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Geochemistry and Mineralogy of Maastrichtian Coals from the Anambra and Gongola Basins of Nigeria: Implications for Coal Quality, Resource Potential, and Agglomeration Characteristics

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ABSTRACT

Anambra and Gongola basins are part of the sedimentary inland basins in Nigeria characterized by fossil fuels and in response to its present energy problem, Nigeria has shifted its power generating focus to coal. The studied coals were obtained from two localities, namely Ankpa and Maiganga in Kogi and Gombe States, respectively. The coals were investigated to determine its quality in terms of use and resource potential. The coals were analyzed by proximate, ultimate, elemental, mineralogy and scanning electron microscopy-energy dispersive spectrometry analyses. The objectives of the study are to determine the coals cokability, rank, paleoenvironments, hydrocarbon potential, and slagging tendency. The average values of moisture content, ash, volatile matter, and fixed carbon are 5.54%, 16.42%, 48.45%, and 30.71%, respectively, for Ankpa coals, while Maiganga recorded 10.68%, 8.60%, 44.33%, and 36.41%, indicating high volatile sub-bituminous non-coking coals that are optimum for combustion and electric power generation. The Van Krevelen plot based on the H/C vs. O/C showed Type IV kerogen. The XRD results, correlation plots, and Detrital Authigenic Index (DAI) values of 7.49 and 13.49 in Ankpa and Maiganga coals, respectively, indicated that Ankpa coals are enriched in authigenic minerals like quartz, pyrite, and calcite, while kaolinite and quartz were probable detrital minerals in the Maiganga coals. The agglomeration of the coals deduced by Base/Acid (B/A), Silicon ratio (G), Silica/Alumina (S/A), Iron/Calcium (I/C), Carbon/Hydrogen (C/H), and Fixed Carbon/Volatile matter (FC/V) showed weak–medium-strong for the Ankpa coals and strong for Maiganga coals.

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Introduction

The coal industry has a significant position within the global energy sector due to its provision of ample and extensively dispersed fossil fuel resources for electricity production (Li et al., 2015). The basins of Anambra, Sokoto, Bida, and the Benue Trough in Nigeria have coal reserves (Fig. 1). For a variety of commercial and technological purposes, different coal properties are frequently examined. The physical properties of coal include density, grindability, abrasiveness, and hardness. The chemical properties consist of volatile matter, moisture content, ash, mineral matter, and fixed carbon. Other properties include thermal and plastic characteristics (free swelling index). The properties of coking and slagging are influenced by the inorganic and organic constituents of coal (Dai et al., 2013; Meng et al., 2017).

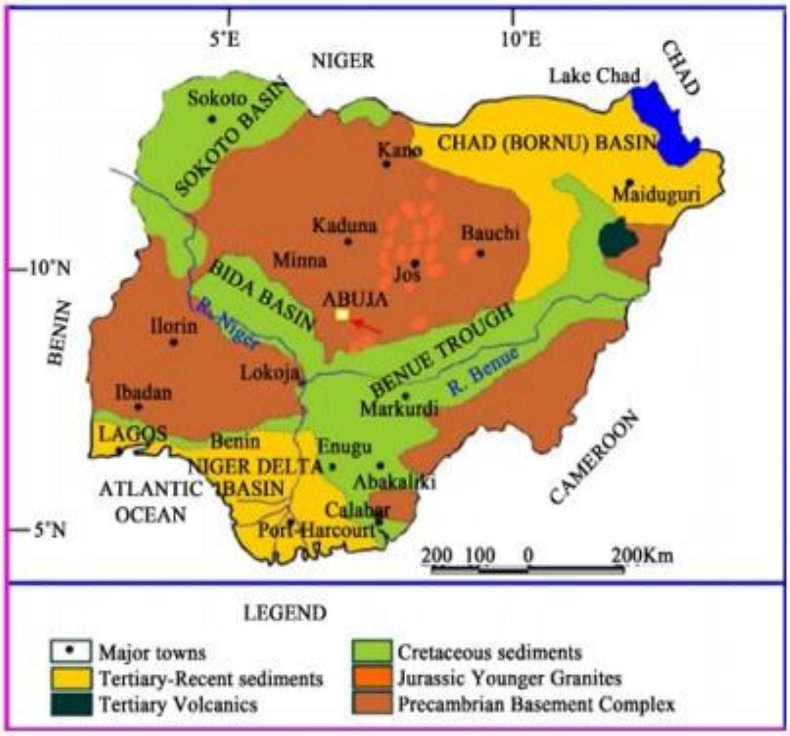

Fig. 1. Nigerian geological map (adapted from Obaje, 2009) showing the NE-SW trending Gongola Basin of Benue Trough and the Anambra Basin

Note: SBT- (Southern section of the Benue Trough), MBT- (Middle section of the Benue Trough), and NBT- (Northern section of the Benue Trough).

Nigeria has adopted electricity production from coal as a key energy source in addition to traditional hydro and thermal sources due to the country's present energy crisis (Ezeme, 2022). The Campanian-Maastrichtian Mamu Formation and the Gombe Formation, which are located in the Anambra and Gongola basins, respectively, include coal reserves in areas like Ankpa, Amansiodo, Ezinmo, Owukpa, Odagbo, Okaba, Inyi, Ogboyaga, and Maiganga. Recently, the Ankpa and Maiganga coal mines in the Ankpa, Kogi, and Gombe states were identified (Jauro et al., 2007; Obaje, 2009; Nyakuma, 2019; Fatoye et al., 2021; Jimoh and Ojo, 2021). However, little to no information has been supplied on the coals' quality, propensity to agglomerate, and potential uses. The objectives of this research are to assess the rank, cokability, power production potential, combustion rate, and slagging potential of coals with the intention of determining their probable suitability for use and resource potential. The

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coordinates of the samples from Ankpa fall within latitudes N 7^0 23’ and N 7^0 26’ 00” and longitudes E 7^0 36’ and E 7^0 39”, while samples from Maiganga fall within latitudes N 9º to N 12º and longitudes E10º to E 12º. These coal deposits vary in origin and formation, rank, paleodepositional condition, paleovegetation, and elemental composition and can be utilized for several purposes based on their properties. The preparation, mining, burning, waste storage, and transportation of the coals have the potential to cause significant environmental harm. The outcome of this research will provide more information as to the utilization and application of coal.

Geological Setting and Stratigraphy of the Anambra and Gongola basins

The Anambra and Gongola Basins are inland sedimentary basins in Nigeria that were created during the Late Jurassic when sea floor expansion caused South America to split off from Africa (Benkhelil, 1989). Sedimentary in nature, the Anambra Basin is situated on the southern edge of the Benue Trough. The Gongola basin is situated in the Northern Benue Trough (Fig. 1). The literature has information on the Anambra basin's growth, including works by Nwajide and Reijers (1996), Nwajide (2005, 2013), and Obaje et al. (1999). Maastrichtian sedimentary successions consisting of sandstones, shales, siltstones, ironstones, and coal seams exist in the Cretaceous Anambra and Gongola basins in the southeastern and northeastern parts of Nigeria, respectively (Fig. 1).

The movement and separation of the two plates during the Late Jurassic era marked the beginning of the formation of sedimentary basins in southeastern Nigeria as reported by (Burke et al., 1971; Benkhelil, 1982). Three major tectonic cycles impacted the basin's sediment deposition, which caused sediments to be displaced within the basin. The Anambra Basin, Abakaliki-Benue Trough, and the Niger Delta Basin were formed as a consequence of this movement (Benkhelil, 1989; Murat, 1972). Within the Abakaliki-Benue Trough, compressional uplift occurred as a consequence of the Santonian events. As the material folded, the zone of greatest sediment thickness migrated along the Abakaliki Basin. After then, it relocated to the Anambra Basin and, later to the Niger Delta Basin during the Tertiary (Nwajide and Reijers, 1996). Four lithostratigraphic successions have been discovered by researchers (e.g, Dim et al., 2017; Obaje et al., 1999; Hoque and Nwajide, 1985; Ekweozor and Udo, 1988; Murat, 1972) in the Anambra Basin. The Owelli, Nkporo, and Enugu Formations comprise the Nkporo Group, which was deposited in the basin during the Campanian epoch. This sedimentation coincided with a temporary marine incursion. Carbonaceous shales and sandstones with a deltaic origin make up the Nkporo Groups (Odunze et al., 2013; Nwajide and Reijers, 1996). The coal bearing unit (Mamu Formation), which developed during the Late Campanian to Early Maastrichtian regressive phase, encircles the Nkporo Group. Sub-bituminous coal deposits coexist with alternating strata of sandstones, mudstones, shale, and grainy shale in the Mamu Formation (Fig. 2) (Akande et al., 2007). Directly next to the coal bearing unit is the Ajali Formation. The Nsukka Formation and the Ajali Formation, which both date to the middle to late Maastrichtian era, are composed of interbeds of clay laminae. Nwajide and Reijers (1996) state that the Nsukka creation is made up of sandstones and black shales with tiny coal fissures buried in the shale. This suggests that the creation of the Niger Delta Basin began during the early Paleogene, when marine transgressions began. The northern Benue Trough is divided into the Yola Basin (or "Arm"), which trends east-west, and the Gongola Basin, which trends north-south, (Fig. 3).

The Albian-Turonian Bima Formation (sandstones), the Maastrichtian Gombe Formation (sandstones, siltstones, shales, ironstone, and coal), the Tertiary Kerri Kerri Formation (sandstones), and the Alluvium comprise the stratigraphy. The oldest rocks in the stratigraphy are the basement rocks.

Methodology

Field sampling was carried out at the coal mines in the two locations. The samples from Ankpa (AK) are borehole samples, while the Maiganga (MG) samples are surface cuttings. A total of 9 coal samples were obtained from two boreholes located at the Ankpa coal mine in Ankpa Kogi State, while 10 surface samples were collected from different phases of the Maiganga mine in Gombe. There are two coal seams (seam 1 and seam 2) at the Ankpa coal mine (Figs. 4 and 5), and (seam A and seam B) at the Maiganga coal mine (Figs. 6, 7, 8 and 9). The boreholes examined at Ankpa are BH-2 (4 samples) and BH-4 (5 samples), respectively, with depths of 16.5m and 27.4m (Figs. 4 and 5). The thickness of seam 1 and seam 2 in BH-2 is 0.5m and 1.4m, respectively. Similarly, the thickness of seams 1 and 2 in BH-4 is 5.6m and 1m, respectively (Figs. 4 and 5). The proximate, ultimate, elemental analyses, X-ray diffraction (XRD), scanning electron microscopy, and energy dispersive X-ray spectrometry (SEM-EDX) analyses of the coals were carried out at the National Steel Raw Materials Exploration Agency (NSRMEA) in Kaduna, Kaduna State, Nigeria.

