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Extraction of Chemical Constituents of Bitumen Using a Mixed Solvent System

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Abstract

Several solvents had been used to extract the SARA (Saturate, Aromatic, Resin and Asphaltene) constituents of bitumen. The quantification of such extracts also abounds in open literature but in this work an attempt was made to determine the quality of extraction as a feed stock for processing bitumen using a mixed solvent system. A mixture of heptane and toluene was used to compare with the standard method using heptane. The components were analysed for functional groups of compound types presented in them using Fourier Transform Infrared Spectrophotometry technique (FTIR). The quality of bitumen component extract was not significantly affected by the method of extraction as recommended by the ASTM. The components are mixture of different class of hydrocarbons such as saturated and unsaturated hydrocarbons which conformed to what had earlier been reported by other researchers.

Keywords

Bitumen, Sara, Ftir, Solvent System

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1. Introduction

Bitumen is a complex mixture, containing a high proportion of poorly soluble asphaltenes. Unpredictable precipitation of this component can cause process problems during bitumen extraction. Consequently, the selection of an appropriate solvent is an important factor in the optimization of bitumen separation by solvent extraction [1]. Bitumen can be gotten as one of the fractions from distillation of crude oil or oil sands. The oils sands extraction process is composed of an extraction step and a characterization step. The first step is the extraction with heated toluene into three components; bitumen, solid content (sand and clay) and water [2].

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The second step is the characterization of bitumen to determine the asphaltene content in the bitumen. Asphaltene is a low value added product present in the bitumen. The higher the asphaltene content, the lower the value of the bitumen [3]. **Figure 1** shows the use of an adsorbent to fractionate the deasphaltened oil [4].

Bitumen comprises three main components, namely, maltenes, resins and asphaltenes. Whereas maltenes are infinitely soluble in paraffinic solvents, and the complete dissolution of resins and asphaltenes requires the use of relatively polar, aromatic solvents, such as benzene or toluene. In conventional practice, asphaltenes are separated from maltenes by adding a large excess of pentane to a solution of bitumen in benzene. However, the solubility of asphaltenes in paraffins increases in proportion to the number of carbon atoms in the solvent and this provides a means of fractionating asphaltenes on the basis of their molecular weight. The selected bitumen solvent must therefore have the proper balance between paraffinic and aromatic components [1].

Considerable research has been performed in an effort to separate bitumen from oil sands using solvent extraction [5] [6]. Several process were suggested to slurry the oil sands in one or multiple non-aqueous solvents followed by filtration and then separation of the solvent from the sand tailings [7] [8].

Hanson *et al*. investigated a solvent extraction process using aromatic hydrocarbons, such as toluene, which included extraction, separation, drying, and solvent recovery, and achieved the circulation of solvent with less environmental impact [9]. However, the major problems of the process are its complexity and high energy consumption. To overcome the high solvent loss and energy consumption of the non-aqueous extraction process, Gantz and Hellwege patented the use of trichloroethylene as a solvent in conjunction with a small amount of a surfactant [10].

Leung and Phillips investigated the use of benzene, toluene, and kerosene as the solvent, and they observed higher mass transfer rates when using solvents with higher aromaticity or lower boiling points [11]. For large-scale operation, the solvents must be easy to recover from the extraction gangue.

Consequently, solvents, such as naphtha and kerosene, can be ruled out. Furthermore, despite their effectiveness in dissolving bitumen, the aromatic solvents are unsuitable because of odor and toxicity.

Sparks and Meadus studied solvent extraction by naphtha as a solvent followed by spherical agglomeration of extracted sands by adding water. Water phase replaced solvents phase in the agglomerates, and agglomerates were separated from the solvent by screening. The optimum added water to sand ratio depended on the fines content of the oil sands but was around 0.13. Bitumen recovery in this process reached 95%, and naphtha content of the extracted sands decreased to around 3% [12] [13].

