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Organic and elemental elucidation of asphaltene fraction of Nigerian crude oils

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HIGHLIGHTS

- We provide data on the organic and elemental composition of the asphaltene component of Nigerian crude oils.
- We provide information on the quality of Nigerian crude oils.
- The study provides information on the properties of asphaltene component.
- The information provided will assist in the refining and processing paths of the natural resource.

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ABSTRACT

This paper provides data on the chemical composition of the asphaltene component of Nigerian crude oils in order to ascertain its properties which can assist in the refining and processing paths of the natural resource. Crude oil samples were collected from three major oil fields in Nigeria and were deasphalted using n-pentane. The organic characteristics of the precipitated asphaltenes were determined using Fourier Transform Infrared (FT-IR) Spectrometry, while the elemental contents were measured by Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-OES) and Carbon and Nitrogen Analyzer. Comparison of the average content of the Nigerian crude oils asphaltene with that of other nations shows that the Nigerian crude oil asphaltene content (3.65%, w/w) is less than that of other nations, except for Russian crude oil, but slightly higher than that of Brazilian crude oil, indicating that asphaltene deposition may pose less problems during Nigerian crude oil development than most of the crude oils from other nations. The IR spectra of the asphaltenes indicate the presence of alkanes, aromatic rings, phenyl rings, alcohols, ethers, carboxylic acids, esters, aldehydes, ketones, anhydrides, organic sulphoxides, sulphate salts and thiobenzophenones, confirming the fact that asphaltenes are composed of high molecular weight polycyclic constituents comprising of nitrogen, sulphur and oxygen heteroatoms. Ten elements (Cr, Cu, Fe, Mn, Ni, S, V, Zn, C and N) are examined and their concentrations determined. The results show that the values of all the elements are comparatively higher in the asphaltenes than the crude oils due to the presence of comparatively high concentrations of porphyrins in the asphaltenes than the crude oils. This is confirmed by their *T*-test values. Cross plot analysis result between the asphaltenes and crude oils using their elemental mean concentrations as variables indicates that *moderate* and positive correlation ($R^2 = 0.53$) exists between them, indicating inter-element and geochemical relationships between them. Elemental clustering analysis results present two groups which are also fairly correlated. As expected, the elements show very close clustering because all the elements are known to associate with petroleum hydrocarbon formation. Also, apart from N, S and C; other elements are transition metals with similar chemical affinity.

1. Introduction

Asphaltenes are usually defined as that fraction of petroleum, which is soluble in toluene and insoluble in n-pentane or n-heptane at a dilution ratio of 40 volumes of solvent per volume of the petroleum sample. Asphaltenes are present in crude oils as colloidally suspended solid particles. Precipitation of asphaltene occurs when the oil loses its capacity to keep those particles dispersed [12,13,6].

Alterations in pressure, temperature, composition and shear rate may cause asphaltene precipitation and deposition. The alterations may occur due different processes used; primary depletion, injection of natural gas or carbon dioxide, acidizing treatments and

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commingled production of incompatible fluids. Asphaltenes have practical uses, such as material for road construction, waterproofing and roofing, curing agents, corrosion inhibitors, stability of oil–water emulsions and in formation wettability, however they are usually ascribed to be a threat in the oil field. Asphaltene deposition may occur at many points along the production system, such as inside the formation pumps, tubing, wellheads, safety valves, flow-lines and surface facilities. Sheer occurrence of asphaltenes in crude oil does not indicate asphaltene-related production problems; minor quantity of asphaltenes when adhere to formation grains, pumps, tubulars, safety valves and flow-lines may not disrupt flow, but dense deposits can bring production to a standstill. Optimizing production in this case calls for the knowledge of the oil composition and the conditions under which its asphaltenes will remain in solution. Asphaltene-deposition problems may also be pronounced in lighter oil containing little content of asphaltenes in reservoir with pressure above bubble point [3,10,8,7].

The possibility of asphaltenes to clog systems continues downstream, and worrisome for refiners, because asphaltenes are significant constituents of the crude oils that are increasingly entering refinery processing streams. Remediation of the heavy organic deposits in the course of petroleum production has been a costly process and it has hampered the production activities in many parts of the world. Solid particles suspended in the crude oil may stick to the walls of the conduits and reservoirs. The toughness of the precipitate may be related to the occurrence of asphaltene in the crude oil even at small levels. Asphaltene is a highly polar compound and usually act as glue and mortar in hardening the deposits and, as a result, preventing oil flow [12,4,5].

