Petroleum and Coal

Article Open Access

CHARACTERIZATION OF ASH CONTENT, COKING TENDENCIES AND EVALUATION OF PHYSICOCHEMICAL PROPERTIES OF OKOBO COALS

Samuel Oluwaseun Oni, Ehinola A. Olugbenga, Gideon Nwafor Chidimma

Department of Geology, University of Ibadan, Ibadan, Oyo State, Nigeria

Received April 18, 2017; Accepted June 12, 2017

Abstract

The mineral content of coal affects the type of ash that will be produced on combustion. Despite the same volatile matter content, the Okobo 1 FSI is 3.7 with ash content of 16.7 while Okobo 2 FSI is 6.8 with an ash content of 8.2. Ash fusion is 1,400ºC, various ash slagging index indices such as silica ratio (Sr), basic to acidic oxide (B/A), and sulphur index (Rs) for Okobo coal are: 85, 0.13, 0.23 respectively implying low slagging characteristics. The Gross Calorific Value GCV of Okobo 1 and Okobo 2 are 20.88 MJ/Kg (8796 Btu/lb) and 19.86MJ/Kg (8536 Btu/lb) respectively congruous with lowest grade of sub-bituminous coal termed the "sub-bituminous C grade" according to ASTM classification. The fixed carbon values are 59.5% (Okobo 1) and 59.7% (Okobo 2) while the moisture content of Okobo 1 is 12.8 and Okobo2 is 23.1, an indication of possible coking with beneficiation. The total alkali of the coal (0.63%) is less than 2%, Silica (SiO_2) is 62.3%, potassium as K_2O, % is 0.53 Fe_2O_3 is 7.96%. The phosphorus oxide content of Okobo coal is 0.07, < 0.1% stipulated while the phosphorus content is 0.011. The Ignitability Index for Okobo1 is 42.5 and Okobo2 is 33, fuel ratio 1.1, Methane content V_{CH4} of Okobo1 and Okobo2 are respectively 10.89 (m^3/tonne) and 11.7(m^3/tonne) corresponding to good ignitability, good fuel reactivity and thus good efficiency and within limits of safe methane emission that may not produce mine fires. CO_2 Emission factor of Okobo1 at 247.8 Ibs/MMBtu and Okobo2= 239.1 Ibs/MMBtu within range prescribed as safe by Clean Air Act of 1990.

Keywords: *Ash content; Mineral matter; Coke; Bituminous coal; Destructive distillation or carbonization; Coal properties*.

1. Introduction

An extensive evaluation of coal quality is central to coal use. Whether coal is to be utilized in direct combustion for energy or power production, or in secondary synthesizing of vital chemicals, reduction of ores to their metal, generating fuels or whatsoever, the coal use is dependent on the quality of the coal. Coal has been proved to be very rewarding material aside its use as fuel/combustion [1]. Much more beneficial uses can be derived from the by-products of coal from its destructive distillation or carbonization. Coke, a proven clean burning fuel is the major by-product with diverse and innumerable uses. It is an indispensable raw material used in the steel industry to reduce and separate iron from its ore. Coke has equally found application in the production of several textile dyes, pharmaceuticals, wood preservatives, and food preservatives [1]. In-depth multidisciplinary research on coal use has established innumerable good benefits majorly from destructive distillation of coal if the undesirable effects will be eliminated before use. For a nation to sustain a vigorous iron and steel industry, it needs plentiful supplies of coking coal, iron ore, and limestone. The nations that possessed all three of these raw materials have been dominant in world affairs – nations such as Great Britain, the United States of America, Russia and Germany (National Energy Strategy, Executive Summary, 1991/1992). Nigeria has limestone in excess (in Afikpo, Ewekoro and Obajana where there has been cement factories) and much iron ore at Ajaokuta and Itakpe both in Kogi state. Nigeria has been an exception because no coking coal has been established except for the upgraded Obi-Lafia coal deposit of the Middle Benue Trough which is geologically the oldest coal deposit in Nigeria inferred to be Turonian–Coniacian in age [2]. The Obi-Lafia coal deposit has been described as coking coal by the National Steel Raw Materials Exploration Agency, NSRMEA as coking coals [3].

The justification for this project is to point attention to the probability of removing the excessive mineral matter in form of ash in Okobo coals, to make an excellent coke. This coal from Okobo (in Kogi state) can be used to reduce the iron ore mined at defunct National Iron Ore Mining Project, NIOMP at Itakpe (in same Kogi state) or combined with the Obajana limestone (also in Kogi state) where Dangote cement was sited. It will be very useful equally in defunct Ajaokuta Steel Rolling Mill, surprisingly "the largest integrated steel complex in the sub-Saharan Africa" "termed the sleeping giant" industry of Africa. There is a large demand for non-coking coals in Kogi state as well especially with the conversion of Dangote gas-fired plants to coal fired plants.

Also several setbacks have been associated with the ASTM D-720 FSI method for FSI determination and it includes proper heating rate, oxidation or weathering of the coal sample, and an excess of fine coal in the analysis sample [4-5]. A non-constant gas pressure change in a gas burner (when not frequently re-calibrated) as a source of heat for FSI will result in a wide variations in the temperature attained in a crucible, variations in the resultant size of the coke button and consequently error in FSI value [4]. Synonymously, most specified quartz crucibles employed for the test are not standard equipment. Since very small variations from standardized crucible dimension and thickness will consequent to wide variations in the resultant size of the button and the size, several errors have been identified with the laboratory test. So, prediction of FSI and several other coal characteristics from coal analysis data can be useful [4,6]. A coal characteristic is vital to be determined at initial stage. This is because when a gasifier, boiler or heating plant is designed to burn a particular type of coal, it must be continually supplied with such or similar coal else undergo an extensive redesign in order to adapt to a different type. The present work is to evaluate the basic parameter will that affect boiler/ gasifier/furnace design as well as coking tendency determinants such as FSI, fixed carbon, ash/mineral matter content, ash fusion temperature and overall ash analysis of Okobo coal using the proximate, ultimate and mineral matter analysis from experimental data obtained at a laboratory level as input variables for the multivariable regression and Adaptive Neuro Fuzzy Inference System (ANFIS) of [4] and Feed-forward Artificial Neural Network (FANN) equations of [7].

2. Experimental, material, methods and procedure

2.1. Material

2.1.1. Regional tectonism and stratigraphy of study area (Anambra basin)

The stratigraphic setting of Southeast Nigeria comprises sediments of three major sedimentary cycles. The first two cycles belong to the Pre-Santonian sediments while the third cycle belongs to Post-Santonian sediments which are found in the Anambra Basin and Afikpo Syncline; [8]. The process started during the early Cretaceous tectonism in Southern Nigeria with the rifting and separation of Africa from South America plate, opening of the South Atlantic and subsequent formation of the Benue aulacogen [9-12]. The Asu river group has been associated with sandstones of the Mamfe formations (Awe, Awi as well as shales, limestones and sandstone of the Abakaliki Formation) [8]. The Asu River Group being the oldest member sediment (Albian) followed by early Cenomanian Odukpani formation, Cenomanian-Turonian Ezeaku group, and late Turonian-Coniacian to early Santonian Awgu shales/group before the Santonian tectonism.

