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Characterization of paraffinic hydrocarbon fraction of Nigerian bitumen using multivariate analytical techniques

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ABSTRACT

Nigerian bitumen paraffinic hydrocarbon (PH) fraction was analyzed to establish the characteristics which might aid the developmental processes of the natural resource. Bitumen samples extracted from the oil sands were deasphalted and paraffinic hydrocarbons (PHs) eluted by column chromatography. The organic components of the PHs were investigated using Fourier transform infrared (FT-IR) spectrometry and Gas chromatography (GC); elemental concentration was determined using Atomic absorption spectrometry, while physical properties by standard methods. The IR spectra showed mainly the presence of $CH(CH_3)$ and $C—H(CH_2)$ functional groups, indicating high purity of the samples. Thirty-one organic compounds were identified and quantified by GC. The PHs had a mean carbon preference index value of 1.035, indicating that the PHs were thermally matured and of petrogenic origin. Principal component analysis using the organics' concentrations as variables indicated that the compounds had similar chemical properties, common sources, and/or maturation age. Elemental concentrations of the PHs were generally low compared with other fraction of Nigerian bitumen and were confirmed by their *T*-test values which indicated significant difference. Elemental cluster analysis showed two groups which were fairly correlated indicating similar sources and/or chemical affinity. The PHs V/Ni ratio 0.10–1.88 (1.12 was close to that of Nigerian bitumen 0.45–2.28 (1.12) which was higher than the average value (0.16) obtained for Nigerian crude oil, while V/V + Ni ratio 0.09–0.65 (0.50) obtained in this study is also close to 0.31–070 (0.50) obtained for Nigerian bitumen. Color of the PHs ranged from colorless to off-white. Values of the analyzed physical parameters confirmed that the PHs contained relatively high concentration of carbon and would tend to burn slower in the combustion chamber of an engine. The study also provided useful information on conversion mechanism and environmental implications of the development of the fossil fuel.

Introduction

Until latest years conventional (light) crude oil has been in abundance and has easily met global demand as a source of energy; but due to sizeable increasing demand for crude oil internationally and continued exhaustion of this natural resource, there is strain in the supply of the fossil fuel. These have led to contemplation of alternative energy sources, among which natural bitumen are possibly the most readily obtainable to complement immediate and lasting requirements. Bitumen is the remains of very large volume of conventional oil that has been generated and then biodegraded, primarily by bacteria. Bitumen resembles residuum produced by refinery distillation of light oil chemically and texturally (Attanasi and Meyer, 2007), but can be upgraded to crude oil (refinery feedstock) before it can be used in refineries to generate gasoline and other petroleum fuels.

Oil sands are naturally occurring mixtures of sand or clay (mineral matter), water and heavy and viscous form of crude oil (bitumen) which is black, sticky and complex mixture of high boiling point range of hydrocarbons and molecules with relatively low hydrogen to carbon ratio (Yoon et al., 2009). Oil sand deposit of Southwestern Nigeria is believed to be one of the largest in the world (Adegoke, 2000) and it has been predicted to be the second largest, it occurs over a 120 km by 6 km belt which stretches from Okitipupa ridge/western edge of Niger delta to as far west of Ijebu-ode in Ogun state (Ekweozor and Nwachukwu, 1989). The exploitation and exploration of the Nigerian natural bitumen deposits can best be described to be at the planning stage (Adegoke and Ibe, 1982; Oboh et al., 2006), and many studies have been carried out on the Nigerian bitumen deposit and its impact on

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the host environments (Asubiojo and Adebiyi, 2014; Adebiyi et al., 2014, 2015; Adebiyi and Thoss, 2015; Adebiyi et al., 2006; Lameed and Ogunsusi, 2002; Adebiyi and Omode, 2007; Oluwole et al., 1993; Coker, 1988; Ekweozor, 1991; Fagbote and Olanipekun, 2010), but there has been scanty literature on the paraffinic fraction of the Nigerian bitumen.

The exploitation of bitumen has environmental impacts due to potential toxic metals and organics. Metals also have negative effects in petroleum industry viz; catalyst poisoning and fouling, corrosion of equipment and pipelines, and particulate emissions into the environment. On the other hand, the metals are often used as tracers in geochemical prospecting. The analysis of these chemical formalities will assist in developing correlations between the bitumen composition and processing characteristics. The distribution of paraffinic hydrocarbon has been used to differentiate the petrogenic and biogenic contributions in complex environmental samples. Thus the distribution of paraffinic hydrocarbon in bitumen can be used to indicate the organic matter source (Akinlua et al., 2007). It is therefore necessary to obtain detailed information on the characteristics and environmental effect of the organics content, trace element and physiochemical properties of the paraffinic hydrocarbon fraction of Nigerian bitumen. The determination of the composition, structures and properties are necessary for the solution of a number of important theoretical and practical problems in the development of the natural resource. The results of the research work will provide useful information on the properties as well as environmental effect of the organic pollutants and trace elements in the yet to be tapped Nigerian bitumen.

