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Characterization of Organic Matter from Bituminous Coals of Lafia-Obi, Middle Benue Trough, Nigeria

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ABSTRACT: The present work deals with a study based on the geochemical techniques such as biomarkers, Rock-Eval pyrolysis, and detailed petrographic study to evaluate hydrocarbon generation potential of coal by collecting nine coal and carbonaceous shale samples from boreholes in Awgu Formation of Middle Benue Trough, Nigeria. The values vitrinite reflectance (0.94–1.15%VR) and Tmax (446–469°C) confirmed that samples are matured enough to generate liquid and gaseous hydrocarbon in coal. The coal samples also contain sufficient quantity of vitrinite and liptinite macerals varying from 70.28% to 74.10 wt%, which confirm the production of liquid hydrocarbon. The cross-plot between H/C and O/C atomic ratio indicates that samples were predominant in the bituminous rank and having kerogen Type III makes it suitable for hydrocarbon generation. Similar results were found in Rock-Eval pyrolysis analysis (Types II-III and Type III kerogen). The homohopane index (C_{35}/C_{31} - C_{35}) and homohopane ratio ($C_{35}\alpha\beta S/C_{34}\alpha\beta S$) range from 0.02 to 0.12 and 0.15 to 0.92 indicates oxic condition during organic matter deposition from Lafia-Obi samples. The Moretane/Hopane, Hopane/Hopane + Moretane, Ts/Ts + Tm, 22S/22S + 22RC$_{32}$homohopane ratios range from 0.06 to 0.14; 0.88 to 0.94; 0.34 to 0.66; and 0.53 to 0.62 and 20S/20S+20R and $\alpha\beta\beta/\alpha\beta\beta+\alpha\alpha\alpha$ C_{29} ratios range from 0.43 to 0.58 and 0.42 to 0.55 indicate samples are within the late oil window/gas phase. Plots of 22S/22S+22R C$_{32}$hopanes against $C_{29}\alpha\beta\beta/\alpha\beta\beta+\alpha\alpha\alpha$ steranes show that Lafia-Obi samples are thermally mature.

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Keywords: Pyrolysis temperature; thermal maturity; petrography; oil yield.

Organic geochemistry deals with the process governing the origin and fate of organic materials such as petroleum (crude oil and natural gas), coal, oil shale and tar sands. Coals are remnants of terrestrial higher plants formed under non-marine and paralic conditions (Tissot and Welte, 1984) and found at its site of deposition as a solid and a relatively pure massive organic substance. Petroleum generation from coal source rocks and its type are fundamentally dependent on the availability of hydrogen (Hunt, 1996; Petersen and Nytoft, 2006). The importance of paraffinicity of coal for generating and expelling liquid hydrocarbons has received great attention (Isasken *et al.*, 1998; Killops *et al.*, 1998). Coal is the major conventional source of energy, which has eventually made the industrial revolution possible and 70% of growing energy demand has been largely met by the coal (Chaurasia and Nikkam, 2016; Chaurasia *et al.*, 2018; Sahu *et al.*, 2018). The unconventional resources are becoming increasingly important for energy requirement and focus has been given by scientists, researchers, and policy makers (Akanksha *et al.*, 2017, 2019; Suman *et al.*, 2017; Yadav *et al.*, 2017). However, the previous study describes that coal can be used as a significant source of liquid and gas hydrocarbons (Obaje and Hamza, 2000; Panwar *et al.* 2016a, b). The atomic ratios of H/C and O/C are also considered for assessment of hydrocarbon potential, maturity, kerogen types, and nature (Fisher *et al*. 1942; Tissot and Welte, 1984; Van Krevelen 1993). The petrographic study reveals the effect of maceral content viz. vitrinite, liptinite, and inertinite for the assessment of liquefaction potential (Chen *et al.*, 2007). However, liptinite and vitrinite group of maceral has higher hydrocarbon generation potential than inertinite group of maceral (Zhong and Qin, 1995). The high-volatile bituminous coals carrying vitrinite reflectance ranging from 0.49 to 1.02% and reactive macerals value >70% are most feasible for liquid hydrocarbon generation (Given *et al*. 1975, 1980; Singh *et al*. 2013). Panwar *et al.* (2019) in their report concluded that most of the bituminous coal samples are per-hydrous in nature; however, some samples also come in the bright band of Seyler's chart (Cornelius, 1978). Rock-Eval pyrolysis is prominently used for determination of hydrocarbon potential in source rocks as well as for maturity of organic material. Since Rock-Eval pyrolysis takes less time and is feasible in nature, a lesser quantity of the sample is needed for analysis (Carvajal-Ortiz and Gentzis,

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2015; Hakimi *et al*. 2013). Maturity of source rocks can also be determined from the biomarker distribution in source rock extracts. Many maturity parameters have been developed from the distribution of terpanes, steranes and polyaromatic hydrocarbons in source rocks (Peters *et al.*, 2005).In the present investigation, six coals, two carbonaceous shales and coaly shale; totaled nine samples were collected from borehole at Lafia-Obi, Middle Benue Trough Nigeria. The objective of this study is to evaluate the hydrocarbon generation potential of coal samples collected from boreholes in Awgu Formation of Middle Benue Trough, Nigeria.

MATERIALS AND METHODS

Geological Settings: The Benue Trough (Fig. 1) 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; Jauro *et al.*, 2007). The Benue Trough is divide at its upper end to; the Gongola arm running north into the Chad basin and the Yola arm terminating eastwards against the Cameroon basement. There are various amounts of uplift and deformation that created a regional unconformity in the Benue Trough. This is because full rifting never developed and its sedimentary fill, accumulated in about 20Ma since Albian time, was folded by complex stress created at the African plate margin in Santonian thereby regarded as ‘Failed Arm’ (Pearson and Obaje, 1999). The Trough contains about 6000 m thick of Cretaceous-Palaeogene sediments that are organic rich in part. The Benue Trough can be physiographically and lithostratigraphically subdivided into lower, middle and upper Benue Trough (Fig. 2). The geology of Benue Trough has been extensively reviewed (Carter *et al.*, 1963; Peters, 1982; Peters and Ekweozor, 1982; Obaje 1994, 2000; Zaborski, 2000; Obaje *et al.*, 2004). Overlying the basal rift sandstones of Late Necomian to Aptian age are thick shales and thin limestone deposited during marine trangression (Peters and Ekweozor, 1982) in the Middle to Late Albian, Late Cenomanian to Early Turonian, Late Turonian to Early Santonian, Campanian to Maastrichtian, Paleocene, and Eocene. The shale limestone sequence formed during Late Cenomanian to Early Turonian includes Odukpani Formation of Calabar area, Eze-Aku/Makurdi Formation that extends from North of Ishiagu in the Lower Benue Trough and Dukul, Gongila and Pindiga Formations of Upper Benue Trough in the North Eastern Nigeria. The limestone beds in these Formations are sufficiently thick in some places. After the deposition of the limestone bearing sequence, the sea became shallower resulting in the formation of swamps particularly in the Anambra basin. The swamps and associated vegetation were later buried under thick sediments to produce coal-bearing rocks.

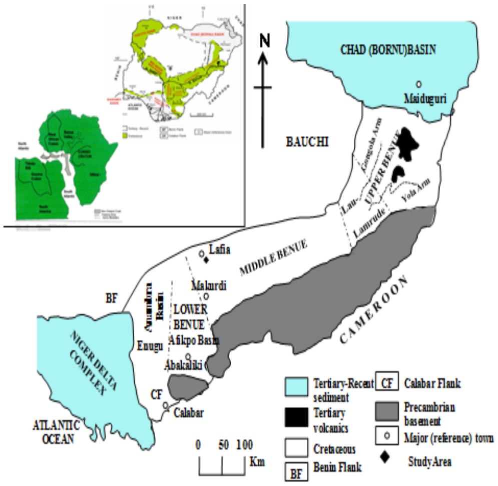

Fig 1: Geological map of Benue Trough, Nigeria (modified after Obaje, 1994).

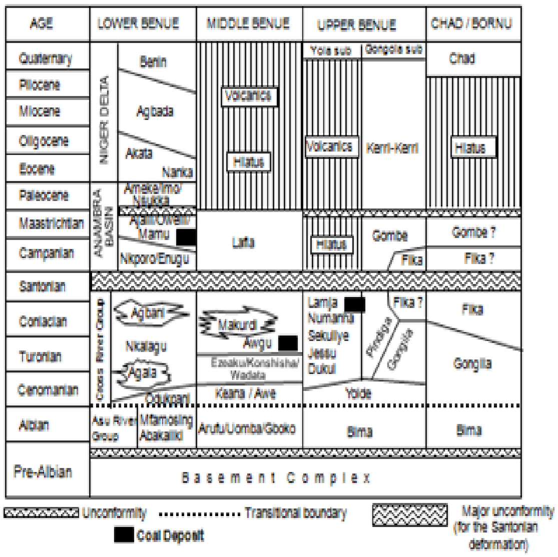

Fig 2: Stratigraphic successions in the Benue trough and the relationship to the Chad basin and the Niger delta (After Obaje *et al.*, 2004).