Prior to the Santonian, the Albian–Coniacian Abakaliki sediments were in the narrow NE-SW-trending, fault-bounded Abakaliki trough. The main depocentre at the pre-Santonian then was this Abakaliki trough which to the west exists a broad stable area (Anambra platform) and existed eastwards is also a relatively stable area (Ikpe platform) [13]. A transcurrent movement in the Santonian causes the folding and uplift of the sediments in the Abakaliki trough and a parallel down-warping of the Anambra terrain to form the Anambra basin. The tectonic movement finally culminated to the Santonian epierogenic folding and uplift of the Abakaliki into anticlinorium along a fault-bounded in NE-SW trending axis as well as corresponding subsidence of the Anambra platform to basin on the west and Afikpo to synclines on the southeast of the Anticlinorium. After the Abakiliki uplift, the Anambra basin and the Afikpo syncline became the main depocenters (depocentre shifted from the former Abakiliki trough, now Abakaliki anticlinorium to the Anambra basin on the northwest and Afikpo syncline on the southeast, [14-15] both of which accommodated sediments ranging from late Cretaceous to early Tertiary. The Nkporo is a major marine transgression that initiated deposition in the new Anambra basin, an embayment of nearly triangular shaped covering about 30,000 km^2.

The Nkporo group started in late Cretaceous within the Campanian – Maastrichtian period comprises of Nkporo Shale, its lateral equivalents which are Enugu Shale and Owelli Sandstone (including Lokoja and Lafia Sandstones) [14,16]. Overlaying these lithostratigraphic units of the Nkporo group in late Maastrichtian is the Mamu formation generally known as the Lower Coal Measure [16-18]. The Mamu formation consist of rhythmic alternation of thick carbonaceous shales and oolitic sandstones that pass upward into mainly fine grained, well sorted sandstones [19]. The Mamu formation is underlain by the Nkporo Shale and overlain by the Ajali Sandstone (formally termed the false-bedded sandstone, [16]) followed by Nsukka Formation (otherwise known as upper coal Measures, [21]. The Mamu formation succession as observed at the abandoned Onyeama coal mine in Enugu outcrop comprises succession of sandstone, siltstone, coal seam, heteroliths and shale, which has been grouped into three major facies as shale facies units, coal facies unit and sandy shale facies unit [21].

Table 1. Stratigraphic sequences in the Anambra basin (*modified after* [22])

Age (my)		Abakaliki–Anambra Basin	Afikpo Basin
30	Oligocene	Ogwashi–Asaba Formation	Ogwashi–Asaba Formation
54.9	Eocene	Ameki/Nanka Formation/Nsugbe Sandstone	Ameki Formation
65	Paleocene	Imo Formation Nsukka Formation	Imo Formation Nsukka Formation
73	Maastrichtian	Ajali Formation Mamu Formation Nkporo/Owelli Sandstone/Enugu Shale (Including Lokoja Sandstone and Lafia Sandstone)	Ajali Formation Mamu Formation Nkporo Shale/Afik-po Sandstone
83	Campanian		
	Santonian	Agjbani Sandstone/Awgu Shale	Non–deposition/erosion
87.5	Coniacian		
88.5	Turonian		Ezeaku Group (Including Amasiri Sandstone)
93	Cenomanian–Albian	Ezeaku Group	
100		Asu River Group	Asu River Group
119	Aptian Barremian Hauterivian	Unamed units	
Precambrian		Basement complex	

The study area (Okobo) is in the coal-rich Mamu formation overlain by irregular thickness of the false bedded Ajali sandstones. At some areas, the Mamu formation is exposed and other areas overlain by Ajali sandstone usually represented by a considerable thickness of red earth. The red earthy sands are formed by the weathering and ferruginization of the formation [16]. The study area (Okobo) is a newly discovered underground (1-8m overburden) non-outcropping coal extension from Okaba coal of Kogi state

2.2. Methodology

Two fresh samples from Okobo mine is collected at 85m interval separation, in air and water proof sample bags to minimize any chemical/physical changes or loss of moisture after which is quickly conveyed to the laboratory and sent to Consulting Industrial Chemists, Analysts & Samplers, INSPECTORATE M&L (PTY) LTD, Johannesburg, South Africa within 2 days of sample collection. The proximate, ultimate, ash, HGI analysis as well as calorific value determination is done with precision under the instrumental test standard Test Methods for proximate analysis of coal by Method ASTM D 2013/ D 346 and standard test method for ash analysis ASTM D3174 – 12.

Table 2. Okobo1 proximate coal analysis report

Parameter	Symbol	As received	Dry basis
Total moisture, %	M	12.8	9.2*
Volatile matter, %	VM	33.6	35.0
Ash content, %	A	16.7	17.4
Fixed carbon, %	FC	36.9	38.4
Total sulphur, %	S	1.73	1.80
GCV, kcal/kg/MJ/kg		4721/19.76	4989/20.88
GCV, Btu/lb		8493	8796
NCV, MJ/kg		19.76	20.88

**inherent moisture*

Table 3. Okobo1 ultimate coal analysis report

Parameter	Symbol	Percentage, %	Parameter	Symbol	Percentage, %
Total carbon	C	59.50	Ash	A	17.4
Hydrogen	H	4.11	Moisture	TM	9.20
Nitrogen	N	1.50	Oxygen	O	6.49
Sulphur	S	1.80			

HGI = 50, P = 0.011 F = 0.004 Cl = 0.002

Table 4. Okobo2 proximate coal analysis report

Parameter	Symbol	As received	Dry basis
Total moisture, %	M	23.10	20.4*
Volatile matter, %	VM	33.60	34.80
Ash content, %	A	8.20	8.50
Fixed carbon, %	FC	35.10	36.30
Total sulphur, %	S	0.60	0.62
GCV, kcal/kg/MJ/kg		4583/19.19	4744/19.86
GCV, Btu/lb		8246	8536
NCV, MJ/kg		18.03	19.21

**inherent moisture*

Table 5. Okobo2 ultimate coal analysis report

Parameter	Symbol	Percentage, %	Parameter	Symbol	Percentage, %
Total carbon	C	55.70	Ash	A	8.50
Hydrogen	H	3.16	Moisture	TM	20.40
Nitrogen	N	1.31	Oxygen	O	10.31
Sulphur	S	0.62			

HGI = 50, P = 0.011 F = Cl =

2.3. Procedure

Common derived parameters for Okobo coal are
1. Coal rank

It is estimated from fixed carbon, calorific value and vitrinite reflectance. According to Rice [23], he derived a formula for estimating vitrinite reflectance of coals whose volatiles is in range of 10% < VM < 40%. The vitrinite reflectance as calculated for Okobo 1 and Okobo 2 are

