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COMPARATIVE STUDY ON THE EXTRACTION STRENGTH OF SOLVENTS ON TAR SAND FROM OKITIPUPA, ONDO STATE

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Abstract
Tar sand, an aggregate of sand, clay, water and bitumen was sampled from Okitipupa area of Ondo State, Nigeria, extracted and optimized using n-hexane and toluene in a soxhlet extractor todetermine solvent effectiveness in extracting the bitumen content and their environmental effect. The experiment was carried out by heating the solvent at and above their boiling temperatures solely to get an optimum yield at a temperature and time of extraction of oil from the tar sand. The analysis gave an optimal yield of 9.07 % at 75°C in 4 h when n-hexane was used and an optimal yield of 21.27 % at 120°C in 4 h when toluene was used. A drastic change in colour was also notice in the sand residue to almost sandy soil nature when toluene was used as solvent compare to when n-hexane was used which shows a slight change from its blackish nature. The change in colour of the black tar sand is an indication of high extraction efficiency. Hence, owing to high demand for conventional oil supply in the country and the urgent need for an alternative source of oil, the bitumen extract can serve as an alternative source of unconventionaloil supply in Nigeria and feedstock in refineries.

1.0 INTRODUCTION

Tar Sand encompasses bitumen which makes up 10 to 20 % of the sand and about 80 to 85 % mineral matter including sand, clay and 4 to 6 % of water. Tar sand has similar compositions as the light crude [12]. These bituminous sands were discovered in Nigeria in the beginning of the 20th century, around 1900 [2]. The Nigeria's tar sands rank amongthe largest deposits in the World. It is second only to the deposits in Venezuela and compatible with the large tar sands deposits in Alberta, Canada and Trinidad [2]. They are believed to have been formed from biodegradation and water-washing of light crude due to lack of cap rock [12]. This impregnated sand contains liquid hydrocarbons, which when processed could be utilized as petroleum products. The bituminous reserves in Nigeria are called tar sands (oilsands). They are viscous oil deposits that must undergo vigorous treatment to convert it into upgraded oil before refining into useful products [12]. Nigeria tar sand belt stretches from east of Ijebu-Ode in Ogun State to Siluko and Akotogbo areas in Okitipupa (Ondo State) and to Edo state. It covers an approximate distance of 110 km [4]. Nigeria's reserve is estimated to be about 30 to 40 billion barrels with potential recovery of 3654 × 10^6bbls [3]. Ogun State

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has more than 40% of Nigeria's reserve, of the estimated 30 to 40 billion barrels of tar sand [13].

Studies into the tar sand reserve in Nigeria have in recent years developed great number of interest from several researchers. [6] carried out comparative study on the physio-chemical characteristics of the Nigeria bituminous sand and that of Alberta in Canada where oil extracted from tar sand contributes about 40% of the oil supply in the country. [7] and [6] characterized the tar sand deposits in Nigeria with respect to the oxide concentration, density and porosity. They deduced that these variables are dependent on the geographical location of the source sample.

Following the increase in the consumption of conventional oil supply and depletion or exhaustion of the Nigeria's oil reserves which currently stands at 36 billion barrels, with the exploitation rate of 2.4 million barrels per day, it is estimated that by the year 2060, the current reserves will be exhausted, at which time; tar sand could constitute an important alternative resource [11], since the Nigeria tar sand has properties similar to petroleumproduct [11].

The recovery of bitumen from tar sand is a difficult process due to its high viscosity. Viscosity can be reduced mainly by injecting steam at 300°C and solvents into the sands. During operation, large volume of water and energy are required in processing than the usually conventional oil extraction method. Surface extraction process is considered the most effective technique in use presently, where tar sand is excavated, washed with hot water before treating with sodium hydroxide (NaOH) to improve bitumen separation from the tar sand. Wetting agents (e.g. caustic soda, sodium silicate) could be used to aid the hot water dilution of tar sand [10].

Researchers have also studied the extraction strength of solvent on tar sand. Benzene when used as solvent for the extraction of bitumen using soxhlet extractor from tar sand deposit in Ondo State at four different locations, operated at three temperatures gave a progressive increase in extraction as temperature changes [8]. [1] deduced that extraction rate and the boiling point of the solvent used are inversely related when they compared the extraction strength of four different solvent at 100^0C, 120^0C, 140^0C for benzene, carbon tetrachloride, toluene and xylene.

The present study was therefore initiated to study the extraction strength of solvents on tar sandin Okitipupa, Ondo State, Nigeria.