Lithology Description: In the middle Benue Trough, the Precambarian Basement is overlain uncomformably by the Asu River Group, and the Keana, Makurdi and Awgu Formation overlie this unconformably while Lafia Formation unconformably overlies the Awgu Formation (Ehinola *et al.*, 2002). Different periods that were recognized in the Middle Benue Trough are Albian, Cenomanian, Turonian, Coniacian, Campanian-Maastrichtian and Paleocene. These periods have been previously described (Ehinola *et al.*, 2002).

Sample Collection and pretreatment: A total of nine samples comprising of six coals, two carbonaceous shales and coaly shale were collected from 2 boreholes (BH94 and BH120) from Lafia-Obi, Awgu Formation. The coal seams and interbedded shale in BH94 and BH120 were sampled between 218-431 m and 131-289 m depths respectively. The detailed lithographic descriptions of the boreholes are presented in Fig. 3. Care was taking to avoid weathered portions of the outcrop and to obtain material sufficient for various geochemical analyses. In the laboratory, the samples were reshaped using a rotating steel cutter to eliminate surface that could be affected by alteration. Chips were cut from the samples and dried in an oven at 105^{o}C for 24 hours. The dried sample was pulverized in a rotating disc mill to yield about 50 g of sample for analytical geochemistry.

Sample Analysis: The TOC and inorganic carbon (TIC) contents were determined using Leco CS 200 carbon analyzer by combustion of 100 mg of sample up to 1600^{o}C, with a thermal gradient of 160^{o}C min^{-1}; the resulting CO$_2$ was quantified by an Infrared detector. The sample with known TOC was analyzed using a Rock-Eval 6, yielding parameters commonly used in source rock characterization, flame ionization detection (FID) for hydrocarbons thermal conductivity detection (TCD) for CO$_2$. The Zeiss standard universal reflected microscope was used for vitrinite reflectance and the reflectance of maceral was analyzed by Scanned Electron Microscope (SEM) at Federal Institute of Geosciences and Natural Resources, Hannover, Germany. The GC-MS analyses of the fractions were performed on a Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5973N Mass spectrometer.

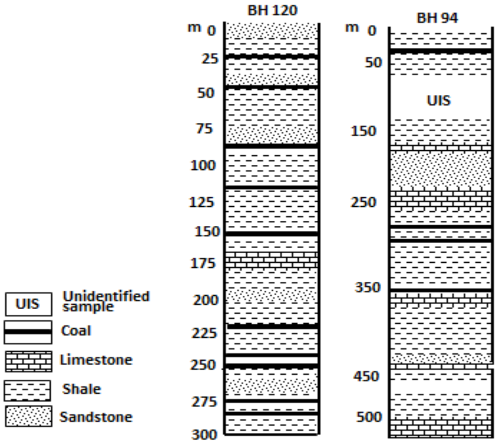

Fig 3: Lithographic section of BH94 and BH120 of Lafia-Obi coal, Awgu Formation (Ehinola *et al.*, 2002).

The gas chromatograph was equipped with a DB-5 MS fused silica capillary column (30 m x 0.25 mm) and helium was used as carrier gas with a flow rate of 1ml/min. The Mass spectrometer was operated with electron impact energy of 70 eV and ion source temperature of 230 ^{o}C. The GC oven temperature was isothermal for 1min at 80 ^{o}C and then programmed from 80 to 280 ^{o}C at 3 oC/min and isothermal for 20 min at 280 ^{o}C. Individual saturated, aromatic and NSO- compounds were monitored by selected ion monitoring (SIM) at a cycle time of 1s.The GC-MS data were acquired and processed with a Hewlett-Packard Chemstation data system.

RESULTS AND DISCUSSION

Biomarker or geochemical fossils are organic compounds found in geosphere whose structure can be unambiguously linked to their biological origin, despite the possibility of some structural alteration due to diagenetic or other processes. Treibs (1934) was the first to develop the biomarker concept with his pioneering work on identification of porphyrins in crude oils and suggested that these porphyrins may have originated from the chlorophyll of plants. All biomarker molecules have definitive chemical structures, which can be related directly or indirectly through a set of diagenetic alterations to biogenic precursors, and cannot be synthesized by abiogenic processes (Simoneit, 2002). The use of biomarkers as indicators of biogenic, paleoenvironmental, and geochemical processes on Earth has been widely accepted (Mackenzie *et al.,* 1982; Johns, 1986; Simoneit *et al.,* 1986; Brassel, 1992; Imbus and Mckirdy, 1993; Mitterer, 1993; Simoneit, 1998). Biomarkers are widely used in petroleum geochemical studies in source rock evaluation, oil-oil or oil-source rock correlations, basin evaluation and reservoir management (Peters *et al.,* 2005).

Rock-Eval Pyrolysis: The C content varies from 76.04wt% to 82.10wt% with a mean of 79.40wt% whilst H ranges between 4.79 to 5.16 wt% with a mean value of 5.03 wt%. Oxygen values range from 8.10wt% to 10.40wt% with a mean value of 8.88wt% whilst Nitrogen ranges between 1.76 to 2.29 wt% with a mean value of 2.06. The S content varies from 0.38wt% to 1.29wt% with a mean value of 0.68wt%. The samples are characterized by low sulphur contents (0.38 to 1.08) except a sample from BH120 with sulphur value of 1.29 wt%. The TOC/S ratio ranges from 8.1 to 52.8, indicating non-marine coal (Berner, 1984; Bechtel *et al.* 2007a, b; Adeosu, 2009). It can be inferred from these results that majority of the samples are of non-marine origin with few samples from BH120 with values ranging between 8.10wt% to 15.00wt% which suggest little marine incursion and/or organic matter deposited in lacustrine environment (Brown and Kenig, 2004; Adeosu, 2009). The TOC/N ratios range from 2.01-22.15 (Table 1). High TOC/N values (13.26-22.15) obtained in three of the samples reflect terrigenous organic matter input (Meyers, 1994; Bechtel *et al.,* 2007a). The low values of (2.01-8.94) recorded in some of the samples, indicating the presence of marine organic matter and/or lacustrine algae (Meyers, 1994; Meyers *et al.,* 2006; Bechtel *et al.*, 2007a). The plot of H/C against O/C ratios (Fig. 4) revealed all the samples plot within the type III evolution path, indicating that the samples are derived mainly from terrigenous organic matter (Van Krevelen *et al.*, 1961; Adeosu, 2009). The TOC values for the carbonaceous shale and coaly shale range between 4.56 wt% to 6.72wt% with a mean value of 5.70wt%. While the coal, TOC values vary between 13.74 wt% to 44.52wt% with a mean value of 27.40wt% (Table 2). The TOC values in all the samples exceeded the minimal 0.5 wt% required for a potential source rock (Tissot and Welte, 1984; Killops and Killops, 1993; Hunt, 1996; Adeosu, 2009). The GP values for the carbonaceous shale and coaly shale range between 3.2mg/g to 5.7mg/g with a mean value of 4.4mg/g. While the coal, GP values vary between 19.1mg/g to 90.8mg/g with a mean value of 42.4mg/g. The GP values are greater than 2 mg/g required for a potential source rock (Tissot and Welte, 1984; Killops and Killops 1993, 2005; Hunt, 1996; Peters *et al.* 2005). The values indicate moderate to good source rock.