$R_o\%$ (Okobo 1) = -2.712 × log (VMdas) + 5.092=0.90

$R_o\%$ (Okobo 2) = -2.712 × log (VMdas) + 5.092=0.91

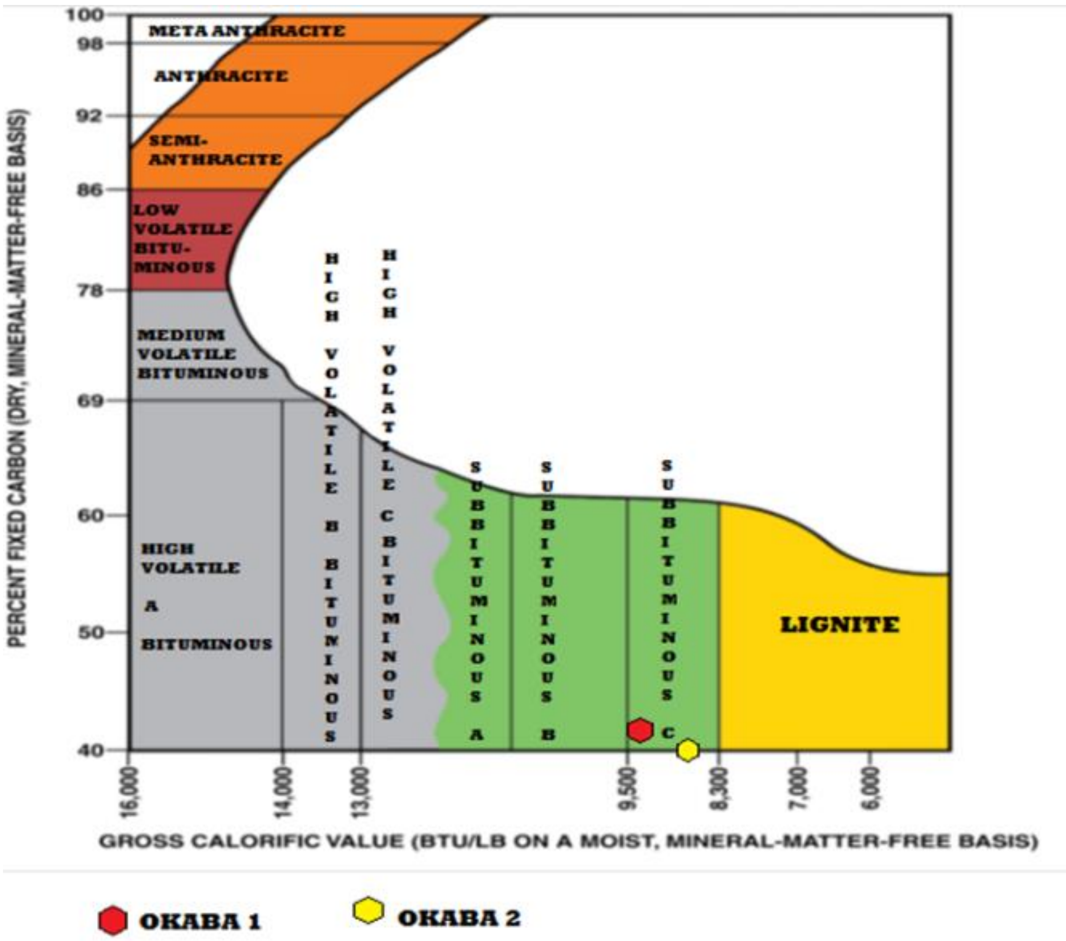

Figure 1. Classification of coals by rank modified from Trumbull (1960) after American Society for Testing and Materials (1999)

Vitrinite reflectance of 0.54-0.95 indicates coal rank of high volatile bituminous [24]. However, the moisture content of 12.8 (Okobo 1) and 23.1 (Okobo 2) do not agree with high volatile bituminous coal. Equally, the Gross Calorific Value GCV of Okobo 1 and Okobo 2 are 20.88 MJ/Kg (8796 Btu/lb) and 19.86MJ/Kg (8536 Btu/lb) respectively consistent with "Sub-bituminous grade" as illustrated in the classification of coal rank by GCV according to Trumbull (1960) in figure 1. Since their calorific values falls between 19.3 MJ/Kg (8,300 Btu/lb) to 22.1 MJ/Kg (9,500 Btu/lb), it also congruous with lowest grade of sub-bituminous coal termed the "sub-bituminous C grade" according to ASTM classification in figure 2. This is more confirmed by their fixed carbon values at 59.5 (Okobo 1) and 59.7 (Okobo 2) matching subbituminous "B" or "C" grade. The lower volatile content giving higher vitrinite reflectance maturity values is unusual and not matching the coal rank. Rather it can be assumed that the relatively high mineral matter (high ash content) suppressed the volatiles to minimal values.

Figure 2. Classification of coals according to ASTM (American Society for Testing Materials) Section 5 volume 5.06

Classification of coals by the American Society for Testing and Materials

rank and group	fixed carbon percentage (dry, mineral-matter-free basis)		volatile matter percentage (dry, mineral-matter-free basis)		caloric value (moist, mineral-matter-free basis)* British thermal units per pound		megajoules per kilogram		agglomerating character
	equal to or greater than	less than	greater than	equal to or less than	equal to or greater than	less than	equal to or greater than	less than	
Anthracitic									
meta-anthracite	98	•••	•••	2	•••	•••	•••	•••	nonagglomerating
anthracite	92	98	2	8	•••	•••	•••	•••	
semianthracite †	86	92	8	14	•••	•••	•••	•••	
Bituminous									
low-volatile bituminous	78	86	14	22	•••	•••	•••	•••	commonly agglomerating §
medium-volatile bituminous	69	78	22	31	•••	•••	•••	•••	
high-volatile A bituminous	•••	69	31	•••	14,000 ‡	•••	32.6	•••	
high-volatile B bituminous	•••	•••	•••	•••	13,000 ‡	14,000	30.2	32.6	
high-volatile C bituminous	•••	•••	•••	•••	11,500	13,000	26.7	30.2	
					10,500	11,500	24.4	26.7	agglomerating
Subbituminous									
subbituminous A	•••	•••	•••	•••	10,500	11,500	24.4	26.7	nonagglomerating
subbituminous B	•••	•••	•••	•••	9,500	10,500	22.1	24.4	
subbituminous C	•••	•••	•••	•••	8,300	9,500	19.3	22.1	
Lignitic									
lignite A	•••	•••	•••	•••	6,300	8,300	14.7	19.3	
lignite B	•••	•••	•••	•••	•••	6,300	•••	14.7	

* Moist coal contains natural inherent moisture but does not include visible water on the surface. † If agglomerating, classify in low-volatile group of the bituminous rank. ‡Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis are classified by fixed carbon, regardless of calorific value. §There may be nonagglomerating varieties in these groups of the bituminous rank; there are also notable exceptions in the high-volatile C bituminous group.

Source: *2000 Annual Book of ASTM Standards*, section 5, volume 5.06.