Wu and Dabros studied the non-aqueous extraction of bitumen by light hydrocarbon solvents followed by centrifuge filtration or regular filtration. The solvent was recovered from flirtation cake by vacuum evaporation at room temperature. They studied different solvents, n-pentane, hexane, cyclopentane, a mixture of n-pentane

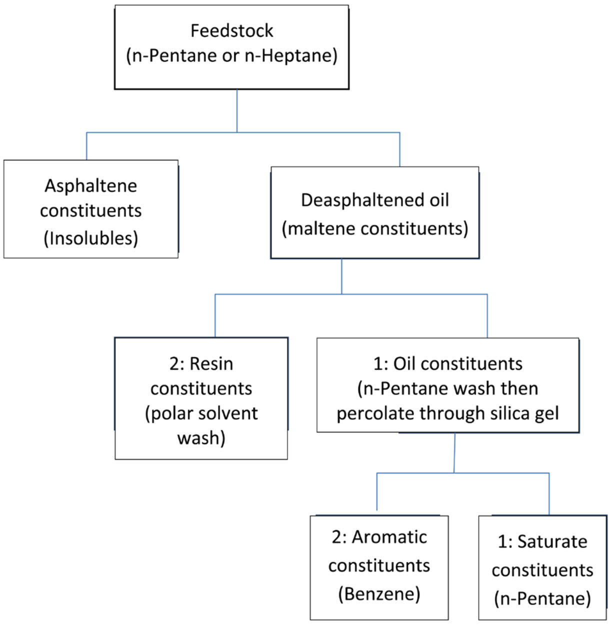

Figure 1. The ASTM D2007 Fractionation procedure.

and cyclopentane and toluene, and suggested cyclopentane as the best solvent. Bitumen recovery using cyclopentane as the solvent reached 90% by a single stage extraction at a solvent to bitumen ratio of over 4. By a three-stage extraction, the bitumen recovery can reach above 95% using a solvent to bitumen ratio of 1. Using pressure filtration instead of centrifuge filtration showed lower bitumen recoveries. The residual solvent content in the extracted oil sands tailings was the lowest for n-pentane and cyclopentane, which have the lowest boiling points among the tested solvents. The residual solvent content for cyclopentane after 20 min vacuum drying was 0.4% of the extracted bitumen or 550 mg/kg in the extraction tailings [14].

Studies by Hooshiar *et al*. [15] and Nikakhtari *et al*. [16] [17] found that bitumen recovery was over 95% for a range of ore grades and solvent blends. Nikakhtari and fellow workers thus, recommended cyclohexane as a potential solvent for bitumen extraction based on high bitumen recovery, low fine solids in the produced bitumen, and rapid evaporation of cyclohexane from the gangue. They found that the migration of fine solids into the product bitumen was very sensitive to the solvent properties, suggesting that choosing a proper solvent blend could control the behavior of these solids. In addition, unlike laboratory reagents, potential low-cost industrial solvents will not be pure but will consist of a mixture of related compounds.

Investigations were conducted by Krupal to evaluate the performance of solvent mixtures to extract bitumen from a high-grade oil sands ore. Solvent mixtures of cycloalkane and n-alkanes were studied on the basis of their Hildebrand solubility parameters, which affect bitumen recovery and fine solids migration during the extraction process, and the results were compared to single solvents. Cyclohexane, cyclopentane, and methylcyclopentane were selected as the cycloalkane solvents, and they were studied in combination with n-alkane solvents, such as n-heptane, n-hexane, or n-pentane, to make up a final solubility parameter between 16.65 and 16.45 MPa1/2 for the final solvent mixture. It was observed that the solubility parameter of the solvent mixture has more impact on the migration of fine solids in bitumen than the recovery of bitumen. The amount of fine solids migrating into the bitumen product followed the order of cycloalkane/n-heptane > cycloalkane/n-hexane > cycloalkane/n-pentane [18]. However, the effect of the mixture on the chemical nature of the SARA component had never been reported in any open literature. The aim of this research therefore is to compare the chemical nature of the extracted constituents to determine if the method of extraction or separation using different solvent systems has any major effect on the SARA constituents and using bitumen sources from Nigeria as our feedstock.