Table 1: Elemental Analysis and Vitrinite Reflectance Data

Sample N0.	**Depth (m)**	**Lithology**	**TOC (%)**	**S (%)**	**C (%)**	**H (%)**	**O (%)**	**N (%)**	**HC**	**O/C**	**C/N**	**TOC/ N**	**TOC/ S**	**VR (%)**
BH218	222.50	Carb. Shale	4.56	0.40	76.55	5.16	10.40	2.27	0.81	0.10	33.72	2.10	11.50	0.94
BH407	412.50	Coaly Shale	6.72	0.45	nd	nd	nd	nd	nd	nd	nd	nd	15.00	nd
BH417	422.00	Coal	13.74	0.38	76.04	4.85	9.38	1.80	0.77	0.09	42.24	7.63	35.90	nd
BH131	136.60	Coal	32.58	1.08	79.81	5.10	8.43	2.29	0.77	0.08	34.85	14.23	31.20	1.02
BH148	148.00	Coal	30.38	0.90	nd	nd	nd	nd	nd	nd	nd	nd	33.90	nd
BH168	173.70	Coal	44.52	1.29	81.45	5.15	8.33	2.01	0.76	0.08	40.52	22.15	34.50	1.08
BH212	216.20	Coal	19.85	0.38	82.10	5.10	8.10	2.22	0.75	0.07	36.98	8.94	52.80	1.15
BH247	247.00	Carb. Shale	5.81	0.72	nd	nd	nd	nd	nd	nd	nd	nd	8.10	nd
BH286	289.00	Coal	23.34	0.51	80.42	4.79	80.42	1.76	0.71	0.08	45.69	13.26	45.40	1.15

nd – not determined; Carb. Shale = carbonaceous shale

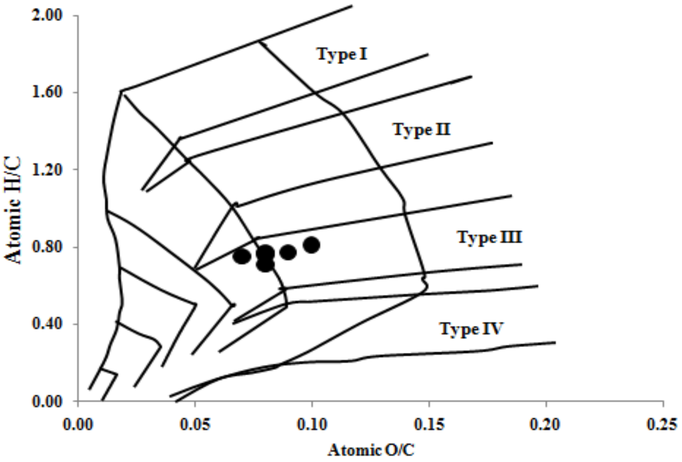

Fig 4: Plot of Atomic H/C against O/C of Coal Samples from Lafia - Obi (After Van Krevelen *et al.*, 1961).

Table 2: TOC and Rock-Eval Pyrolysis Data.

Sample N0.	**Depth (m)**	**Lithology**	**TOC (%)**	**Tmax (ºC)**	**S_1 (mg/g)**	**S_2 (mg/g)**	**S_3 (mg/g)**	**PI (S_1/S_1+S_2)**	**HI (mg/g TOC)**	**OI (mg/g TOC)**	**GP (S_1+S_2) (mg/g)**
BH218	222.50	Carb. Shale	4.56	446.00	0.91	4.82	1.10	0.16	105.00	24.00	5.70
BH407	412.50	Coaly Shale	6.72	447.00	0.89	3.55	0.64	0.20	52.00	9.00	4.40
BH417	422.00	Coal	13.74	453.00	1.92	17.76	2.08	0.10	129.00	15.00	19.70
BH131	136.60	Coal	32.58	451.00	12.88	77.92	2.36	0.14	239.00	7.00	90.80
BH148	148.00	Coal	30.38	469.00	3.58	25.16	2.48	0.12	82.00	8.00	28.70
BH168	173.70	Coal	44.52	459.00	10.28	57.84	3.42	0.15	129.00	7.00	68.10
BH212	216.20	Coal	19.85	455.00	4.32	23.48	1.44	0.16	118.00	7.00	27.80
BH247	247.00	Carb. Shale	5.81	454.00	0.82	2.40	0.88	0.25	41.00	15.00	3.20
BH286	289.00	Coal	23.34	455.00	2.34	16.76	2.86	0.12	72.00	12.00	19.10

S_1= hydrocarbon already present in the sample which are mainly stripped at temperatures about 300 ºC; S_2= hydrocarbons generated through thermal cracking of kerogen at temperatures in the range of 300-650 ºC; S_3= CO_2 that is generated from the kerogen at the same time the S_2 hydrocarbons are being generated; Tmax = Temperature of maximum generation of S_2 peak; Carb. Shale = carbonaceous shale

The HI values in Awgu samples range from 41-239 mg/gTOC (av. 107.3). These low HI values indicate type III kerogen, capable of generating gas only (Peters, 1986; Sachsenhofer *et al.*, 2000a). Plots of HI against OI, S2 vs. TOC and Tmax against HI for the samples are shown in Figs. 5, 6 and 7 respectively. The samples fall within type III evolution path on the plots of HI vs OI (Fig. 5) and S2 vs. TOC (Fig. 6), indicating gas prone (Killops and Killops 1993, 2005; Adeosu, 2009). The potential of the samples to generate mainly gas was further confirmed on the plot of Tmax vs HI where all the samples were plotted within the gas prone zone (Fig. 7).

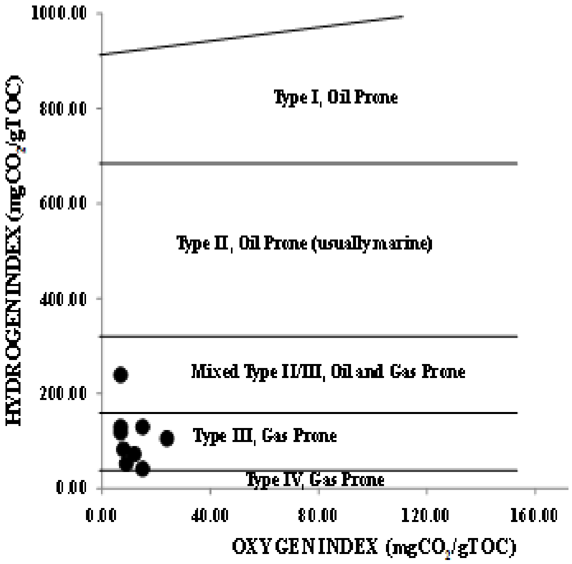

Fig 5: Plots of HI vs OI of Coal Samples from Lafia - Obi (After Van Krevelen *et al.*, 1961)

The Tmax and PI values in Lafia - Obi samples ranges from 446 to 469 ºC (av. 454) and 0.10 to 0.29 (av. 0.15) respectively. These values indicate organic matter within the main phase of oil generation-late oil window. The Vitrinite reflectance (VR) values of Awgu samples range from 0.94-1.14 %R0 (av. 1.07). These values show that the samples are at the peak of oil generation (Killops and Killops, 2005; Peters *et al.*, 2005; Adeosu, 2009). The high vitrinite reflectance recorded for Awgu Formation samples at the shallow depth is probably due to the activity of erosion, which has exposed the coal seam to the surface. Vitrinite reflectance values were estimated from the plots of HI vs. Tmax for the Awgu samples (Fig. 8). Majority of the samples have VR of about 1.0 %R0. These values agreed with the vitrinite reflectance data obtained from the petrographic analysis. The samples also fall within the oil/condensate field (Fig. 9).

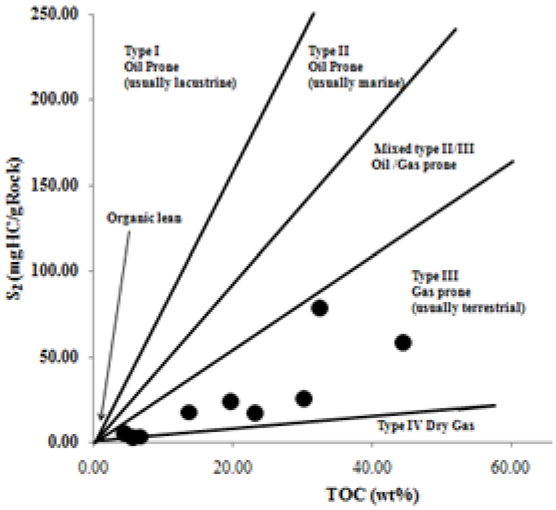

Fig 6: Plots of S2 vs TOC of Coal Samples from Lafia - Obi (After Langford and Blanc-Valleron, 1990)

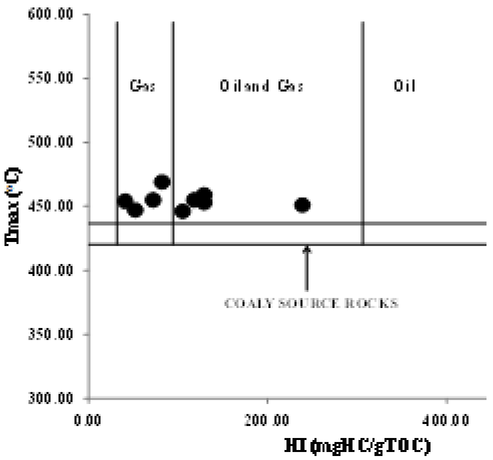

Fig 7: Plot of Tmax vs HI. Of Coal Samples from Lafia - Obi (After modified by Akande *et al.*, 2007).