However, the value of vitrinite reflectance (R_o) in coking coal has been set in the range of 0.85-1.35%, which is just perfect for Okobo coal to coke if the mineral mater is reduced. Soft coking coal has a lower value while hard coking coal has higher value. Okobo coal may be classified in accordance with soft coking coals

2. Free swelling index FSI

This is a unique caking property of coals of the bituminous group which is an essential factor for coals required for coking. Knowledge of the swelling property of a coal can be used to predict or explain the behaviour of the coal during carbonisation or in other processes such as gasification, liquefaction, and combustion. The free swelling index is a measure of the volume increase of a coal when heated under specific conditions and is reported in numbers from 0 to 9, a non-swelling sample is given 0 with higher values considered superior in coking [5, 26-27]. The free swelling index (FSI) test entails heating a standard powder of the coal in a crucible and comparing the result with a standard profile (0-9). As many kinds of caking/swelling (mostly bituminous) coals are heated in an inert atmosphere, it passes through a region where it becomes very plastic, softens, swells and then re solidifies to form a plastic mass. The escaping volatiles pass through this plastic material which makes the residue re-solidifies to a carbon-rich solid upon further heating. Coals that pass through a plastic stage on heating are called caking coals. A caking coal which will re-solidify on heating to form/yield a satisfactory a hard, very strong, carbon-rich porous mass suitable for use as a reducing agent in the metallurgical industry (coke) is termed "coking" coals. Confusingly, the words caking and coking are used interchangeably but they are not synonymous. All coking coals are necessarily caking, but not all caking coals will yield/form coking coals. The caking behaviour is critical to coke making; successful coke must be strong and not powdery. There are series of other derived test that may be used to classify the caking properties of coals, which are the Roga test and Gray-King index. Gray-King index is essentially the same except the residue is compared with a number of previously made standard cakes. The minimum value of the Gray King test in coking coals is normally G5.

Table 6. The correlation between Swelling index and Gray –King value

Gray king	A	B	C	D	E	F	G	G1	G2	G3	G4	G5	G6	G7	G8	G9
Swelling Index	1	1	1.5	2	3	3	4	5	5	6	6	7	7	8	9	9

From feed-forward Artificial Neural Network (FANN) equations of (Chelgani *et al.* [24] modified by Oni [25]).

FSI = 33.379 – 0.779**O** – 0.23**C** – 1.787**N** - 0.437(**H_{ult}** + 0.1119**M**) – 0.318**A** – 0.362**S**.

where A = Ash content; O = oxygen; C = carbon; N = nitrogen; M = moisture; H_{ult} = hydrogen on dry basis from ultimate analysis; Sp (total sulphur) = pyritic sulphur and So = organic sulphur.

The Okobo1 FSI is 3.7 while Okobo2 FSI is 6.8

The swelling index of coals is a function of the reactive components in a coal to fuse with the inert material during destructive distillation to make a strong coke. The inorganic components of the coal remain in the coke. This inorganic component (mineral matter) is proxied by the percentage ash, thus implying the ash content (mineral matter) of the coal will have a negative correlation with coking tendencies and thus may reduce coke quality [28-29]. Consequently, the caking tendency (FSI) of coal decreases with increasing of mineral matter, most especially calcium-containing substances that reduce coking properties by deteriorating thermoplastic properties hence decrease their swelling index [30].

This is as observed in the Okobo1 coal with 33.6% volatile matter but relatively poor FSI (3.7 FSI) than expected; as compared to normal Okobo2 FSI of 6.8 with same volatile matter. The excessive ash content of Okobo1 (16.7), relative to lesser volatile of Okobo2 (8.2) is responsible for the low FSI. According to Blackmore who rated metallurgical coal with good swelling abilities to be consistent with 33-36% volatile matter, the coal would have made an excellent coke for steel industry especially if the mineral matter can be removed. Low rank coals (very low carbon content and very high volatile matter) such as peat/lignite or high rank coals such as anthracite (very high carbon content and very low volatile matter) lack melting and fusing abilities and show no swelling value [5,31]. The Free Swelling Index of bituminous coal increases as the rank increases, peaking in medium volatile bituminous rank range [4,27].

Considering table 7, which compares Okobo1 coal with some coal samples from West Virginia in USA [32] it is very glaring how increase ash content, > or = 11.4 can drastically reduce coal's FSI. If volatile matter is the paramount variable for FSI reduction, JHM-54 or JHM-57 (max or min) would have the least of the FSI from Virginia coals. If it's moisture, VAT-I or JHM-54 (max or min) would equally have least FSI from Virginia coals. It will be observed that the excessive ash content of VAT-6 is responsible for the FSI dropping drastically to 1.5 despite its close value of volatile matter to VAT-3 (a difference of 2). Even when the ash content is as high as 8.9 in VAT-3, the FSI is still high (8.0). Similarly the same excessive ash content of Okobo1 (16.7) is responsible for the FSI dropping drastically to 3.7 despite same volatile matter content, even with as much ash content as 8.2 in Okobo2 (FSI 6.8). Conclusions can be made that an ash content greater than or equal to 11.4 will drastically reduce the FSI of any coal to poor FSI grade (0-2). Trent [32], who worked on chemical properties of the 12 coal samples of Pocahontas field, West Virginia equally suggested "probably because they contain somewhat higher percentages of ash". The excessive percentage of ash is confirmed and as same factor reducing the FSI of Okobo 1 coals despite good volatility grade (33-36) as explained by Blackmore (1985).

Table 7. Comparing of volatile matter, ash/mineral matter, moisture and FSI of Okobo Coal with some coal samples from the Pocahontas Field, West Virginia USA after Trent *et al.* [32]

Sample	Volatile matter	Ash	Moisture	FSI
VAT-I, (wl87040)	26.2	2.1	9.4	7.0
JHM-54, (d170150)	27.8	3.9	0.9	7.0
VAT-3, (wl87042J)	25.1	8.9	3.0	8.0
VAT-6, (w191522)	22.5	11.4	6.2	1.5
JHM-57 (d170153)	20.8	7.6	1.9	9.0
Okobo coal 1	33.6	16.7	12.8	3.7
Okobo coal 2	33.6	8.2	23.1	6.8

3. Fluidity

Fluidity is a function of the quantity of organic sulphur content in coal. As explained by Clark *et al.* [33] and Yarzab *et al.* [34], similar maceral composition and rank coals but with greater organic sulphur content show a greater tendency to form coke. The recovery of sulphur contents from coal (to be used as a good raw material in sulphur production) had turned out to be an exciting area and on trial for research related to coal quality. In metallurgical coal, organic sulphur alone is to be limited to 0.6% maximum in as dried condition. According to Schweinfurth [1], river-borne sediments tend to be richer in some elements, such as iron, whereas ocean-borne sediments tend to be richer in other elements, such as sulphur. It follows that ocean borne coal tend to have higher fluidity and higher coking abilities. Coking coals have dialation value of 55% minimum and fluidity of 600 ddpm minimum [12]. Higher fluidity value gives better flow-ability in the coking ovens. Weathering and oxidation may also reduce fluidity. According to Nelson [35], exposure of bituminous and sub-bituminous coals to oxygen at ambient temperatures can result in a very rapid reduction in the fluidity that is exhibited when they are heated and a significant narrowing of the coals plastic temperature range. According to Williams [36], the acceptable level for total sulphur in coking coal blends for furnace coke production should be less than 1.60%. It implies Okobo2 with total sulphur content of (0.62 % sulphur) is more suitable than Okobo1 (1.80% sulphur). For Okobo1 to be used as coking coal, the sulphur content must be reduced. Sulphur and iron combined as pyrite (FeS) has a moderate effect on fluidity while Fe_2O_3, has a major effect. Obviously if pyrite oxidizes or magnetite is introduced by heavy cleaning, fluidity will be affected [51].