2.0 METHODOLOGY

A Complete set of Soxhlet Extractors were employed in the extraction process. The samples collected were first crushed using a mortar and pistol to increase the surface area and sieve to attain the required particle size (500m). The particle size was kept constant throughout theexperiment. 60g of the grinded and sieved sample was weighed using a digital weighing balance before charging into the thimble of the extractor. The n-hexane/toluene solvent (250ml) was charge into the extraction flask. The whole setup was held in the heating mantle (Figure 1). The extraction begins by switching on the heating mantle. The n-hexane and toluene were heated above their boiling temperatures; 60–80°C for n-hexane and 110–130°C for toluene in 4 h of the extraction respectively. The experiment was stopped after 4hrs of extraction and the sample re- weighed to determine the percentage yield. The same procedure was carried out when the temperature was kept constant and the time varied between one to four hours (1–4hrs). The thimble was removed and the enveloped sample was replaced with another 60g of the tar sand. This procedure was carried out for five different runs to determine the optimum temperature and time.

Figure 1: Experimental setup for the extraction of oil from tar sand

3.0 RESULTS AND DISCUSSION

3.1 Analysis of Tar Sand Samples from Okitipupa

The samples obtained from this location were analyzed using Scanning electron microscope before and after extraction to check the morphology of the tar sand as shown in Figures 2a, 2b and 2c respectively.

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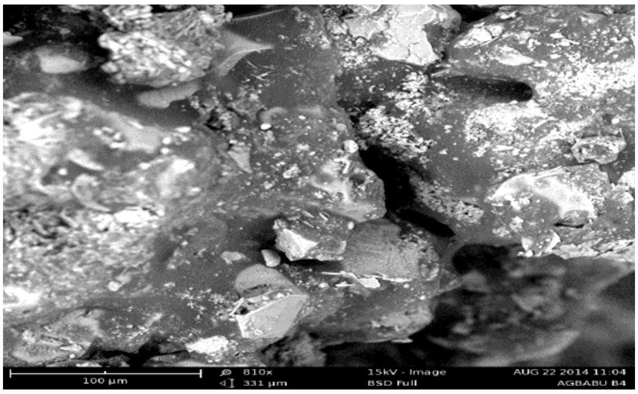

Figure 2a: Tar sand from Okitipupa before extraction

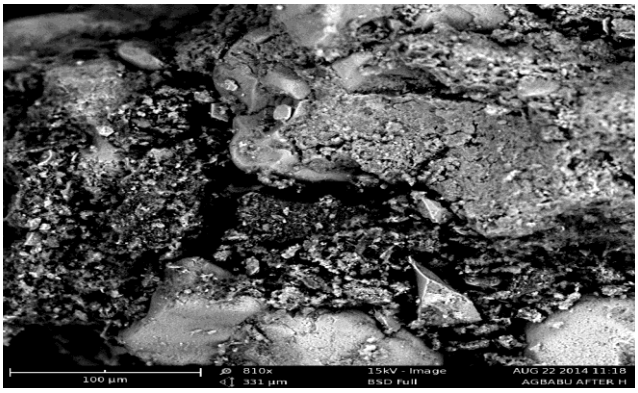

Figure 2b: Tar sand from Okitipupa after extraction with n-hexane

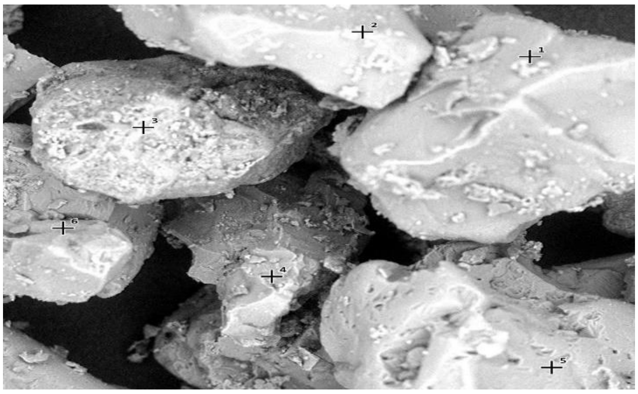

Figure 2c: Tar sand from Okitipupa after extraction with toluene

The Figure 2a shows the morphology of the tar sand sample before extraction. There are no pores opening because the surface is covered by the oil in the tar sand. After extraction, the crystalline surface of the tar sand was revealed as some of the oil that covered its surface hasbeen removed as shown in Figure 2b when n-hexane was used. The crystalline form of the tar sand was disrupted due to the effect of solvent and temperature in relation to time as the extractible yield (bitumen) was obtained.