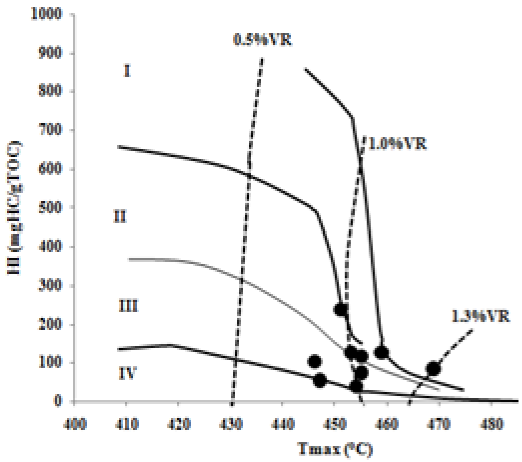

Fig 8: Plots of HI vs Tmax of Coal Samples from Lafia - Obi.

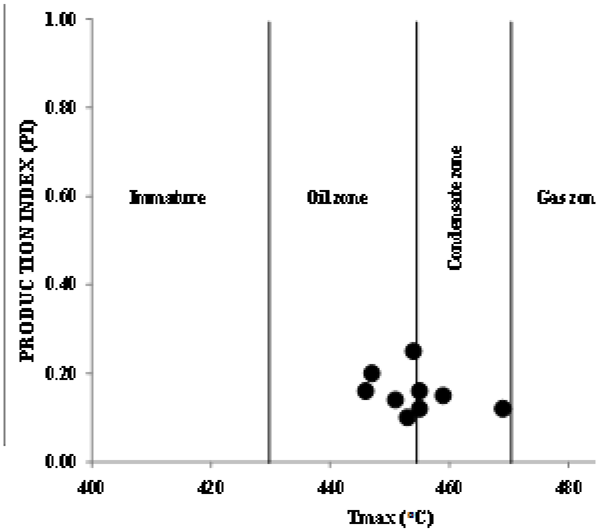

Fig 9: Plots of PI vs Tmax of Coal Samples from Lafia - Obi.

Petrographic and liquefaction potential: The maceral composition in coal is influenced by several parameters such as source material, environmental of deposition (pH, water table), and maturation of organic matter under aerobic and anaerobic bacteria activity (Moore, 2012). The petrographic study adduced that vitrinite maceral (textinite and ulminite) is mostly observed in all samples (Panwar *et al.*, 2019). The vitrinite maceral is found to be 59.10–65.34 wt%. The liptinite content of samples varies between 9.40 and11.24 wt%. Similarly, the inertinite maceral is found to be 24.59–29.72 wt% as on dry ash free basis. The liquefaction potential is highly influenced by nature and amount of maceral present in coal (Chen and Ma, 2002; Panwar *et al.*, 2019). Vitrinite, liptinite, and inertinite contents are mostly used for assessment of liquefaction potential (Chen *et al.*, 2007; Panwar *et al.*, 2019). Liptinite is primarily composed of chitin tissue (containing high aliphatic compound) of higher plants and is capable to generate oil potential. However, liptinite and vitrinite maceral has higher oil generation potential than inertinite (Panwar *et al.*, 2019. Further, the literature review for high volatile coal with reactive macerals implies that more than 70 wt% are suitable for liquefaction (Davis *et al.*, 1976) but in the existing coal samples from Lafia-Obi have sufficient concentration of reactive macerals (vitrinite + liptinite) and it varies from 70.28% to 75.41 wt% which shows the credibility to produce liquid hydrocarbon (Panwar *et al.*, 2019).

Table 3: Macerals analysis, conversion and oil yield of coal samples.

Sample N0.	Depth (m)	Lithology	Vitinite (%)	Liptinite (%)	Inertinite (%)	Conversion (%)	Oil Yield (%)	Rm (%)	VR (%)
BH218	222.50	Carb Shale	60.95	11.04	28.02	91.00	60.64	71.98	0.94
BH407	412.50	Coaly Shale	59.10	11.19	29.72	90.66	60.26	70.28	nd
BH417	422.00	Coal	61.98	9.45	28.57	90.89	60.51	71.43	nd
BH131	136.60	Coal	61.05	10.59	28.36	90.93	60.56	71.64	1.02
BH148	148.00	Coal	61.50	9.71	28.79	90.84	60.47	71.21	nd
BH168	173.70	Coal	62.98	11.06	25.96	91.41	61.09	74.04	1.08
BH212	216.20	Coal	64.46	9.64	25.90	91.42	61.10	74.10	1.15
BH247	247.00	Carb Shale	61.24	9.40	29.36	90.73	60.34	70.64	nd
BH286	289.00	Coal	59.65	10.98	29.36	90.73	60.34	70.64	1.15

VR, vitrinite reflectance (%); V, vitrinite (%); L, liptinite (%); I, inertinite (%); RM, reactive macerals

The empirical equations formed by Guyot (1978) and Jin and Shi (1997) are used to estimate the conversion of coal into oil and oil-yield (Table 3):

$$RF = 1000Rmax = RM \tag{1}$$

$$Conversion\ (\%) = 0.2RM + 76{:}6 \tag{2}$$

$$Oil\text{ - }yield\ (\%) = 0.22RM + 44{:}8 \tag{3}$$

where Rmax is the maximum reflectance of vitrinite and RM is reactive macerals. While the statistical study shows that vitrinite (R^2 = 0.77) and oil-yield (R^2 = 0.99) formed strong positive correlation with conversion (%), as shown in Figs. 10 and 11. However, inertinite ($R^2 = -1.00$) stabilized negative correlation with conversion (%), as shown in Fig. 12.

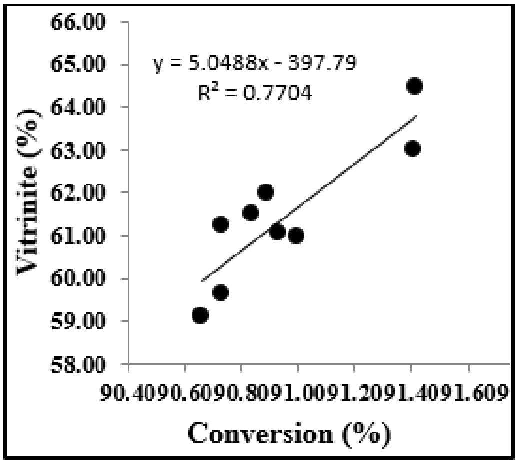

Fig 10: Correlation between conversion and vitrinite maceral for studied samples.

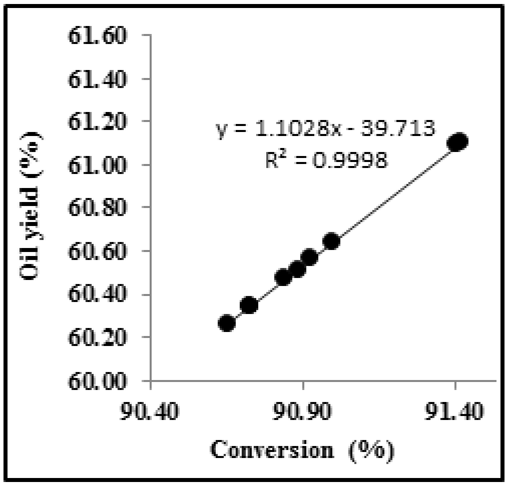

Fig 11: Correlation between conversion and oil yield for studied samples.

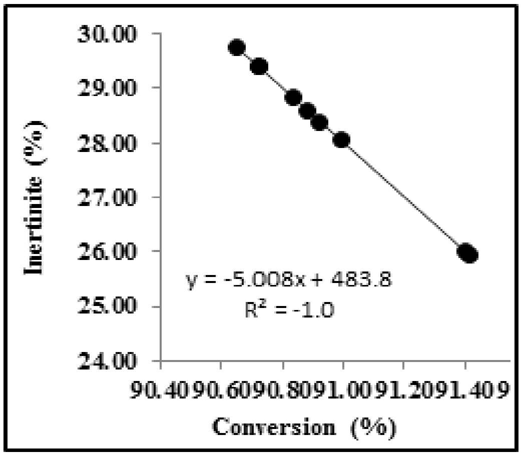

Fig 12: Correlation between conversion and inertinite maceral for studied samples

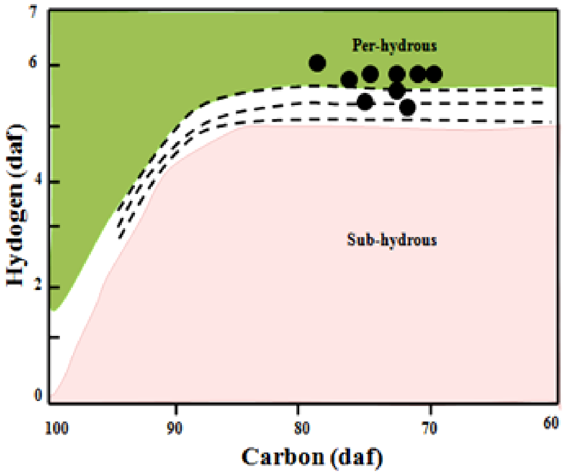

Fig 13: Carbon and hydrogen content of investigated samples in the Seyler's chart (after Cornelius, 1978).