4. Hardgroove grindability index, HGI

HGI = 67 - 3.16 O- 3.02 N- 0.23 H -2.37 C - 0.00585 GCV (Btu/Ib) - 1.53 S + 3 FC – 1A + 3 VM + 1.13M=60

The HGI from experimental analysis for both Okobo 1 and Okobo2 is 50. This implies a relatively hard coal, which may not be easy to grind. The high mineral matter content of the coal may be inferred as the factor reducing the HGI (increasing hardness) to bituminous anthracite range of 50

5. Ash analysis

Ash analysis is used to characterize the slagging and fouling potential of coal in the boiler. The ash residue of coals follows no precise pattern, but appears to depend in part on the local geology of the particular coal seam. The presence of ash/minerals in coal is undesirable but can be of advantage when removed and used as a raw material elsewhere. The fusion temperature/melting point of the ash are major determinant for designing furnaces and boilers. When the ash fusion temperature is low, then the molten ash is collected at the bottom of the furnace as bottom ash, in a simple boiler design [1]. Contrarily when the fusion temperature is relatively high, there is a fly ash (the part of the ash that does not melt easily) that will be blown through the furnace or boiler with the flue gas to be collected in giant filter bags or electrostatic precipitators, at the bottom of the flue stack. This makes the boiler required a different and more complex design [1]. Coal's fly-ash is very useful in cement industry used mainly as an additive in concrete. It may be also used as structural fill, as road-base material, waste stabilization, grit for snow and ice control, roofing granules and small amounts being used as soil pH control for agricultural applications. The mineral content of coal affects the type of ash that will be produced on combustion. Coals very high in iron-bearing minerals like pyrite/siderite, will have low ash fusion temperatures and high slagging tendencies while coals relatively rich in aluminium-bearing minerals such as kaolinite or illite will have high fusion temperatures [1]. The Okobo coal have relatively high Fe_2O_3 of 7.96% as compared to Indian coals and as reported by Garba *et al.* [37]. Major oxides from ash analysis (Table 8).

Alkalis (Na_2O, K_2O): The alkalis value of the coking coals is to be controlled and it is to be limited to 2% maximum (sum for both) in coal ash. High alkali content is not desirable in blast furnace. It also affects the lining of the blast furnace adversely [12]. The total alkalis of Okobo coal (0.63%) is less than 2%

Iron Oxide, Fe2O_3: The content of iron is another important parameter in determining the ash slagging potential. High iron content (in form of pyrite) usually lowers the melting point of slag, which results in a high slagging potential according to Frandsen *et al.* [38]. The Iron content of 7.96% in the studied coal will contribute a raise in the coal slagging tendencies.

Silica (SiO_2) and Alumina (Al_2O_3): The silica content of the Okobo coal from analysis of ash results in table 8 is 62.3% (between 55-65%) matching Indian coals, the alumina is assuming 25%, Na_2O is 0.07% (lower than Indian coal used as reference (0.1-0.3), potassium as K_2O, % is 0.53 congruous to Indian coal (between 0.7 - 1.5) and Fe_2O_3 is 7.96% greater than 6% as compared to Indian coals in figure 3. All this is an indication of high-ash coals as compared and interpreted with ash characteristics in coals as shown in figure 3. The coals will subsequently possess high resistivity because the high ash content is coupled with much lower Na_2O and high (Silica + Alumina) between 80 - 95 % matching Indian coals of figure 5. Silicon actually strengthens the ferrite ($ZnFe_2O_3$, produced in ash during deformation) by dissolving in it, and at the same time causes brittleness by causing the cementite (Fe_3C, produce on ash fusing) to break down to graphite. When, however, silicon is present in amounts in excess of that necessary to completely decompose all the cementite, it will cause hardness and brittleness to increase. Considering the desired and unwanted effects silica in coke can have on metals, the optimum value as (observed in Okobo coals) is advised for use in coking coals.

Phosphorus oxide P_2O_5/Phosphorus: High-phosphorus coals have great fluidity. High phosphorus contents should be avoided in coal since it enhances brittleness and lowers strength considerably when in coke and is used with metal. Its presence tends to promote increased shrinkage. Phosphorus oxide content of metallurgical coal is to be limited to 0.1% (maximum on 'air dried or dry basis) condition as excess phosphorus will be absorbed into the hot metal in blast furnace creating difficulties in de-phosphorization during steelmaking. The phosphorus oxide content of Okobo coal is 0.07, < 0.1% while the phosphorus content is 0.011 in accordance with safe limit of Gray *et al.* [39] (1978) as < 0.03% and Bustin *et al.* [40] of < 0.012%. Phosphorus content of Okobo coals within coking limit.

Sulphur: Organic sulphur levels in coking coals are to be limited to 0.6% maximum in as dried condition. Higher sulphur results into increase in the sulphur content of hot metal in the furnace. Pyritic sulphur has adverse effect on the quality of iron but this type of inorganic sulphur in form of pyrite is easily oxidized and removed by the limestone washing. The organic sulphur is bound to the crystal lattice in coals and not removed by washing. The effect of sulphur (organic) has the opposite effect to silica as it tends to stabilise cementite, inhibits decomposition of carbon in ash and increase cementation until optimum value of 0.6 is reached.

Manganese oxide (Mn): The effect of sulphur may be controlled by the amount of manganese present. Manganese combines with sulphur to form manganese sulphide, MnS, which, unlike iron(II) sulphide, is insoluble in the molten iron and floats to the top to join the slag. The manganese oxide content is 0.07 which is optimum for coke production in coals

Ash fusion temperature (AFT): Ash Fusion Temperature in coking coals is to be higher than coking temperature. AFT value in the coking coals should be 1450ºC minimum. Low ash-fusion coal are coal that when burned typically produces ash that has a melting point below 2,450°F (1344ºC). The ash fusion temperature of Okobo coal is 1,400ºC (table 8).