The extend of disintegration from the crystalline form of the tar sand is solely dependent on the solvent used in the course of extraction and the applied temperature since different solvent have varying effect on the sample. The vigorous nature of thesolvent on the sample is notice in the amount of pore space created after extraction i.e. how disintegrated the sample is after extraction. Figure 2c shows the morphological change that occurred when the oil in the tar sand had been extracted using toluene. The extent of the extraction is seen in the porous nature of the tar sand morphology in comparison to the morphology in Figure 2a.

Table 1, shows the EDX analysis of tar sand from Okitipupa area of Ondo State before and after extraction. However, the analysis is a point data analysis, so the composition at a specific point may deviate from another.

Table 1: Elemental Composition of Tar Sand from Okitipupa

Element	Concentration Before	Concentration after Extraction	
Name		N-hexane	Toluene
Carbon	11.0	38.3	55.7
Nitrogen	14.6	40.9	0
Oxygen	32.1	0	32.7
Fluorine	25.5	0	0
Strontium	4.0	20.8	11.6
Lead	12.8	0	0

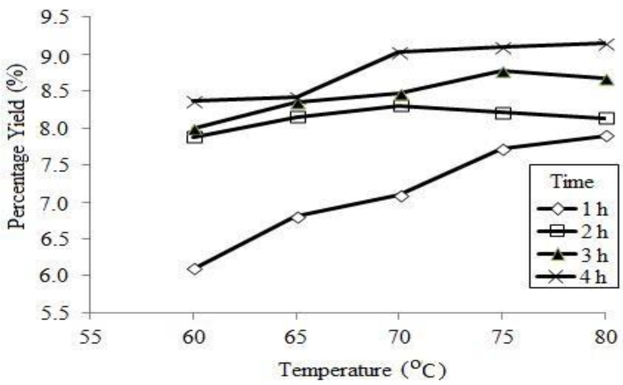

Figure 3a: Interactive effects of time and temperature on oil yield using n-hexane as solvent

3.2 Extraction of Bitumen from Okitipupa's Tar Sand Using N-Hexane and Toluene

Experimental conditions were set from preliminary experiment and twenty (20) different runs were generated by MINTAB software. In the extraction process, 60g of tar sand was used each for n-hexane and toluene solvents and the yields were obtained, each dependent on time and temperature. The inter-relationship between these factors shows their effects as extractionproceed. This progressive effect as time and temperature increase is shown in Figure 3a and 3b.

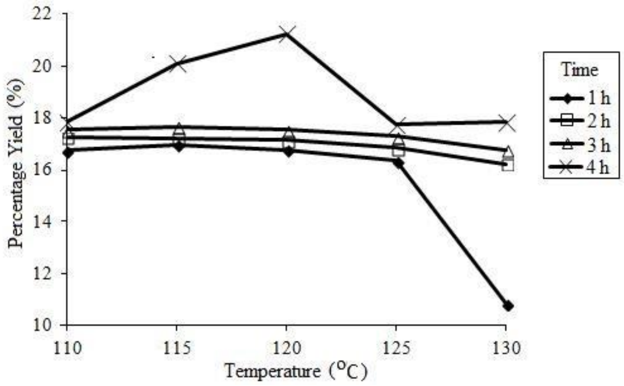

Figure 3b: Interactive effects of time and temperature on oil yield using toluene as solvent

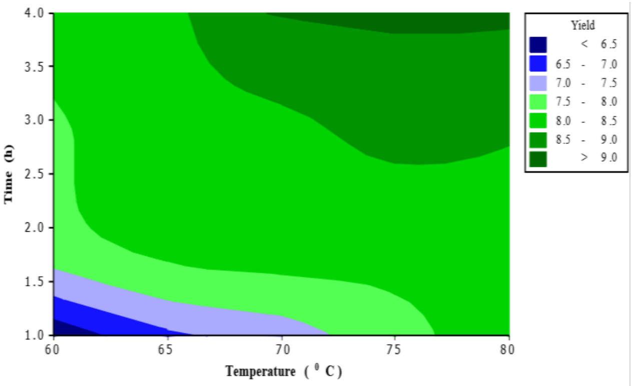

Figure 4a: Contour plot on the effects of time and temperature on oil yield using n-hexaneas solvent

