

# Ultimate Analysis of some Nigerian coal: Ranking and Suitable Application

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**Abstract**— Ultimate analysis was carried out to determine the elemental composition of some Nigerian coal samples viz: Garin Maiganga (GMGA3 – top layer and GMGB – base layer), Chikila (CHK), Lamza (LMZ) and Afuzie (AFZ); in order to ascertain their ranks for appropriate utilization. Carbon, hydrogen and oxygen were theoretically (numerically) determined and the results fall between 78.26 – 83.37 %, 5.73 – 6.00 % and 7.98 – 12.55 % respectively. Sulphur and nitrogen were determined conventionally by Eschka and Kjeldah method respectively; and the sulphur content fall between 0.68 – 0.87 %, while that of nitrogen was between 1.98 – 2.54 %. Generally, the coal samples had low elemental contents (with the exception of carbon), which implies low mineral compounds which are undesirable because of their adverse effect on operational system, environment, products and ultimate users, and so they are safe for various application taking advantage of their high carbon contents. The investigation of the coal samples revealed that all are of sub-bituminous rank and are of good grade (low sulphur content) that can be utilized for gasification, liquefaction, power generation and coking technology – both conventional and formed coke making, for domestic and industrial fuel making.

**Index Terms**— ultimate analysis, rank, sub-bituminous, liquefaction, gasification, power generation, coke.

## I. INTRODUCTION

### 1.1 Background Information

Coal, a solid fuel is composed primarily of carbon along with variable quantities of other elements, chiefly hydrogen, sulphur, oxygen, nitrogen as well as trace amounts of other elements including mineral matter [1]. Coal forms when dead plant matter is converted into peat, which in turn is converted into lignite, then sub-bituminous coal, bituminous coal, and lastly anthracite. This involves biological and geological processes that take place over a long period of time. Heat and pressure acts on it to finally convert it into coal. It is literally known as a mineral substance of vegetable origin that is chemically and physically heterogeneous. It has combustible substance that consists of both organic and inorganic compounds or elements which make it a major energy source worldwide, especially among many developing countries, and will continue to be for many years to come [2; 3]. Coal is an organic combustible black or brownish-black rock consists of

more than 50 percent by weight, and more than 70 percent by volume of carbonaceous material including inherent moisture and water of constitution as well as associated inorganic substances [4]. Ultimate analysis also known as elemental analysis is dependent on quantitative analysis of various major elements present in solid fuel (coal), such as carbon, hydrogen, sulphur, oxygen and nitrogen. It is essential to know the elemental composition of solid fuel in order to determine its rank as well as grade for evaluation of its suitable application as a chemical feedstock or as a fuel in power generation. By elemental analysis of coal, empirical formula can be generated such as:  $C_{137}H_{97}O_9NS$  for bituminous coal and  $C_{240}H_{90}O_4NS$  for high-grade anthracite [5].

In the five major coal ranks (from peat to anthracite), organic constituents such as carbon, hydrogen and oxygen are rank dependent variables but the major inorganic elements (nitrogen and sulphur) contents depend on chemistry of the area of occurrence and precursory plant of the coal. The composition of carbon, hydrogen and oxygen in peat is 5 – 60 %, 6.0 – 6.5 % and 30 – 35 %; lignite, 60 – 75 %, 5.8 – 6.5 % and 22 – 26 %; sub-bituminous and bituminous, 75 – 90 %, 4.0 – 5.8 % and 7.0 – 15 %; and anthracite, 90 – 95 %, 2.0 – 4.0 % and 3.0 – 5.0 %, respectively. It is widely noticed that Sub-bituminous and bituminous coals are the most useful amongst coal rank [6; 7].

All these elements in coal except nitrogen (which is found in either organic or inorganic form) are generally present in inorganic combination in coals: carbon is present in carbonates of calcium, magnesium and iron; hydrogen in free water and water of hydration; oxygen in oxides, water, sulphates, and silicates; and sulphur in sulphides and sulphate. All these inorganic compounds affect the efficiency of the blast furnace as well as other boilers, and so choice of low content inorganic coal is very crucial for fuel making. Coal which comprises of many elements also occurs in association with minerals and this led to large numbers of distinct mineral phases in the coal as many as 50 – 60 minerals [8; 4; 9]. These minerals may be excluded minerals (i.e. the mineral is separate from the maceral) or included minerals – the mineral remaining closely associated with the organic matter [10; 11]. These minerals fall into one of the major eight groups: aluminosilicates, sulphides, carbonates, phosphates, sulphates, oxides, hydroxides and silicates. But the common major minerals identified in association with coals are quartz, kaolinite, illite, calcite, pyrite, plagioclase, feldspar and gypsum, and occasionally dolomite, ankerite, siderite, iron-oxyhydroxides and sulphates [12].

