ASSESSMENT OF ALIPHATIC BIOMARKERS IN SOME SELECTED COAL DEPOSITS IN NORTHERN NIGERIA

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Abstract: This research investigates the distribution of *n*-alkanes (m/z 85), Steranes (m/z 218) and hopanes (m/z 191) in Chikila, Lamja, Lafia Obi, Maiganga and Okaba coals from Northern Nigeria in order to assess their source organic matter, depositional environment and thermal maturity using GC-MS. The results revealed that the source organic matter of the coals is terrestrial higher plants while the depositional environment is terrestrial under oxic condition. The coals have the potential to generate oil but are not yet thermally matured.
Keywords: Aliphatic, biomarkers, coals, hopanes, *n*-alkanes, steranes, Northern Nigeria

Introduction

Biomarkers are complex molecular fossils derived from biochemicals, particularly lipids, in once-living organisms. Biomarkers can be determined in both petroleum and extracts of petroleum source rocks; therefore, they provide a method to correlate the two and can be used by geochemists to interpret the characteristics of petroleum source rocks when only oil samples are available (Peters *et al*., 2005). Biomarkers can also give useful information on the organic matter in the source rock, environmental conditions during diagenesis and catagenesis, degree of biodegradation and some phases of lithology (Hunt. 1991).

Inland sedimentary basins in Northern Nigeria have been highly under-explored mainly because of the little knowledge of their geology compared to the Niger delta (Obaje *et al.*, 2006).

The total reliance on oil and oil-derived foreign exchange in planning the nation's economy resulted in the demotion of coal to the background. Prior to the discovery of oil at Oloibiri in Bayelsa State in 1956, coal played a significant role in Nigeria's economic development (Fatoye and Gideon, 2013).

The debate on hydrocarbon generation and migration within coal has strengthened since the early work by Brooks and Smith (1969) who proposed that certain oils originated from coals. Today, it is widely accepted that some coals can truly generate oil (Hunt, 1991). Petroleum generation from coal source rocks and its type depends on the availability of hydrogen (Hunt, 1996; Petersen and Nytoft, 2006). The significance of paraffinicity of coal for generating and expelling liquid hydrocarbons has received great consideration (Isasken *et al.*, 1998; Killops *et al.*, 1998).

Marketable hydrocarbon accumulations have lately been discovered in Chad and Sudan within this rift trend (Obaje *et al.*, 2006); therefore there is a need for the analysis of coals in the Benue Trough. The Nigeria coal deposits are reported to be within the Benue Trough (Carter *et al*., 1963; Obaje *et al.*, 1994) which is subdivided into Lower, Middle and Upper portions. The Benue Trough is considered to have formed by the incipient rifting during the breakaway of South America from Africa and the opening of south Atlantic in Early Cretaceous (Albian) times (Whiteman, 1982). It trends SSW-NNE for about 800 km in length and 150 km in width (Abubakar *et al.*, 2006). The Benue Trough divides at its upper end to the Gongola arm running north into the Chad basin and the Yola arm terminating eastwards against the Cameron basement. Despite the huge reserves of coal in Nigeria, its petroleum potential has not been broadly studied (Fatoye and Gideon, 2013).

The aliphatic biomarkers such as steranes, n-alkanes and hopanes can give information on the source organic matter, depositional environment and thermal maturity of coals. This research investigates the distribution of aliphatic biomarkers in Chikila, Lamja, Lafia Obi, Maiganga and Okaba coals in order to assess their source organic matter, depositional environment and thermal maturity.

Materials and Methods

Sampling

The coal samples were collected from exposed coal seams in Nasarawa State (Lafia, Obi coal), Kogi State (Okaba coal), Gombe State (Maiganga coal) and Adamawa State (Chikila and Lamja coals) in the Benue Trough (Fig. 1) after scrapping of the top 30 cm. The samples were pulverized and stored in a polythene bag for subsequent use. The gross sample was reduced to representative sample by cone and quatery (Speight, 2005).

