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

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ABSTRACT

Tar sand, an aggregate of sand, clay, water and bitumen, was sampled from the Okitipupa area of Ondo State, Nigeria, extracted and optimized using n-hexane and toluene in a soxhlet extractor. This was meant to determine, which among the two solvents (n-hexane and toluene) is best for the extraction of bitumen from the tar sand, and also to determine the operating conditions (temperature and time) of the extraction and, to ultimately evaluate the properties of the extracted oil. The experiment was carried out by heating the solvent at and above their boiling temperatures to get the temperature-time conditions for optimal yield of oil from the tar sand. The analysis gave an optimal yield of 9.07 % at 75^{o}C in 4 h when n-hexane was used and an optimal yield of 21.27 % at 120^{o}C in 4 h when toluene was used. A drastic change in colour was also noticed in the sand residue to almost sandy soil nature when toluene was used as solvent compared 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 the 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 unconventional oil supply in Nigeria and feedstock in refineries.

Keywords: Tar sand, Solvent extraction strength, N-Hexane, Toluene, XRF and SEM analysis

INTRODUCTION

Tar Sand encompasses bitumen which makes up 10 to 20 % of the sand and about 80 to 85 % mineral matters, including sand, clay and 4 to 6 % of water. Tar sand has similar compositions as light crude [1]. These bituminous sands were discovered in Nigeria at the beginning of the 20th

century, around 1900 [2]. Nigeria's tar sands rank among the largest deposits in the World. It is second only to the deposits in Venezuela and compatible with the large tar sand deposits in Alberta, Canada and Trinidad [2]. They are believed to have been formed from biodegradation and water-washing of light crude due to a lack of cap rock [1]. 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 them into upgraded oil before refining into useful products [1]. Nigeria's 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 [3]. Nigeria's reserve is estimated to be about 30 to 40 billion barrels with a potential recovery of 3654×10^6 bbls [4]. Ogun State has more than 40% of Nigeria's reserve, of the estimated 30 to 40 billion barrels of tar sand [5].

Studies into the tar sand reserve in Nigeria have, in recent years, developed a great number of interest from several researchers. Coker and Ekweozor [6] carried out a 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. Enu [7] and Ekweozor [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 Nigeria's oil reserves which currently stands at 36 billion barrels, with an 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 [8] since the Nigeria tar sand has properties similar to petroleum product [8].

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, a large volume of water and energy are required in processing than the usual conventional oil extraction method. The surface extraction process is considered the most effective technique in use presently, where tar sand is excavated and 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 [9].

Researchers have also studied the extraction strength of solvent on tar sand. Benzene, when used as a solvent for the extraction of bitumen using a soxhlet extractor from tar sand deposit in Ondo State at four different locations, operating at three temperatures, gave a progressive increase in extraction as temperature changes [10]. Adebayo and Kazim [11] deduced that the extraction rate and the boiling point of the solvent used are inversely related when they compared the extraction strength of four different solvents at 100^{o}C, 120^{o}C, and 140^{o}C for benzene, carbon tetrachloride, toluene and xylene.

The present study was therefore initiated to study the extraction strength of non-polar solvents (n-hexane and toluene) on tar sand from Okitipupa, Ondo State, Nigeria. The choice of non-polar solvents, stems out from the results of some previous researches. Ahmad et al. [12] showed that the lower the polarity of solvent, the greater the extractable from the containers; and Zarrinmehr et al. [13] in their work on 'the effect of solvents polarity and extraction conditions on the microalgal lipids yield, fatty acids profile, and biodiesel properties' affirmed that the polarity of solvents also affected FAMEs composition of microalgal lipids; and concluded that the lipids yield extracted by hexane and chloroform (non-polar solvents) were higher than that by methanol (polar solvent). Therefore, n-hexane and toluene were selected the investigation in this study.