2. Materials and Method

2.1. Collection of Samples

Bituminous sand samples were collected from Agbabu, in Ondo State, Southwest Nigeria (**Figure 2**), by scooping the viscous bituminous sand samples into air light plastic containers and conveying the samples immediately to the laboratory for processing and analysis.

All solvents were double distilled analytical grade. The adsorbent was (supplied by Heloatta, Akure, Nigeria) was activated in a muffle furnace at 600˚C for 6 hours. The chromatographic column tubing of 1 m long and 0.04 m internal diameter was constructed in Federal University of Technology Akure, Ondo state.

2.2. Determination of Asphaltene and Raffinate Components of Bitumen

A modified ASTM-2007 method was used as follows. A mixture of 50/50vol% heptane/toluene in the modified method instead of 100 vol% heptane or pentane in the standard method. Exactly 200 ml n-heptane/toluene mixture was added to 20 g of bitumen in an Erlenmeyer flask. This was refluxed at 98˚C for about 6 hours. After cooling, the extract was decanted into another flask, the residue left was thoroughly rinsed with n-heptane/toluene into the second flask containing the extract and pure residue was taken as asphaltene while the extract was taken as raffinate after solvent removal using rotary evaporator. The procedure was repeated with 100vol% heptane in the standard method

2.3. Column Chromatographic Fractionation of Raffinate into Oil and Resins

A chromatographic column was carefully and neatly packed with activated neutral alumina after pre-wetting with n-heptane. The raffinate was introduced into the column after dissolution in 100 ml n-heptane. The oil component being the least polar came out first as expected, the process continued with more n-heptane being added until n-heptane coming out was colourless. The remaining resins were progressively eluted with increasing polar

