Compositional Significance of Light Hydrocarbons in Niger Delta Crude Oils

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Abstract: Crude oils from the tertiary Niger Delta were analyzed for their light hydrocarbon content. Ratios of three ring (P2, P3) and five ring (N2) preference were found to have no compositional variation of significance among the Niger Delta oils. However six ring (N1) preference (N1) had high compositional ratios and revealed the tertiary Niger Delta oils as exhibiting high six ring preference. Heptane ratio and invariance and maturity parameter among the C_7 light hydrocarbons discriminated the oils into two families namely marine and terrigenous and also revealed the tertiary Niger Delta oils as mature. Further confirmation of these two sources for crude oils in the tertiary Niger Delta were obtained from multivariate plots of each crude oil on a star diagram which showed the Eastern and Central oils were closely matched by their similar path followed on the star diagram and grossly different from the western oil which followed different pattern. [Nature and Science 2010;8(8):130-135]. (ISSN: 1545-0740).

Key words: light hydrocarbon, Niger delta, ring preference, star plot, invariance ratio

1. Introduction

The composition and distribution of certain chemical fossil can indicate the dominant source of sedimentary organic matter, whether marine or terrestrially derived (Osuji and Antia, 2005). The light hydrocarbons (LHs) are an important component in petroleum and account for over 50% of the carbon in petroleum (Mango, 1997). It is widely believed that the LHs are products of thermal cracking of higher hydrocarbons (Tissot and Welte, 1984). However, recent hypothesis suggests their formation by steady state catalysis of *n*-alkane parent into daughter iso- and cycloalkanes via three-, five- and six-carbon ring closure within the organic matter in a source rock (Mango, 1990, 1994). This hypothesis is supported by invariant ratios among the C_7 LHs (Peters et al, 2005). This invariance in the composition of C_7 LHs is unique and remains constant over the course of petroleum generation for a homologous oil suites (sets of oils from a common source), but distinctly different from another suite of homologous oils (Eneogwe, 2004, Mango, 1987, 1994). Thus genetically related oils can be differentiated from unrelated oils on the assumption that the same source material and environment of deposition will produce the same oil in which the case a chemical fossil compound in the source rock would be expected to appear in the oil it generated. Oils displaying a uniform overall geochemical composition show large compositional variations in their LHs reflecting variations in three ring preference (3RP), five ring preference (5RP) and six ring preference (6RP) (Mango, 1994).The LHs provide information regarding the source of the oil, environment of deposition, maturity (Mango, 1990, 1994; Thompson, 1983; BeMent et al.,1994) and have proven effective in source rock/crude oil and crude oil/crude oil correlations which are usually based on the recognition of compositional similarities (Onyema and Manilla, 2010; Zhang et al, 2005; Eneogwe and Ekundayo, 2004; Ten Haven, 1996; Halpern, 1995). This paper focuses on the compositional characteristics of the C_7 light hydrocarbons in selected crude oils from Niger Delta, Nigeria and their significance.

2. Geological Setting of the Niger Delta

The Niger Delta is one of the world's largest tertiary delta system and is situated on the West African continental margin at the apex of the Gulf of Guinea (Doust, 1990). The Niger Delta basin covers an area of $75,000 km^2$ (Sonibare et al., 2008). It formed during the continental breakup in the cretaceous era, with the delta developing from Paleocene. The lithostratigraphic sequence of the Niger Delta is divided into three formations. The Akata formation (Paleocene to Recent), at the base of the delta, consists of thick shale deposited under marine conditions. The overlying Agbada formation (Eocene into the Recent) consists of interbedded shale and sandstones and is overlain by the Benin formation (latest Eocene to Recent), which is composed of coastal plain sands (Sonibare et al., 2008, Short and Stauble, 1967). The source rocks for crude oil in the Niger Delta are the marine shale facies of the upper Akata formation and the shale interbedded with paralic sandstone of the lower Agbada formation. One petroleum system has been identified in the Niger Delta province referred to as the tertiary Niger Delta (Akata-Agbada) petroleum system (Tuttle et al., 1999).