METHODOLOGY

A complete set of Soxhlet Extractors was employed in the extraction process. The samples collected were first crushed using a mortar and pistol to increase the surface area and sieved to attain the required particle size (500 μm). The particle size was kept constant throughout the experiment. Sixty (60) g of the 500-μm sample was weighed using a digital weighing balance before charging into the thimble of the extractor. The n-hexane/toluene solvent (250 ml) was charged into the extraction flask. The whole setup was held in the heating mantle (Plate 1). The extraction begins by switching on the heating mantle. The n-hexane and toluene were heated above their boiling temperatures; 60–80^{o}C for n-hexane and 110–130^{o}C for toluene in 4 h of the extraction, respectively. The experiment was stopped after 4 h of extraction and the sample reweighed to determine the percentage yield. The same procedure was carried out when the temperature was kept constant at (60^{o}C, 65^{o}C, 70^{o}C, 75^{o}C and 80^{o}C for n-hexane; and 110^{o}C, 115^{o}C, 120^{o}C, 125^{o}C and 130^{o}C for chloroform) and the time varied between one to four hours (1–4 h). The thimble was removed, and the enveloped sample was replaced with another 60 g of tar sand. This procedure was carried out for five different runs to determine the optimum temperature and time.

Characterization of tar-sand and the oil from it

The morphology of the tar-sand before and after extraction was examined by the use of surface electron microscopy (SEM) and the compositions of the tar-sand was also evaluated by EDX-point analysis. The elemental compositions of oil from the tar-sand were obtained by passing X-ray fluorescence (XRF) through the oil. The specific gravity of the oil was measured at 60^{o}C by taking a ratio of the density of equal volume of the oil and that of water at the same condition. The American Petroleum Institute (API) specific gravity was evaluated by the use of equation (1).

$$API = \frac{141.5}{sp.gr.60/60} - 131.5 \quad (1)$$

where *sp.gr.60/60* is the specific gravity of the oil at 60^{o}C.

RESULTS AND DISCUSSION

Analysis of Tar Sand Samples from Okitipupa

The samples obtained from this location were analyzed using a Scanning electron microscope before and after extraction to check the morphology of the tar sand, as shown in Figures 1a, 1b and 1c, respectively.