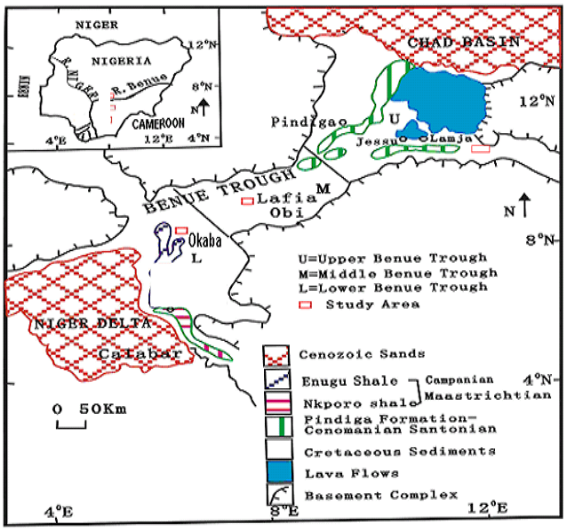

Fig. 1: Geological Map of Benue Trough, Nigeria (modified after Obaje, 1994)

Extraction

The extraction of the biomarkers was done using Soxhlet extractor. Coal samples (50 g) were weighed into an extraction thimble. The solvents used for the extraction were dichloromethane and methanol (93 and 7%, respectively). Each sample was extracted for 24 h. The solvents were evaporated using rotary evaporator. Column chromatography was conducted on each extract to recover the aliphatic hydrocarbons (Usman, 2015).

Column preparation

1 g of alumina was measured and poured into a 5 cm^3 beaker that is properly washed and rinsed with the solvent after drying. 50 mg of the extract was measured and transferred onto the center of alumina and was shaken until the extract was uniformly distributed in the alumina.

A glass column was rinsed with n-hexane and small piece of cotton wool was inserted into the column. Silica gel (10 g) was measured and wetted with *n*-hexane which was transferred and packed into the column to form stationary phase. Then, a 1 cm thick layer was formed by adding alumina then the sample was loaded and covered with another 1 cm thick layer of the alumina. Saturated compounds were eluted using 40cm^3 n-hexane (Usman, 2015).

GC/MS conditioning and analysis

Saturated hydrocarbon fraction from the column chromatography were analysed using GC/MS (Agilent 6980N GC coupled with Agilent 5973MSD). The run involves injection of the sample solution (1 µl) into the injection port of the GC machine. The machine was equipped with a 30 m long polysilohexane capillary column with 20 µm internal diameter and 1.0 µ film thickness. Helium gas was used as a carrier gas. The GC temperature program involves an initial temperature of 50°C and a heating rate of 5°C to the final temperature of 300°C with initial and final hold time of 5 min. The data was acquired using Chemsation software on Dell personal computer. The MSD was set to monitor selected ions (SIM) for aliphatic hydrocarbon analysis. The chromatographic peaks were obtained and compared with standard peaks for identification and the peaks were manually integrated to obtain the peak areas which were used to calculate the biomarker parameters.

Results and Discussion

The results of the aliphatic hydrocarbon parameters are shown on Table 1. High proportions of long chain C_{27}-C_{31} alkanes relative to the total n-alkane especially n-C_{27} and n-C_{29} are typical of terrestrial higher plants, where they occur as main components of waxes (Bray and Evans, 1961). The coal samples analysed have significant proportions of long chain C_{27}-C_{31} members. This indicates that the coals are from terrestrial higher plants. Hopanoids are considered biomarkers for bacteria and cyanobacteria. However, the C_{30} hopanes have been found in some cryptogams; moss, fern (Bechtel *et al*., 2007). The coals contain reasonable amount of the hopanes in various proportions. These compounds could be from both higher plants as well as the bacteria involved in the degradation of the plant debris during diagenesis (Hunt, 1991).

Table 1: The results of the aliphatic hydrocarbon parameters

Samples	CPI	OEP	Pr/Ph	DEW	Paq	TAR	%C_{27}	%C_{28}	%C_{29}	I (%)	II (%)	III (%)
Lamja	0.91	0.73	3.37	3.60	0.22	0.14	8.54	35.9	55.57	54.87	49.25	1.17
Chikila	0.90	1.10	7.80	1.11	0.23	0.04	9.52	45.56	44.92	55.13	40.44	1.37
Maiganga	0.99	0.91	4.68	1.59	0.14	0.01	6.54	41.24	52.22	41.52	42.35	3.82
Lafia Obi	0.69	1.22	3.23	1.65	0.59	1.69	-	-	-	23.42	43.81	1.54
Okaba	0.43	0.53	3.18	3.42	0.20	0.15	7.27	69.60	23.13	30.12	43.45	1.76