3. Materials and Methods

3.1 Samples

Crude oil samples were collected from the tertiary Niger Delta, Nigeria. The crude oil samples were obtained from producing well heads by field technicians, with the assistance of the Department of Petroleum Resources (DPR). Five crude oil samples were collected from the Eastern Niger Delta (KA-1, US-3), Central Niger Delta (ET-3, NY-7) and Western Niger Delta (EV-5) and used for this study.

3.2 Analytical Methods

The light hydrocarbons were analyzed using the Hewlett Packard (HP) model 6890 gas chromatography (GC) fitted to a fused silica capillary column (30m x 0.25µm) and equipped with a flame ionization detector (FID) Helium was used as the carrier gas and a split ratio of 100:1. 1µl was injected with the aid of a HP 6890 automatic liquid sampler (ALS) fitted to the GC. Oven temperature was programmed with a 15min hold at 35^{o}C and ramped at 2^{o}C from 35^{o}C to 70^{o}C, 3^{o}C/min from 70 to 120^{o}. The final temperature was held for 20mins. Separated components were detected by FID and area integration of each peak was processed by the HP chemstation software. Light hydrocarbon peak identification was based on data presented by Mango (1987, 1990 and 1994).

For the purpose of investigating the selected tertiary Niger Delta crude oils, ratios and multivariate plot using gas chromatographic analysis of the C_7 LHs will be used. Ratios (eq. 1-3) will have to be virtually invariant within a family of oils (oils derived from the same source rock). Maturity of the selected tertiary Niger Delta oils from certain C_7 LHs ratio (eq. 4) will also be assessed. Multivariate plots of star diagram which consist of a series of ratios of chromatographic peaks will be used to investigate for differences and/or similarities among the oil samples.

$$\text{Heptane Ratio } (H) = \frac{n\text{-C7}}{(\Sigma \text{ CyC6 } + \text{ C7 HCs})} \times 100 \quad \text{------- 1}$$

$$\text{Invariance Ratio } (k_1) = \frac{\text{2MC6 } + \text{ 2,3DMC5}}{\text{3MC6 } + \text{ 2,4DMC5}} \quad \text{---------- 2}$$

$$\text{Invariance Ratio } (k_2) = \frac{P_3}{P_2 + N_2} \quad \text{------------------ 3}$$

$$C_7 \text{ MaturityParameter} = \frac{\text{2,4-DMC}_5}{\text{2,3-DMC}_5} \quad \text{-------------- 4}$$

4. Results and discussion

C_7 light hydrocarbons which constitute the bulk of carbon in petroleum include: ***n***-heptane, cyclohexanes, cyclopentanes and the isoalkanes. The six carbon ring compounds N1 originate from the ***n***-heptane parent, P1. Second parent P2 (mono branched isoalkane) forms five carbon ring compound N2 and P3 (poly branched isoalkane). All the oil samples analyzed contained C_7 LHs which makes the Niger Delta oils suitable for this study. GC fingerprints (fig. 1-5) of all the Niger Delta crude oil samples showed well resolved peaks for these characteristic C_7 LHs.

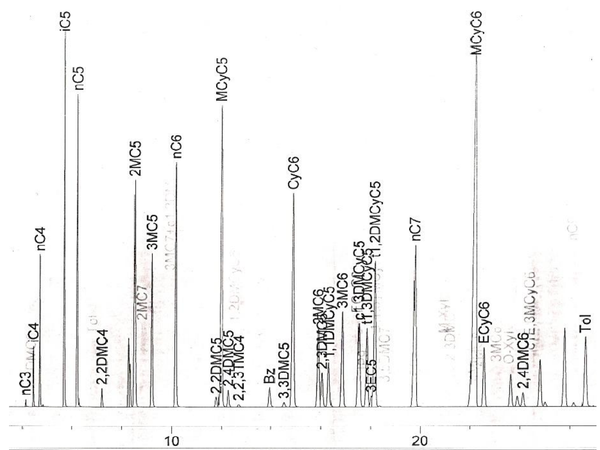

Figure 1: Gas Chromatographic Fingerprint of Oil Sample NY-7 showing characteristic C_7LHs.

