Comparative Assessment of Carbon Preference Index and Degree of Waxiness in Different Crude Oils as Indicator of Maturity and Organic Matter Input: A Case Study of Ebocha and Kwali Crude Oil Niger Delta, Nigeria

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Abstract

Chemical fingerprinting of two crude oil samples (Ebocha and Kwali) crudes from Niger Delta region of Nigeria were carried out and hydrocarbon range of n-C₈H₁₈ to n-C₄₀H₈₂ were obtained. In this study, the Carbon Preference Index (CPI) and the Degree of Waxiness of the two crude oil samples were calculated. The results of the American Petroleum Institute (°API) gravity Ebocha 38.45° and Kwali crude 47.07° show that the crudes are light crudes. The viscosity Ebocha 3.68 and Kwali 3.46 correlate with °API gravity suggesting light crudes while the results from the Carbon Preference Index (CPI) 0.99 and 1.0 which indicate the two crude oil blends are mature crudes. The degree of waxiness of the two crudes is equal, Ebocha 4.4 and Kwali 4.4 which indicate that the two crudes are derived from terrestrial organic source. The geochemical analyses of the two crudes from different exploration well in Niger Delta are an indicator that both crudes have a common geological and formative history.

Keywords: Chemical fingerprinting; Carbon preference index; Degree of waxiness; Maturity; Terrestrial organic source

Introduction

Chemical fingerprinting of Niger Delta crude oil to ascertain the degree of waxiness and Carbon Preference Index (CPI) value is important because it gives information on the organic matter input. CPI is the first maturity indicator applied to crude oil [1]. Crude oil varies widely in appearance, behaviour and viscosity from field to field, therefore characterization and source identification from various fields cannot be over emphasized. The properties and composition of any petroleum systems is controlled by complex geological, physicochemical and biological processes during generation as well as accumulation in reservoirs. Niger Delta, as a case study for this research is one of the major hydrocarbon provinces of the world with an estimated reserve of 183 trillion cubic feet of natural gas and about 23 billion barrels of oil [2]. Generally the ratio of abundance of odd number paraffins, specifically calculated over the C₂₄-C₃₄ range has significance in the maturity of crude oil. Hydrocarbons derived predominantly from terrestrial sources and/or at low maturity exhibit a predominance of odd-numbered alkanes resulting in a high CPI; this feature disappears with increasing maturation level as CPI approaches 1.0 [3]. A waxy crude oil usually consists of a variety of light and intermediate hydrocarbons (paraffin, aromatics, naphthenic etc), a variety of other heavy organic non-hydrocarbon compounds even though at very low concentration includes resins, asphaltenes, diamondoids, mercaptans, organo-metalics etc. The distribution of n-alkanes in crude oils can be used to indicate the organic matter source [4]. This research work aims at determination of some bulk properties of the crude oil such as °API gravity, viscosity, density and geochemical parameter such as degree of waxiness and carbon preference index of the two crude oil (Ebocha and Kwali) from Niger Delta in order to understand the type and quality of the crude oils. Moreover, their correlation studies, degree of thermal maturity, organic matter source and depositional environment were ascertained.
Materials

The two crude oil samples (Kwali and Ebocha crude) which are collected from two oil well heads of Nigerian Agip Company limited, Niger Delta, Nigeria.

The Methodology

Physical properties of the crude oils

The physical properties of the crude oils were determined using ASTM methods, i.e density, specific gravity (ASTM D 1298-95), viscosity (ASTM D445-01) and API gravity (ASTM D287-92).

Precipitation of asphaltenes

N-pentane was added to crude oil sample in the ratio of 40mL of n-pentane to 1g of the crude oil sample. The mixture was thoroughly agitated with a magnetic stirrer and left to equilibrate for 48hour (floculation time). The samples were centrifuged for 1hour at a speed of 2000rpm for 2hour after pouring it into various centrifuge tubes. After which asphaltene precipitates were removed from the crude.

Maltene fractionation

The deasphalted crude oil samples were weighed again and were fractionated by column chromatography on activated silica gel. Slurry method was used in packing the column in order to avoid voids, bubbles and crack saturate fractions of the crude oil was eluded using (100ml) n-heptane. The saturate fractions were recovered after rotary evaporation of the solvents.

Gas Chromatography (GC-FID) analysis of the saturate

Gas chromatograph in line with ASTM D 3328-00 standard test method equipped with flame ionization detector (FID) and Restek 15m MXT-1 columns. Injection volume was 1µL with helium as the mobile phase. Injection and detection temperatures of 250 °C and 280 °C respectively were adopted to obtain their profiles, carbon number ranges and major compounds of distribution patterns.

