CHARACTERISATION OF LIGNITES FROM OHORDUA AND AZAGBA-OGWASHI AND THEIR EXTRACTED HUMIC ACIDS: SUITABILITY FOR SOIL BENEFICIATION/CONDITIONING.

PRESENTED

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IN PARTIAL FULFILLMENT FOR THE REQUIREMENT OF THE AWARD OF DEGREE OF MASTER OF SCIENCE (M.Sc) IN GEOLOGY (MINERAL EXPORATION)

APRIL, 2019

CERTIFICATION

This is to certify that this project work described in this thesis was carried out by Abdulmajeed, OCHU, in the Department of Geology, Faculty of Physical Sciences, University of Benin, Benin-City, Edo State, Nigeria, under the supervision of Professor Asuen, G. O.

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DEDICATION

With the whole of my being, I dedicate this work to the Almighty God for His unmerited favour bestowed on me to soar high above every challenges, ensuring that this work sees the light of day.

ACKNOWLEDGEMENT

To God Almighty, the giver of life, strength and wisdom. The whole appreciation in the entire universe would never measure up to your loving-kindness and tender-mercies. My big appreciation goes to Professor Asuen, G.O, who stood by me through thick and thin, to ensure a good quality output. I am grateful sir for your fatherly guidance. Also, to the Head of Department, Prof. Akujieze C.N for his mental prowess and intellectual sagacity in ensuring the smooth running of the post graduate programme. . I also acknowledge Dr. Imasuen, O.I., for standing by me when I needed him most, who was also my course Lecturer; I am sincerely grateful sir. May God continually bless and protect you. To Dr. Salami, I sincerely appreciate you sir for teaching me diligence, persistence and focus I sincerely learnt from your humility. I acknowledge my external supervisor,. Also to a man whom I can’t eliminate out even in my sleep, Mr Festus; I thank you for your direction, knowledge and input in the success of this project Your cheerful nature had endeared many to you. Special thanks to Dr (Mrs) Ariyo of Federal University Otuoke, for her moral support, indeed you have been a mother to me.To my colleagues and friends Mr. Bassey, Mr Ayo, Mr Oziggy, Mr Ejiro ,Mr Odia, Mr Julius, Mr Osazie, Mr Precious,Mr Bode, Mr Isreal Bamang, Miss Amaka, Miss Osas, Miss Faith andMiss Janet.Also my sincere thank you goes to the Head of Department, Physics FUO and all staff of Physics Laboratory Unit FUO.A very big appreciation to my wonderful parents, Mr and Late (Mrs) Ochu Suleiman. To my loving and lovely Sister Late (Mrs) Salihat Ochu and my one and only brother Ochu Muhydeen, you all mean so much to me. Special acknowledgement to my spiritual parents, Pastor and Pastor (Mrs) Mike Daniel, whose teachings and impartations had risen the giant in me, your prayers, advice and support I can’t understimate. I also want to acknowledge Pastor and Pastor (Mrs) Egede Emmanuel who have also been a medium of inspiration and advice to me. I love you all.

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LIST OF ABBREVIATIONS

HA (Humic acid)

CEC (cation exchange capacity)

C (Carbon)

H (Hydrogen)

N (Nitrogen)

S (Sulphur)

O (Oxygen)

OH (Ohordua)

AO (Azagba-Ogwashi)

LOC (Location)

