content in the bitumen tar sand. Levels of ash content were low at the temperatures of 100 and 150°C from the four locations analyzed. For Agbabu bitumen, their mean values of ash content range from 0.18-0.26%, Olowo/Irele bitumen ash content was 0.25-0.36%; Iwopin bitumen ash content was 0.30-0.47% while for Oshosu/Ofosu the bitumen ash content was 0.42-0.50%. In all the parameters considered, the ash content is less than 1%. This implies that there is negligible amount of inorganic matter in the oil. Moreover, oil sand has high concentration of fine divided mineral matter such as clay minerals in the interstices; it is possible some inorganic matter was left behind in the sand residue, which was not analyzed.

The results obtained in Table 4 showed that there is low sulphur content in the bitumen at both 100 and 150°C. Agbabu bitumen has sulphur content range from 0.26-0.35%; Olowo/Irele bitumen has sulphur content range of 0.58-0.63%; Iwopin bitumen contained 1.26-1.47% of sulphur. The low sulphur content indicates that the oils are quality oil. However, the sulphur content decreases as the temperature increases. It is likely that the sulphur content has been diminished by; (I) age and method of storage of tar sand samples and (II) the method of extraction of bitumen[3]. The extent of these factors on the value of sulphur content has not been determined. Moreover, it is suspected by researchers that prolonged storage of tar sands samples in contact with air probable resulted in oxidation and evaporation of some of the light sulphur compounds in the bitumen[3].

Five relatively distinct compound types were obtained after elution from the dual packed gel absorption column. These include saturates, monoaromatics, diaromatics, polyaromatics and polars/resins (Table 5).

The saturates consists of normal and branched saturated hydrocarbons comprising the alkanes as well as unsaturated naphthenes. Monoaromatics are compounds with only one aromatic ring regardless of the number of the saturated rings. A diaromatic has two rings which may be condensed, joined by single bond or is totally separated by the alkane chains or naphthenic rings. A polyaromatic has three or more aromatic rings. Polar materials are those compounds containing such heteroatoms as sulphur, oxygen and nitrogen[3].

From these findings, there is a decrease in the saturate and polyaromatics as the temperature moves from 100 to 150°C. This implies that the saturate and polyaromatics decomposed to the gaseous products and volatile liquids[5]. The polyaromatic decomposed to monoaromatics and diaromatics, resulting to an increase in the monoamonetics and diaromatics. The increase in the polars and resins can be attributed to coking, polymarizetion and condensation reactions of carbon atoms. It should be noted that coking reduces the quality of hydrocarbon products.

Furthermore, the effect of coking increases as the temperature increases. This explains the reason behind increase in the quantity of saturates at 100°C and less of the polars and resins at this temperature. Since more of the saturate is required, 100°C is recommended. At this temperature the coking effect is low compared to 150°C. At 200°C, the reactor busted. It is assumed that the gaseous products and volatile matter produced during the pyrolysis led to the busting because the quantity of the samples in the reactor was much for that temperature.

We noticed an increase in the monoaromatics, diaromatics, polars resins and a decrease in the saturate and polyaromatics for increase in temperature. Based on these findings, from this study, it is possible to develop

Table 5: The constituents of saturates, monoaromatis, diaromatics polyaromatics and polar resins available in the tar sands at 100 and 150°C

	Saturates		Monoaromatics		Diaromatics		Polyaromatics		Polar resins	
Location	100°C	150°C	100°C	150°C	100°C	150°C	100°C	150°C	100°C	150°C
Olowo/Irele	8.03	6.42	3.25	4.40	2.17	3.66	2.61	2.44	4.28	5.45
Iwopin	7.61	5.94	2.81	4.05	2.07	3.22	2.36	2.24	4.37	5.38
Agbabu	36.63	34.69	14.95	16.15	12.28	14.91	10.69	8.66	23.46	25.01
Ohosu/Ofosu	4.99	3.91	1.97	2.52	1.26	1.96	1.45	1.20	2.70	3.54

Data are means of triplicate determinations

a technology for upgrading the bitumen derived from tar sands into high-grade oils. If judiciously taped and processed, the tar sands could provide feedstocks for the petrochemical industry in the country.

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