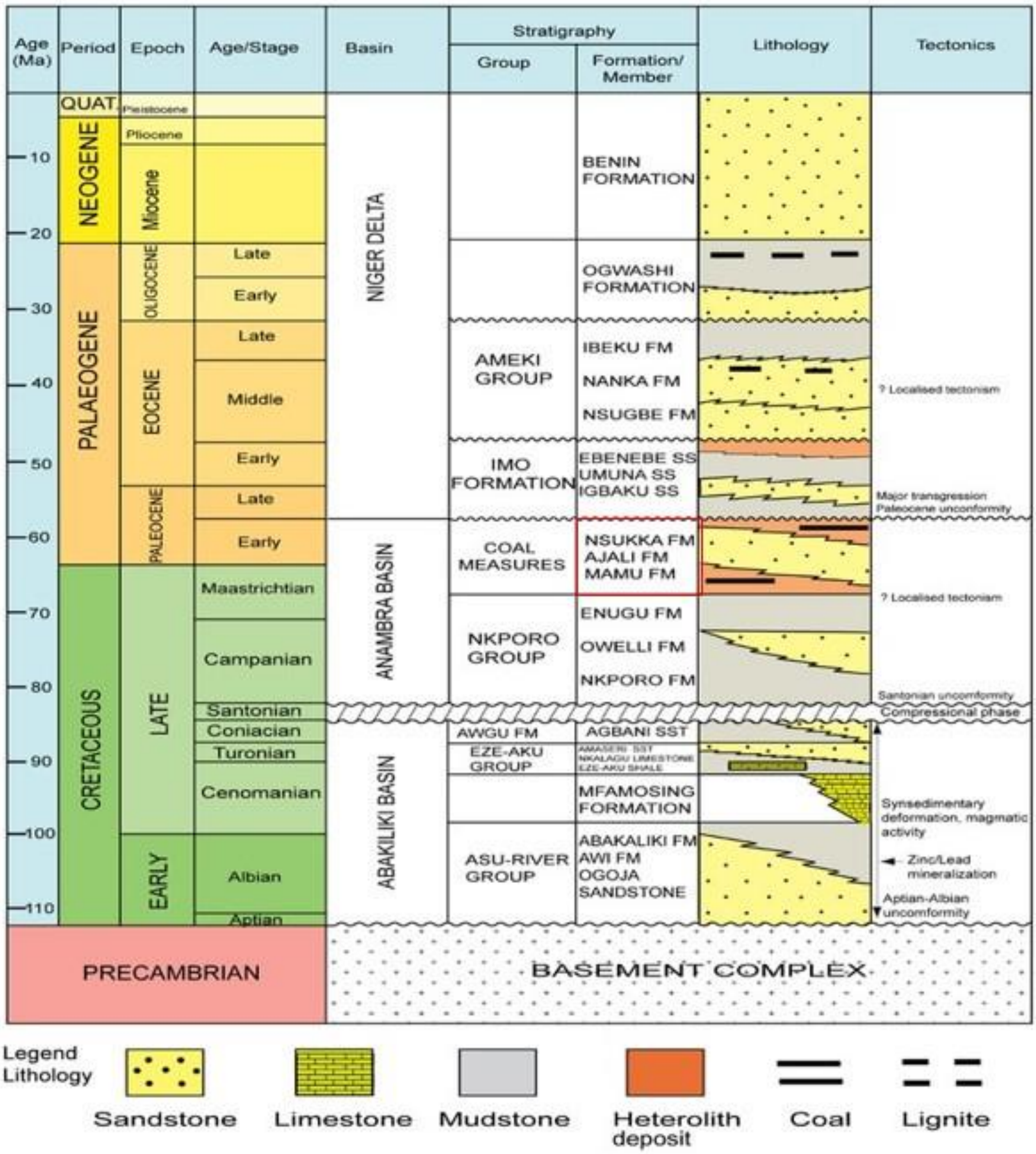

Fig. 2. Anambra Basin Stratigraphic Succession (modified after Ekwenye et al., 2016)

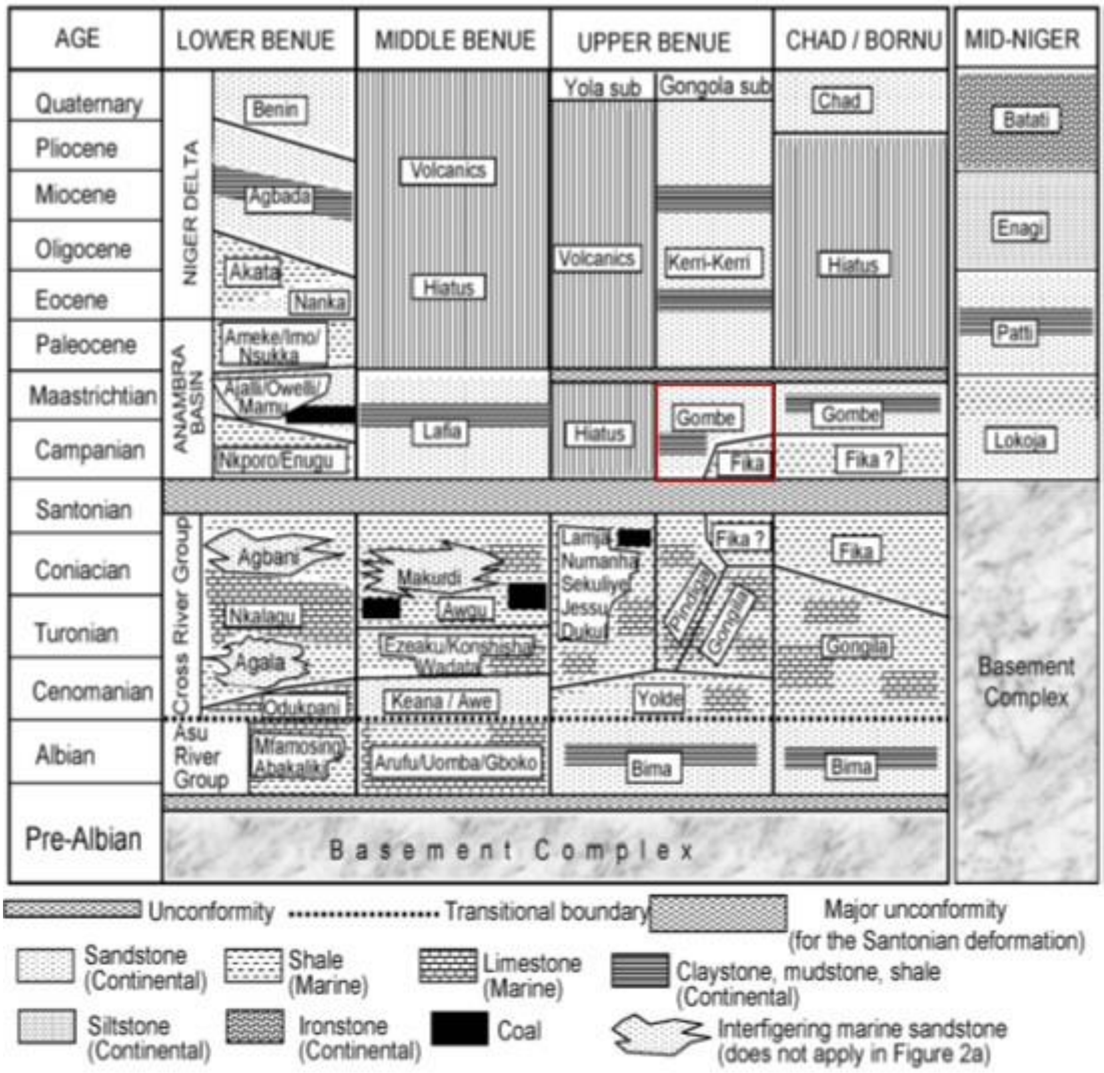

Fig. 3. The stratigraphic succession of the upper Benue Trough, the red box indicate the Gombe Formation (modified after Obaje et al., 2006)

Proximate analysis will be used to assess the quality of the coals by evaluating their moisture, volatile matter, ash, and fixed carbon contents. Subsequently, the ultimate analysis will be conducted to evaluate the carbon, hydrogen, oxygen, nitrogen, and sulfur compositions. The elemental composition and characterization of the coal will be investigated to determine the major, trace, and rare earth elements. Other analyses include the XRD analysis for mineralogical composition. A total of nineteen coal samples (9 samples from Ankpa coal and 10 samples from Maiganga coal) were subjected to proximate analysis (Table 1). Five samples each from the two locations were analyzed by ultimate analyses (Table 2), and six samples were analyzed by XRD. Fifteen coal samples from Ankpa and Maiganga were analyzed by X ray fluorescence (XRF) (Table 3). Two samples from Ankpa coals were analyzed by SEM-EDX. The Proximate Analyzer (VG0STBR model) was used to systematically evaluate the moisture, volatile matter, and ash content of coal samples at different temperatures and residence durations. The residual component reverted to the fixed carbon content. The coal samples underwent a drying process to maintain a uniform quality within the temperature range of 105 °C to 110 °C. The resultant mass was used in order to ascertain the moisture content. The coal sample was exposed to atmospheric conditions and exposed to a temperature of 900 ± 10 °C for a period of 7 minutes. We determined the volatile content by subtracting the moisture content from the reduced mass. We subjected the coal sample to a muffle furnace, raising the temperature to 500 °C for more than 30 minutes, to determine the ash content. The temperature was then maintained at this level for another 30 minutes and then further raised to 815 ± 10 °C. The mass of the residue was measured after a duration of one hour in order to determine its ash content. The Ultimate Analyzer (Advant'X model) performed the comprehensive analysis to determine the relative amounts of carbon, hydrogen, oxygen, nitrogen, and sulfur. The method of testing adhered to the guidelines outlined in the American Society for Testing and Materials (ASTM) standards (ASTM D3173-11, 2011; ASTM D3174-11, 2011).

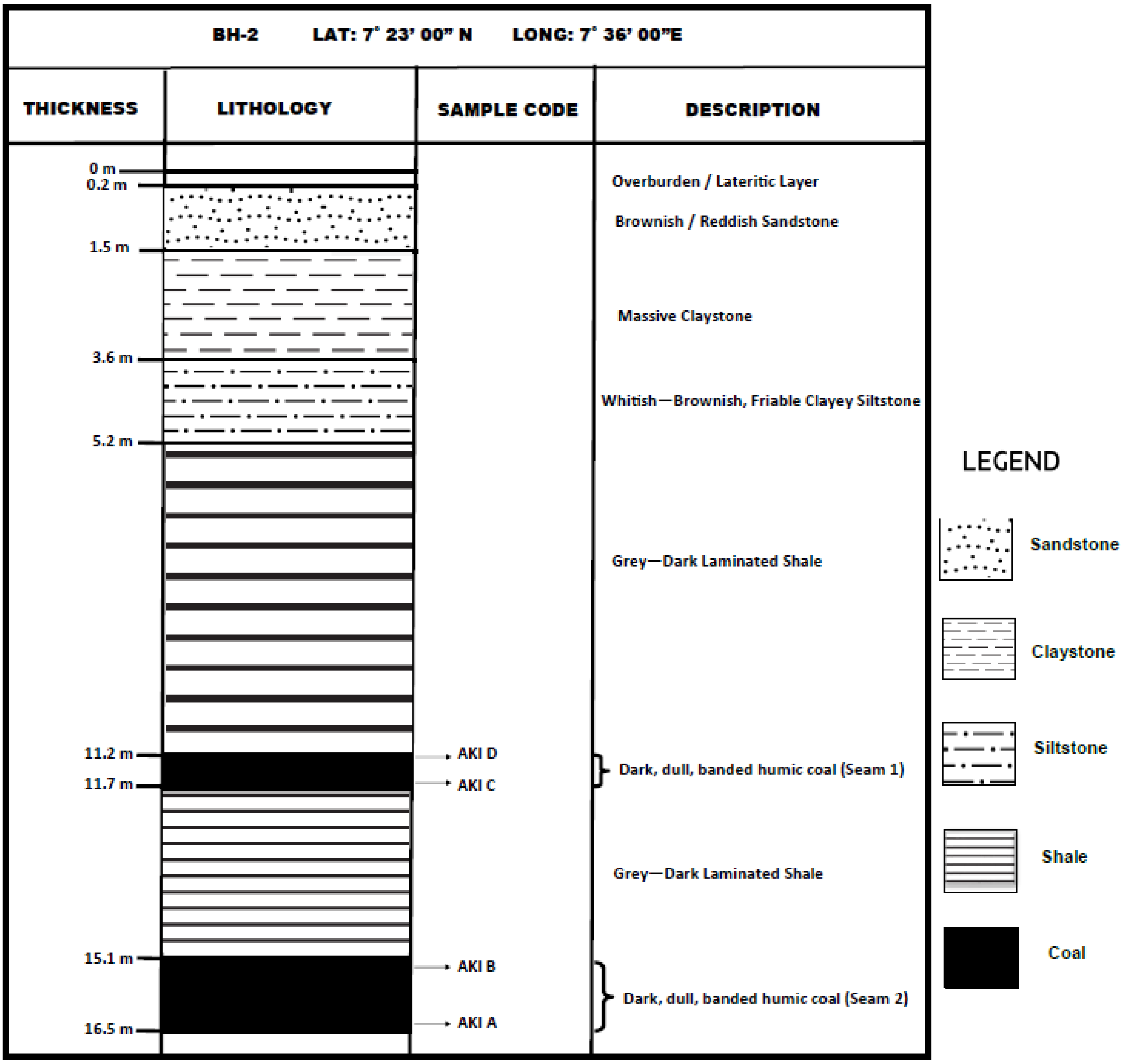

Fig. 4. Lithologic description of samples from borehole 2 at Ankpa mine (N 007° 23' 00" and E 007° 36" 00")