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

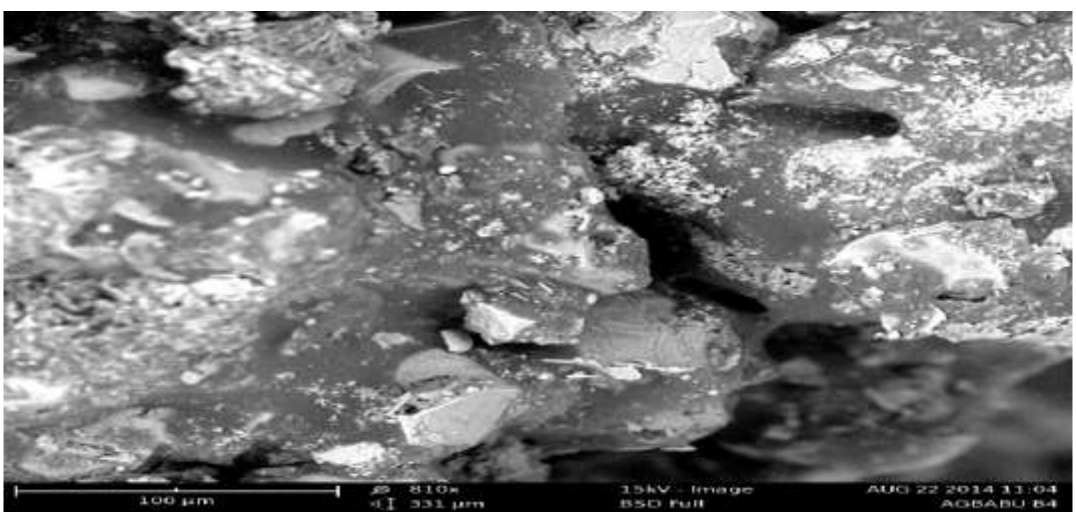

Figure 1a: Tar sand from Okitipupa before extraction

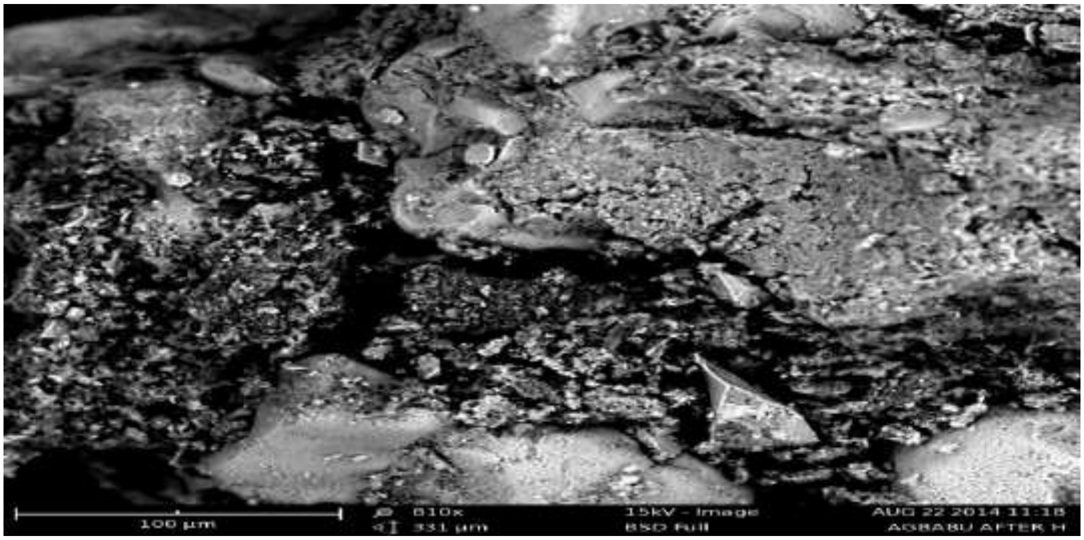

Figure 1b: Tar sand from Okitipupa after extraction with n-hexane

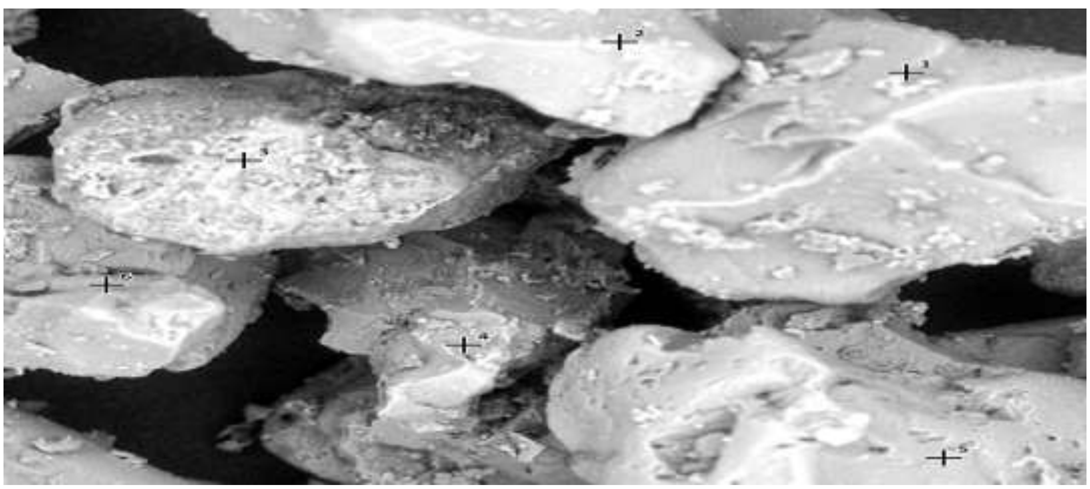

Figure 1c: Tar sand from Okitipupa after extraction with toluene

Figure 1a 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 had been removed, as shown in Figure 1b 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 extent 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 solvents have varying effects on the sample. The vigorous nature of the solvent on the sample is noticed in the amount of pore space created after extraction, that is, how disintegrated the sample is after extraction. Figure 1c 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 1a.

Table 1 shows the EDX analysis of tar sand from the 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 Name	Concentration Before	Concentration after Extraction N-hexane	Concentration after Extraction 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

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 MINITAB software. In the extraction process, 60 g 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 extraction proceeds. This progressive effect as time and temperature increase is shown in Figures 2a and 2b.