In high temperature coal carbonization, the coking process time is between 12 to 30 hours (metallurgical coke is between 12 – 18 hours while foundry coke is 28 – 30 hours) depending upon the oven width, flue temperature and the type of coke required. At these temperatures, practically all the

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volatile matter is driven off as gases or liquids, leaving behind a residue that consists principally of carbon with minor amounts of hydrogen, nitrogen, sulfur, phosphorus, chlorine, oxygen and so forth [13; 14; 15].

This paper reports the elemental composition of some Nigerian coals and its application in ranking of the coals. Objectively, this will indicate the area of utilization or application.

## II. MATERIALS AND METHOD

### 2.1 Material

The materials used for this study include five different coal samples collected from Garin Maiganga (GMG<sub>A3</sub> – top layer and GMG<sub>B</sub> – base layer), Chikila (CHK), Lamza (LMZ) and Afuzie (AFZ), all from Nigeria.

### 2.2 Methodology

#### 2.2.1 Theoretical (numerical) determination of carbon and hydrogen

Coal has various characteristics which include elementary composition, coking properties, calorific values, etc. Relationship exists between these characteristic values which make them to be dependent on each other. Based on the Seyler's formulae and other similar calculations (e.g. Dulong's, Spooner or Channivala's formulae) which relate proximate and ultimate analysis, some formulae have been emanated to include that of Mazumdar (dispensing the need for calorific value test and applicable to wide range of coals) for determination of composition of carbon and hydrogen; using the knowledge of other coal characteristics like moisture (M) and volatile matter (V) content on dry ash free basis. These formulae apply to coals of more than 18 % volatile matter and gives results to ± 1 % [16; 17]. The values of proximate results obtained from [18] were used for the carbon and hydrogen elemental determination in the formulae below.

$$\% \text{ Carbon} = 97 - 0.27V - M(0.6 - 0.01M)$$

$$\% \text{ Hydrogen} = 3.6 + 0.05V - 0.0035M^2 (1 - 0.02M)$$

Oxygen was obtained by subtracting from 100 the sum of the other components of the ultimate analysis: percentages of carbon, hydrogen, nitrogen and sulphur in the coal sample [19].

$$\% \text{ oxygen} = 100 - (\text{carbon} + \text{hydrogen} + \text{nitrogen} + \text{sulphur}) \%$$

#### 2.2.2 Determination of sulphur in coal by Eschka method [19]

This was done by igniting 1 g of coke sample and Eschka mixture (2 parts of calcium magnesium oxide with 1 part anhydrous sodium carbonate). The sulphur is dissolved in water and then precipitated as barium sulphate. The precipitate is then filtered, ashed and weighed. The total sulphur content was calculated using the formula below:

$$\% S_t = \frac{A - B}{C} \times 13.74$$

where  $S_t$  = total sulphur

A = mass of barium sulphate from sample

B = mass of barium sulphate from blank

C = mass of sample used

#### 2.2.3 Determination of nitrogen by Kjeldah method [20]

Coal sample (2.00 g) was weighed into Kjeldah digestion flask, about 20 cm<sup>3</sup> of sulphuric acid and 1.00 g each of copper sulphate and potassium sulphate (catalysts) was added into the flask. The flask was then slightly heated in an inclined position and allowed to boil for about 6 hrs forming NH<sub>4</sub><sup>+</sup> SO<sub>4</sub>. The mixture was then diluted with 100 cm<sup>3</sup> of distilled water and allowed to cool down. Thereafter the flask was connected to Kjeldah distillation apparatus and excess 50 % of sodium hydroxide was added to the mixture, to convert the NH<sub>4</sub><sup>+</sup> ion to ammonia gas followed by boiling and condensation of the gas in a 2 % boric acid for about 30 min, using bromo cresol green and methyl red as indicators in the receiving flask. The resulting alkaline distillate was titrated against 0.1 M hydrochloric acid. The same procedure was repeated for the blank, and percentage nitrogen (% N) was calculated using the formula:

$$\% N = \frac{V_2 - V_1}{\text{Weight of the sample (g)}} \times 0.1 \times 14 \times 100$$

where  $V_1$  and  $V_2$  are the volumes of hydrochloric acid used in the sample and the blank respectively.

#### 2.2.4 Calorific value determination of Coal [19]

The calorific value was determined based on ASTM [19] – D3286 using AC-350 calorimeter. This was done by burning the sample in a controlled environment. The heat released by combustion is proportional to the heating value of the substance. The coal or coke sample was placed in a high pressure atmospheric environment called combustion vessel surrounded by water. Resistance wire was used in igniting the sample. The temperature of the water surrounding the combustion vessel was measured every six seconds by an electronic thermometer. The difference in water temperature between pre-fire and post-fire was processed by the microprocessor in the system and the calorific value (result) was readout.