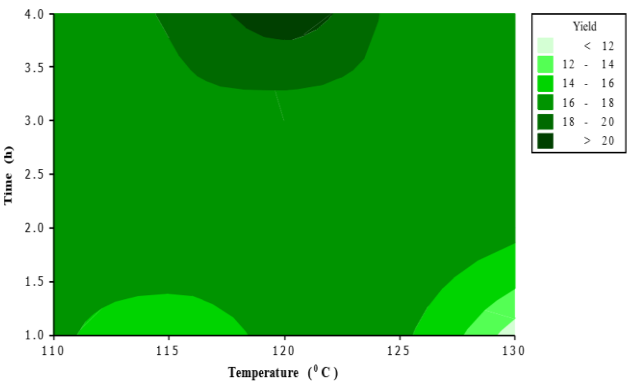

Figure 4b: Contour plot on the effects of time and temperature on oil yield using toluene as solvent

An increase in the yield of oil extracted from the tar sand as time and temperature increase wasnoticed in the Figure 3a. Hence, extraction is said to increase as the solvent is heated above its boiling temperature with respect to time. At low heating rate, the extract was proportional to the extraction time. The maximum yield was obtained at 75^{0}C which correspond to 9.07% in 4hrs when n-hexane was used as solvent. But it is economical advisable to extract at 70^{0}C (which correspond to 9.03% in 4hrs since the difference in yields (0.04%) at 70^{0}C and 75^{0}C is very negligible, hence 70^{0}C may be considered optimum, so as to save some amount of energy. The percent yield at 120^{0}C shown in Figure 3b when toluene was used as solvent gave a clear indication of the effectiveness of solvent boiling temperature in the course of extraction. At this temperature it is without doubt that the optimum yield was achieved at a stretch of 4hrs. The decrease yield observed from the graph begins above the boiling range of toluene. This interaction is also presented in the ANOVA contour plot of yield vs. time and temperature (Figure 4a and 4b).

The yield distribution in correlation with time and temperature as extraction proceeds from 60^{0}C to 80^{0}C is better depicted in the Figure 4a contour plot. From 65^{0}C to 80^{0}C, yield obtained was between 8.5 to 9.0%, assuring 70^{0}C extraction temperature as the most economically operating condition. This optimum yield was achieved at a lesser time of 3.5hrs. Figure 4b contour plot shows the best possible distribution of extract as time and temperature were altered. The optimal yield 21.27% was achieved at a temperature of 120^{0}C in 4hrs. But extraction is more economical at 115^{0}C for 4hrs with extract yield of 20.2%. In comparison, extraction with toluene is preferable to n-hexane solvent with respect to yield, time and temperature.

3.3 Characterization of Oil Extracted from Tar Sand

The oil extract from the tar sand was characterized and the result presented in Tables 2 and 3.

Table 2: Properties of Oil Extracted from Tar Sand

Experimental test	Sample from Okitipupa	Standard value*
Specific gravity @ 60ºC	0.94	0.204-1.837
API Specific gravity @ 60^{0}C	17.76	Below 20
Viscosity @ 60ºC (cp)	95.5	Below 10,000
Acid value (mg KOH/g)	2.81	1.5-5
Moisture Content	0.09	0.36

Source: [5]*

Table 3: X-Ray Fluorescence analysis of the oil extracted from tar sand

Experimental test	Sample from Okitipupa	Standard value*
Ultimate analysis		
Carbon	84.07	83
Hydrogen	12.40	10.4
Sulphur	0.95	4.8
Nitrogen	0.09	0.36
Oxygen	0.45	0.94
Trace elements		
Fe	0.3	-
Ni	0.02	-
As	0.21	-
Cr	0.25	-
Pb	0.004	-
Ca	0.001	-
Hg	0.3	-

V	0.001	-
Bi	0.02	-
Ag	-	-
Nd	0.002	-

Source: [5]* and [9]*

4.0 CONCLUSION

The effectiveness of bitumen extraction depends on the nature of solvent used. Extraction with toluene is preferable to n-hexane solvent with respect to yield, time and temperature. At 115ºC, 20.2% yield was obtained at a time of 4hrs compared to n-hexane optimal of 8.5 to 9.0% at 70ºCin 3.5hrs. Toluene has a better yield during extraction than n-hexane but at a higher temperature. Itis preferred for extraction of bitumen from tar sand because of its non-carcinogenic nature whichmakes the environment free from toxic substances; even at lower temperature and time the yield supersede that of n-hexane.

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