Coal quality analysis: The results of the proximate and ultimate analyses are summarized in Table 4. It has been observed from the analysis that samples have moderate moisture content ranging from 3.13 to 6.67 wt%. Samples content higher value of volatile matter which varies from 32.66 to 36.19 wt%. Similarly, ash content and fixed carbon content vary from 10.59 to 22.16 wt% and 40.44 to 50.67 wt% (dry basis). The samples have higher carbon and hydrogen content ranging from 65.62 to 79.80 wt% and 3.67 to 6.97 wt% on dry ash free basis, respectively. The hydrogen and carbon composition on dry ash free basis was evaluated through the Seyler's diagram (Fig. 13) and it can be concluded that most of the samples are per-hydrous in nature; however, some samples also come in the bright band of Seyler's chart (Cornelius, 1978; Panwar *et al.*, 2019).

Table 4: Proximate analysis result of coal samples.

Sample N0.	**Depth (m)**	**Lithology**	**M (%)**	**A (%)**	**VM (%)**	**FC (%)**
BH218	222.50	Carb Shale	4.31	21.05	34.20	40.44
BH407	412.50	Coaly Shale	4.10	21.08	33.47	41.35
BH417	422.00	Coal	6.67	15.48	34.42	43.43
BH131	136.60	Coal	4.32	15.09	36.19	44.40
BH148	148.00	Coal	4.31	14.91	35.43	45.35
BH168	173.70	Coal	4.38	14.33	35.58	45.71
BH212	216.20	Coal	3.47	13.97	35.76	46.80
BH247	247.00	Carb Shale	3.13	22.16	32.66	45.18
BH286	289.00	Coal	3.76	16.13	34.67	45.44

M, moisture; A, ash; VM, volatile matter (%) and FC, fixed carbon (%); Carb = carbonaceous

Biomarker Geochemistry: The source, depositional environment and thermal maturity status of the organic matter contained in the samples were determined based on the distributions and abundance of aliphatic biomarkers in the coal extracts. The *m/z* 85 mass chromatograms showing the distribution of *n*-alkane and isoprenoids in the samples are shown in Figs.14, 15 and 16. Geochemical parameters calculated from the alkane distribution are given in Table 5. The *n*-alkane distribution in Lafia – Obi sample ranges from C_{14}-C_{35} maximizing at n-C_{16} or n-C_{18} (Fig.14). This pattern of distribution indicates organic matter derived from both marine and terrestrial (Peters *et al.*, 2005; Adeosu, 2009). The samples plotted within the terrestrial organic matter zone on the plots of Pr/nC_{17} vs. Ph/nC_{18} in Fig. 15. Pr/Ph ratio calculated for the Awgu samples range from 3.04 to 11.07 (Table 5).

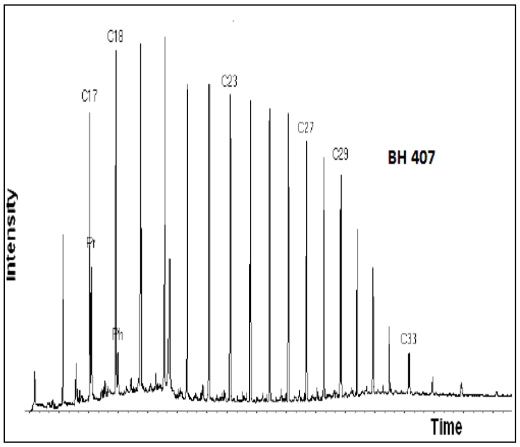

Fig 13: *m/z* 85 Mass chromatograms of aliphatic fractions of Lafia - Obi samples showing the distribution of *n*-Alkanes.

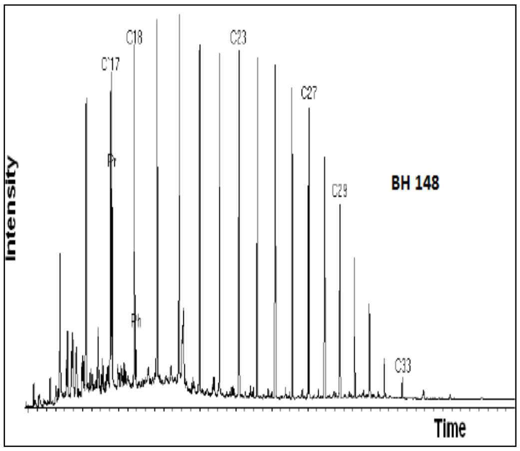

Fig 14: (contd.): *m/z* 85 Mass chromatograms of aliphatic fractions of Lafia - Obi samples (BH 120) showing the distribution of *n*-Alkanes.

Table 5: *n*-Alkanes and Isoprenoids Parameters

Sample N0.	**Depth (m)**	**Lithology**	**Pr/Ph**	**Pr/n C_{17}**	**Ph/n C_{18}**	**CPI**	**CPI (1)**	**OEP (1)**	**OEP (2)**	**C_{range}**	**C_{max}**
BH218	222.50	Carb Shale	6.14	1.81	0.23	1.12	1.08	1.03	1.06	C_{13-36}	C_{23}
BH407	412.50	Coaly Shale	3.16	0.50	0.13	1.02	1.01	0.98	1.00	C_{14-37}	C_{18},C_{20}
BH417	422.00	Coal	5.49	0.30	0.03	1.07	1.02	0.99	1.00	C_{16-32}	C_{18}
BH131	136.60	Coal	3.52	0.24	0.06	1.05	1.02	0.99	1.02	C_{13-35}	C_{19}
BH148	148.00	Coal	5.25	0.68	0.11	1.09	1.04	0.99	1.06	C_{13-35}	C_{20}
BH168	173.70	Coal	6.52	0.54	0.08	1.10	1.05	0.99	1.05	C_{13-35}	C_{16}
BH212	216.20	Coal	4.60	0.28	0.06	1.07	1.04	1.01	1.03	C_{13-35}	C_{16},C_{18},C_{20}
BH247	247.00	Carb. Shale	11.07	1.69	0.09	1.04	0.99	0.98	0.99	C_{15-33}	C_{27}
BH286	289.00	Coal	3.04	0.34	0.08	1.06	1.03	0.99	1.03	C_{13}-C_{35}	C_{18},C_{20},C_{21},C_{22}

Pr- Pristane, Ph- Phytane; $CPI = ½[(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}/C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33}/C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]$, $CPI\ (1) = 2(C_{23} + C_{25} + C_{27} + C_{29})/[C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30}]$; $OEP\ (1) = C_{21} + 6C_{23} + C_{25}/\ 4(C_{22} + C_{24})$, $OEP\ (2) = C_{25} + 6C_{27} + C_{29}/\ 4(C_{26} + C_{28})$; *Carb = carbonaceous*

All the samples have Pr/Ph ratio greater than 3.0, typical of land plant detritus deposited under aerobic (oxic) condition (Peters *et al.,* 2005; Adeosu, 2009). The Carbon Preference Index (CPI) and Odd-Over-Even Predominance (OEP) values range from 0.98 to 1.12 and 0.98 to 1.06 respectively. These values reflect high maturity status of the samples (Peters *et al.,* 2005). Also, the plots of CPI against OEP show that the samples are thermally mature (Fig. 16). Lafia - Obi samples have *n*-fatty acids ranging from C_{14} to C_{30}, maximizing at nC_{16} or nC_{18} (Fig. 17). The short chain/long chain saturated fatty acid (ATRFA) ratios for the samples which range from 0.97-1.00, indicate both terrestrial and marine organic matter derived material (Wilkes *et al.,* 1999). Abundance of short chain saturated *n*-fatty acids ($<nC_{20}$) in the samples reflects mixed input of microorganisms and algae (Duan *et al.,* 1997; Killops and Killops, 2005). The nC_{16} and nC_{18} are prominent in all the samples. These compounds are ubiquitous and can also reflect higher plant input e.g. seed and leaf oils of gymnosperms (Volkman *et al.,* 1998; Volkman, 1998). The appreciable amount of long chain saturated *n*-fatty acids ($>C_{20}$) in the samples can be attributed to curticular waxes of higher plants (Cranwell, 1974; Adeosu, 2009).