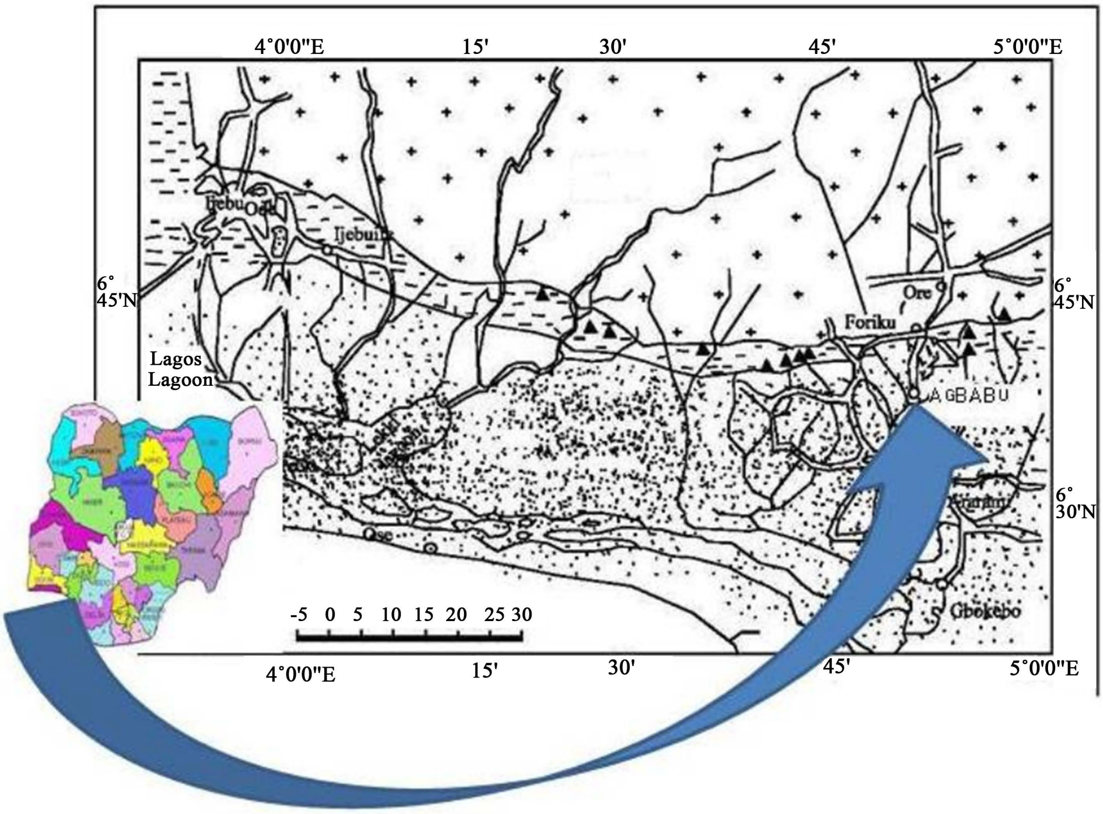

Figure 2. Showing the location of our sample collection [19].

solvents; toluene, trichloromethane and ethanol until solvent coming out in each elusion were colourless. The eluents were recovered from the bitumen components by rotary evaporation [20].

2.4. Structural Characterization by Fourier Transform Infrared (FTIR)-Spectroscopy

The bitumen components (asphaltene, oil, and resins) were investigated for functional assignment by infrared spectroscopy using a Shimadzu FTIR-8300 spectrometer. The spectra of the homogenized material, in the form of KBr discs, were analysed in the range of 400 to 4000 cm^{-1}.

2.5. Atomic Absorption Spectroscope (AAS) Determination of Trace Metal Contents in Bitumen Components

Sample preparation for analysis was done by dry ashing and dissolution of the ash in mineral acids [21]. Duplicate of 1 g sample of oil component contained in crucibles with lids was placed in a furnace maintained at 500˚C for 5 hours. 1 mL of 2 M HCI was added to the ashed sample in the crucible and allowed to boil to dryness on a water bath. After drying, another batch of 1 mL 2 M HCI was added, but left to boil only for few minutes before being transferred into 50 ml volumetric flask. The crucible was rinsed several times with double distilled water into this flask and made up to the graduating mark with double distilled water. The solution was subjected to AAS analysis using the Bulk model 200 A Atomic Absorption Spectrophotometer to determine the presence and concentration of metals.

3. Results and Discussion

The saturate (Oil) components of the Agbabu bitumen are 36.80% and 36.20 for the standard method and the modified method respectively. These values are greater than most of the values reported by some researchers [19] [22] [23] but the discrepancy is not significant. The values obtained in the standard method corresponds to what was reported by Oderinde and Olanipekun [24]; Adebiyi and Omode [20], however, the values are less than the 51.5% and 39.6% reported by Ells [25] for the oil components of the Alberta and Bermudez respectively.

The Nigerian bitumen is richer in the saturates (oil) components than the Athabasca and Cold lake bitumen [26] and a number of Chinese and Middle Eastern vacuum resids reported by Liu *et al*. [27].

The functional group assignment for the bitumen components using standard and the modified method is presented in **Tables 1-5**, while the IR spectrum of four (as a representation) of the samples are presented in **Figures 3-6**.