## III. RESULTS AND DISCUSSION

Table 1, shows the ultimate and calorific value analysis results of the coal samples. The percentages of the elemental carbon and hydrogen of the coal samples were close to each other, and fell within the ranges of 78.26 – 83.37 % and 5.73 – 6.00 %, respectively. All the coal samples show low sulphur content of less than 1 %. The coal samples revealed reasonable oxygen contents that fell between 7.98 and 12.55 %. The CHK coal had the highest nitrogen content of 2.54 %, followed by GMG<sub>A3</sub> and LMZ coal samples with 2.41 % and 2.24 %, respectively. AFZ coal had 2.08 % and GMG<sub>B</sub> coal sample the least content of 1.98 %. The AFZ coal sample recorded the highest calorific value of 6,752.70 cal/g closely followed by GMG<sub>B</sub> and GMG<sub>A3</sub> with 5,641.40 and 6,606.10 cal/g, respectively. The LMZ coal sample had 5,019.70 cal/g and CHK coal sample had the least heating value of 4,875.60 cal/g.

**Table i:** Ultimate and calorific value analysis results of the coal samples

S/N	Sample coal	Calorific value (cal/g)	Elemental composition				
			(%) carbon	(%) hydrogen	(%) sulphur	(%) nitrogen	(%) oxygen
1	LMZ	5,019.70 ±23.06	83.37 ±1.09	5.73 ±0.27	0.68 ±0.03	2.24 ±1.08	7.98 ±0.82
2	CHK	4,875.60 ±21.48	78.26 ±1.10	5.89 ±0.51	0.76 ±0.02	2.54 ±0.94	12.55 ±0.91
3	AFZ	6,752.70 ±19.94	82.55 ±1.03	6.00 ±0.60	0.85 ±0.06	2.08 ±0.76	8.52 ±0.88
4	GMG <sub>B</sub>	5,641.40 ±25.99	81.35 ±1.22	5.76 ±0.56	0.69 ±0.09	1.98 ±0.91	10.22 ±0.6
5	GMG <sub>A3</sub>	5,606.10 ±23.04	80.83 ±1.27	5.91 ±1.04	0.87 ±0.05	2.41 ±0.15	9.98 ±0.18

### 3.1 Ultimate Chemical Composition

The importance of ultimate analysis of coal is also to decide the extent of coalification. Moreover, the ultimate and physical properties of coal influence its behaviour and reaction during heat treatment, and so knowledge of these properties is important for the coal utilization [21]. From lignite (the lowest coal rank) to anthracite being the highest form of coal, the carbon in the pure coal substance increases progressively while the hydrogen shows small change [22; 6]. Some of the important ultimate analysis parameters shown in Table 1 are hereby discussed:

**Oxygen:** The oxygen content is an important index for coal ranking. The younger coal is richer in the elemental oxygen than that of the more matured coal. Oxygen exists in the form of mineral compounds within the coal mass. For example, the hematite ( $\text{Fe}_2\text{O}_3$ ) content of LMZ and AFZ are 27.94 and 40.74 %, respectively; GMG has magnetite ( $\text{Fe}_3\text{O}_4$ ) content of 12.29 % [23]. Even though LMZ and AFZ have high values of hematite, all these oxide minerals have supplementary advantages of various applications in metallurgy [9]. The lower the oxygen content of coal or coke the higher the calorific value. Oxygen content decreases from lignite to anthracite, with a corresponding decrease in moisture holding capacity and an increase in the caking power of the coal for coke production decreases [7]. The oxygen contents of these coal samples are within the desired range for most utilization.

**Sulphur:** By definition, sulphur is part of ultimate analysis. Sulphur in coal is distributed between the organic matter as ash, and relatively extensive washing generally tends to reduce the sulphur content. World coal contains 1 to 3 % sulphur [7]. Some of the sulphur in coal escapes with the volatiles during carbonization, thus the sulphur content in the coke is slightly less than that of the coal. The sulphur content of metallurgical coal is critical and less than 1 % is the widely accepted limit for most applications [24]. Sulphur is associated with coal mass as mineral (e.g. barite –  $\text{BaSO}_4$ , gypsum –  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , pyrite/marcasite –  $\text{FeS}_2$ , galena –  $\text{PbS}$ , etc). It exists in 3 forms – pyritic, organic and sulphate. Even though it increases calorific value but is undesirable

because of its detrimental effects on materials and environment. The oxidization product of sulphur in presence of moisture causes corrosion of equipment and pollution. When used in steel making it badly affects properties of iron and steel. The formation of di- and tri- sulphur oxide during high-temperature treatment of coal or coke gives rise to sulphuric acid that causes industrial fumes [1]. The removal of sulphur compounds during coal preparation process (beneficiation) also results in loss of some coal mass (i.e., decreased recovery). The technology and cost of separation of sulphur is determined by its type of distribution [25]. It is possible to desulphurise the coal, but it's a relatively costly operation. Sulphur fixation agent otherwise known as desulfurizing agent can be added to convert most of the sulphur into less harmful substance – salt (ash) instead of liberating it as sulphur dioxide ( $\text{SO}_2$ ) into the atmosphere polluting the environment and eventually contributing to acid rain as well as global dimming [26; 27]. Sulphur is therefore a very important quality index, which can be regulated easily only by the choice of coal(s) for carbonization or other applications [1; 25], and this justified the safe utilization of these coal samples because of their low sulphur contents which are below the maximum limit of 1.2 %, required for consistent iron quality in metallurgical operation, briquette or power generation [28].