This research focuses on the analysis of the organic compound types of the paraffinic hydrocarbons present in samples of Nigerian bitumen obtained from five selected locations in Nigeria using Fourier-Transform Infrared Spectroscopy (FT-IR) and Gas Chromatography coupled with Flame Ionization Detector (GC-FID). Other measured characteristics of the paraffinic hydrocarbons are the concentrations of some trace elements that may have exploitation, processing and environmental effects by Atomic Absorption Spectrometry (AAS), as well as the measurement of the physical properties (Refractive index, color, carbon residue and flash point).

Experimental

Study area and sample collection

The Nigerian part of the Dahomey Basin strata contain various fossil fuel deposits which include oil sand deposits, occurring in a blinking belt extending from east of Ijebu-Ode to Okitipupa area. The area of study is latitudes 60 31′N and 60 34′N and longitudes 40 48′E and 40 50′E Agbabu in Odigbo Local Government Area of Ondo state. The study area consists of farm settlements of which the inhabitants are farmers that deal mainly in crop and fish farming (Asubiojo and Adebiyi, 2014). Figs. 1 and 2 show map of the sample location in Ondo State of Nigeria and the geological map of the study area, indicating the natural deposit out-crops, respectively.

Oil sand samples were collected from five different locations namely – Olowo-Irele, Ilubirin, Mile 2, Agbabu, and Orisunbare communities in Ondo State, Nigeria. These were areas where there were bitumen out-crops in areas of shallow overburden (Olowo-Irele, Ilubirin, Mile 2 and Orisunbare) and an uncapped well (Agbabu) dug following the pioneering work of the Geological Consultancy Unit of the University of Ife (now Obafemi Awolowo University) in 1980. The samples were collected by scooping the viscous oil sands into air tight containers and conveyed immediately to the laboratory for analysis and each sample was labeled according to the name of the community from which the sample was collected.

Extraction of bitumen from oil sand and fractionation

A measured amount of each oil sand sample was taken and tied in a thimble and dropped inside the soxhlet extractor connected to a heating mantle and chiller using toluene as extracting solvent. To ensure exhaustive extraction, the process lasted for about 48 h. At completion, the toluene was recovered from the oil sands using a rotary evaporator under a controlled temperature and transferred.

The ASTM (1998) separation method was used to fractionate the bitumen into operationally defined fractions. This method involves precipitating bitumen fractions by mixing whole bitumen in n-pentane (deasphalting). The n-pentane soluble are then separated by adsorption on silica gel and subsequent desorption of the saturates (paraffinic fraction) with n-hexane at an approximately rate of 0.5 ml/min with 100% n-hexane for saturates. The n-hexane (paraffinic fraction) eluates obtained was concentrated using a stream of nitrogen gas. Prior to Gas chromatographic (GC) analysis, the concentrated samples were reconstituted with 2 mL n-hexane.

Qualitative and quantitative analyses of organic components

Infrared spectroscopy

Identification of the functional groups of organic compounds present was determined using a Perkin Elmer Model 100 infrared spectrophotometer loaded with Infrared Data Manager (IRDM) software and coupled with Samsung ML-3051N printer. Infrared spectra for the raw samples of the paraffinic hydrocarbon fraction were recorded on the infrared spectrophotometer. All IR spectra were obtained using a 0.1-mm path length sample KCl cell. Spectra were recorded using the following settings; number of scans 4; gain 1; apodization weak; and resolution 4. Salt plates and windows of sealed cells were of KCl.

Gas chromatography/flame ionization detector (GC-FID) analysis

Identification and quantitative analysis of paraffinic hydrocarbons in the bitumen samples was performed with Agilent 7890A Gas chromatograph coupled with flame ionization detector (FID). High Resolution GC Capillary Column (HP-5, length 30 m, internal diameter 0.32 mm and film 0.25 μm (thickness) temperature limit of −60 °C to 325 °C was used. The injector temperature was 310 °C and the detector temperature was 310 °C. The oven temperature program had an initial temperature of 45 °C for 2 min and ramped at the rate of 5 °C/min to 305 °C and held for 5 min. Helium was used as the carrier gas at a flow-rate of 1 mL/min. Splitless injection was used and the sample volume injected was 1 μL. External Paraffinic Hydrocarbons standard, NEOCHEMA n-alkanes mix 31 (C10–C40) in cyclohexane Cat. No. 14670 was used for the calibration and quantification of the Paraffinic Hydrocarbons. CHEM STATION software was used for data acquisition.

Metal analysis

Extracted PHs measured 10 g was placed in a covered porcelain crucible and heated at 500 °C in a muffle furnace for 2 h to ash it. The crucible was brought out of the furnace and allowed to cool. The residue (ash) was dissolved with 10 ml of 0.02 M nitric acid to facilitate the complete extraction of the trace metals from the sample. A glass rod was then used to stir and crushed all the acid soluble elements in the ashes. The digest was then filtered into a 100 ml volumetric flask; the residue was further washed with 10 ml 0.02 M nitric acid solution. It was diluted with distilled water to the mark. The solution was later analyzed using Atomic Absorption Spectrophotometer, AAS (Buck Scientific VGP 210).

Blank determination was carried out to check for background levels of the metals in the reagents used for the digestion