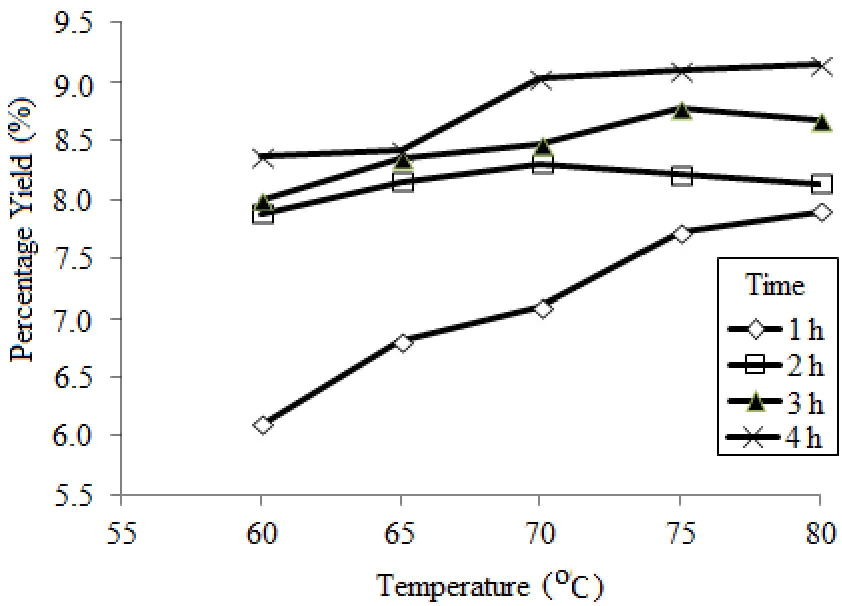

Figure 2a: Interactive effects of time and temperature on oil yield using n-hexane as solvent

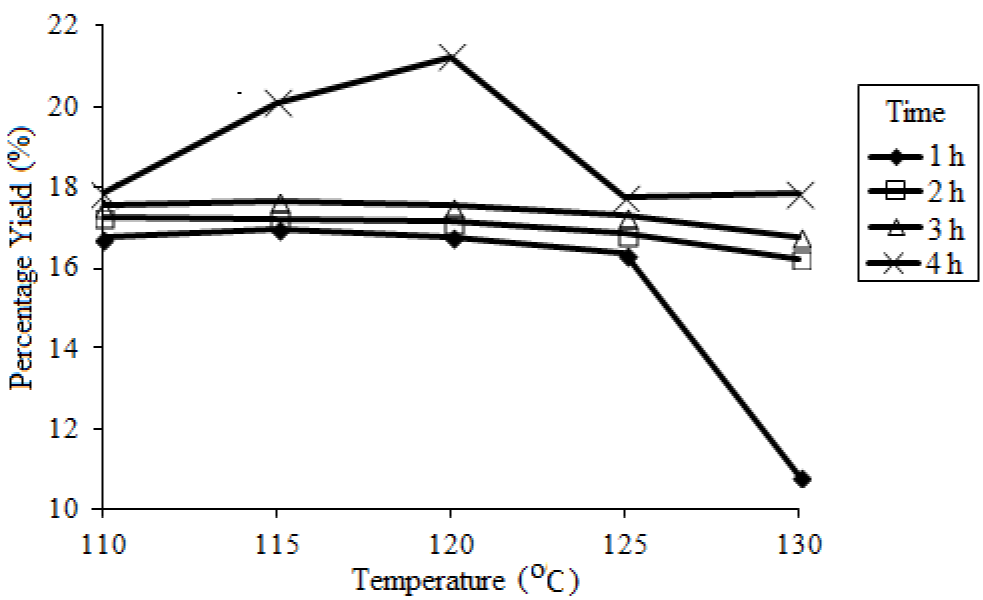

Figure 2b: Interactive effects of time and temperature on oil yield using toluene as solvent

An increase in the yield of oil extracted from the tar sand as time and temperature increased was noticed in Figure 2a. Hence, extraction is said to increase as the solvent is heated above its boiling temperature with respect to time. At a low heating rate, the extract was proportional to the extraction time. The maximum yield was obtained at $75^{o}C$, which corresponds to 9.07% in 4 h when n-hexane was used as a solvent. But it is economically advisable to extract at $70^{o}C$ (which corresponds to 9.03% in 4 h since the difference in yields (0.04%) at $70^{o}C$ and $75^{o}C$ is very negligible. Hence, $70^{o}C$ may be considered optimum, so as to save some amount of energy. The percent yield at $120^{o}C$ shown in Figure 2b 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 a doubt that the optimum yield was achieved at a stretch of 4 h. The decrease in 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 (Figures 3a and 3b).