Pr/ph = Pristane/Phytane ratio DeW = Degree of Waxiness Paq = Alkane proxy TAR = Terrigenous versus aquatic ratio CPI = Carbon Preference Index OEP = Odd-Even predominance I= 31αβ22S/(22S + 22R) II= 32αβ22S/(22S + 22R) III = C30 βα/(βα +αβ)

The marine organic matter is associated with Pr/Ph ratios of less than 2.0, ratios between 2.0 and 3.0 indicates lacustrine organic matter, while ratios greater than 3.0 indicates terrestrial organic matter (Peters and Moldowan, 1993). This further indicates the terrestrial organic matter in the coals because their ratios are greater than 3.0. Also, alkane proxy (Paq) parameter which was suggested by Ficken *et al*. (2000) revealed that the range from 0.01 to 0.23 is associated with terrestrial waxes while the range from 0.48 to 0.94 are linked with submerged floating species of macrophytes. All the coal samples are within the first range given; therefore they are linked to terrestrial plants.

According to Moldowan *et al.* (1985), the relative percentages of C_{27}, C_{28}, C_{29} steranes can give information on the organic facies of source rocks. The amount of C_{27} ranges from 6.54% for Maiganga and 9.52% for Chikila. The amount of C_{28} steranes ranges from 35.90% for lamja to 69.60% for Okaba coal. The amount of C_{29} steranes falls within the range of 23.13% to 55.57%; therefore, the steranes in these samples have a significant contribution of the source organic matter from higher plant.

Peters and Moldowan (1993) reported that the Pr/Ph ratio of less than 1.0 may indicate hypersaline, anoxic or lacustrine environment, Pr/Ph ratio equals to 2.5 indicates a marine environment with considerable amount of terrestrial input while high Pr/Ph ratio of greater than 3.0 indicates terrestrial organic matter input under oxic conditions. The samples analysed are in the range of 3.18 to 7.80 and this is an indicative of terrestrial input under oxic conditions. This is further supported by the higher relative proportions of moretanes (βα-hopanes) and C_{29} hopanes in the extracts which have been observed to indicate terrestrial depositional environment (Hoffmann *et al.*, 1984).

CPI values below 1.0 indicate carbonate facies, while values higher than 1.0 indicate lacustrine environment or salisiclastic source rock (Tissot and Welte, 1984). The coal values obtained are all below 1.0; therefore, this may indicate carbonate facies as the depositional environment. The 30βα/30αβ of C_{30} hopanes is an important parameter that indicates the type of environment to which the extract is obtained. All the coals have values above 0.5 indicating terrestrial input (Peters *et a*l., 2005). Furthermore, the degree of waxinesss (DEW) parameter shows that all the coals have values significantly higher than 1.0 further indicating oxic condition for source organic matter (Finken *et al*., 2000).

The thermal maturity parameters indicate the degree of maturity which the organic matter of the coals had attained. CPI is an important maturity parameter. All coals having the CPI and OEP values above or below 1.0 indicate low thermal maturity (Peters *et al.*, 2005). According to this all coals are thermally immature. This is collaborated by the hopane-based 22S/(22S + 22R) maturity parameter. The 22S/(22S + 22R) for C_{31} hopanes is a maturity parameter used for immature to early mature petroleum stage of oil window. It has the maximum values of 60% according to the biomarker maturity scale reported by Hunt (1996). The values obtained are from the range 23.42% for Lafia Obi coal to 55.13% for Chikila coal. The values acquired for all the coals are not up to the maximum value but Lamja and Chikila coals are closer to maturity. Also another similar parameter is 22S/(22S + 22R) for C_{32} hopanes which was prescribed by Peters and Moldowan (1993). The values of this parameter for the coal samples are within the range of 40.44% for Chikila to 49.254% for Lamja. All these concur that the coals are not matured (Hunt, 1996).

The βα/(βα +αβ) of C_{30} hopanes is a very important parameter. The values for the coals analysed are in the range of 1.37 for Chikila to 3.82% for Maiganga. By this, it can be said that the coals might be closer to maturity since the maximum equilibrium value is 5% (Peters and Moldowan, 1993).