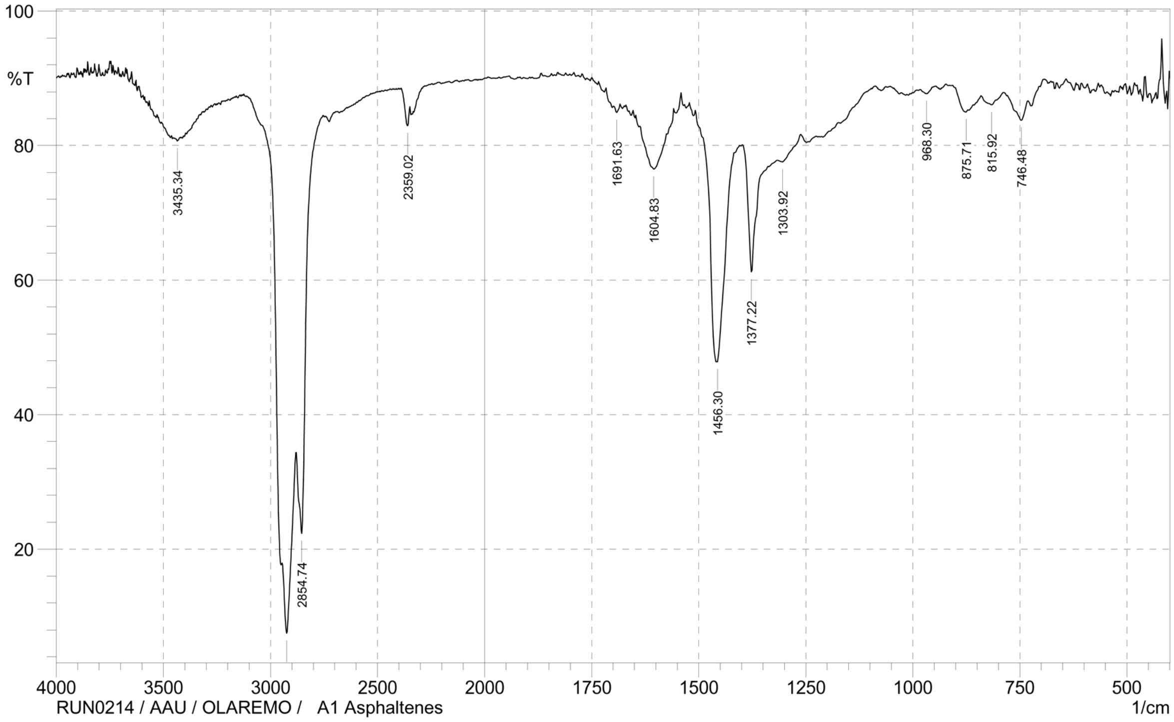

Figure 3. FTIR Spectra for SARA (Asphatene) extraction with 50% Heptane, 50% Toluene.

Table 1. Comparation of FTIR peaks of Asphaltene.

50% Heptane, 50% Toluene	100% Heptane	Functional Group
	669.32	Aliphatic Halogen compounds
746.48	746.48	Aromatic
815.92		Aromatic
875.71	883.43	Aromatic
968.3		Alkanes
1303.92	1303.92	Aromatic amines
1377.22	1377.22	Organic sulfates
1456.3	1458.23	Alkanes
1604.83	1610.61	Carbonyls
1691.63	1697.41	Carboxylic acid
2359.02	2360.95	Si-H, Thio/Sulfides, Phosphines, Arsines, Borones
2854.74	2854.74	Alkane
2924.18	2924.18	Alkane
3435.34	3437.26	Alcohols, Phenols

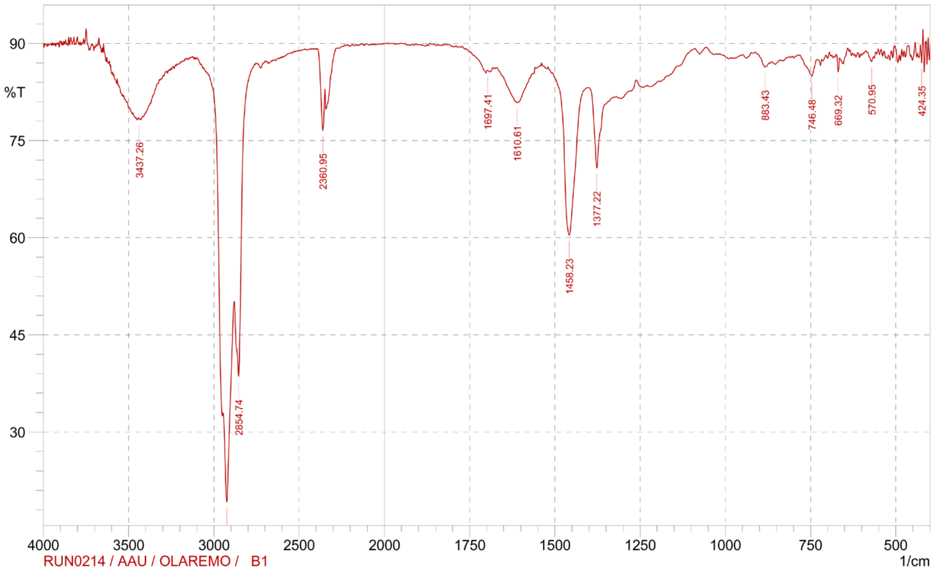

Figure 4. FTIR Spectra for SARA (Asphatene) extraction with 100% Heptane.