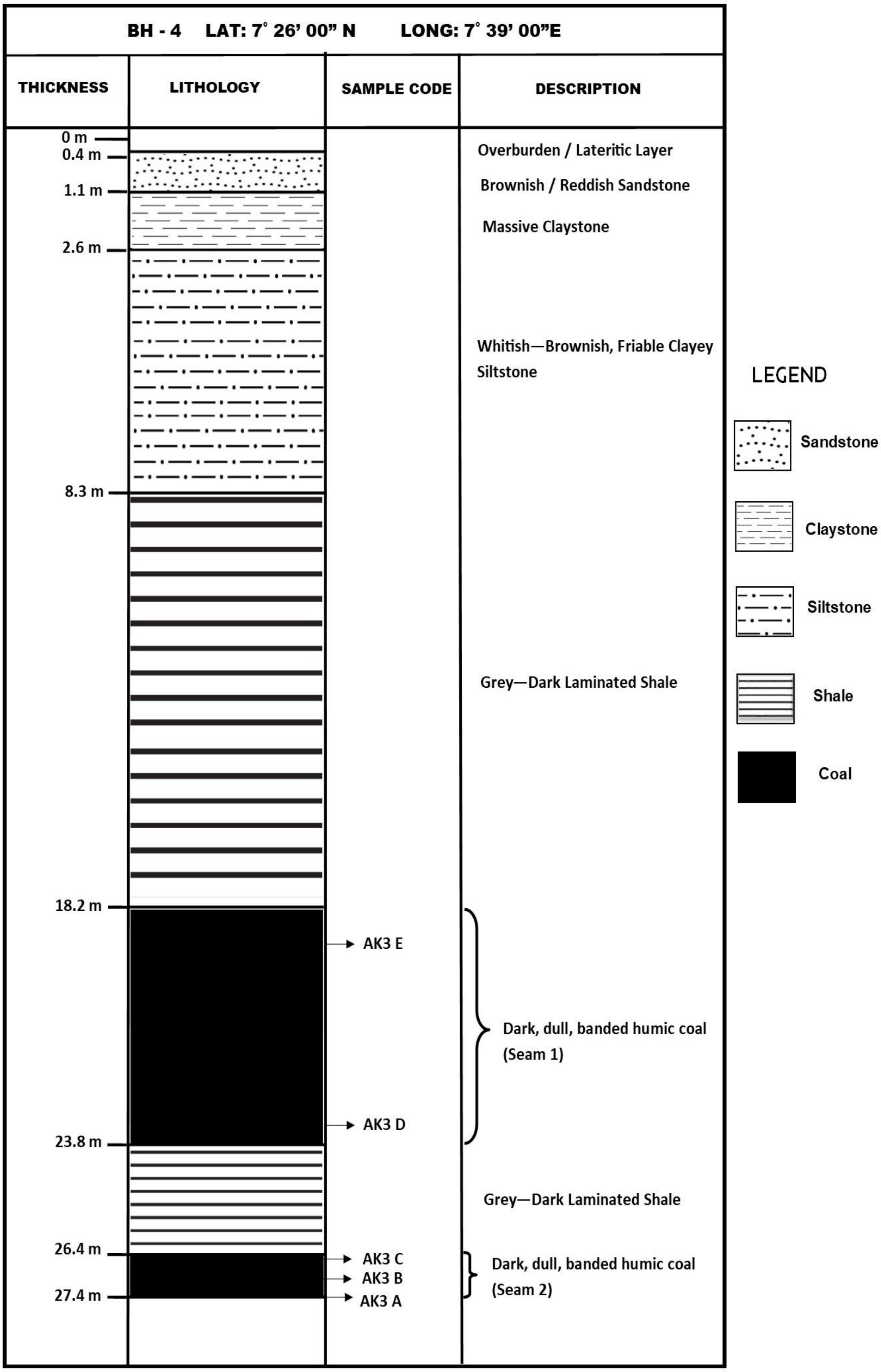

Fig. 5. Lithologic description of samples from borehole 4 at Ankpa mine (N 007° 26' 00" and E 007° 39" 00")

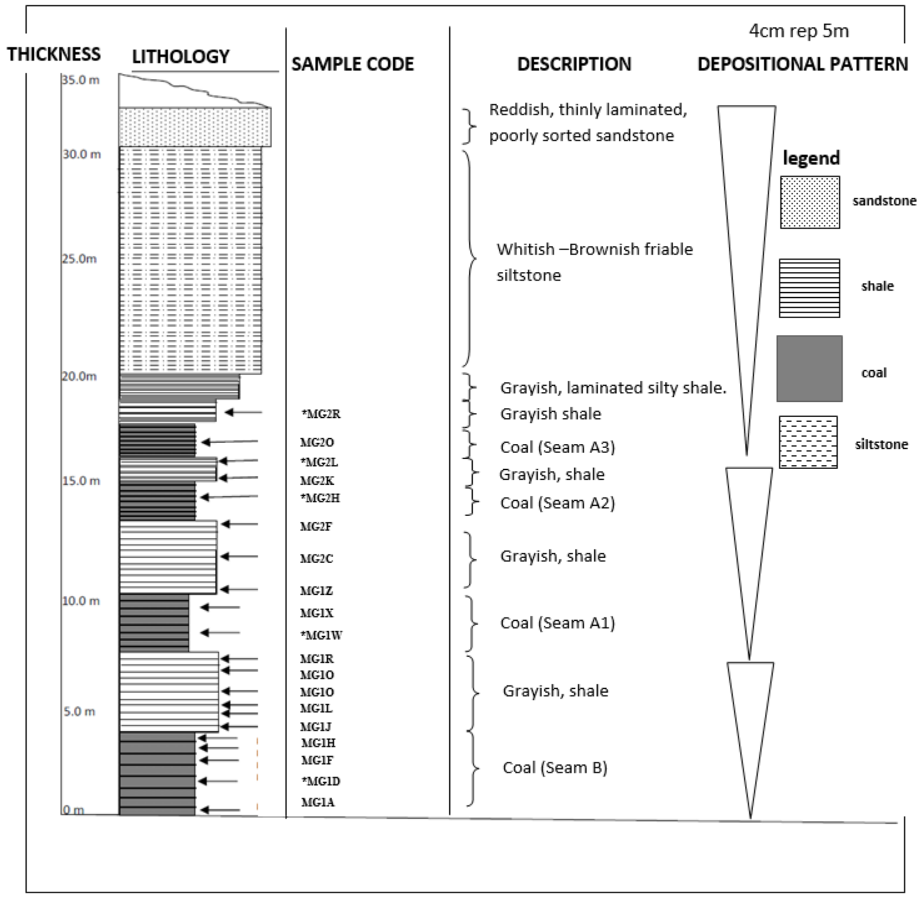

Fig. 6. The lithologic sequence at Maiganga mine exhibits an upward coarsening, transitioning from coal, shale, and siltstone to sandstone Jimoh and Ojo (2016). Phase I is located at coordinates (10^0 02' 39" N, 11^0 12' 17" E)

Fig. 7. Maiganga mine in panoramic perspective. A coarsening upward sequence is indicated by the coal seams at the base grade into sandstone, siltstone, and shale (10^0 02' 39" N, 11^0 12' 17" E)

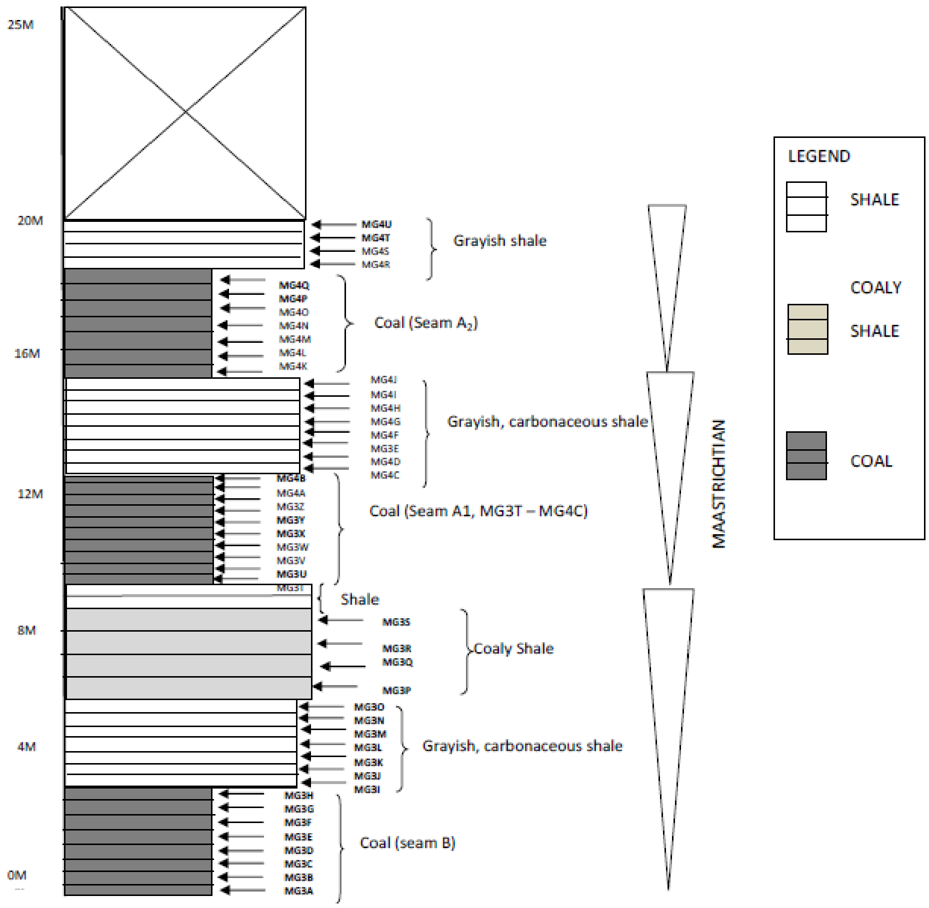

Fig. 8. Lithologic succession of the Gombe Formation (Phase II) at the Maiganga mine (Jimoh and Ojo, 2016)

Fig. 9. The dull-lustering, fractured seam B coal at the Maiganga mine is most likely the result of dehydration or stresses in the crust during coalification (10^0 02' 39" N, 11^0 12' 17" E)

The study of ash composition was conducted in accordance with the (ASTM D-4326 (2004) standard, using XRF equipment to ascertain the relative proportions of major-element oxides, namely Si, Al, Fe, Ti, Mg, Ca, Na, and K.