Conclusion

The distribution of aliphatic biomarkers was determined in Chikila, Lamja, Lafia Obi, Maiganga and Okaba coals from Northern Nigeria. The organic geochemical parameters revealed that the source organic matter of the coals is terrestrial higher plants while the depositional environment is terrestrial under oxic condition. The coals have the potential to generate hydrocarbons but are not substantially matured.

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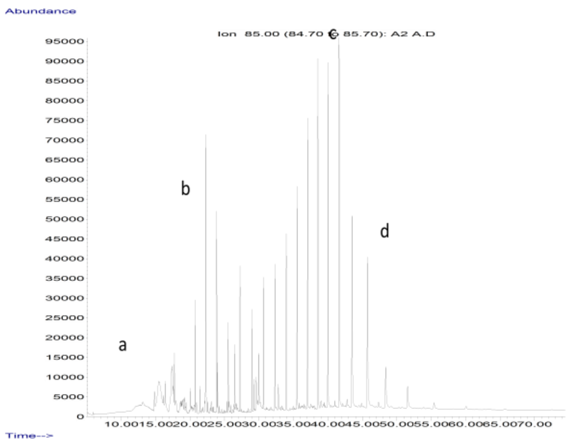

Fig. 2: Mass chromatogram showing distribution of the n-alkanes with *m/z* 85

a = C_{15} *n*- Pentadecane; **b** = C_{19} *n*- Nonadecane; **c** = C_{30} *n*-Triacontane; **d** = C_{32} *n*- Dotriacontane

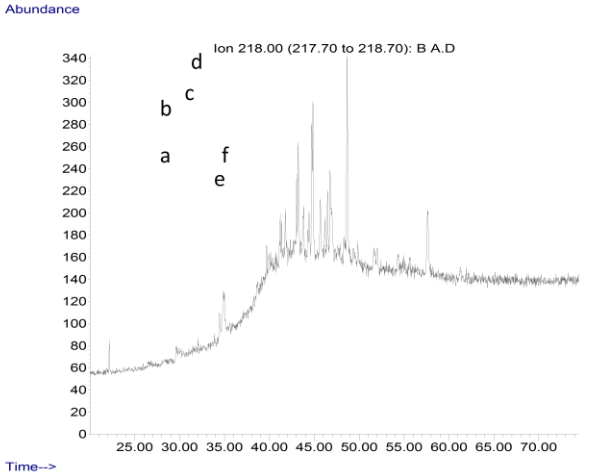

Fig. 3: Mass chromatogram showing steranes with *m/z 2*18
a- 27 5α (H), 14β (H), 17β (H), 20S; **b-** 27 5α (H), 14β (H), 17β (H), 20R; **c-** 28 5α (H), 14β (H), 17β (H), 20S **d-** 28 5α (H), 14β (H), 17β (H), 20R; **e-** 29 5α (H), 14β (H), 17β (H), 20S; **f-** 29 5α (H), 14β (H), 17 β (H), 20R; **h-** 28 5α (H), 14β (H), 17β (H), 20R **g** -28 5α (H), 14β (H), 17β (H), 20S

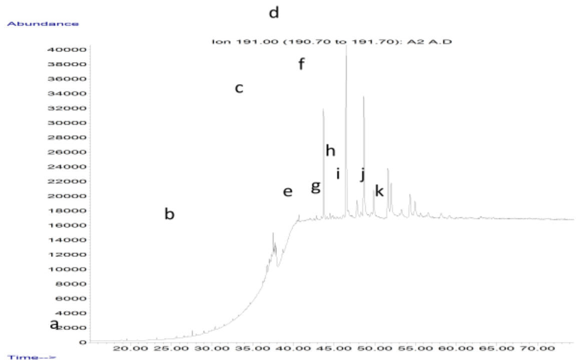

Fig. 4: Mass chromatogram showing distribution of the hopanes with *m/z* 191
b= Tm 17α (H) - 22,29,30-trisnorhopane; **c=** 29 17α (H) - 21β(H) norhopane; **d=** 30 17α(H)-21β(H) Hopane; **e=** 30 17β(H)-21α(H) moretane; **f=** 31 17α(H), 21β(H), 22S homohopane; **g=** 31 17α(H), 21β(H), 22R homohopane; **h=** 32 17α(H), 21β(H), 22S bishomohopane; **i**=32 17α(H), 21β(H),22R bishomohopane; **j=** 33 17α(H), 21β(H),22S trishomohopane j-33 17α(H), 21β(H), 22R trishomohopane