Results and Discussion

Table 1: Some physical properties (viscosity, densities oAPI gravity) of the crude.

| Crude Sample | Viscosity (Centistokes) | Density (G/Cm³) | 0API Gravity (Degree) |
|--------------|-------------------------|----------------|----------------------|
| Ebocha       | 3.68                    | 0.8326         | 38.45                |
| Kwali        | 3.46                    | 0.7924         | 47.07                |

Some physical properties determined for the two crudes are as shown on Table 1. 0API gravity, density and viscosity show the quality of the crude oil in terms of the presence of light molecular weight hydrocarbons. The relative density value of Ebocha crude (0.8326) and Kwali crude (0.7924) which is less than 1.0 show that the crudes are light and hence can float in water. The API values are 38.45 and 47.07 for Ebocha and Kwali crude oil respectively which interprets that the crude is light crude. Generally, crude oil samples with API gravity greater than 31 are classified aslight asphaltenes, those with API gravity between 22.3 are classified as medium crude while those with API gravity 20 and less are referred to as heavy crudes [5] (API,2011). Viscosity results give valuable information concerning the composition of crude oils. This is a measure of the shear strength of the liquid and therefore indicates the flowing ability of crude oil [6]. The results show that crude oil blende sampled from Ebocha (3.46) and Kwali (3.68) are light crudes and can flow rapidly during spillage, shipment or pipes. The viscosity results also show bacteria effect on crude oil and infer that crudes used for this study are biodegradable. The occurrence of biodegradation in a reservoir affects the fluid properties like density, viscosity, etc [7]. The viscosity results summarizes that Ebocha crude oil is slightly more viscous than Kwali crude oil.

Table 2: Hydrocarbon profile of crude oils.

| Parameter | Carbon Chain | Concentration of Ebocha Crude (Mg/L) | Concentration of Kwali Crude (Mg/L) |
|-----------|--------------|---------------------------------------|-------------------------------------|
| n-Octane  | C-8          | -                                     | 1.615                               |
| n-Nonane  | C-9          | -                                     | 1.724                               |
| n-Decane  | C-10         | -                                     | 1.854                               |
| n-Undecane| C-11         | 1.864                                 | 2.047                               |
| n-Dodecane| C-12         | 2.058                                 | 2.146                               |
| n-Tridecane| C-13        | 2.381                                 | 2.367                               |
| n-Tetradecane| C-14      | 2.612                                 | 2.615                               |

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Gas chromatographic analysis data of the hydrocarbon profile of the various crude oil is shown in Table 2 and Figure 1 & 2. The results of the total concentrations Table 2 show that Kwali crude has the highest concentration (528.864mg/L) of n-alkanes while Ebocha crude has the least (504.206mg/L). The n-alkanes determined in the chromatogram ranges from C8-C40. Low molecular weight hydrocarbons (n-C8) were not observed probably because of evaporative loss during sample processing. The results of the carbon preference index and the degree of waxiness are shown in (Table 3).

Table 3: Value of CPI and degree of waxiness.

| Crude Oil Sample | Degree of Waxiness | Carbon Preference Index |
|------------------|--------------------|-------------------------|
| Ebocha           | 4.4                | 0.999                   |
| Kwali            | 4.4                | 1                       |

The table shows the value of carbon preference index (CPI) and degree of waxiness for two crude oil samples: Ebocha and Kwali. The CPI for Ebocha is 0.999 and for Kwali is 1.0. The degree of waxiness for both samples is 4.4. The CPI values indicate the maturity and organic matter input of the crude oils, with lower values suggesting higher maturity and more organic matter input. The degree of waxiness is a measure of the relative abundance of certain hydrocarbon components in the crude oil, with higher values indicating greater waxiness.
The carbon preference index (CPI) value of Ebocha (0.99) and Kwali crude oil (1.0) show that the two crude oil blends are mature crude. CPI is affected by source and maturity of crude oils [8]. CPI of petroleum oils of about 1.00 indicate mature samples and also can be used in source identification. The results of the degree of waxiness of the two crudes are equal, Ebocha (4.4) and Kwali (4.4) which indicates that the two crudes are derived from mixed organic matter with high contribution of aterrigenous organic matter input. Crude oil with degree of waxiness greater than 1 is said to be terrestrial organic source.

**Conclusion**

The maturation levels of samples and organic matter input obtained from calculations of degree of waxiness and carbon preference index (CPI) on Table 3 and some physical parameters of the crudes were determined Table 1. The two crude oil under study showed similar characteristics in terms of maturity and organic matter source. Saturated hydrocarbon molecular composition of these crude oils revealed that the crudes were formed in source rocks containing mixed kerogen (marine and terrestrial) deposited in a toxic environment. In this research, saturated hydrocarbons fractions were extracted from crude oil and different fractions of n-alkanes were analysed using gas chromatographic analyses. The bulk properties of the crudes (density and viscosity) reveal that both crudes are light crudes (biodegraded) and this correlate with the result of Carbon Preference Index (CPI) which indicate that the crudes are mature. Oil source correlation studies based on degree of waxiness which
records the digenetic evolution of the parent materials of crude oil indicate that the crudes are formed from source rock containing kerogen of terrestrial origin deposited in a toxic environment. The two crude oil under study (Ebocha and Kwali) have similar characteristics in terms of maturity, parent material and formation environment. Determination of these parameters in crude is important in oil and gas industry because it gives information on the flow rate, maturity and deposition environment of the crudes. The lower the value of density, viscosity, CPI and degree of waxiness, the higher the flow rate of the crude and the lesser it will create problem in refinery. Heavy and immature crudes may contain heavy organics such as asphaltenes which has detrimental impacts in petroleum operation such as refining and transportations. The knowledge of the degree of waxiness will help a geochemist or petroleum geologist to identify the source of oil spillage and also to identify crudes of similar origin with the information of diagenetic evolution of the parent material.

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