The high ash resistivity may escalate to high flue gas temperatures and high particulate emissions reducing ESP efficiency. Apart from physical effects of high ash coals such as slagging and fouling on the reactor walls and heat transfer tubes, some studies reported in the literature show that the nature and amount of ash does affect some of the combustion processes. Saxena and Rehmat [41] studied theoretically the effect of basic oxide and ash content on coal combustion in a fluidized bed. They showed that the burning time of the coal would increase due to the presence of the ash layer. The combustion rate would be reduced thereby reducing the combustion efficiency. The presence of excess ash and the consequent decrease in oxygen diffusion rate (due to a thicker ash layer) may lead to substantial reduction in char combustion as this is the governing rate for combustion and significantly affecting the overall combustion parameters. As observed in Indian coals, the high percentage of ash has always necessitates higher amount of primary amount of air required for combustion. Liu *et al.* [42] reported that the evolution of char reactivity can be correlated with incipient melting of mineral matter. The structural alteration of melted minerals has a direct influence on carbon conversion. When minerals melt, they cover the surface of the chars thereby hindering carbon conversion.

Table 8. Analysis of Okobo Ash using XRF (X-Ray Fluorescence)

Analysis of the ash	value	Analysis of the ash	value
Loss of ignition (1000°C), %wt.	1.94	Calcium as CaO, %	1.54
Total silica as SiO2	62.3	Magnesium as MgO, %	1.18
Aluminium as Al_2O_3, %	21.7	Sodium as Na_2O, %	0.10
Total Iron as Fe_2O_3, %	7.96	Potassium as K_2O, %	0.53
Titanium as TiO_2, %	1.99	Manganese as MnO, %	0.07
Phosphorus as P_2O_5, %	0.07	Sulphur as SO_3 %	1.42

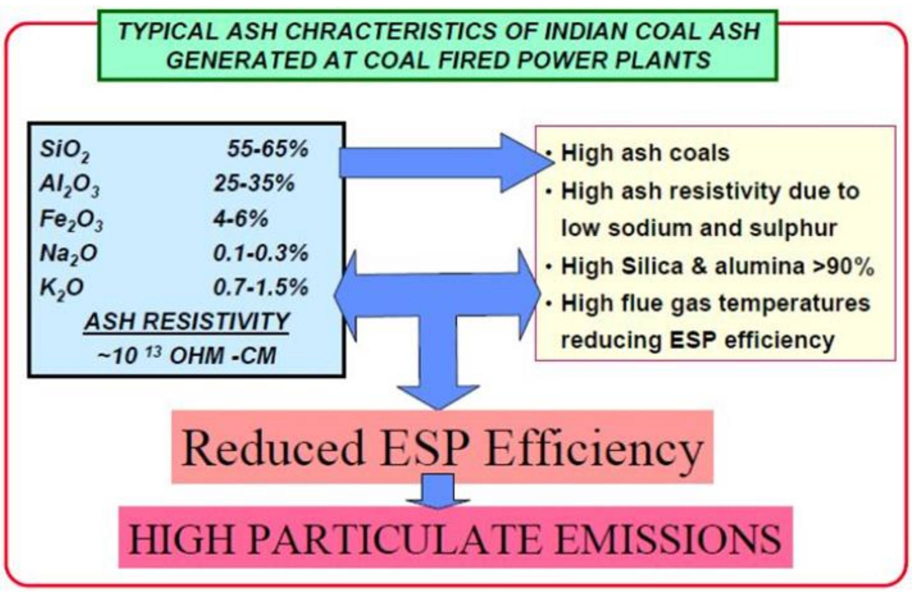

Figure 3. Ash characteristics from Indian coals as a function of basic oxide observed at coal fired stations. Source [27]

6. Slagging Index

The performance of the coal samples may be described by some indices like basic to acidic oxide (B/A), silica ratio, iron index and sulphur/iron slagging index [37]. Specifically, it is believed that the basic to acidic oxides ratio (B/A) of the coals determines the melting behaviour of coal ash systems and may be used to describe the effect of ash content prior to combustion [43]. A decrease in the B/A of the coal will raise its fusibility, leads into higher ash fusion temperatures and hence decreases its slagging potential. Deductions can therefore be made that low basic to acidic (B/A) ratio will reduced slagging properties. Lawrence *et al.* [43] stated that extremely good coals have B/A ≤ 0.11. In high sulphur coals such as observed in this study, it has been established that there is strong correlation between (B/A) ratio and sulphur content. The sulphur slagging index is a more accurate indices defined as the product of (B/A) and sulphur in (pyrite in form of FeS_2). These indices have been established on coal ash properties and have been used to describe Nigerian coals [37].

$B/A = (Fe_2O_3+CaO+MgO+Na_2O+K_2O)/(SiO_2+Al_2O_3+TiO_2)$

$Sr = (100*SiO_2)/(SiO_2+ Fe_2O_3+CaO+MgO)$; $Rs = B/(A*S)$

where B/A is basic to acidic oxide; Sr is silica ratio and Rs is sulphur index. Fe index is the percentage iron (3^+) oxide as obtained from the analysis of ash. Garba *et al.* [37] indicate the various range of slagging index of coal and equivalent interpretation in table 9

Table 9. Summary of coal slagging indices after Garba *et al.* [37]

Ratio	Low	Medium	High	Severe
B/A	< 0.50	0.50 - < 1.00	1.00 - <1.75	> 1.75
Sr	72 – 80	65 – 72	50 – 65	-
Rs	< 0.60	0.60–2.0	2.00–2.60	> 2.60
Fe index	< 6 %	6–7 %	> 7 %	-

From the ash analysis, the values obtained for basic to acidic oxide (B/A), silica ratio (Sr), and sulphur index (Rs) for Okobo coal are: 0.13 (low, less than 0.50), 85 (very low, greater than 80) and 0.23 (low, less than 0.6) respectively as compared to standardized range of value for coal slagging indices after Garba *et al*. [37]. The values match minimal slagging character in coals.

7. Fuel ratio

FR = Fixed Carbon / Volatile Matter= 1.1.

Fuel Ratio is commonly used to evaluate the combustibility of coals. When the Fuel ratio percentage of a coal is high, the unburnt in combustion will increase which leads to poor boiler efficiency. Fuel ratio also gives a good indication of the fuel reactivity. The Okobo fuel ratio is low indicative of little or no unburns, good fuel reactivity and thus good efficiency in boilers.

8. Ignitability Index [44]

Ignitability index (II) =
(coal calorific value in kcal/kg – 81*FC in%)/(volatile matter in % + moisture in %)

If the ignitability index is 35 or considerably less, measures for ignitability improvement should be taken. The II for Okobo1 is 42.5 and Okobo2 is 33. This implies that ignitability measures may need to be taken for combustion of Okobo2 coals.

9. Methane content

Methane is always present in coal and may constitute serious safety hazard in coal mining. It is a normal by-product of the coal-forming process. At a given temperature and pressure, higher rank coals will have more volumes of methane than lower rank coal [45]. Although much of the gas formed during coalification migrates away from the coal, a significant portion is still retained in the coal [45]. The estimated methane content of a coal can has been utilized in resource evaluation and mine planning. In mining, the amount and rate of methane released depend on several factors such as nature of the coal, age of the mine, production rate, underground/open cast, permeability of the coal etc. Estimation of coal methane content can be used to predict the gassiness of a mine and possibility of mine fires.