Table 2. Comparation of FTIR peaks of Heptane extract.

50% Heptane, 50% Toluene	100% Heptane	Vibrational response
653.89	669.32	Alkyl halides
721.4	744.55	Aromatics
854.49	875.71	Aromatics
1298.14		Alkyl halides
1377.22	1377.22	Organo sulfate
1458.23		Alkanes
1608.69	1612.54	Primary amine
2360.95	2359.02	Si-H, Thio/Sulfides, Phosphines, Arsines, Borones
2854.74	2854.74	Alkane
2924.19	2924.18	Alkane
3425.69	3439.19	Alcohols, Phenols

Table 3. Comparation of FTIR peaks of Toluene extract.

50% Heptane, 50% Toluene	100% Heptane	Vibrational response
744.55	746.48	Aromatic
815.92		Aromatic
875.71	881.5	Aromatic
1031.95	1030.7	Aliphatic amines
1305.85	1305.85	Aromatic amines
1377.22	1377.22	Organo sulfates
1456.3	1458.23	Alkanes
1602.9	1608.69	Alkanes
1695.49	1697.41	Carboxylic acid
	2359.02	Si-H, Thio/Sulfides, Phosphines, Arsines, Borones
2852.81	2852.81	Alkane
2924.18	2924.18	Alkane
	2951.19	Alkane
3435.34	3435.34	Alcohols, Phenols

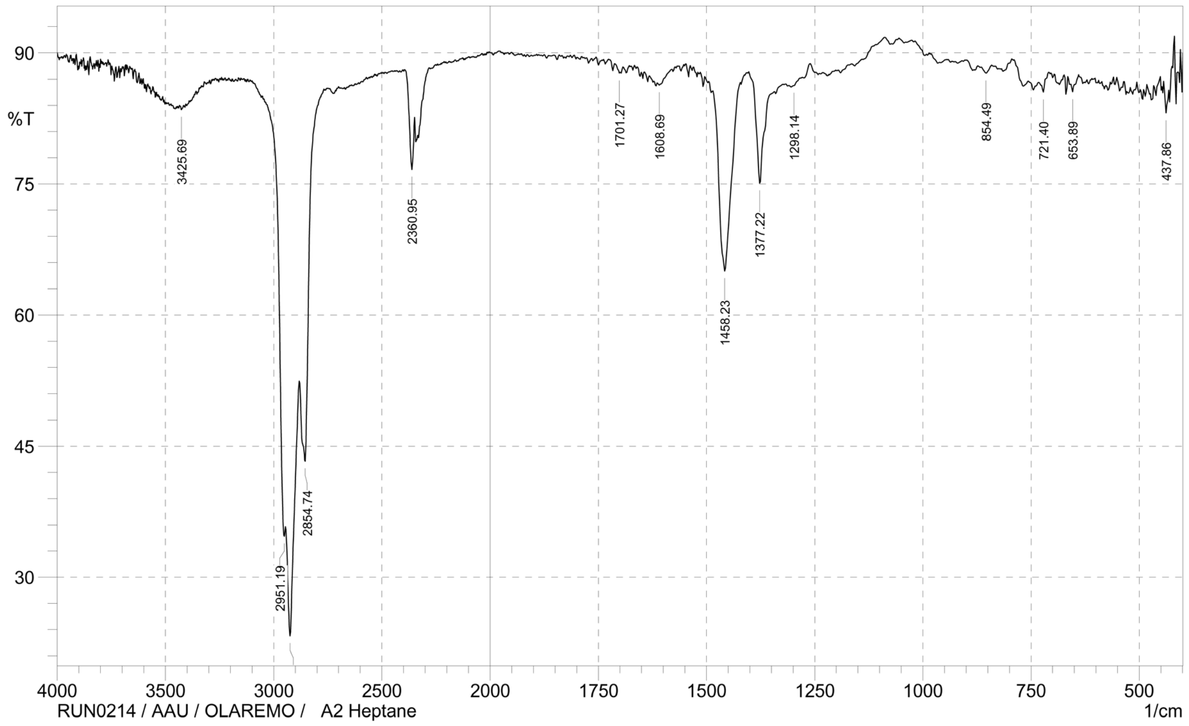

Figure 5. FTIR Spectra for SARA extraction (Oil) with 50% Heptane, 50% Toluene.