**Hydrogen:** It is one of the major constituents but minor element in terms of effect on coal utilization. Hydrogen is mostly associated with volatile matter and forms part of the combustible component in coal. It increases calorific value of coal and coke, and remains as coke oven gas in metallurgy. Hydrogen occurs in minute content: peat to bituminous contains 3.0 – 5.6 %, while anthracite contains only 2 – 4% hydrogen [6]. The hydrogen contents of these coal samples are generally within the normal range in coals.

**Nitrogen:** The presence of nitrogen in the coal reduces oxidation, and is found in coal mass mostly in low amount (as the case of these coal samples). Under certain combustion conditions a portion of nitrogen is emitted to the atmosphere as the polluting nitrogen oxides. Nitrogen originates from

protein and represent up to 1 – 3 % in coal. Nitrogen decreases calorific value and as coal matures, extractable nitrogen decreases. Its proportion does not depend on rank of coal [7].

**Carbon:** Carbon content is an important parameter in estimating the amount of coke yield from a sample of coal on carbonization [29: 30]. It is an important element for most application, and the greater its percentage composition the better is the coal in quality and rank. It is a major yardstick used in determining the rough estimate of calorific value of coal, which is also a rank dependent variable parameter, and so ultimate analysis prior to carbonization is important [31; 32]. In this study, the coal samples have appreciable heating value in an increasing order of AFZ > GMG<sub>B</sub> > GMG<sub>A3</sub> > LMZ > CHK, that can be used for energy generation taking advantage of their low ash and sulphur contents. It was noticed that carbon contents of the coal samples has no linear relationship with the corresponding calorific values, which may be due to certain elemental variables such as majorly sulphur, nitrogen, oxygen and mineral contents. The most important constituents of coal which are carbon and hydrogen account for 70 to 95 % and 2 to 6 % respectively by weight on dry, ash-free basis [4]. Fixed carbon differs from the ultimate carbon content of the coal because during heat treatment some carbon substances are lost with the volatiles.

In this work, the elemental carbon of the coal samples (which is between 78.26 – 83.37 %), confirms that they are all sub-bituminous in rank [6], which is in agreement with [18]. Tar yield of coal is known to possess a linear relationship with carbon [33]. The study found that the coal samples have high elemental carbon contents which are within a short range (Figure 1) but their tar yields were reported to be low (below 17 %) [34]. This may be due to their high volatile matter contents which were previously reported [18]. This implies that these coals would be suitably utilized only in conventional or formed coking technology for metallurgical coke production. On the whole, all the parameters are within the acceptable range for liquefaction, gasification, coking technology and power generation.

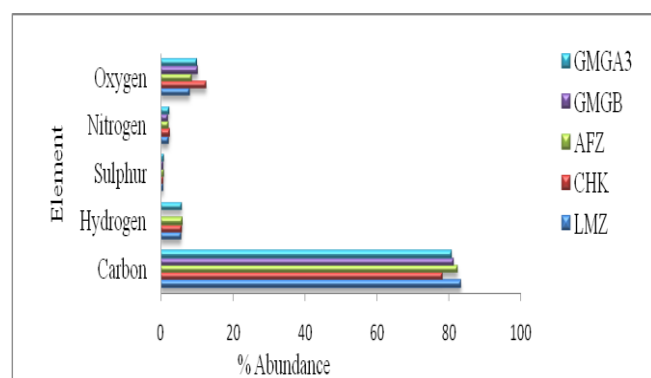


Figure 1: Profile of elemental composition of the coal samples

#### IV. CONCLUSION

The elemental composition (particularly the high carbon contents of between 78.26 – 83.37 %) of the coal samples confirms that they are all sub-bituminous in rank with low contents of other elements. The advantage of low content of these substances (especially sulphur) in the coals adjudged that they are potential materials for liquefaction, gasification

as well as blend additive for conventional and formed coking technology in the production industrial or domestic fuel (coke). The low contents of these elements further indicate low inorganic or mineral substances which make them safe for utilization. The high carbon contents of these coal sample and the adequate heating values as well as the low tar yield (which portrays low caking tendency), make them a good source of energy for power generation.

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