$V_{CH4} = -325.6 \times \log(VM_{daf}/37.8)$ (m^3/tonne)

V_{CH4} Okobo1 = $-325.6 \times \log$-(0.92593) (m^3/tonne) V_{CH4} Okobo1 = 10.89 (m^3/tonne)

V_{CH4} Okobo2 = $-325.6 \times \log$(-0.92063) (m3/tonne) V_{CH4} Okobo2 = 11.7(m3/tonne)

Studies of the major coal-bearing basins in the world suggest that more than 50% of the estimated in situ coal bedded methane CBM resources is found in coals at depths below 1500m [46]. We can draw a strong suggestion that coals beneath less than 10m overburden mined as open cast may not constitute fire hazards.

10. CO_2 Emission factor

Ibs of CO2/ MMBtu (gross) = % Carbon/GCV X 36,640 in Ibs/MMBtu
Ibs of CO2/ MMBtu (gross) Okobo1= 247.8 Ibs/MMBtu
Ibs of CO2/ MMBtu (gross) Okobo2= 239.1 Ibs/MMBtu

3. Results and discussion

Okobo coals are "sub-bituminous C grade" according to ASTM classification. The volatile matter range is perfect for coking coals as well as the FSI values, if the mineral matter will be reduced. For Okobo coal to be used as coking coal, the sulphur content should be slightly reduced by washing with limestone. With low HGI of 50, the coal is strong and will be very hard to grind. High ash content in coal is undesirable as its lower the ash fusion temperature and reduces fusibility resulting in high slag volume and low blast furnace efficiency. However from basic ash analysis, the most of the major oxide in ash are within coking limits, confirmed by high possibility of low slagging tendency of the coal in boilers. As observed from Ignitability Index, the coal will ignite easily with minimal effort. The methane quantity emitted by per tonne of Okobo coals is negligible and may not amount to mine fires in open cast mines. However, if the gas is constrained in an enclose without vents; and underground mining system is used, it may accumulate to poise fire hazards. The CO_2 emission factor is within the internationally accepted value required by the U.S. Environmental Protection Agency (USEPA) [47], and federal law of the 1990 Clean Air Act [49]. According to McCabe, [48] low ash coals originate from raised or domed-shaped mires while higher ash coals originate from low-lying or floating mires.

Conclusion

Okobo coals posses optimum properties that is required for coking except for high moisture and ash content which could be corrected by beneficiation. Okobo coal is inferred to form from low-lying mires because of relatively high ash content. High-ash Nigerian coal is rich in resins and waxes and is of potential interest as a source of chemicals and also for utilization in the manufacture of plastics [50]. Sub-bituminous coals in the Lower and Upper Benue Trough are best for chemical production, the coals can be used for the production of benzene, chloroform and coal tar [3].It will be assumed that Okobo coals are waxy, resinous and can be useful in chemicals and plastic production. The coal will have good fuel reactivity; minimal or no combustible unburns when burnt in boilers.

Acknowledgements

I am appreciative of Mr Nicholas Nelson, executive Chairman of EMEMINE Nig *Ltd*., a subsidiary Equatorial Mining and Exploration plc. I will like to equally acknowledge Mr Robert Maduakor for his immense advice and guidance. Special appreciation will go to my queen, Mrs Diamond Temitope Oni for her support and understanding.

References

[1] Schweinfurth SP. An introduction to coal quality. in Pierce BS and Dennen KO. eds., The National Coal Resource Assessment Overview: U.S. Geological Survey professional Paper 1625–F, Chapter C, The Chemistry and Technology of Coal. CRC Press, Berkeley California, pp. 217–229.

[2] Obaje NG, Hamza H. Liquid hydrocarbon source-rock potential of mid-Cretaceous coals and coal measures in the Middle Benue Trough of Nigeria. Int Journal Earth Sciences 2000; 89(1):130–139.

[3] Fatoye FB and Gideon YB. Appraisal of the Economic Geology of Nigerian Coal Resources. Journal of Environment and Earth Science, 2013; 3(11): 25-31.

[4] Khorami MTi, Chelgani SCh, Hower JC, Jorjani E. Studies of relationships between Free Swelling Index (FSI) and coal quality by regression and Adaptive Neuro Fuzzy Inference System. International Journal of Coal Geology, 2011; 85(1): 65–71.

[5] Speight GJ. Handbook of Coal Analysis. Wiley-Interscience, Chichester, West Sussex, England, 2005.pp. 141–149.

[6] Swartzman E, Behnke GC. Using Electric Furnaces and Heaters to Determine the Free-Swelling Index of Coal The American Institute of Mining, Metallurgical, and Petroleum Engineers. Publication Date: Jan 1, 1952.

[7] Chelgani SCh, Hower JC, Hart B. Estimation of free-swelling index based on coal analysis using multivariable regression and artificial neural network. Fuel Processing Technology, 2011; 92 (3): 349–355.

[8] Nwajde CS, Reijers TJA. 1996c. Anambra Basin Excursion Guide. In Reijers, TJA. (Ed.), Selected Chapters on Geology pp.149-197.
Nwajide CS and Reijers TJA. 1996b. Geology of the Southern Anambra Basin. In Reijers, TJA., (Ed.), Selected Chapters on Geology. pp.131-148.

[9] Burke KC, Dessauvagie TFJ and Whiteman AJ. 1970. Geological history of the Benue Valley and Adjacent areas. In Dessavaugie TFJ and Whiteman AJ. (Eds.), African Geology: University of Ibadan Press, pp.181-186.

[10] Hoque M. Significance of Textural and Petrographic attributes of several Cretaceous Sandstones, Southern Nigeria. Journal of Geology Society, India. 1976 17: 514-521.

[11] Olade MA Evolution of Nigeria is Benue trough (Aulacogen) A tectonic, Geological magazine, 1975; 112(6): 575-583.

[12] www.coalsalesonline.com

[13] Murat RC. Stratigraphy and paleogeography of the Cretaceous and Lower Tertiary in Southern Nigeria. In T.F. J. Dessauvigie and A.J. Whiteman eds. African Geology, University of Ibadan Press, 1972. pp.635 - 648.

[14] Kogbe CA. The Cretaceous and Paleogene Sediments of Southern Nigeria. Geology of Nigeria 2nd Edition. Rock View (Nig) Ltd, 1989: 325-334.

[15] Nwachukwu SO. The Tectonic Evolution of the Southern Portion of the Benue Trough, Nigeria. Geological Magazine, 1972; 109: 411-419.

[16] Reyment RA. Aspect of the Geology of Nigeria. Ibadan University Press, 1695: 145p.

[17] Simpson A. The geology of parts of Onitsha, Owerri and Benue Provinces: the Nigerian Coalfield. Geological Survey of Nigeria Bulletin, 1954; 24: 1 -40.

[18] Simpson A. 1955. The Nigerian Coalfield. The geology of parts of Owerri and Benue provinces. Bull. Geol. Surv. Nigeria, 1955; 24: 5-24.

[19] Obi CG. Depositional Model for the Campanian-Maastrichtian Succession, Anambra Basin, Southeastern Nigeria. Ph.D Thesis, 2000, University of Nigeria, Nsukka, Nigeria.