ABSTRACT

This research gives attention to the non-energy use of Lignite samples collected from Ohordua town of Edo State and Azagba-Ogwashi in Delta State. A total of six composite Lignite samples,from ten sampled points were subjected to analytical study, with a view to determining their humic content and properties for use in soil beneficiation and conditioning.Proximate and Ultimate analytical technique was used to characterize the lignite from which humic acid was extracted under alkaline condition, and precipitated using acidic medium of 6M HCl.X-Ray Diffraction and X-Ray Fluorescence analytical methods were employed to determine the mineralogical and elemental composition of the samples respectively,while Ultra-Violent visible spectroscopy was used for organic characterization of the humic acid.Proximate analyses of the Lignite show percentage composition of Ohordua and Azagba-Ogwashi Lignite respectively,Fixed Carbon (65.22 wt% and 67.16wt%),Moisture Content (26 wt% and 25.4wt%) and Ash (5.02 wt% and 4.5 wt%).Ultimate analyses shows Hydrogen (6.60 wt% and 6.22wt%), Nitrogen (1.34 wt% and 1.19wt%,) Sulphur (0.77 wt% and 0.70wt%), Oxygen (26.07 wt% and 24.73 wt%), for Ohordua and Azagba-Ogwashi respectively.The analytical results suggest the existing lignite with varying thickness is of Lignite rank. The Ultimate analyses of the extracted Humic acid show Carbon (57.5wt% and 55.8wt%)%, Hydrogen (5.1 wt% and 3.9wt%), Nitrogen (2.5 wt% and 1.1wt%), Sulphur (Nil and 0.3wt%) and Oxygen (34.9 wt% and 38.9wt%,) for Ohordua and Azagba-Ogwashi, respectively.The mineralogical composition in the lignite samples shows Kaolinite was the main clay mineral identified. Non clay minerals such as anorthite, drierite, yeelimite, spurite, belite, wollastonite, hematite, pyrite, bauxite and quartz were detected.For Ultra-Violent visible spectroscopy characterization of the Humic Acid, E_2/E_3 and E_4/E_6 absorption values for Ohordua (21.69 and 4.50) respectively, while Azagba-Ogwashi reveal (19.39 and 4.6) respectively. The humic substance has percentage aromaticity values of 33.90% and 34.06%, total acidity has 10.4% and 10.1%, COOH has 3.4% and 3.3%, Phenolic has 7.0% and 6.8% and acidity ratio has 0.49% and 0.48%, for Ohordua and Azagba-Ogwashi, respectively which depicts the Humic Acid has a high degree of Humification and a very good total acidity ratio. Results from this research indicate that the Lignite from both locations are similar in geochemistry, mineralogy and organic properties. Although,humification is high in both samples, Ohordua Lignite with lesser aromaticity and E4/E6 ratio, higher E2/E3 ratio and higher acidity ratio is more suitable for soil beneficiation and conditioning than that of Azagba-Ogwashi.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

Humic acid (HA) is a complex organic molecule with high molecular weight ranging from approximately 5,000–100,000 Daltons. It is dark brown or black, soluble in alkaline solution and insoluble in acidic condition (Fulcrum Health Limited 2004).The role of HA in improving agricultural soils is well established, especially in soils with low organic matter (Pettit 2002).Humic acid has long been used in enhancing crop productivity and soil fertility. It also plays an important role in human health and animal husbandry (Enviromate 2002). Many reports on its medicinal values have also been published (Anon. 1999; Enviromate 2002).The market for humate is expanding. Humic acid products mainly as plant growth enhancers and as an ingredient in fertilizer. products are widely distributed throughout the world. The largest markets are in Europe and also in Asia (Anon. 2004). Malaysia imports almost all its humic acid (HA) requirements in solid as well as in liquid forms. Most common high purity commercial HA are in the form of K, Na, and Ca humates while unprocessed HA of varying quality from naturally occurring low rank and oxidized coals are also found in the market. Humic acid contains many functional chemical groups that help to physically modify and improve the chemical properties of the soil and biologically stimulate plant growth (Burdick 1965; Anon. 2003). These functional groups including the aromatic backbone and amines (R-NH2) cause HA to be biologically active. The oxygen containing functional groups (carboxyl, phenol, hydroxyl and ketone) tend to increase the cation exchange capacity (CEC) of the soil. Traditionally, HA is extracted from lignite, brown coals and humified organic materials. Earlier work on extracting humic acids from peat with alkaline and sodium pyrophosphate solution had been attempted (Gracia et al.,1993). The amount of extractable HA from humic substances and its chemical characteristics depend on several factors. These include the types of organic material from which HA is extracted, temperature, grain size, frequency of extraction, the extracting agent and its strength and drying procedure. Extracting HA under elevated temperature greatly enhanced HA recovery (Sasaki and Oyamada,1966; Asing et al.,2004).Therefore, it is absolutely essential that when HA content is stated, it is to be accompanied by the method of determination. Much of the extraction techniques of commercial HA remain proprietary. Therefore, with the abundant availability of lignite, sub-bituminous coals and composted biomass in Nigeria, it may have commercial value if methods are developed to extract HA from these local sources. The objectives of this study were to fine tune the method of extracting HA from low quality coals and to characterize their chemical properties with respect to each other. Lignite has been used as a fuel for decades. Simple burning of this raw material is highly inefficient use of valuable matter. Lignite can be used as a versatile and interesting substance in several application fields due to its specific properties and composition. This project is aimed at non-energy and cost-effective use of lignite in Nigeria.Hence, this project is to bring out concordant views and make objective submission of the characterization of the Ohordua and Azagba-Ogwashi Lignite with respect to their humic acid content (extraction) and its suitability for soil beneficiation and conditioning.