Figure 6. FTIR Spectra for SARA (Oil) extraction with 100% Heptane.

Saturated hydrocarbon and aromatic compounds are present in all the components separated indicating the high quality of the Nigerian bitumen in agreement with the previous work of Adebiyi and Omode [20]; Moschopedis *et al*. [28] that reported more hydrocarbons (oil) that are saturates and aromatics which can be generated from the pyrolysis of asphaltene at 300˚C - 350˚C.

Table 4. Comparation of FTIR peaks of Ethanol extract.

50% Heptane, 50% Toluene	100% Heptane	Vibrational response
542.02	540.34	Alkyl halide
744.55	721.4	Aromatic
1010.73	1012.66	Alcohols, carboxylic acids ,esters, ethers
1377.22	1377.22	Organic sulfate
1458.23	1460.16	Alkanes
1604.83	1604.83	Primary amines
	1658.84	Alkanes
1707.06	1705.13	Carboxylic acid
2366.74	2360.95	Si-H, Thio/Sulfides, Phosphines, Arsines, Borones
2854.74	2854.74	Alkane
2924.18	2924.18	Alkane
2953.12		Alkane
3443.05	3431.48	Alcohols, Phenols

Table 5. Comparation of FTIR peaks of Chloroform extract.

50% Heptane, 50% Toluene	100% Heptane	Vibrational response
721.4	721.4	Aromatics
	827.49	Aromatics
968.3	966.37	Alkenes
1080.17	1080.17	Aliphatic Amine
1186.26	1188.19	Alkyl halides
1290.42	1288.49	Alkyl halides
1377.22	1377.22	Organic sulfate
1460.16	1464.02	Alkanes
1707.06	1707.06	Carboxylic acid
2360.95		Si-H, Thio/Sulfides, Phosphines, Arsines, Borones
2852.81	2854.74	Alkane
2924.18	2924.18	Alkane
2955.04		Alkane
3433.41	3425.69	Alcohols, Phenols

In the current investigation, the presence of different class of hydrocarbon discovered in all the components conformed to the earlier report by various researches on studies on Nigerian bitumen. Worthy of note however is that the quality and components of the hydrocarbon is not affected by the method of extraction whether in the standard or modified method.

Table 6 below compares the results obtained in this work for the oil components of Nigerian bitumen with previous reports as detailed in the table.

Table 6. Average trace metal concentrations of Nigerian bitumen, ppm.

Metal	Obiajunwa and Nwachukwa 2000 [29]	Ipinmoroti and Aiyesanmi 2001 [30]	Adebiyi and Omode 2007 [20]	Present study
Zn	119.00	7.00	100.94	120.00
Ni	NDT	21.00	20.22	11.20
Cu	72.00	BDL	ND	ND
Pb	69	80.00	57.49	12.68
V	NDT	37.00	7.59	13.80
Fe	48,300.00	234.00	204.93	210.44
Mn	216.00	NDT	12.41	11.67

NDT: not determined, BDL: below detection limits (0.02 ppm for Cu).

The understanding of the metals present in bitumen is very important as they have effect during thermal and catalytic processing [31]-[37]. Metals during catalytic upgrading cause catalyst poisoning and deactivation.

4. Conclusion

The quality of bitumen component extracted is not significantly affected by the method of extraction as recommended by the ASTM 2007. Nigeria bitumen was used to test run this hypothesis and was observed to be true. From our results, the components are mixture of different classes of hydrocarbon hence; the bitumen is a huge reservoir of petrochemicals which can be vital for the chemical industry development.

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