Nigeria is endowed with huge deposits of crude oil. She is the 13th major world oil producer, and there are investigations [1,11] which are still on-going on the deposits, but there are few references to the asphaltene fraction of the crude oils. This article therefore characterizes the asphaltene fraction of crude oils obtained from three major Nigerian crude oil deposits using Fourier Transform Infrared (FT-IR) Spectrometry for compound types, while Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-OES) and carbon/nitrogen (C/N) analyzer were used for elemental composition elucidation. This will give insight to the contents and nature of the asphaltene fraction as well as assisting the refining and processing paths of Nigerian crude oils.

2. Experimental

2.1. Precipitation of asphaltene from crude oil

Samples of crude oil were collected from Belema, Imo and Eket oil fields in the Niger Delta area, Nigeria. Asphaltenes for this work were precipitated with n-pentane using a solvent to the crude oil ratio of 40:1. The precipitated asphaltenes were separated from maltenes (n-pentane solubles) by filtration and then washed with an equal volume of n-pentane. The solvent (n-pentane) was then removed using stream of N_2 gas followed by drying of the asphaltene at 70 °C in oven. The total yield (%/weight) was then calculated and reported.

2.2. Spectroscopic analyses

2.2.1. Infrared (IR) spectroscopy identification of functional groups in the asphaltene fraction

Infrared (IR) spectra were recorded on a Perkin Elmer Model spectrum 100 Fourier Transform Infrared Spectrometer coupled with Samsung ML-3051N printer. Solutions for obtaining the IR spectra were prepared by dissolving 30–50 mg of sample in 1.00 ml of Nujol (spectroscopic grade). 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.

2.2.2. Elemental characterization

2.2.2.1. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis. Measured weight (0.50 g) each of the asphaltene samples was put in a covered crucible and placed in a Gallenhamp muffle furnace which was maintained at 550 °C for 5 h. After ashing and cooling, 1 ml of 2 M HCl was added to the sample and allowed to boil to near dryness. This was followed by another batch of 1 ml of 2 M HCl but left to boil only for a few minutes before being transferred into a 50 ml volumetric flask. The crucible was rinsed several times with deionized water into the flask and then made up to the graduating mark. The above procedure was strictly followed in the preparation of the blank sample. All the digested samples were stored in thoroughly cleaned plastic bottles for elemental analysis using Inductively Coupled Plasma-Optical Emission Spectrometer ICP-OES (model Varian 71 O-ES ICP Optical Emission Spectrometer).

2.2.2.2. Carbon–nitrogen analysis. 0.150 g samples were weighed in a tin crucible and placed in the auto sampler and introduced into the high temperature combustion furnace. At 1100 °C the carbon was completely oxidized to CO_2 and nitrogen converted into NO_y in the presence of oxygen. After the catalyst furnace where the oxidation reaction usually takes place, the sample passed through a Peltier cooler to remove moisture formed by condensation. Then the sample gas splitted and transferred, by the carrier gas helium to the reduction oven. In the reduction oven of 600 °C NO_y was reduced, in the presence of a copper reductor, to N_2. Then first the CO_2 was measured by Non Dispersive Infra-red Detection (NDIR) for total carbon and subsequently the by-products, water and carbon dioxide were removed by an absorber. Secondly the N_2 gas was measured by Thermal Conductivity Detection (TCD).

2.3. Quality assurance and quality control

An Analar grade ethylenediaminetetraacetic acid (EDTA) with N (41.03%) and C (9.57%) was used as standard reference material for C and N analysis. The analyzed EDTA was prepared following the same protocols as the asphaltene samples, and the results N (40.93%) and C (9.60%) obtained were in good agreement with the stated certified values. The C/N Analyzer, IR spectrometer and ICP-OES used were calibrated using in-house calibration standards.

2.4. Data analysis

The overall data obtained on the elemental investigation of the asphaltenes were statistically analyzed and interpreted using descriptive and inferential technique viz; variation diagrams, *T*-test, cluster and cross plot analyses. Cross plot analysis using gross elemental concentrations as variables was carried out in this study to establish inter-elemental relationship the Nigerian crude oil and its asphaltene fraction. The cross plot analysis was carried out using Microsoft Excel. The cluster analysis was carried out using the furthest neighbor (complete linkage) grouping of the hierarchical cluster analysis in the Statistical Package for Social Scientist (SPSS) package. This was done to group the analyzed elements into families. The concentrations of the analyzed elements in the Nigerian crude oil and its asphaltene were also subjected to statistical analysis using *T*-test. The *T*-test was calculated using Microsoft excel. The data were analyzed using *T*-test to know whether there was significant difference between the concentrations of each element in the two set of samples. Level of parameter was considered *significant* if *T*-test value was less than 0.05.