The mineralogy of the coal samples was determined using X-ray diffraction (XRD) analysis. This study was performed using a Rigaku D/max-2500/PC powder diffractometer that was equipped with radiation from Ni filtered Cu-K³ and a scintillation detector. To eliminate the adsorbed water, the pulverized samples underwent oven-drying at a temperature of 100 °C for a duration of 10 hours. The samples were manually placed into rectangular aluminum sample holders using a spatula that had been cleansed with alcohol. The samples were thereafter firmly affixed into the instrument sample container. The specimens underwent step scanning within the theta scale range of 5 to 85 degrees, with the intervals being 0.02. Each step was tallied for a duration of 0.5 seconds. In order to ascertain the mineral phases and main elements present in the selected coal samples, the SEM was outfitted with an EDX. Before conducting the SEM-EDX analysis, the samples underwent a process of crushing and grinding to a size of 1 mm. Subsequently, they were transformed into polished pellets and coated with conductive carbon. The scanning electron microscope was run with a beam current of 40–60 mA and an accelerating voltage of 20 kV.

Results and Discussion

Lithologic Description

In Ankpa, the lithologies in the boreholes include coals, shales, siltstones, claystones, sandstones, and laterites (Figs. 4 and 5). The samples were logged and described to reveal the lithology. The depths of BH-2 and BH-4 are 16.5m and 27.4 m, respectively. The two boreholes consist of two coal seams (1 and 2), with the shale intercalations occurring between the coal seams. The coal seams 1 and 2 in BH-2 are 0.5m and 1.4m thick, respectively, while in BH-4, the thickness of the coal seams is 5.6m and 1m, respectively (Figs. 4 and 5). The coals are humic, banded, and dull in appearance, based on the physical observation. The Maiganga coals are surface cuttings characterized by dull luster and banding. The coal seam B (phase I) in Maiganga has a thickness of 4.3m (Fig. 6). The shale and clayey siltstone units are located above it, whereas seam A consists of three sub-seams: seam A1, seam A2, and seam A3. These sub-seams have thicknesses of 2.4, 1.8, and 1.4 meters, respectively (Fig. 6). Shales and siltstones interbed the coal seams (Figs. 7 and 8). Figure 9 illustrates the presence of cleats and partitions within the seams, which are likely attributed to dehydration and pressures experienced in the upper crust during the processes of coalification or devolatilization.

Proximate and Ultimate Analyses

Tables 1 and 2, respectively, provide the findings from the coals' proximate and ultimate analysis. The moisture content, ash content, volatile matter content, and fixed carbon content were all determined by proximate analysis. The ultimate analysis determines the percentages of carbon, hydrogen, oxygen, nitrogen, and sulfur in Table 2. There is a range of 2.10 to 7.5% for moisture content, 4.45 to 26.8% for ash content, 40.10 to 56.9% for volatile matter, and 20.45 to 39.24% for fixed carbon in Ankpa coals. The average values for the following parameters: ash content, volatile matter, permanent carbon, and calorific value are 5.54%, 16.42%, 48.45%, 30.71%, and 25.46 MJ/kg, respectively, for Ankpa coals (Table 1). For Maiganga coals, the moisture content ranges from 5.48–19.03%, the ash content varies from 4.65–12.55%, the volatile matter ranges from 36.89–54.58%, and the fixed carbon ranges from 26.46–48.27%. The averages of these parameters are 10.68%, 8.60%, 44.33%, and 36.41%, respectively (Table 1).

The ultimate results of Ankpa and Maiganga coals indicated that carbon has the highest percentage, followed by oxygen, hydrogen, nitrogen, and sulfur. The average values of C, H, O, N, and S in Ankpa coals are 59.67, 5.08, 13.35, 2.14, and 1.96, respectively, while in Maiganga, the average values are 64.12, 5.96, 26.56, 0.84, and 0.70, respectively (Table 2).

Coal Quality

Numerous studies have delved into the correlation between the proximate characteristics of coal and its coking ability (e.g Chelgani et al., 2011; Yu et al., 2013; Fatoye et al., 2021; Jimoh et al., 2023). It has been consistently observed that as the moisture content of coal samples increases, the coking ability decreases (Jimoh and Ojo, 2021; Chelgani et al., 2011). The average value of the moisture content (5.54%) in Ankpa and (10.68%) in Maiganga coals seems to be high, probably which may not be suitable for coking as a result of oxidation (Chelgani et al., 2011). Ash content impacts systems that handle coal and ash, furnaces, heaters, and pollution control equipment. Ryemshak and Jauro (2013) have shown that the presence of ash content has an adverse impact on the volume, structure, and performance of blast furnace coke. The Ankpa coals have higher ash contents than the Maiganga coals, indicating elevated incombustible content, and would be of restricted use (Chukwu et al., 2016). According to Chukwu et al. (2016), coal's heating value and quality are determined by its grade, which is defined as the quantity of fixed carbon and mineral matter contained in the coal. The coke yield of coal samples is determined by the fixed carbon content, as demonstrated by studies conducted by Schobert (1987) and Diez et al. (2002). The coking ability is enhanced when the fixed carbon content rises (Ryan et al., 1998). The average values of the fixed carbon in Ankpa and Maiganga coals are low, suggesting the coals have limited capacity for coking. Thermal power plants and other small industries could utilize these coals for their combustion processes.

Table 1. Proximate data of coal samples obtained from Ankpa and Maiganga (as received)

S/N	Samples code	Sample type	Lithology	M (%)	Ash (%)	VM (%)	FC (%)	CV (MJ/Kg)	FC/V
1	AK1A^	Borehole	Coal	4.11	20.04	51.90	23.95	26.24	0.46
2	AK1B^	Borehole	Coal	6.69	21.30	43.70	28.31	23.94	0.65
3	AK1C^	Borehole	Coal	5.41	10.05	45.82	38.72	25.01	0.85
4	AK1D^	Borehole	Coal	7.61	4.45	48.70	39.24	26.70	0.81
5	AK3A^	Borehole	Coal	8.75	13.90	56.90	20.45	28.85	0.36
6	AK3B^	Borehole	Coal	8.52	7.70	52.30	31.48	27.71	0.60
7	AK3C^	Borehole	Coal	2.70	19.60	40.10	37.60	21.21	0.94
8	AK3D^	Borehole	Coal	2.10	26.80	52.90	28.20	26.99	0.53
9	AK3E^	Borehole	Coal	3.95	23.90	43.70	28.45	22.51	0.65
		Average		**5.54**	**16.42**	**48.45**	**30.71**	**25.46**	**0.65**
10	MG1C	Surface	Coal	11.09	4.65	39.79	44.58	5737	1.12
11	MG1H	Surface	Coal	9.89	5.13	36.89	48.27	5758	1.31
12	MG1V	Surface	Coal	5.48	11.28	54.09	29.15	5198	0.54
13	MG1X	Surface	Coal	8.41	7.92	39.49	44.30	5583	1.12
14	MG1Y	Surface	Coal	7.97	10.99	54.58	26.46	4658	0.48
15	MG2G	Surface	Coal	14.14	6.57	37.31	41.78	5399	1.12
16	MG2O	Surface	Coal	9.45	12.55	40.34	37.46	4957	0.92
17	MG3A	Surface	Coal	19.03	6.25	44.63	30.09	5241	0.67
18	MG3E	Surface	Coal	11.55	9.41	45.66	33.38	5432	0.73
19	MG3H	Surface	Coal	9.75	11.20	50.47	28.58	4969	0.57
	Average			**10.68**	**8.60**	**44.33**	**36.41**	**5293**	**0.86**

Note: ^ Proximate data obtained from (Jimoh et al., 2023). M- Moisture content, VM-Volatile matter, FC-Fixed carbon, CV- Calorific Value, FC/V- Fixed carbon /Volatile.

Table 2. Ultimate data of Ankpa and Maiganga coal samples (in %)

Sample code	C	H	O	N	S	C/H	H/C	O/C
AK3A	72.42	6.14	9.57	1.83	1.82	11.79	0.08	0.13
AK3B	73.61	6.88	11.94	2.9	1.59	10.70	0.09	0.16
AK3C	23.28	1.73	18.46	1.42	4.15	13.46	0.07	0.79
AK3D	58.78	4.68	14.43	2.41	0.73	12.56	0.08	0.25
AK3E	70.27	5.97	12.35	2.15	1.51	11.77	0.08	0.18
AVG	**59.67**	**5.08**	**13.35**	**2.14**	**1.96**			
MG1C	65.2	6.5	25.6	0.94	0.6	10.03	0.10	0.39
MG1V	60.3	5.4	27.3	0.8	1.1	11.17	0.09	0.45
MG1Y	62.4	6.7	25.1	0.76	0.5	9.31	0.11	0.40
MG3E	66.2	5.1	28.3	0.78	0.7	12.98	0.08	0.43
MG3H	66.5	6.1	26.5	0.91	0.62	10.90	0.09	0.40
AVG	**64.12**	**5.96**	**26.56**	**0.84**	**0.70**			

Note: C- carbon, H-hydrogen, O-oxygen, N-Nitrogen, S- Sulphur, C/H- Carbon/hydrogen, H/C- Hydrogen /carbon, O/C -Oxygen/carbon, AVG - Average

Table 3. Major Elemental Compositions of Ankpa and Maiganga coal samples

S/N	Sample code	Sample type	Lithology	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	MgO (%)	P_2O_5 (%)	K_2O (%)	CaO (%)	Na_2O (%)	DAI
1	AK1A	Borehole	Coal	24.24	7.99	2.37	2.65	0.91	1.26	0.61	0.48	0.38	9.54
2	AK1B	Borehole	Coal	15.56	4.23	3.87	3.15	0.65	1.10	0.89	0.46	0.29	4.84
3	AK1C	Borehole	Coal	11.02	3.25	2.53	1.38	0.81	1.44	0.24	0.56	0.42	4.18
4	AK1D	Borehole	Coal	25.56	6.12	3.39	1.48	0.61	0.87	0.65	0.36	0.20	7.80
5	AK3A	Borehole	Coal	11.51	3.80	4.62	0.93	0.51	1.47	0.60	1.34	0.51	2.68
6	AK3B	Borehole	Coal	6.52	3.93	2.69	1.05	0.23	1.58	1.06	0.46	0.63	3.90
7	AK3C	Borehole	Coal	58.04	19.29	8.69	2.02	1.13	1.86	2.96	1.22	0.57	7.51
8	AK3D	Borehole	Coal	36.82	5.80	1.04	1.65	0.70	1.21	1.01	0.31	0.44	22.30
9	AK3E	Borehole	Coal	11.92	4.59	3.89	1.08	0.56	0.71	0.31	0.70	0.59	3.59
	Average			**22.35**	**6.56**	**3.68**	**1.71**	**0.68**	**1.28**	**0.93**	**0.65**	**0.45**	**7.37**
10	MG1C	Surface	Coal	5.88	5.89	0.66	0.38	0.65	0.46	0.35	2.10	1.53	24.01
11	MG1V	Surface	Coal	2.92	5.85	0.76	0.13	0.86	0.36	1.12	1.79	1.34	17.60
12	MG1Y	Surface	Coal	3.86	6.02	1.85	0.20	0.49	0.38	0.26	1.67	1.23	8.41
13	MG2O	Surface	Coal	3.69	5.93	1.25	0.15	0.71	0.39	0.51	1.76	1.28	11.72
14	MG3H	Surface	Coal	2.56	6.05	4.80	0.11	0.83	0.38	2.06	1.35	1.17	4.67
15	MG3E	Surface	Coal	2.82	6.03	0.96	0.21	0.42	0.41	0.65	2.04	1.89	14.54
	Average			**3.62**	**5.96**	**1.71**	**0.20**	**0.66**	**0.40**	**0.83**	**1.79**	**1.41**	**13.49**

Detrital /Authigenic Index (DAI)=(SiO_2+Al_2O_3+K_2O+Na_2O+TiO_2) / (Fe_2O_3+CaO+MgO+SO_3+P_2O_5+MnO).