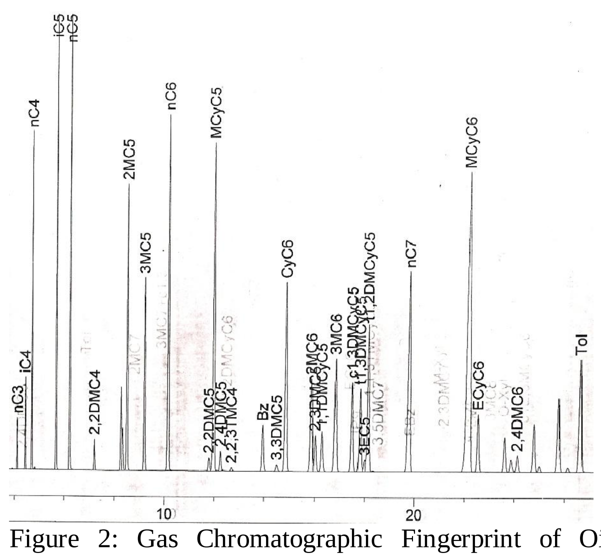

Figure 2: Gas Chromatographic Fingerprint of Oil Sample ET-3 showing characteristic C_7 LHs.

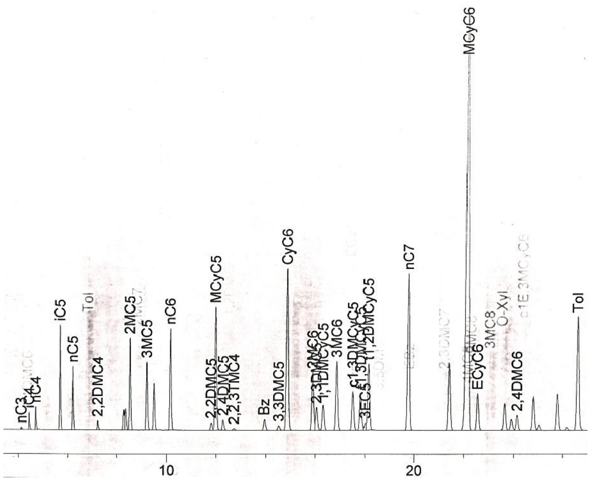

Figure 3: Gas Chromatographic Fingerprint of Oil Sample KA-1 showing characteristic C_7 LHs.

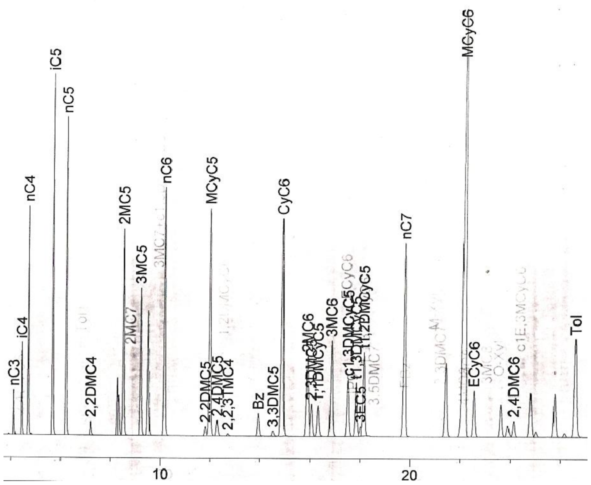

Figure 4: Gas Chromatographic Fingerprint of Oil Sample US-3 showing characteristic C_7 LHs.