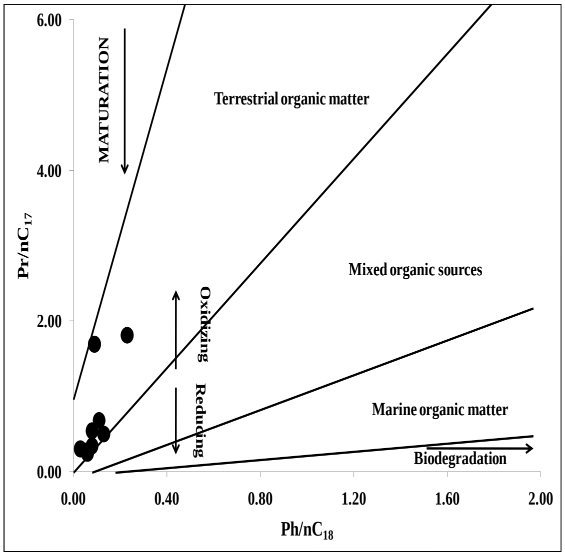

Fig 15: Plots of Pr/nC_{17} against Ph/nC_{18} of Lafia - Obi samples.

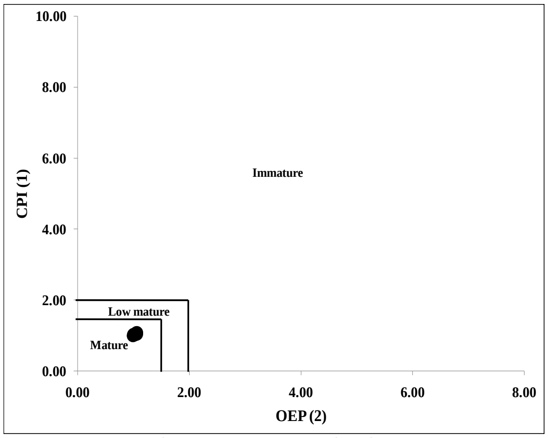

Fig 16: Plots of CPI against OEP of Lafia - Obi samples.

The carbon preference index (CPIFA) of the long chain *n*-fatty acids (C_{24}-C_{30}) range between 1.98 and 3.29 (Table 6), indicating a strong even over odd predominance. These values inferred high maturity status for the samples (Wilkes *et al.*, 1999; Adeosu, 2009). The distribution of straight chain *n*-alkan-2-ones range from nC_{14}-nC_{33} a maximizing at nC_{17} (Fig. 18). Similar distribution has previously been observed in *stalagmites* (Xie *et al.*, 2003; Bai *et al.*, 2006). However, some of the samples maximize at nC_{23} or nC_{25} (Fig. 19), an indication of contribution from higher plants, microalgae and phytoplankton organic matter inputs (Hernandez *et al.*, 2001; Gonzalez-Vila *et al.*, 2003). A series of tricyclic terpanes ranging from C19 to C_{29} are observed in Awgu samples (Fig. 19). Higher percentages of C_{19}-C_{21} compared to C_{23} tricyclic terpanes indicate organic matter derived from terrestrial origin (Ozcelik and Altunsoy, 2005; Adeosu, 2009). The C_{24} tetracyclic terpane is present in appreciable amounts in all the samples. The C_{24}tetra/C_{26}tri (R+S) ratios range between 0.96 and 3.45 (Table 7), probably reflecting terrigenous organic matter input (Philp and Gilbert, 1986). Various ratios of tricyclic terpanes have been used to distinguish marine carbonate, lacustrine, paralic, coal/resin and evaporitic source depositional environments (De Grande *et al.*, 1993; Tuo *et al.*, 1999; Yangming *et al.*, 2005; Peters *et al.*, 2005; Adeosu, 2009). C_{22}/C_{21} tricyclic terpane ratio in the samples range from 0.16 to 0.42, suggesting organic matter deposited in lacustrine-fluvial/deltaic depositional environment (Peters *et al.*, 2005). C_{24}tetra/C_{30} hopane ratio has also been used to assess depositional environment of source rock (Peters *et al.*, 2005; Adeosu, 2009). C_{24}tetra/C30hopane ratios in the sample range between 0.11 and 0.43. These values also indicate organic matter deposited in lacustrine-fluvial/deltaic depositional environment (Peters *et al.*, 2005; Adeosu, 2009).

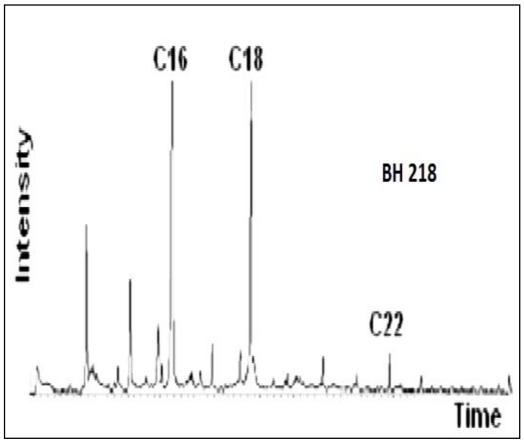

Fig 17: *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Lafia - Obi samples (Numbers refer to carbon chain lengths of *n*-fatty acids).

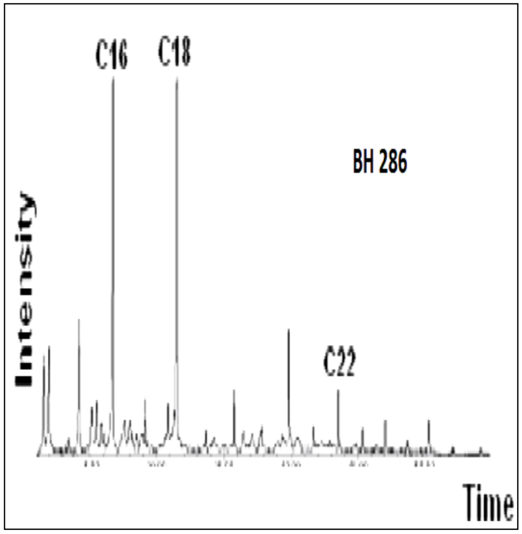

Fig 17: (contd.): *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Lafia - Obi samples (Numbers refer to carbon chain lengths of *n*-fatty acids).

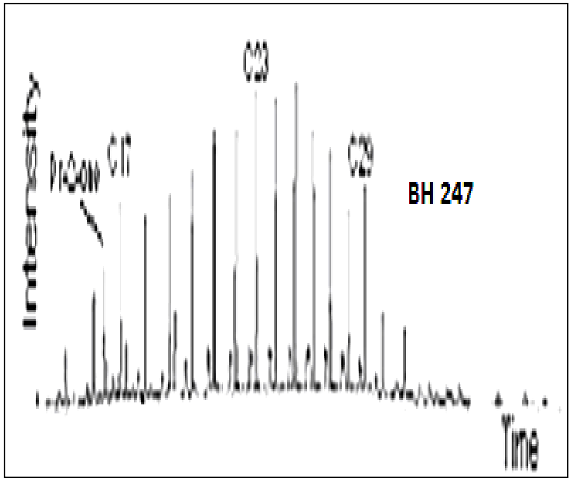

Fig 18: *m/z* 58 mass chromatograms showing the distributions of alkan-2-ones in Lafia - Obi samples (Numbers refer to carbon chain lengths of alkan-2-ones)

Table 6: Parameters calculated from *n*-Fatty acids and alkanones composition of Lafia – Obi coal.