The storage and burning behavior of coal are influenced by its volatile matter concentration (Barnes, 2015). The higher the level of volatile matter, the greater the risk of spontaneous combustion. Also, high volatile matter yields lower coke. In the studied samples, the volatile matter for Ankpa and Maiganga coals is high, indicating low cokability. The coals' high volatiles are advantageous for combustion applications and fueling (Guo et al., 2018). The significant moisture content found in the analyzed coals (up to 10%), along with the high volatile matter (>36%) and ash (>10%), suggest that these coals are non-coking in nature (Dıez et al., 2002; Zhang et al., 2014). The calorific value indicates the degree of heat content in the coals. According to Hower et al. (2014), power plant coals have a calorific value ranging from 9.5 MJ/kg to 27M/kg. The average calorific value of the coals in the study area would be suitable for heating and power generation.

According to the findings of the ultimate analysis, it is anticipated that the carbon content would positively impact the coking ability, similar to the effect seen with fixed carbon. According to Speight (2015), there is a positive correlation between carbon concentration and cokability. The hydrogen content significantly affects the coking ability, decreasing as the rank increases (Zhang et al., 2014). The nitrogen and sulfur concentrations in coal create challenges in its use and lead to pollution. Sulfur has an intricate effect on cokability and leads to corrosion and clogging of boiler tubes, as well as air pollution when emitted in flue gases (Mochizuki et al., 2013). A value of 0.8% sulfur (air-dried) is required in coking coals, and sulfur emitted from coal burning, such as H_2S, does not impact coking or slagging (Mochizuki et al., 2013). The average total sulfur contents (both organic and inorganic) in the studied samples are 1.96% and 0.70% in Ankpa and Maiganga coals, respectively (Table 2), indicating non-coking coals, especially Ankpa coals.

The fixed carbon to volatile matter ratio (FC/V) is an important factor in understanding the coking properties of coal. Higher ratios are generally associated with better coking properties. Fixed carbon enhances coke strength, whereas volatile matter enhances coal plasticity, aiding in the formation of a cohesive mass during coking. The average FC/V values for Ankpa and Maiganga coals are low, measuring 0.65 and 0.86, respectively (Table 1), suggesting poor coking potential. The oxygen and nitrogen concentrations on the coking ability are significant because the high value is probably a results of oxidation. Furthermore, the average ratio of carbon to hydrogen (C/H) in both samples is low (Table 2), subsequently reducing the coking ability.

Thus, the coals from these locations have low quality due to their high moisture content, volatile matter, ash, and low percentage of fixed carbon. The required percentages for high quality coal are 10-20% for ash and 20-30% for volatile matter, while the fixed carbon should be greater than 69% (Hower et al., 2014).

Rank and Kerogen Classification

According to Ryan et al. (1998), the presence of fixed carbon may serve as an indicator of the coal rank within the lignite and bituminous coal range. Nevertheless, the vitrinite reflectance (R) serves as a very effective indicator for the determination of coal rank. Based on the low fixed carbon, the coals of Ankpa and Maiganga are classified as low rank coals, specifically medium-high volatile sub-bituminous coals. These coals exhibit low nitrogen, high oxygen, and moderate sulfur contents, as described by Guo et al. (2018). The Van Krevelen diagram was initially introduced by Van Krevelen (1961) as a means to characterize coals based on the overall atomic composition of the three primary elements: C, O, and H. The kerogen classification is based on the plot of H/C versus O/C in the Van Krevelen diagram. Figure 10 shows that the samples are dominated by Type IV kerogen and hence have no potential for hydrocarbon generation.

Geochemistry

Table 3 presents the chemical composition (major elements) of the coal samples in the study areas. All of these elements may be found in coal, in its organic and inorganic forms, and they all have different relationships to different parts of coal (Vassilev and Vassileva, 1997). The dominant major elemental components in Ankpa coals are Si, Al, Fe, and Ti. The components that are found in the smallest quantities are Ca, Mg, Na, K, and P. This is consistent with the results of the EDX, as shown in (Figs. 19A-C and 20A-C). In Maiganga coals, Al is the most predominant element, followed by Si, Ca, and Fe. In Ankpa coals, SiO_2 ranges from 6.52% to

58.04% (average 22.35%), Al_2O_3 ranges from 3.80% to 19.29% (average 6.56%) while Fe_2O_3 ranges from 1.04% to 8.69% (average 3.68%). The average values for TiO_2, MgO, P_2O_5, K_2O, CaO, and Na_2O are 1.71, 0.68, 1.28, 0.93, 0.65, and 0.45%, respectively (Table 3). The SiO_2 content in Maiganga coals ranged from 2.56% to 5.88% (average 3.62%), and Al_2O_3 ranged from 5.85% to 6.05% (average 5.96%). The average percentage concentrations of Fe_2O_3, TiO_2, MgO, P_2O_5, K_2O, CaO, and Na_2O are 1.71, 0.20, 0.66, 0.40, 0.83, 1.79, and 1.41%, respectively (Table 3).

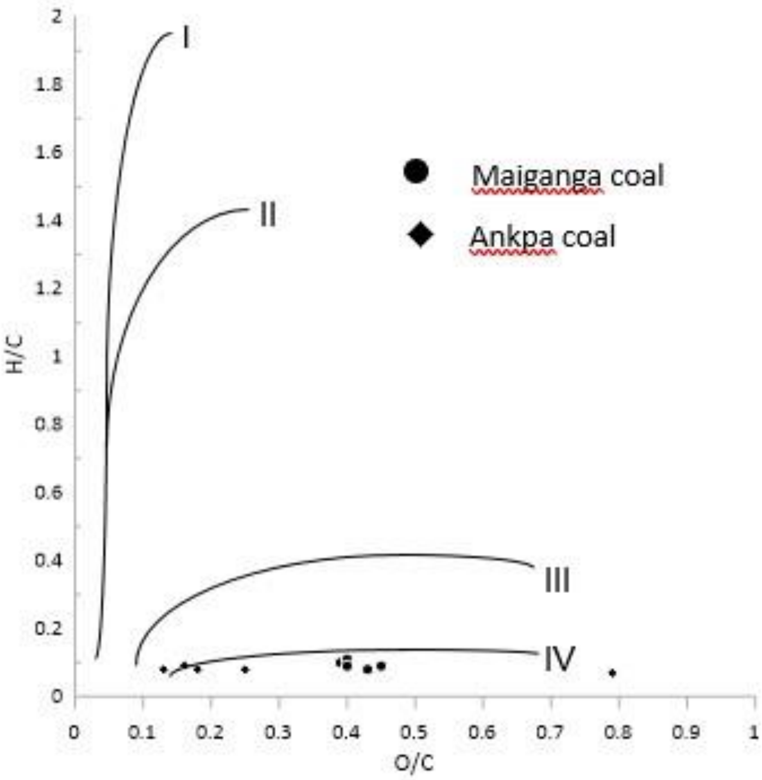

Fig. 10. A graph of H/C vs. O/C of coals from Ankpa and Maiganga indicating Type IV kerogen (after Van Krevelen 1961)

The Si/Al ratio in the coal samples is more than 2, mostly seen in Ankpa coals. This suggests that quartz and clay minerals are prevalent, possibly originating from detrital sources (Finkelman, 1995; Swaine, 1990, Dai et al., 2012). This is supported by the mineralogy of the coals presented in (Tables 6 and 7). The average value of the ratio K_2O/Na_2O in Ankpa and Maiganga coals is 2.15%, and 0.63% indicates the presence of K-bearing minerals. The relatively low average value of Fe_2O_3 (1.71%) in Maiganga coals indicates the possible absence or low content of iron-bearing minerals such as pyrite. Additionally, the low TiO_2 and MgO values may suggest the presence of kaolinite.

Genetic characteristics and Depositional Environments

To determine the environment of deposition, the AKF ternary diagram after Englund and Jorgensen (1973) using the major oxides, (A) Al_2O_3 – K (K_2O + CaO + MgO) – F (Fe_2O_3 + MgO), was adopted. The coal samples were deposited mostly in paralic environment, with a few samples plotted in continental settings (Fig. 11).

Both detrital and authigenic minerals are present in coal, and their distribution within the inorganic matter exhibits variability (Eskenazy, 1980). Carbonates, Sulfides, and sulfates of iron (Fe), magnesium (Mg), and calcium (Ca) make up most of the authigenic minerals in coals (Vassilev et al., 1994). The Detrital/Authigenic Index (DAI) represents the chemical composition of various index minerals found in coal. Based on the DAI values, some genetic information with respect to the formation of the coals could be deduced (Vassilev and Vassileva, 2009). The DAI values of 7.49 and 13.49 in Ankpa and Maiganga coals, respectively (Table 3), indicate that the coals in the study areas are enriched in elements associated with probable authigenic and detrital minerals. This is corroborated by the positive correlation (Fig. 12A-H) between (SiO_2 vs. Al_2O_3), (SiO_2 and TiO_2), (SiO_2 and MgO), and (K_2O and Na_2O) in Ankpa coals, suggesting an authigenic origin, while the negative correlation in Maiganga coals indicate a detrital origin (Vassilev and Vassileva, 2009). During the process of coalification, detrital minerals such as quartz, kaolinite, illite, muscovite, rutile, apatite, as well as Fe and Al oxyhydroxides often exhibit stability.

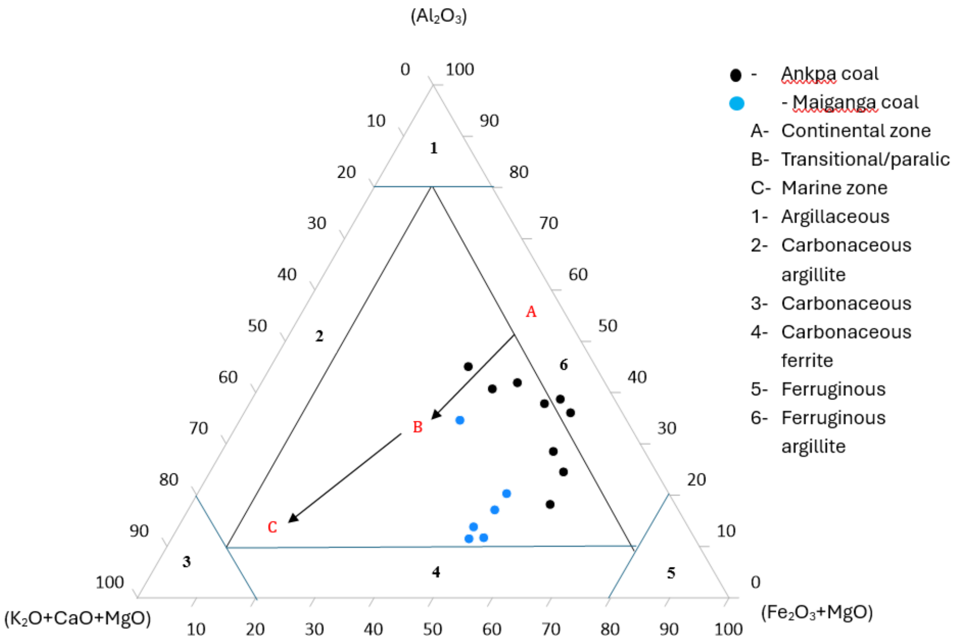

Fig. 11. Al_2O_3 - (K_2O+CaO+MgO) - (Fe_2O_3+MgO) [AKF] Ternary plot of Ankpa and Maiganga coal samples. Samples were deposited within continental and paralic depositional environment

Agglomeration Tendency

A significant quantity of inorganic elements may be found in coal, resulting in the formation of various inorganic oxides referred to as mineral compositions. These compositions include SiO_2, TiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, Mn_3O_4, SO_3, Fe_2O_3, and others (Ghosh and Chatterjee, 2008). At elevated temperatures, minerals undergo a sequence of transformations, leading to the occurrence of slagging phenomena at a certain temperature threshold. In research conducted by Liu et al. (2013), the melting behavior of coal samples was investigated using XRD and SEM. The findings revealed a negative correlation between the ash fusion temperatures (AFTs) and the Fe_2O_3 concentration. The AFTs exhibited a minimum value of 30% CaO, followed by a further rise. Shao et al. (2007) did a study on sludge combustion and found that phosphates, along with the eutectics of Fe_2O_3 and SiO_2, had a big effect on how the bed agglomerated. Combining compounds with low melting points with alkalis achieves this. The slagging indices used to determine the agglomeration level in the coals includes ratios of Base/Acid (B/A), Silicon ratio (G), Silica/Alumina (S/A), Iron/Calcium (I/C), Carbon/Hydrogen (C/H), and Fixed Carbon/Volatile matter (FC/V) (Table 4). The Base/Acid ratio (B/A) is a comprehensive measure

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that measures the slagging characteristics of coal. Basic oxides lower the AFTs and enhance ash fluidity, whereas acidic oxides have contrasting effects (Guo et al., 2018). Consequently, the likelihood of slagging increases as the Base/Acid ratio increases.