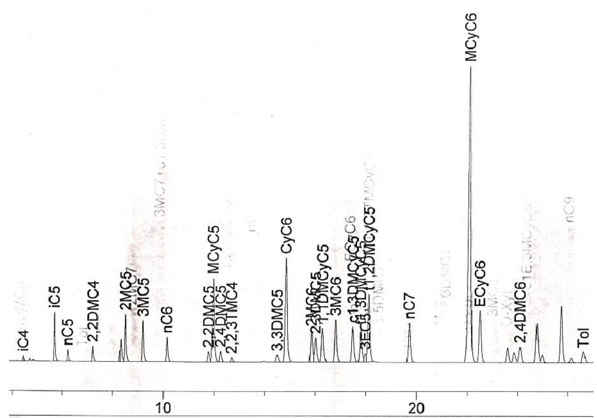

Figure 5: Gas Chromatographic Fingerprint of Oil Sample EV-5 showing characteristic C_7 LHs.

4.1 Compositional characteristic of Light Hydrocarbons

The results of the compositional characteristic of the five crude oil samples are presented in table 1.

Compositional ratio of *n*-heptane parent P1 discriminated between the samples. The data showed low P1 ratio for the western Niger Delta oil EV-5 (5.29%) and separated clearly from the Eastern, KA-1 (13.00%), US-3(14.24%) and Central, NY-7 (11.85%), ET-3 (15.70%) crude oils. The compositional ratios of P2, P3 (isoalkanes) and N2 (cyclopentanes) ranged from 9.73 to 13.27%, 4.05 to 7.90% and 8.57 to 14.71% with no compositional variation of significance. The six carbon ring N1 LHs was observed to be high compositional ratio ranging from 38.47 to 55.17%. This revealed the Niger Delta oils as exhibiting high six ring preference (6RP).

Table 1: Summary of C_7 Light Hydrocarbon Compositional Characteristics Parameters for Crude Oils from the NigerDelta.

LH	**Eastern Niger Delta**		**Central Niger Delta**		**Western Niger Delta**
Variables	**KA-1**	**US-3**	**NY-7**	**ET-3**	**EV-5**
P1	529.28	872.67	1195.51	2144.66	63.22
P2	423.77	781.78	1209.04	1812.59	116.26
P3	164.76	305.47	496.03	689.52	94.39
N2	349.05	640.06	1484.21	1899.12	167.93
N1	2247.10	2934.17	4256.61	5255.32	549.60
Total C_7	4072.82	6127.83	10087.06	13661.91	1194.35

Ratios are calculated from peak area of each C_7 LH compounds from the GC

4.2 Light Hydrocarbon Composition of Source and Maturity

The C_7 light hydrocarbon composition obtained by GC was used to discriminate between the tertiary Niger Delta crude oil samples and their proposed source. Thompson (1983) used the heptane ratio (*H*) as an indicator of the source (kerogen type) of crude oil, while Mango (1987, 1990) showed a remarkable invariance in the ratios of the sum of concentrations of certain C_7 LHs in crude oils. These invariant ratios (k_1 and k_2) are almost constant throughout hydrocarbon generation, regardless of their absolute concentration, among oils from the same source. Table 2 presents C_7 LHs source parameters for the selected tertiary Niger Delta crude oils.

Table 2: Summary of C_7 Light Hydrocarbon Source Parameters for Crude Oils from the Niger Delta.

LH Parameters	**Eastern Niger Delta**		**Central Niger Delta**		**Western Niger Delta**
	KA-1	**US-3**	**NY-7**	**ET-3**	**EV-5**
H	11.46	12.30	10.33	14.00	4.64
k_1	1.03	1.02	1.03	0.98	1.08
k_2	0.21	0.21	0.18	0.19	0.33
C_7 maturity	0.37	0.40	0.41	0.45	0.35