Sample N0.	Depth (m)	Lithology	ATR_{FA}	CPI_{LFA}	Pr-2-one/C_{17}	CPI (alkanone)
BH218	222.50	Carb Shale	0.99	nd	0.58	0.84
BH407	412.50	Coaly Shale	0.99	nd	0.80	0.85
BH417	422.00	Coal	1.00	nd	1.09	1.14
BH131	136.60	Coal	0.99	nd	0.51	0.89
BH148	148.00	Coal	0.99	2.46	0.60	0.76
BH168	173.70	Coal	0.99	1.98	0.39	1.01
BH212	216.20	Coal	0.99	3.29	1.59	0.76
BH247	247.00	Carb Shale	0.97	3.20	0.86	0.93
BH286	289.00	Coal	0.98	nd	0.82	1.20

ATR_{FA} = Short chain/long chain saturated fatty acid; CPI_{LFA}= Carbon Preference Index (Long chain fatty acids)
CPI (alkanones) = Carbon Preference Index (alkan-2-ones); $ATR_{FA} = C_{14} + C_{16} + C_{18} / C_{14} + C_{16} + C_{18} + C_{26} + C_{28} + C_{30}$;
$CPI_{LFA}=½\{(C_{24}+C_{26}+C_{28}+C_{30}/C_{21}+C_{23}+C_{25}+C_{27})+(C_{24}+C_{26}+C_{28}+C_{30}/C_{23}+C_{25}+C_{27}+C_{29})\}$
CPI (alkanones)$=1/2\{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+C_{32}) + (C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/ C_{24}+C_{26}+C_{28}+C_{30}+C_{32}+_{34}\}\}$ and nd = Not determined. Carb = carbonaceous

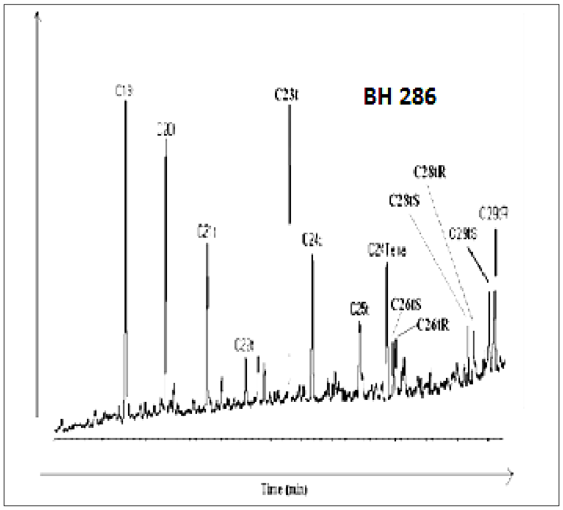

Fig 19: *m/z* 191 showing the distribution of tricyclic and tetracyclic terpane in Lafia - Obi samples.

(Fig. 20), indicating significant contribution of prokaryotic organisms (i.e. bacteria, cyanobacteria and blue algae) to the source organic matter. The sterane/hopane ratio is often used as a measure of relative inputs of eukaryotic versus prokaryotic debris (Peters and Moldowan, 1993; Adeosu, 2009). The sterane/hopane ratio values range from 0.04-0.51(Table 8). The ratio values (<0.6) according to (Tissot and Welte, 1984; Peters and Moldowan, 1993; Sachsenhofer *et al.*, 2000a; Norgate *et al.*, 1999) indicative of the incorporation of high level of bacterial inputs commonly associated with terrigenous organic matter in coals (non-marine organic matter).

The appreciable quantity of homohopanes (C_{31}-C_{35}) in all the samples, suggest that bacteriohopanetetrol and other polyfunctional C_{35} hopanoids; bacteriohopanepolyols, aminopolyols etc. (Wang *et al.*, 1996), common in prokaryotic micro-organisms (Ourrisson *et al.*, 1979; Rohmer, 1987; Adeosu, 2009) were significant contributors to the biomass. C_{29} and $C_{30}αβ$-hopane occur in appreciable amount in all the Lafia - Obi coaly shale samples. The occurrence of 18α(H)-28-noroleanane, 18α(H)- and 18β(H)-oleanane in Lafia - Obi coaly shale samples is notable. Oleananes are regarded as reliable marker for angiosperm; being significant constituents of wood, roots and bark in Cretaceous or younger effective source rocks in deltaic petroleum system (Moldowan *et al.*, 1994; Nytoft *et al.*, 2002; Peters *et al.*, 2005; Ozcelik and Altunsoy, 2005; Otto *et al.*, 2005; Bechtel *et al.*, 2007b). The C_{35}/C_{30} hopane ratio values range from 0.03 to 0.26, which reflects organic matter deposited in lacustrine-fluvial/deltaic environments (Peters *et al.*, 2005). The homohopane index (C_{35}/C_{31} - C_{35}) and homohopane ratio ($C_{35}αβS/C_{34}αβS$) range from 0.02 to 0.12 and 0.15 to 0.92 respectively (Table 8). The low homohopane index of the samples indicates oxic condition during organic matter deposition (Peters and Moldowan, 1991; Killops and Killops, 2005; Peters *et al.*, 2005; Yangming *et al.*, 2005; Adeosu, 2009).

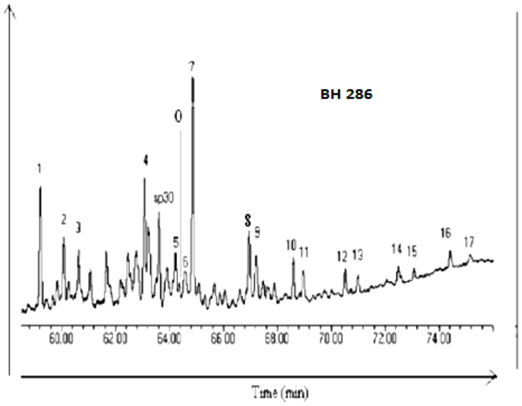

Fig 20: *m/z* 191 Mass chromatogram showing the distribution of hopanes in Lafia - Obi samples.

Table 7: Tri- and tetracyclic terpanes source and depositional environment parameters.

Sample N0.	Depth (m)	Lithology	C_{24}tetra/ C_{30}hopane	C_{24}tetra/ C_{26}(R+S)tri	C_{22}/C_{21} triterpane	%C_{19}-C_{21} triterpane	%C_{23} triterpane
BH218	222.50	Carb Shale	0.10	2.50	0.24	83.70	16.30
BH407	412.50	Coaly Shale	0.18	2.47	0.24	77.30	22.70
BH417	422.00	Coal	0.43	2.84	0.23	82.50	17.50
BH131	136.60	Coal	0.18	2.55	0.17	82.40	17.60
BH148	148.00	Coal	0.24	2.14	0.26	86.20	13.80
BH168	173.70	Coal	0.24	3.45	0.17	84.70	15.30
BH212	216.20	Coal	0.21	2.29	0.42	93.60	6.40
BH247	247.00	Carb Shale	0.32	0.96	0.16	82.10	17.90
BH286	289.00	Coal	0.18	1.33	0.27	72.70	27.30

nd – Not determined; C_{24}tetra/C_{30}hopane = C_{24}tetracyclic terpane/C_{30} hopane; C_{24}tetra/C_{26}(R+S) tri = C_{24}tetracyclic terpane/C_{26}(R+S) tricyclic terpane; Carb = carbonaceous

Table 8: Source and depositional environment parameters computed from the hopane and sterane distributions in the coals.

Sample N0.	Depth (m)	Lithology	C_{27} Ster. (%)	C_{28} Ster. (%)	C_{29} Ster. (%)	C_{27} Diast. (%)	%C_{28} Diast. (%)	%C_{29} Diast. (%)	C_{27}/ C_{29} Ster.	%Diat. / Ster.	Ster./ Hop.	C_{35}/ C_{30} Hop.	C_{35}/ C_{34} αβS Hop.	Homo Hop./ index
BH218	222.50	Carb. Shale	25.43	20.04	54.53	27.46	54.50	18.14	0.47	55.74	0.11	0.06	0.43	0.06
BH407	412.50	Coaly Shale	18.13	28.27	53.60	21.58	32.14	46.28	0.34	68.03	0.11	0.06	0.25	0.04
BH417	422.00	Coal	24.04	29.02	46.94	30.53	31.25	38.22	0.51	67.35	0.51	0.07	0.15	0.05
BH131	136.60	Coal	17.47	29.66	52.87	15.05	33.05	51.90	0.33	55.13	0.27	0.03	0.34	0.04
BH148	148.00	Coal	23.19	23.28	53.53	10.79	32.29	56.93	0.43	73.80	0.32	0.03	0.37	0.04
BH168	173.70	Coal	16.14	26.10	57.77	19.42	42.67	37.91	0.28	46.81	0.43	0.03	0.35	0.05
BH212	216.20	Coal	18.71	36.88	44.41	27.97	45.89	26.14	0.42	70.97	0.04	0.06	0.33	0.06
BH247	247.00	Carb Shale	31.89	31.20	36.91	25.86	42.26	31.89	0.86	62.81	0.11	0.26	0.58	0.10
BH286	289.00	Coal	17.58	32.90	49.52	24.41	29.04	46.55	0.36	67.92	0.13	0.11	0.89	0.10

Sterane/Hopane = C_{27}+C_{28}+C_{29} steranes/[(C_{29}+C_{30}) αβhopane + (C_{31}+C_{32}+C_{33}) αβ(R+S) homohopane]; C_{35}/C_{30} = C_{35}αβ(R+S) homohopane/ C_{30}αβ hopane + C_{30}βα moretane; Homohopane ratio = C_{35}/C_{34} αβS = C_{35}αβS/C_{34}αβS homohopane; Homohopane index = C_{35}/ C_{31}+C_{32}+C_{33}+C_{34}+C_{35}) αβ(R+S) homohopane; carb = carbpnaceous

Table 9: Maturity parameters computed from the hopane and sterane distributions in the coals.

