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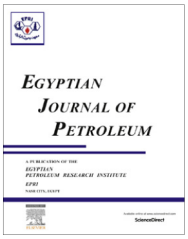

FULL LENGTH ARTICLE

Assessment of aromatics to saturate ratios in three Niger Delta crudes

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Abstract This study was designed to determine the aromatics to saturate ratios in three Nigerian Niger Delta crude oils to ascertain the crude oil source with the highest asphaltene risk. Three crude oil samples were collected from different locations: Kokori, Afiesere and Nembe in the Niger Delta region, Nigeria. The physical properties of the crudes (viscosity, density, API gravity) were determined. Saturates, aromatics, resins, asphaltenes (SARA) fractionation method was employed to separate different components in the crude oil. The composition and concentration of the saturates and aromatics hydrocarbon fractions were determined using a gas chromatograph. Results showed that API gravities ranged from 34° to 39° indicating that the three crudes are light. *n*-Heptane precipitation showed that Kokori crude had the highest weight percent concentration of asphaltenes (2.33%) and Afiesere crude, the least (1.91%). The gas chromatographic analysis of the saturates and aromatics showed that the total concentrations (mg/L) of all the saturates in Kokori, Afiesere, and Nembe were 871.26, 885.56, and 780.21 respectively while the total concentration of all the aromatics in the crudes were 80.15, 89.73 and 75.11 respectively. The aromatics to saturate ratios were computed and the results showed that this ratio decreased in the order Kokori crude < Nembe crude < Afiesere crude. This implies that Kokori crude with the lowest ratio will cause most asphaltene deposition problems than the other crudes.

1. Introduction

Asphaltenes are constituents of heavy organics in crudes. They are components of the solid deposits that narrow pipeline bores and obstruct fluid flow in the petroleum industry. They also contain trace elements and polyaromatics which are deleterious to health and constitute environmental pollutants if not professionally handled. Aromatics to saturate ratios are part of the parameters that govern asphaltene availability in crudes. In refinery processing, the qualities of crude oils are critical to refining cost. Crude oils in general can be divided into three basic categories namely light, medium and heavy. The criterion

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is based on the composition of the fractions derived from crude oil refining. The analysis of crude oil is necessary to determine the properties that can assist in resolving process problems as well as properties that indicate the function and performance of the product [1]. Fuel properties are determined experimentally in the laboratory on fluid samples taken from the process under study. It is necessary to analyse crude oils in terms of their saturates, aromatics, resins, asphaltene (SARA) composition in order to address and mitigate process problems such as asphaltene precipitation that can clog wells, pipelines, surface facilities and subsurface formations in the upstream operations, while in the downstream refining of heavy crude oils, it can lead to coking, fouling and catalyst deactivation. These problems are undesirable because they reduce productivity, limit fluid flow and are costly, hence laboratory analysis can assist to remediate such problems.

Chromatographic techniques have been extensively used for hydrocarbons group type determination, such as SARA fractionation. This area of study was first introduced by Jewel et al. where they developed the basis for SARA fractionation. This study discusses parameters such as SARA composition and asphaltene stability [2]. Asphaltene stability of crude oils can be determined from the ratio of aromatics to saturates in the crude oil [3] and this can be used to mitigate crude oil fouling. The main parameter that controls the stability of asphaltene in a crude oil is the aromatics to saturate ratio. If this ratio decreases, asphaltene will flocculate and form larger aggregates [4]. These asphaltene aggregates are highly notorious for the problems they cause as solid deposits.

The Niger Delta is one of the world's largest tertiary delta systems and an extremely prolific hydrocarbon province. It is situated on the West African continental margin at the apex of the Gulf of Guinea [5]. It occupies an area of about 75,000 km^2 with clastic sequence which reaches a maximum thickness of 9000–12,000 m of sediment and a total sediment volume of 500,000 km^3 [6].

Afiesere is located in Ughelli in Ughelli North Local Government Area, Delta State, Nigeria. The estimate terrain elevation above sea level is 12 m. Kokori is one of the six sub-urban states of the Agbon kingdom in Ethiope East Local Government Area, Delta State, Nigeria. It has a land area of 196 square kilometres while Nembe is located in Nembe Local Government Area, Bayelsa State, Nigeria.

2. Materials and methods

2.1. Materials

The three crudes namely Afiesere, Kokori and Nembe crudes were collected from Shell Petroleum Development Company (SPDC) located in Afiesere, Delta State and in Nembe, Bayelsa State respectively and stored in plastic containers.

The reagents *n*-heptane, toluene, dichloromethane, methanol and silica gel were of Aldrich analytical grade and were used without further purification.

2.2. Methods

The physical properties of the crude oils were determined using ASTM methods, i.e. density, specific gravity (ASTM D1298-95), API gravity (ASTM D287-92) and viscosity (ASTM D 445 01).

2.2.1. Precipitation of asphaltene

The crude oils (20 g) were mixed with *n*-heptane (800 ml) in the ratio of 40 ml of *n*-heptane to 1 g of crude oil. The mixture was thoroughly agitated with a magnetic stirrer and left to equilibrate for 48 h (normally, this is sufficient time for flocculation). The samples were transferred into centrifuge tubes and centrifuged at a speed of 2000 rpm for 30 min to obtain the asphaltene (*n*-heptane insoluble fraction) which was a shiny black amorphous solid. The resulting asphaltene was dried in an oven at 105 °C for 30 min and weighed.

2.2.2. Maltene fractionation

The deasphalted crude oils (maltenes) were fractionated by column chromatography on activated silica gel. The saturates, aromatics and the resins were eluted using *n*-heptane (100 ml), toluene(100 ml) and a 1:1 volume mixture of dichloromethane and methanol (100 ml) respectively. The fractions were recovered after rotary evaporation of the solvent.

2.2.3. Gas chromatography (GC-FID)

The saturate and aromatic hydrocarbon fractions obtained above were subjected to gas chromatography (GC) analysis using Buck Scientific Gas Chromatograph, Model 910 equipped with flame ionization detector (FID) and Restek 15 m MXT-1 columns. Injection volume was 1 μL with helium as the mobile phase. Injection and detection temperatures were 250 °C and 280 °C respectively.

3. Results and discussion

Some physical properties determined for the three crudes are shown in Table 1. The physical properties of crude oils are useful for initial screening and tentative identification of genetically related oils. Density/specific gravity gives an idea about the presence of light and high molecular weight hydrocarbons. The lesser the value of specific gravity, the lighter the amount of hydrocarbons in the petroleum [7]. Nembe crude had the lowest specific gravity than the other crude samples. This implies that the hydrocarbon content of the Kokori and Afiesere crudes will be more than that of Nembe crude.

Table 1 Some physical properties of the crudes.

Parameter	Unit	Kokori crude	Afiesere crude	Nembe crude
Density	g/ml	0.854	0.836	0.828
Specific gravity	g/ml	0.854	0.836	0.828
API gravity	°	34.19	37.76	39.39
Viscosity	P	8.64	6.40	4.48

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