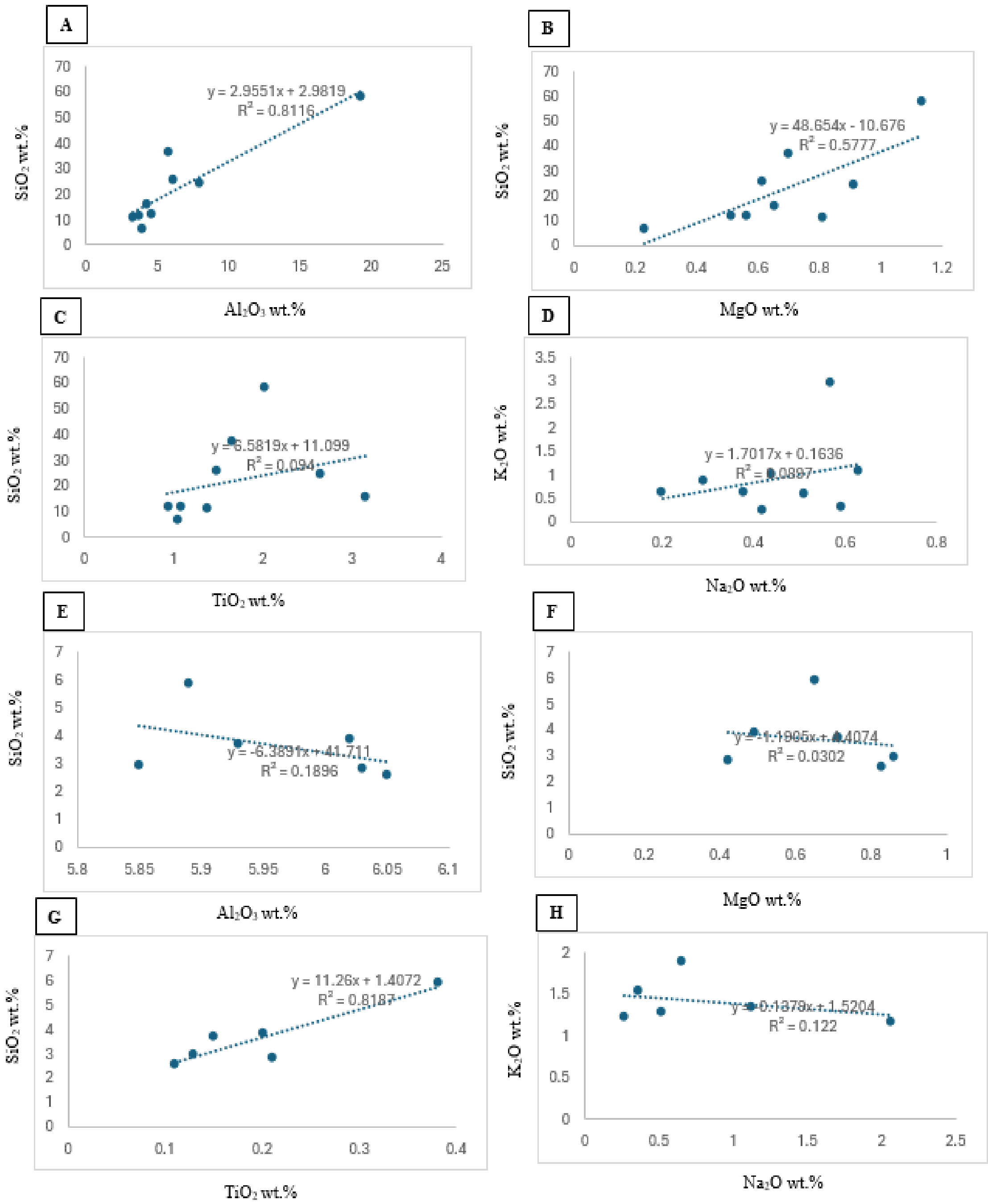


Fig. 12. Positive correlation plots of (A) SiO_2 vs Al_2O_3, (B) SiO_2 vs MgO, (C) SiO_2 vs TiO_2, and (D) K_2O vs Na_2O, for the Ankpa coals and negative correlation plots of (E) SiO_2 vs Al_2O_3, (F) SiO_2 vs MgO, (G) SiO_2 vs TiO_2, and (H) K_2O vs Na_2O for the Maiganga coals

Table 4. Comparison of slagging discriminant indices of coals from Ankpa and Maiganga coal mines (^ data obtained from Jimoh et al., 2023).

Sample Code	C/H	FC/V	B/A	G	S/A	I/C	Agglomeration Degree
AK1A^	-	0.46	0.14 (Weakly)	86.6 (Weakly)	3.03 (Strongly)	4.94 (Weakly)	Weakly
AK1B^	-	0.65	0.26 (Medium)	75.8 (Medium)	3.68 (Strongly)	8.41 (Weakly)	Medium
AK1C^	-	0.85	0.29 (Medium)	73.9 (Medium)	3.39 (Strongly)	4.52 (Weakly)	Medium
AK1D^	-	0.81	0.16 (Weakly)	85.4 (Weakly)	4.18 (Strongly)	9.42 (Weakly)	Weakly
AK3A^	11.79	0.36	0.47 (Strongly)	64.0 (Strongly)	3.03 (Strongly)	3.45 (Weakly)	Strongly
AK3B^	10.70	0.60	0.44 (Strongly)	65.9 (Strongly)	1.66 (Weakly)	5.85 (Weakly)	Weakly-Strongly
AK3C^	13.46	0.94	0.18 (Weakly)	84.0 (Weakly)	3.01 (Strongly)	7.12 (Weakly)	Weakly
AK3D^	12.56	0.53	0.08 (Weakly)	94.7 (Weakly)	6.35 (Strongly)	3.35 (Weakly)	Weakly
AK3E^	11.77	0.65	0.34 (Medium)	69.8 (Medium)	2.60 (Medium)	5.56 (Weakly)	Medium
MG1C	10.03	1.12	0.44 (Strongly)	63.29 (Strongly)	1.00 (Weakly)	0.31 (Medium)	Strongly
MG1V	11.17	1.31	0.66 (Strongly)	46.13 (Strongly)	0.50 (Weakly)	0.42 (Medium)	Strongly
MG1Y	9.31	0.54	0.55 (Strongly)	49.05 (Strongly)	0.64 (Weakly)	1.11 (Medium)	Strongly
MG3E	12.98	0.73	0.66 (Strongly)	45.19 (Strongly)	0.47 (Weakly)	3.56 (Weakly)	Weakly-Strongly
MG3H	10.90	0.57	1.17 (Strongly)	26.83 (Strongly)	0.42 (Weakly)	0.47 (Medium)	Strongly

Note: FC/V = Fixed carbon/Volatile matter, C/H = Carbon/Hydrogen, B/A, Base/Acid ratio = (Fe_2O_3+ CaO + MgO +Na_2O+ K_2O) / (SiO_2 + Al_2O_3+TiO_2), G, Silicon ratio = 100•SiO_2/(SiO_2 + Fe_2O_3 + CaO + MgO), I/C = Fe_2O_3/CaO, S/A = SiO_2/Al_2O_3

The assessment of coal slagging heavily relies on the silicon ratio, which is a critical parameter. However, it fails to include the influence of Al_2O_3 on the occurrence of slagging (Guo et al., 2018). The primary emphasis of the silicon ratio (G) is in the concentration of silica, which constitutes the main constituent inside the coal. The value of the silicon ratio exhibits an upward trend as the ash fusion temperatures rise. According to Guo et al. (2018), an elevation in the silica/alumina ratio increases the occurrence of slagging. Based on the discriminant limits in Table 5 (Guo et al., 2018) and using the elemental composition of the coal samples in Table 3, the slagging tendencies of the coal samples were deduced (Table 4). The indices S/A (strongly) and I/C (weakly) are consistent for the Ankpa coals, likewise, the indices B/A and G indicate weakly-medium slagging tendencies, with few samples exhibiting a strong slagging tendency. The Maiganga coals showed consistency with B/A (strongly), G (strongly), and S/A (weakly) tendencies. The agglomeration level of the Ankpa coal ranges from weak to medium to strong, while the Maiganga coals have a significant agglomeration level. The combination of many agglomeration indicators causes the agglomeration level to vary. The Ankpa coals can be compared to coals from the East Kalimantan in Indonesia and Witbank coalfield in South Africa having lower coking qualities and weak agglomeration tendencies while Maiganga coals are comparable to coals from the Shanxi province, Datong coalfield, and Heilongjiang province in China.

Table 5. The constraints of the indicator for slagging coals from Heilongjiang Province (Guo et al., 2018)

Tendency of slagging			
Index	**Weakly**	**Medium**	**Strongly**
B/A	< 0.206	0.206-0.4	> 0.4
G	> 78.8	78.8-66.1	< 66.1
SiO_2/Al_2O_3	< 1.87	1.87 – 2.65	> 2.65
Fe_2O_3/CaO	Out of 0.3-3	0.3 -3	Near 1

Mineralogical Composition

The result of the XRD is presented in Tables 6 and 7. The primary mineral phases that have been identified in the diffractograms from the Maiganga coals include quartz, kaolinite, calcite, vermiculite, and microcline (Table 7, Figs. 13, 14, 15 and 16). Other minerals observed in the samples include illite, chlorite, muscovite, and graphite. The identification of quartz, kaolinite, calcite, chlorite, and microcline substantiates the inferences from XRF and EDX results. In Ankpa coals, pyrite and illite were recorded in addition to quartz, calcite, and chlorite (Table 6, Figs. 17 and 18). The prevalence of quartz in the coal samples that were examined mostly originates from detrital sources. The coals contain a significant amount of quartz due to their inherent stability and inertness during burning. Quartz is often found in coal deposits as discrete, angular particles of different sizes, dispersed between organic debris and clay minerals, suggesting a detrital source. The SEM-EDX images (Figs. 19A-C and 20A-C), confirms the presence of detrital chlorite in the Ankpa coals, illite is also disseminated as fine grained within the detrital quartz and contains minor elements such as Ca, Mg, Fe, and Na. The mineral pyrite and the calcite in Ankpa coals are of authigenic origin (Vassilev and Vassileva, 1996). The percentage of non-metallic graphite in Ankpa coal is high.