Sample N0.	Depth (m)	Lithology	Mor./ Hop.	Hop./Hop . + Mor.	Ts/Ts +Tm	22S/22S+22 RC_{32} HH	20S/20S + 20RC_{29} Sterane	Bβ/ββ + αα C_{29} Sterane
BH218	222.50	Carb Shale	0.12	0.89	0.61	0.60	0.58	0.47
BH407	412.50	Coaly Shale	0.08	0.92	0.46	0.62	0.43	0.55
BH417	422.00	Coal	0.11	0.90	0.64	0.61	0.44	0.51
BH131	136.60	Coal	0.10	0.91	0.46	0.61	0.44	0.48
BH148	148.00	Coal	0.09	0.92	0.53	0.60	0.48	0.49
BH168	173.70	Coal	0.09	0.92	0.34	0.58	0.45	0.54
BH212	216.20	Coal	0.06	0.94	0.59	0.58	0.44	0.42
BH247	247.00	Carb Shale	0.14	0.88	0.49	0.53	0.45	0.48
BH286	289.00	Coal	0.08	0.93	0.66	0.61	0.44	0.51

Mor/Hop = Moretane/Hopane (C_{30}); Hop/Hop + Mor = Hopane/Hopane + Moretane (C_{30}); C_{32}HH = C_{32}homohopane; Carb.=Carbonaceous

Hopanes with αβ epimers are more prominent in all the samples while no ββ-epimer is detected. Homohopanes ranging from C_{31}-C_{35} showed notable predominance of the 22S over the 22R epimer (Fig. 20). These observations reflect high maturity status of the samples (Miranda *et al.*, 1999; Peters *et al.*, 2005; Tuo *et al.*, 2007, Adeosu, 2009). The Moretane/Hopane, Hopane/Hopane + Moretane, Ts/Ts + Tm, 22S/22S + 22RC32 homohopane ratios range from 0.06 to 0.14; 0.88 to 0.94; 0.34 to 0.66; and 0.53 to 0.62 respectively. These values indicate samples are within the late oil window/gas phase (Seifert and Moldowan, 1980; Mackenzie, 1984; Seifert and Moldowan, 1986; Peters and Moldowan, 1993; Kagya, 1996; Tuo *et al.*, 1999; Peters *et al.*, 2005; Adeosu, 2009).

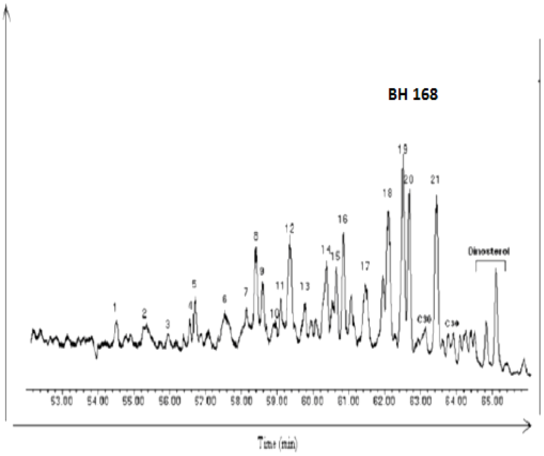

Fig 21: *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in Lafia - Obi samples.

The occurrence of C_{27} to C_{29} steranes and diasteranes were detected in Lafia - Obi coaly samples (Fig. 21). The sterane and diasterane distributions for all the samples occur in the order of $C_{29}>C_{28}>C_{27}$ (Table 6). The predominance of C_{29} sterane over C_{27} sterane reflects a greater input of terrestrial relative to marine organic matter (Huang and Meinschein, 1979; Volkman, 1988; Kagya, 1996; Sari and Bahtiyar, 1999; Otto *et al.*, 2005; Peters *et al.*, 2005). The ternary plots of sterane distribution in Lafia - Obi samples (Fig. 22) indicate organic matter derived from terrestrial materials deposited in lacustrine – fluvial/deltaic settings (Huang and Meinschein, 1979; Killops and Killops, 1993, 2005; Peters *et al.*, 2005). The diasterane ternary plots (Fig. 23) also show that Lafia - Obi samples are from terrestrial organic matter. This observation is supported by C_{27}/C_{29} ratios (Table 9), which range from 0.28 to 0.56 (Peters *et al.*, 2005). The dominance of dinosterol over C_{30} steranes in these samples reflects typical fresh water lacustrine source rocks (Köhler and Clausing, 2000; Peters *et al.*, 2005; Adeosu, 2009). The 20S/20S+20R and αββ/αββ+ααα C_{29} ratios range from 0.43 to 0.58 and 0.42 to 0.55 respectively. These values show that the samples are within the oil generative window (Peters *et al.*, 2005; Adeosu, 2009). Plots of 22S/22S+22R C_{32} hopanes against C_{29}αββ/αββ+ααα steranes show that Awgu samples are thermally mature (Fig. 24).

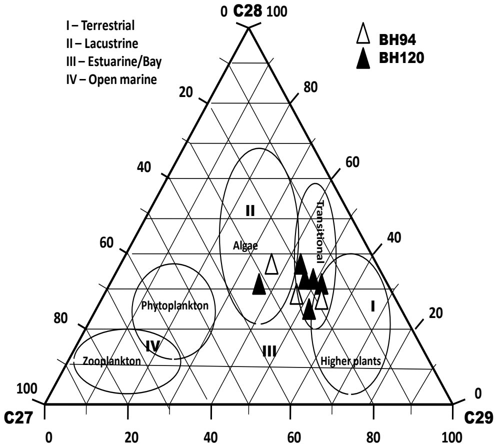

Fig 22: Ternary plots of C_{27}, C_{28} and C_{29} steranes distributions in Lafia - Obi coal (After Huang and Meinschein, 1979).

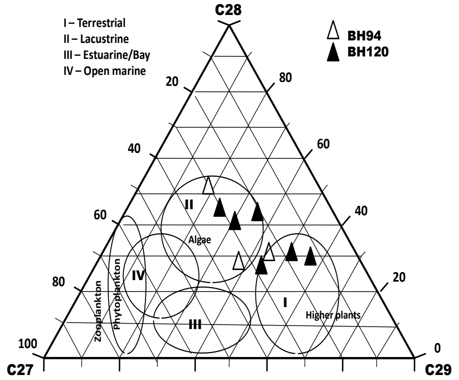

Fig 23: Ternary plots of C_{27}, C_{28} and C_{29} diasteranes distributions in Lafia - Obi coal (After Huang and Meinschein, 1979).

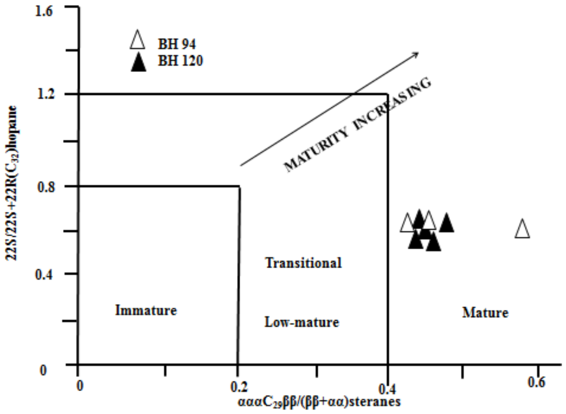

Fig 24: Plots of 22S/22S+22R C32 hopanes against C_{29}αββ/αββ+ααα steranes (After Inaba *et al.*, 2001).

Conclusion: The low sulphur contents indicate coal derived from non-marine organic matter. Various plots from the Rock-Eval pyrolysis data showed that, Lafia-Obi samples are mainly type III which has potential to generate gas. The distributions of *n*-alkanes and *n*-alkan-2-ones showed that Lafia-Obi samples were formed from organic matter derived from both terrestrial and marine organic matter. The Pr/Ph ratios and the abundance of C_{29} steranes and diasteranes of samples from Lafia-Obi samples reflect organic matter deposition under oxic conditions in freshwater-lacustrine depositional environment.

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