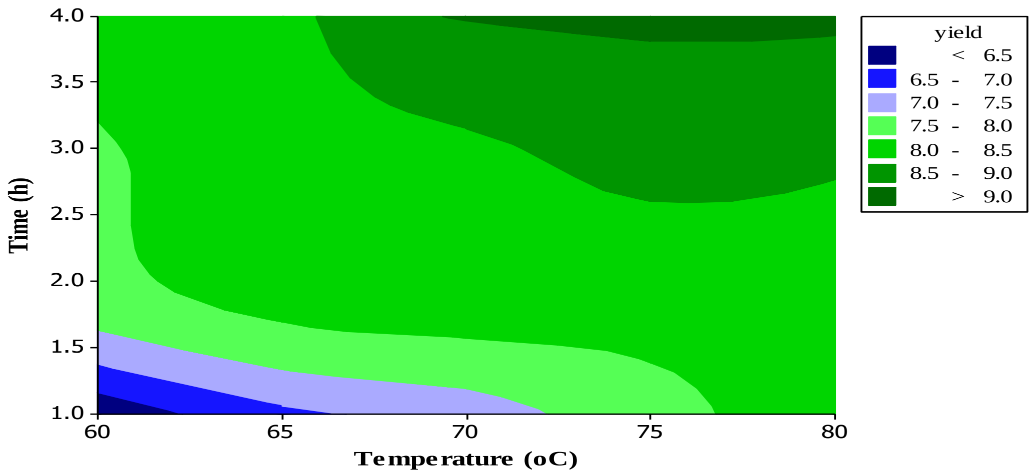

Figure 3a: Contour plot on the effects of time and temperature on oil yield using n-hexane as solvent

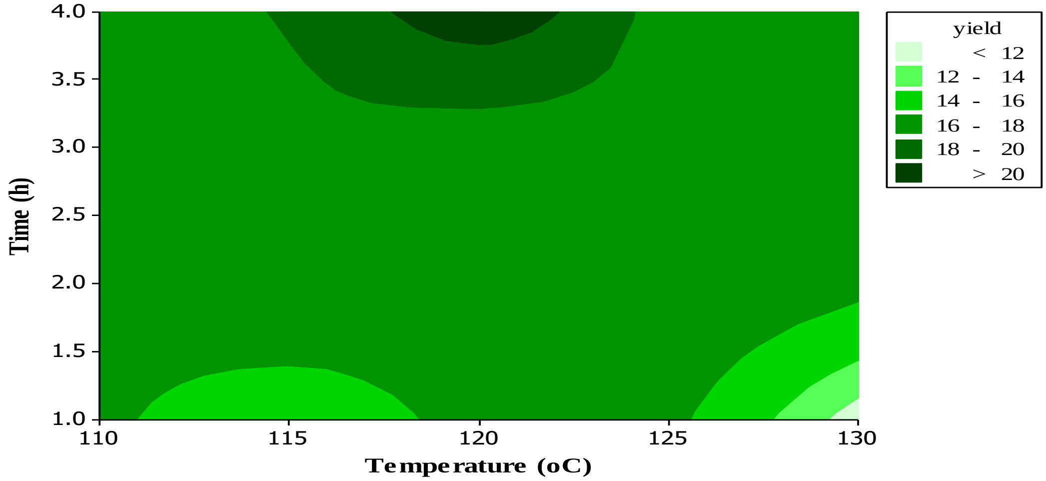

Figure 3b: Contour plot on the effects of time and temperature on oil yield using toluene as solvent

The yield distribution in correlation with time and temperature as extraction proceeds from 60°C to 80°C is better depicted in the Figure 3a contour plot. From 65°C to 80°C, the yield obtained was between 8.5% to 9.0%, assuring 70°C extraction temperature as the most economically operating condition. This optimum yield was achieved at a lesser time of 3.5 h. Figure 3b 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°C in 4 h. But extraction is more economical at 115°C for 4 h with an extract yield of 20.2%. In comparison, extraction with toluene is preferable to n-hexane solvent with respect to yield, time and temperature.

Characterization of Oil Extracted from Tar Sand

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

Table 2: Properties of Oil Extracted from Tar Sand

Experimental test	Sample from Okitipupa	Standard value*
Specific gravity @ 60°C	0.948	0.204-1.837
API Specific gravity @ 60°C	17.76	Below 20

Viscosity @ 60^{o}C (cp)	95.5	Below 10,000
Acid value (mg KOH/g)	2.81	1.5-5
Moisture Content	0.09	0.36

Source: Ante [14] *

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: Ante [14]* and Intisar [15]*

Conclusion

The effectiveness of bitumen extraction depends on the nature of the solvent used. Extraction with toluene is preferable to n-hexane solvent with respect to yield, time and temperature. At 115^{o}C, 20.2% yield was obtained at a time of 4 h compared to n-hexane optimal of 8.5 to 9.0% at 70^{o}C in 3.5 h. Toluene has a better yield during extraction than n-hexane but at a higher temperature. It is preferred for extraction of bitumen from tar sand because of its non-carcinogenic nature, which makes the environment free from toxic substances; even at lower temperatures and time, the yield supersedes that of n-hexane.