Table 6. XRD data of coal samples obtained from Ankpa Coals in percentage

Code	Lithology	Q	Py	I	Ca	S	Ch	G
AK3A	Coal	35.1	2.1	1.1	3.2	0.06	0.6	57.8
AK3D	Coal	10.2	2.0	8.8	1.0	1.7	10.4	66

Table 7. XRD data of coal ash samples obtained from Maiganga in percentage

Code	Lithology	Q	K	Mu	Ch	Ca	Mi	V
MG1V	Coal	47	2	-	-	13	23	16
MG1Y	Coal	61	-	-	8	6	16	9
MG3E	Coal	37	22	6	-	10	-	25
MG3H	Coal	69	12	6	-	-	0.1	13

Q-Quartz, Ka-Kaolinite, I-Illite, Py-Pyrite, Ch-Chlorite, G-Graphite, Ca-Calcite, Mi-Microcline V-Vermiculite, Mu-Muscovite and S-Sulfur

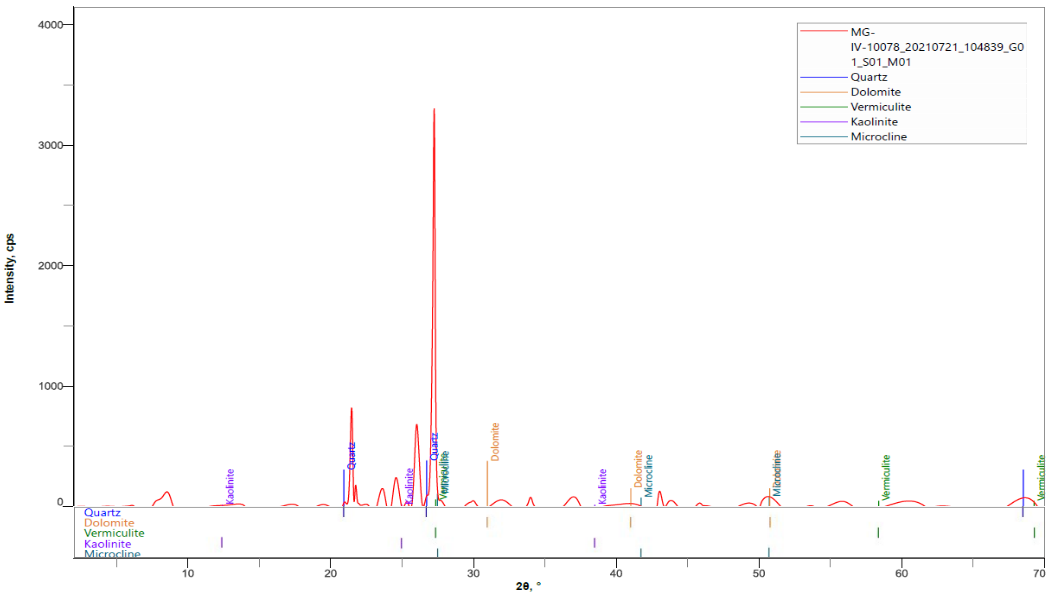


Fig. 13. Diffractogram of sample MG1V from Maiganga mine

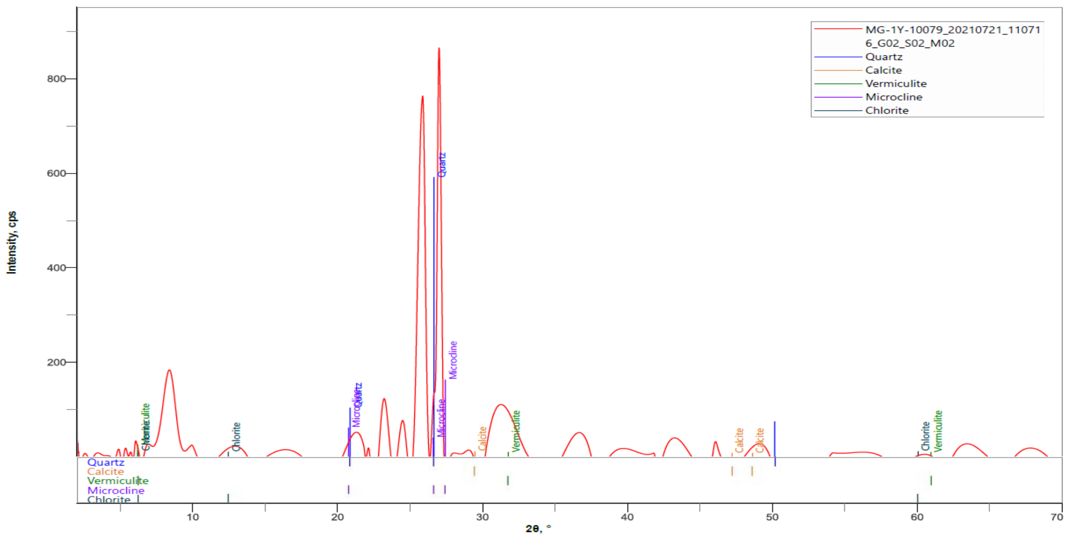


Fig. 14. Diffractogram of sample MG1Y from Maiganga mine

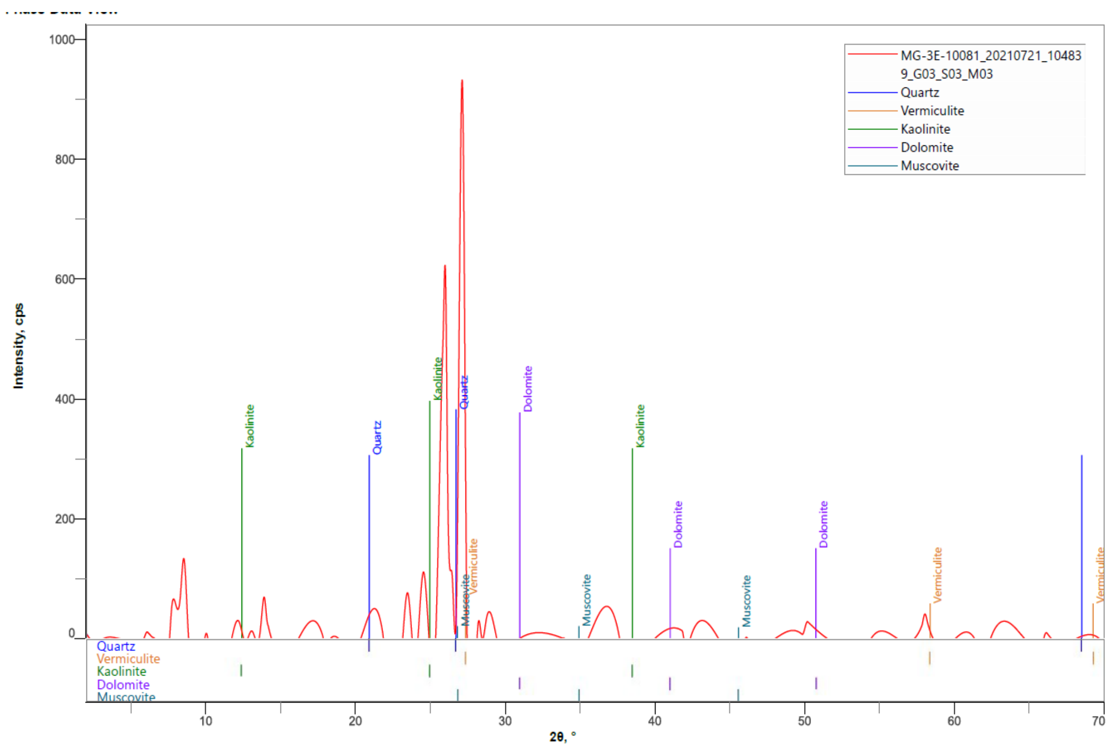


Fig. 15. Diffractogram of sample MG3E from Maiganga mine

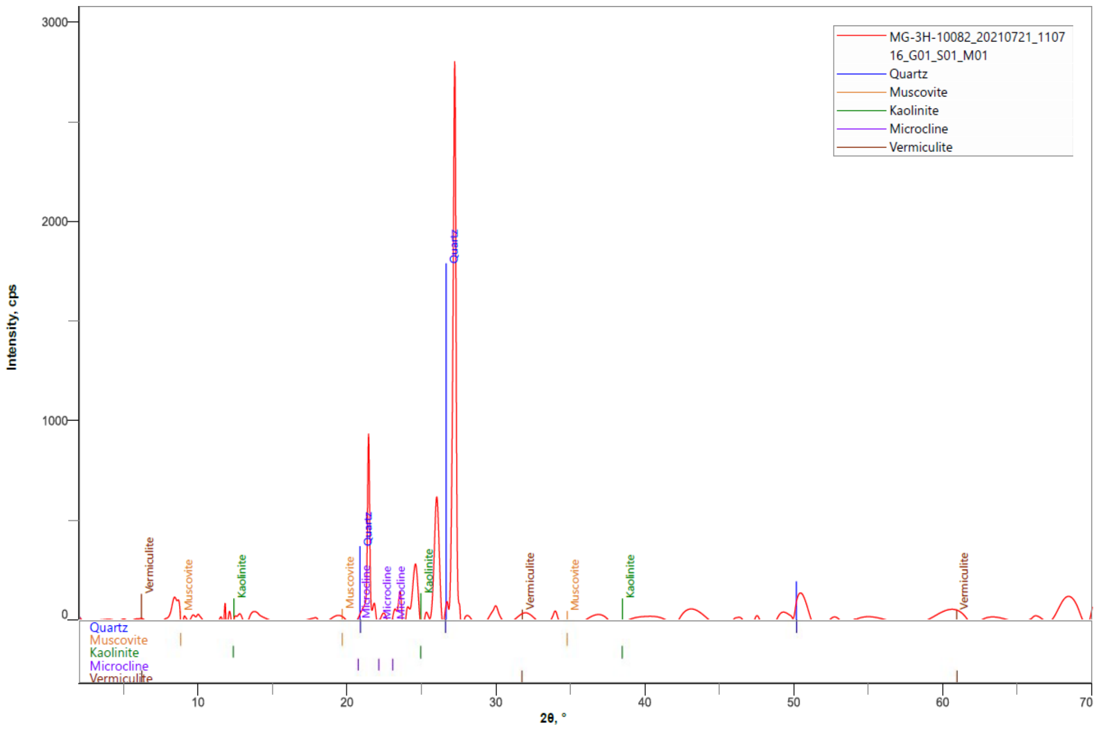


Fig. 16. Diffractogram of sample MG3H from Maiganga mine

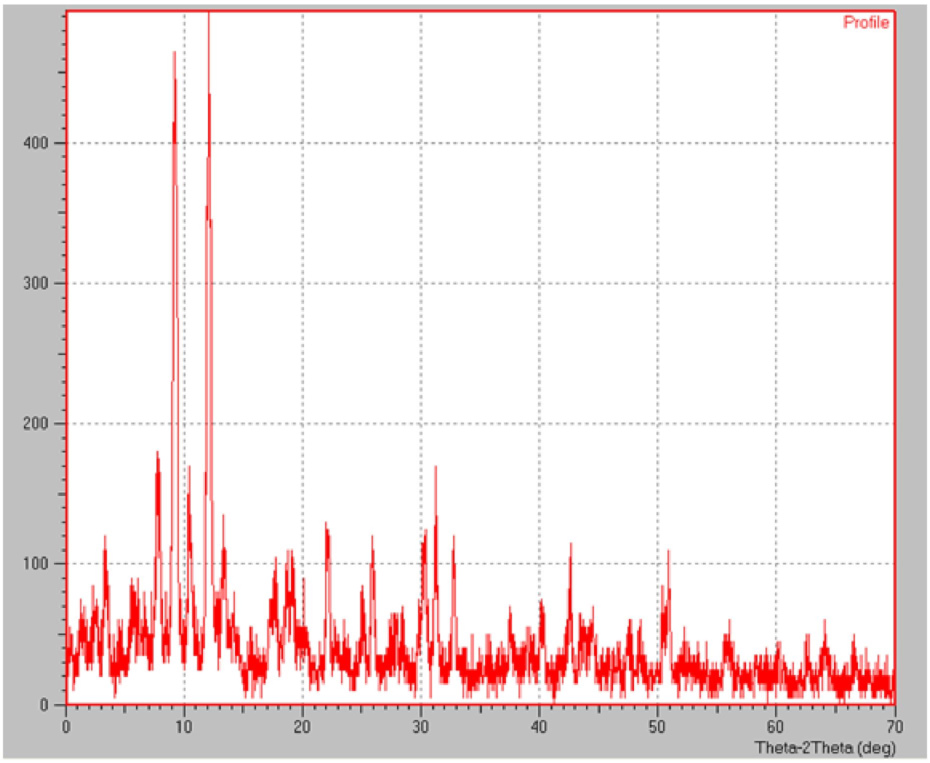


Fig. 17. Diffractogram of sample AK3D from Ankpa mine

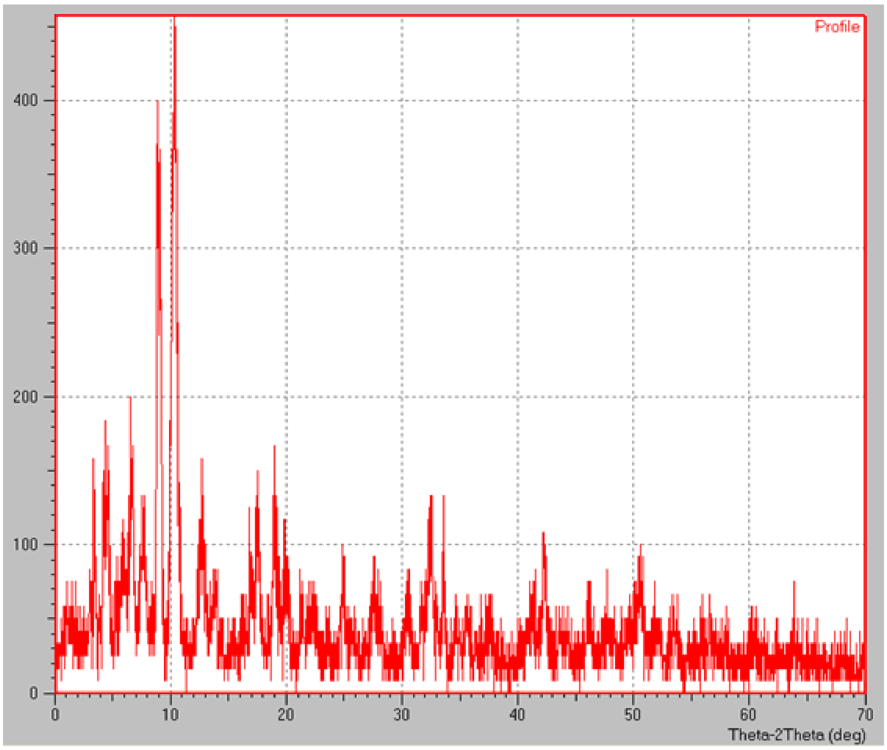
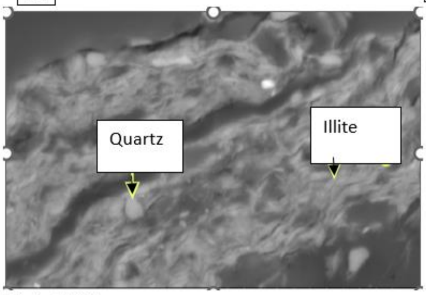


Fig. 18. Diffractogram of sample AK3A from Ankpa mine

A



Mode: 20kV

B

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	19.32	27.13
13	Al	Aluminium	7.56	10.21
26	Fe	Iron	2.18	6.08
19	K	Potassium	1.26	2.46
47	Ag	Silver	0.45	2.44
22	Ti	Titanium	0.51	1.21
20	Ca	Calcium	0.43	0.87
15	P	Phosphorus	0.52	0.81
12	Mg	Magnesium	0.56	0.68
11	Na	Sodium	0.36	0.42
9	F	Fluorine	0.41	0.39

C

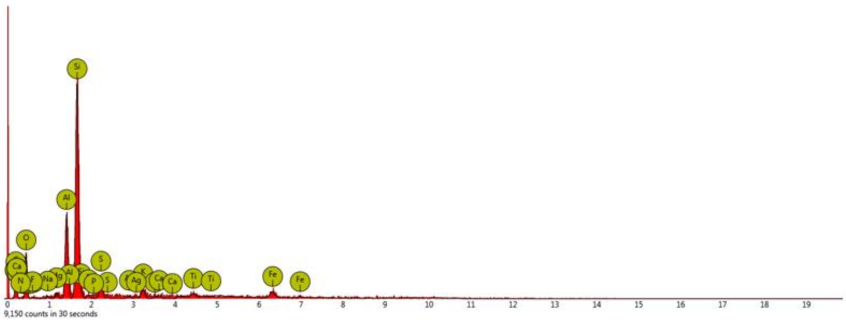
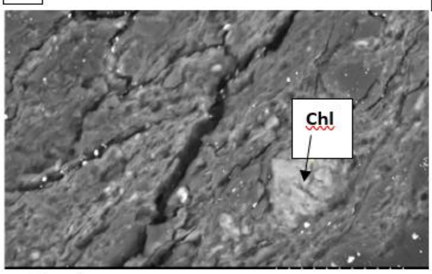


Fig. 19. A: SEM image of the Ankpa coal sample AK3A having illite dispersed in detrital quartz, B: elemental compositions of the coal sample, and C: EDX spectra of the coal sample

A



Mode: 20kV

B

Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	5.83	11.33
13	Al	Aluminium	2.26	4.23
26	Fe	Iron	0.43	1.66
22	Ti	Titanium	0.48	1.59
12	Mg	Magnesium	0.33	0.55
15	P	Phosphorus	0.26	0.55
19	K	Potassium	0.19	0.51
20	Ca	Calcium	0.12	0.34
11	Na	Sodium	0.18	0.28
9	F	Fluorine	0.08	0.10

C

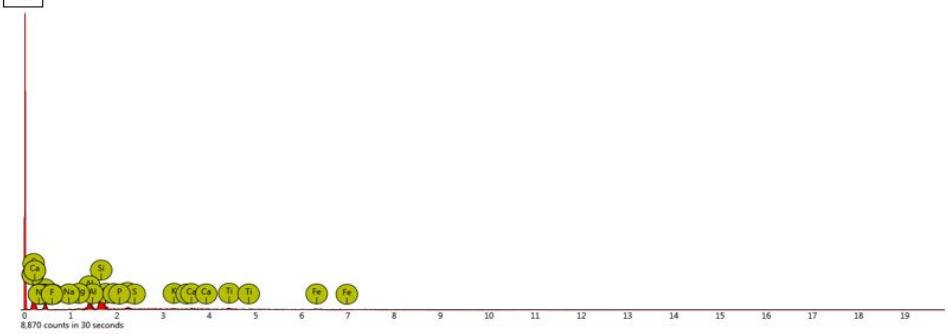


Fig. 20. A: SEM image of the Ankpa coal sample AK3D showing chlorite, B: elemental compositions of the coal sample, and C: EDX spectra of the coal sample

Conclusions

The lithology in the study areas include coals, shales, siltstones, claystones, and sandstones. The coals are banded and classified as humic coals. The proximate analyses revealed that the coals are characterized by high moisture content, high volatile matter, low fixed carbon, high ash content, low FC/V, and low C/H, indicating low cokability potential. The high volatile matter in the coals may support fueling and combustion purposes. The coals are classified as low-rank coals, specifically sub-bituminous coals deposited in continental-paralic environments. The coals are characterized by Type IV kerogen, indicating no potential for hydrocarbon generation. The geochemical composition of the Ankpa coal showed a higher percentage of SiO_2 than Maiganga coals, but