[20] Tatham RH. Seismic Applications in the Exploration for and Development and Production of Unconventional Hydrocarbon Resources. (An overview). (2012), Dept of Geological Sciences, Jackson School of Geoscience, Univ. of Texas at Austin

[21] Adeigbe OC and Salufu A E., Geology and depositional environment of Campano-maastrichtian sediments in the Anambra basin, Southeastern nigeria: evidence from field relationship And sedimentological study. Earth sciences research journal. Earth Sci. Res. J., 2009; 13(2): 148-166.

[22] Nwajide CS. 2005. Anambra Basin of Nigeria: Synoptic Basin Analysis as a Basis for Evaluating its Hydrocarbon Prospectivity. Hydrocarbon Potentials of the Anambra Basin. PTDF Chair, pp: 2-46.

[23] Rice DD. Composition and origins of coalbed gas. In B. E. Law, & D. D. Rice (Eds.), Studies in Geology: Vol. 38. Hydrocarbons from Coal (1993) (pp. 159 - 184). American Association of Petroleum Geologist.

[24] Chelgani SCh, Hower JC. Jorjani E, Mesroghli Sh. Bagherieh AH. Prediction of coal grindability based on petrography, proximate and ultimate analysis using multiple regression and artificial neural network models. Fuel processing technology, 2008; 89(1): 13–20.

[24] Taylor GH, Teichmüller M, Davis A, Diessel CFK, Littke R and Robert P., Organic Petrology: Gerbrüder Borntraeger, 1998, Berlin, 704 p. International Journal of Earth Sciences.

[25] Oni OS, Olugbenga EA. Estimation and assessment of free swelling index and some petrographic properties from chemical analysis of coals across river Niger. Pet Coal 2017; 59(3): 273-287.

[26] Speight JG. Handbook of Coal Analysis, 2005, John Wiley & Sons, Inc.,pp. 145–148.

[27] http://www.eecpowerindia.com

[28] Ryan B, Leeder R, Price JT, Gransden JF. The effect of coal preparation on the quality of clean coal and coke, Geological Fieldwork, 1999: 247–275.

[29] Toroglu I. The effects of ash and maceral composition of Azdavay and Kurucasile (Turkey) coals on coking properties, Energy Sources, Part A, 2006;28: 263–279.

[30] Khan MR, Jenkins RG. Influence of added calcium compounds on swelling, plastic, and pyrolysis behaviour of coal devolatilized at elevated pressures. Fuel, 1986; 65(9): 1203-1208.

[31] Ghosh A, Chatterjee A. Ironmaking and Steelmaking: Theory and Practice. Prentice-Hall of India Private Limited, New Delhi, 2008, pp. 141–143.
[32] Trent VA, Medlin JH, Coleman SL and Stanton RW. Chemical analyses and physical properties of 12 coal samples from the Pocahontas field, Tazewell County, Virginia, and McDowell County, West Virginia.1982; (Geological Survey bulletin ; 1528) Bibliography: p. Supt. of Docs. no.: I 19.3:1528
[33] Wrigley EA. The Supply of Raw Materials in the Industrial revolution, Economic History Review, 1962; 15(1): 1-16.
[34] Mahajan OP, Yarzab R, Walker PL.Jr. Unification of coal-char gasification reaction mechanisms. Fuel, 1978; 57(10): 643-646.
[35] Nelson CR. Coal weathering: Chemical processes and pathways. Chemistry of coal weathering. In: Coal Science and Technology 14. Charles R Nelson (Ed.), Elsevier, Amsterdam, 1989: 1 – 32.
[36] Williams K. Primary Coal-Analytical Needs. J. Pure and Applied Chemistry, 1977; 49: 1465-1473.
[37] Garba MU, Musa U, Azare P, Ishaq K, Onoduku S and Mohammad YS. Characterization and ash chemistry of selected Nigerian coals For solid fuel combustion. Pet Coal, 2016; 58(6): 646-654.
[38] Laursen K, Frandsen F and Larsen OH. Ash deposition trials at three power stations in Denmark. Energy and Fuels 1998; 12: 429–42.
[39] Gray RT, Goscinsky JS and Shoeberger RW. Selection of coals for coke making. Paper presented at joint Conference for Iron and Steel Society (ISE) and Society for Mineral Engineering (AIME). Pittsburgh, Pennsylvania, October 3, 1978.
[40] Bustin RM, Cameron AR, Greve DA and Kalkreuth WD. 1985. Coal Petrology. Its principles, methods and applications. Geological Association Canada. Short Course Notes. vol. 3, 230pp.
[41] Saxena S, Rehmat A. A mathematical model for char combustion in a fluidized bed, in: Proceedings of the 6th International Conference on Fluidized Bed Combustion, 1980; 3: 1138–1149.
[42] Liu H, Luo C, Kato S, Uemiya S, Kaneko M and Toshinori Kojima. Kinetics of CO2/Char gasification at elevated temperatures: Part I Experimental results Fuel Processing Technology, 2006; 87: 775-781.
[43] Lawrence A, Kumar R, Nandakumar K and Narayanan K. A novel tool for assessing slagging propensity of coals in pf boiler. Fuel, 2008; 87:946–50.
[44] Asthana AK. India Coal Blending and its effects on boiler performance. http://knowledgeplatform.in/wp-content/uploads/2015/11/Coal-Blending-and-its-effects-on-Boiler-Performance.pdf.
[45] Kim AG. Estimating methane content of bituminous coalbeds from adsorption data / by Ann G. Kim. [Washington]: U.S. Dept. of the Interior, Bureau of Mines, 1977.
[46] Larry T. Coal Geology, Second Edition. Dargo Associates Ltd. A John Wiley & Sons, Ltd., Publication. 2013.
[47] Energy Information Administration, 2000. Annual energy review 1999: Washington, D.C., U.S. Department of Energy, Office of Energy Markets and End Use, DOE/EIA-0384(99), 374 p.
[48] McCabe PJ. 1991, Geology of coal; Environments of deposition, in Gluskoter, H.J., Rice D.D., and Taylor, R.B., eds., Economic Geology, U.S.: Boulder, CO, Geological Society of America, The Geology of North America, v. P-2, p. 469-482.
[49] U.S. Department of Energy, 2000, Clean coal technology—Clean coal technology demonstration program, program update as of September 1999: Washington, D.C., Assistant Secretary for Fossil Energy, DOE/FE-0415, 304 p.
[50] Fatoye FB, Gideon YB. Appraisal of the Economic Geology of Nigerian Coal Resources. Journal of Environment and Earth Science2013; 3(11): 25-31.
[51] Price JT, Gmnsden JF, Khan MA and Ryan BD. Effect of Selected Minerals on High Temperature Properties of Coke. Abstract. Ironmaking Proceedings, Iron and Steel Society/American Institute of Miig, Metallurgical and Petroleum Engineers, 1992

To whom correspondence should be addressed: talk2nicesam@hotmail.com