REFERENCES

[1] Odunaike, R.K. Fasunwon, O.O. Akinyemi, L.P. and Odusote, O.O. "Physico-Chemical Characterization of Oil Sands at Imeri in Ogun state of South West, Nigeria", *Research Journal of Recent Sciences*, **2**(8): 1-7; 2013.

[2] Adegoke, O.S. "Historical perspective of bitumen tar sand development in South Western Nigeria": *Paper delivered at International Summit on Bitumen in Nigeria,* Akure, Nigeria, 2000.

[3] Ako, B.J. *Exploration strategies for bitumen saturated sands in Nigeria*: Elueze, A.A. (Ed). Prospects for Investment in Mineral Resources of South Western Nigeria. *Nigeria Mining and Geosciences Society (N.M.G.S)*. p. 61-66; 2003.

[4] Adegoke, O.S. Omatsola, M.E. and Coker, S.J.L. **“**The Geology of the Nigerian Tar Sands, in Meyer, Edition”. The Proceedings of *5th Unitar International Conference on Heavy Crude and Tar Sands: Technical Reports*, 369-385, 1991.

[5] Tetede, E.O. Bitumen Development in Ogun State: *Power Point Presentation at the Ogun State Economic Summit during the stakeholders meeting slides*, 1-16; 2006.

[6] Ekweozor, C.M. (1985) Nigerian Tar Sands, Bitumen Chemical Properties and their Relation to Origin, Production and Processing, *Book of Abstracts, 21st Annual Conference, Mining and Geoscience Society*, Jos, Nigeria. 11-15 March 1985.

[7] Enu, E.I. “Textural Characteristic of the Nigerian Tar Sands”, *Sedimentary Geology*, **44:** 65-81; 1985.

[8] Nfor, B.N. and Nwali, M.A. **“**Extraction of oil from the Tar Sands of Ofosu and Environs, Edo State, Mid-Western Nigeria: A Way to Meet Increasing Energy Demand”, *Archives of Applied Science Research*, **3**(3): 45-48; 2011.

[9] Miller, J. and Misra, M. “Hot water process development for Utah tar sands”, *Fuel Processing Technology*, **6:** 27-59; 1982.

[10] Ibisi, N.E, Okwu, D.E., and Ekwenchi, M.M. “Evaluation of the Chemical Composition of Tar Sands of Southwestern, Nigeria”, *Journal of Engineering and Applied Sciences*, **1(2)**: 138-142; 2006.

[11] Adebayo, T.A. and Kazim, D.A. “Comparative study on the Rate of Extraction of Crude bitumen from Nigerian Oil sands Using Various Solvents”. *Asian Transactions on Engineering*, **1**(2): 68-71; 2013.

[12] Ahmad, I., Sabah A., Anwar, Z., Arif, A., Arsalan, A., and Qadeer, K. “Effect of solvent polarity on the extraction of components of pharmaceutical plastic containers”, *Pakistan Journal of Pharmaceutical Science* **30**(1): 247-252; 2017.

[13] Zarrinmehr, M.J., Daneshvar, E., Nigam, S., Gopinath, K.P., Biswas, J.K., Kwon, E.E., Wang, H., Farhadian, O., and Bhatnagar, A. “The effect of solvents polarity and extraction

conditions on the microalgal lipids yield, fatty acids profile, and biodiesel properties", *Bioresource Technology* **344:** 126303; 2022.

[14] Ante, J. Petroleum Refining and Petrochemical Processes, Faculty of Chemical Engineering and Technology University of Zagreb; 2012, Accessed on 07/05/2017 @ http://www.fkit.unizg.hr/_download/repository/PRPP_2013_Crude_oil_composition.pdf.

[15] Intisar, H.K. "Ministry of Higher Education and scientific research: Properties of Petroleum Product", University of Technology Malaysia, Chemical Engineering Department (2009).