generally, the composition showed an abundance of the following elements: Si, Al, and Fe in the coals. The DAI of the coals suggests a composition enriched in elements associated with detrital minerals for the Maiganga coals and authigenic minerals for Ankpa coal. The XRD inferences revealed the presence of quartz and clay minerals such as kaolinite and illite. Authigenic minerals in the coals include pyrite and calcite. The slagging tendency of the coals was deduced by the following indices: Base/Acid (B/A), Silica (G), Silica/Alumina (S/A), Iron/Calcium (I/C), Carbon/Hydrogen (C/H), and Fixed Carbon/Volatile Matter (FC/V), which indicate weak–medium-strong agglomeration for the Ankpa coals while the agglomeration level of Maiganga coals is strong.

Authors contribution statement

Jimoh Ayoola Yusuf conceived the research, interpreted data, and wrote the paper; Saadu Mariam Bolaji: Interpreted and plot some data. Jimoh Ajadi: Interpreted and plot some data; Aminu Shakirat: Interpreted and assisted with writing of the draft: Akinpelu Mutiu: analysis tools and plotting of some data.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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زمین‌شیمی و کانی‌شناسی زغال‌های ماستریشتین از حوضه‌های آنامبرا و گنگولای نیجریه: کاربردهایی برای کیفیت زغال، ظرفیت منابع و ویژگی‌های تجمعی

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تجمع

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چکیده

آنامبرا و گنگولا بخشی از حوضه‌های داخلی رسوبی در نیجریه هستند که با سوخت‌های فسیلی مشخص می‌شوند و نیجریه برای حل مشکل انرژی فعلی خود، تمرکز تولید برق خود را به زغال‌سنگ منتقل کرده است. زغال‌های مورد بررسی به ترتیب از دو منطقه آنکپا و مایگانگا در ایالات کوگی و گومبه به دست آمده‌اند. زغال‌ها برای تعیین کیفیت و استفاده و پتانسیل منابع خود مورد بررسی قرار گرفتند. این زغال‌ها با استفاده از تجزیه‌های مجاورتی، نهایی، عناصری، کانی‌شناسی و میکروسکوپی الکترونیکی تجزیه‌شده‌اند. هدف این پژوهش تعیین قابلیت کک‌سازی، رتبه‌بندی، محیط‌های پالئوآنوی، پتانسیل هیدروکربن و تمایل به ذوب‌کردگی زغال‌هاست. مقادیر میانگین محتوای رطوبت، خاکستر، ماده فرار و کربن ثابت برای زغال‌های آنکپا به ترتیب ۵/۵۴، ۱۶/۴۳، ۴۸/۴۵ و ۳۰/۷۱ درصد و برای زغال‌های مایگانگا به ترتیب ۱۰/۶۸، ۸/۶۰، ۴۴/۳۳ . ۳۶/۴۱ درصد بوده که نشان‌دهنده زغال‌های نون- ککینگ زیربیتومینوس با محتوای فرار بالاست و برای سوخت و تولید برق مناسب هستند. نمودار ون کرولن بر اساس H/C در برابر O/C نشان داد که کروژن نوع IV وجود دارد. نتایج XRD، نمودارهای همبستگی و مقادیر شاخص مواد آلوده و غیرماده‌ای (DAI) به ترتیب ۷/۴۹ و ۱۳/۴۶ برای زغال‌های آنکپا و مایگانگا نشان‌داد که زغال‌های آنکپا با مواد برجایی مانند کوارتز، پیریت و کلسیت غنی شده‌اند؛ در حالی که کائولنیت و کوارتز احتمالی مواد آواری در زغال‌های مایگانگا هستند. به طور خلاصه، تجمع زغال‌های آنکپا بر اساس نسبت اسید/ پایه (B/A)، نسبت سیلیسیم (G)، نسبت سیلیس/ آلومینا (S/A)، نسبت آهن/ کلسیم (I/C)، نسبت کربن/ هیدروژن (C/H) و نسبت کربن ثابت/ ماده تبخیرپذیر (FC/V) به ترتیب نشان‌دهنده تجمع ضعیف، متوسط و قوی برای زغال‌های آنکپا و تجمع قوی برای زغال‌های مایگانگا بود.

استناد به این مقاله

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