The crude oils produced from the tertiary Niger Delta basin have heptane ratios that ranged from 4.64 to 14.00 (Table 2). *H* allowed two different oil sets to be discriminated. The data showed that oils KA-1(11.46), US-3 (12.30), NY-7 (10.33) and ET-3 (14.00) have *H* close and separate from EV-5 (4.64). Mango (1987) showed the invariance in the ratio of isoheptanes, k_1, remains remarkably constant in all primary oils and variations can be explained by the variations in homologous sets. k_1 of the Eastern (KA-1= 1.03; US-3= 1.02) and Central (NY-7= 1.03; ET-3= 0.98) crude oils remains remarkably constant but distinct from the Western EV-5 (1.08) crude oil. This result strongly suggests at least two distinctly different source rocks responsible for oils in the tertiary Niger Delta and supports the grouping by *H*. Invariance ratio of isoheptanes and dimethylcyclopentanes, k_2, is a reliable indicator of source organic matter. Zhang et al (2005) reported that marine oils are characterized by low k_2 values (average 0.23) and terrigenous oils by high k_2 values (average 0.35). k_2 data (table 2) for oils from the Niger Delta classifies oil sample EV-5 (0.33) as terrigenous source organic matter input and KA-1 (0.21), US-3 (0.21), NY-7 (0.18) and ET-3 (0.19) as marine source organic matter. C_7 maturity parameter (Table 2) as defined by BeMent et al. (1994) show all the tertiary Niger Delta oils to be mature with crude oil sample ET-3 being the most mature (0.45) and oil sample EV-5 being the least mature (0.35).

4.3 C_7 Light Hydrocarbon Correlation

Multivariate plot, such as the star diagram consisting of a series of ratios of chromatographic peaks, have been used to correlate primary oils based on source related chemical differences (Onyema, 2005; Volk et al, 2005; Ali *et al*, 2002, Halpern, 1995). Comparisons of the Niger Delta oils using gas chromatographic analysis of C_7 LHs was put in pictorial form of a star diagram to make correlation of the fluids easier. The ratios used for the star diagram represent a random selection of C_7 LH compounds. A star diagram of selected ratios of chromatographic peaks on six (6) axes is presented in fig. 6.

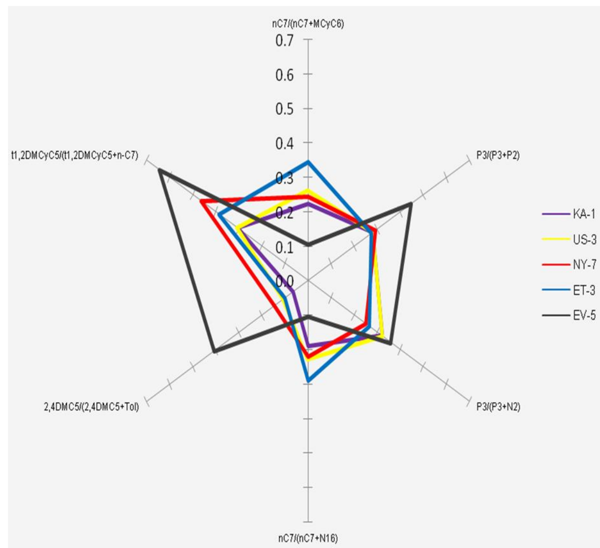

Figure 6. Selected ratios of chromatographic peaks on six (6) axes

The star diagram showed that oil samples KA-1 and US-3 (Eastern) oils followed patterns that were similar suggesting a close grouping among the oils and is reflective of oil generation from the same source rock (marine). Crude oils NY-7 and ET-3 were closely matched and shown on their plots to follow fairly similar path as the Eastern oils. However gross difference was observed in the star plot of EV-5 (Western) oil which followed patterns different from those of the Eastern and Central oils. This difference in path followed by the oils is in line with differences in source rocks between the oils (Ali et al., 2002) further confirming different sources for the western Niger Delta oils.

Conclusion

All the tertiary Niger Delta crude oils used in the study were shown to contain the C_7 LHs: *n*-heptane, isoalkanes, cyclopentanes and cyclohexanes. From the gas chromatographic data provided, all the tertiary Niger Delta oils were shown to mature and exhibit high six ring preference (6RP). Heptane ratio allowed two distinct oil sets to be discriminated. C_7 LH invariance among the crude oils, although relatively constant, separated the Niger Delta oils into two source-related families: terrigenous for the Western oil and marine for the Central and Eastern. Similar patterns followed by the Central and Eastern oils were different from the Western further affirming 2 homologous sources for crude oils in the tertiary Niger Delta.

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