1.2 THE NIGERIA LIGNITE DEPOSITS

The Nigerian lignite zone, of mid-Tertiary age, extends from Orlu in the southeast, through Nnewi, in a 16 to 20 km wide belt across the Niger River, to Ogwashi-Uku in Delta State (Okezie & Onuogu, 1985). In the west of River Niger, there are several areas (Obomkpa, Ibusa, Okpanam, Illah, Agbor and Ubiaja) hosting lignite fields, whereas the most important seams east of the Niger are found at Oba and Nnewi (Nigeria has the largest known lignite deposit in Africa with proven reserves exceeding 300 million tons (Orajaka *et al*.,1990).Coal is an important source rock for natural gas and crude oil (Murchison, 1987; Hunt, 1991; Mpanju *et al*., 1991; Clayton, 1993; Hendrix *et al*., 1995; Sykes and Snowdon, 2002; Petersen and Nytoft, 2006; Davis *et al*., 2007). The coal deposits of Nigeria occur in the Benue Trough (Obaje, 2009). The Benue Trough of Nigeria, subdivided into Lower, Middle and Upper regions (Obaje *et al*., 2004), is a sedimentary basin that extends from the Gulf of Guinea in the south to the Chad Basin in the north in a NE-SW trend Studies of the Nigerian lignite deposits date back to more than 80 years (Wilson, 1924; Du Preez, 1945, 1946; Simpson, 1949, 1954; Da Swardt and Piper, 1957; Chene *et al*., 1978; Okezie and Onuogu, 1985; Oboh-Ikuenobe *et al*., 2005; Olobaniyi and Ogala, 2011). Relatively little has been written about the hydrocarbon potential of the Nigerian lignite deposits. Okezie and Onuogu, 1985 presented data from chemical and gas analysis of lignites and showed that the lignite deposits have high calorific values, low sulphur but are generally rich in hydrocarbons, resins and waxes. Nwadinigwe (1992) studied the wax and resin characteristics of Nigeria’s lignite and sub-bituminous coals and concluded that the lower the coal rank the higher the total amount of wax and resin extracted from it. Akande *et al*. (1992) examined the rank, petrographic composition and depositional environment of selected Upper Cretaceous and Tertiary coal of southern Nigeria and concluded that thermal maturation in the Cretaceous successions increases from the post-Santonian (Campanian-Maastrichtian) Anambra Basin into the older Benue Trough where strong diagenetic to anchimetamorphic (that is, very low grade metamorphism) conditions were reached. Obaje and Hamza (2000) investigated the liquid hydrocarbon potential of mid-Cretaceous coals and coal measures in the middle Benue Trough of Nigeria and also subdivided the coal beds into three different coal facies, namely: a vitrinite-fusinite, a trimaceritic and shaly coal facies. Ogala,(2011) The study of the organic matter content, depositional environment and thermal maturity of the Tertiary lignite series in the Azagba-Ogwashi Formation study show that the lignites have appreciable amounts of organic matter (TOC of up to 63.54 wt.%) to generate both oil and gas. The lignites are thermally immature with regards to petroleum generation. The lignites are dominated by huminite but contain high liptinite contents in all the samples and are classified as Type II-III and Type III kerogen by both Rock-Eval and elemental atomic ratios (H/C and O/C). The HI values range from 157 to 402 mg HC/g TOC, suggesting potential for both oil and gas generation. Nigerian Coal has been used extensively as a source of power generation both industrially and domestically (Odesola et al.,2013) .Coal accumulation in Nigeria took place mainly during upper Cretaceous and Tertiary times, resulting in the formation of extensive lignite, sub-bituminous and bituminous coal deposits in the Benue trough and Anambra Basin, (Akande *et al.*,1992).The Ogwashi-Asaba formation occurs extensively within the Niger Delta Basin.(Wilson.,1925) first described and named the lignite group in Southern Nigeria. Lithologically, it consists of a sequence of coarse-grained sandstones, light-coloured clays and carbonaceous shales, within which are continental lignite seam intercalations (Reyment, 1965; Kogbe, 1976; Jan du Chene *et al.*, 1978). Nigeria has the largest known lignite deposits in Africa, proven reserves exceeding 300 million tons (Orajaka *et al.*,1990).Lignite is mined in open pits in Nigeria and is used mainly as a substitute for wood as fuel in domestic cooking. The pertinent literature on Nigerian lignite deposits' major and trace element composition is scarce (Adedosu *et al.*, 2007; Olobaniyi and Ogala, 2011).

Coal is heterogeneous sediment having both organic and inorganic fractions; it contains variable amounts of almost all the elements included in the periodic table (Christanis *et al.*,1998; Orem and Finkelman, 2003). Most elements contained in coal usually show a close association with organic matter or with the coal's inorganic fraction. Changes in the elements' affinity with either the organic or inorganic fraction may also occur during coalification (Christanis *et al.,*1998). Several researchers have attempted to study the geochemical features of trace elements contained in coal to understand and evaluate trace elements' mode of occurrence as well as their behavior during combustion (Gluskoter *et al*,1977; Swaine, 1990; Finkelman, 1994; Meij, 1995; Spears and Zheng, 1999; Davidson, 2000; Vassilev *et al.*, 2001). Previous studies on trace elements in Nigerian coal have revealed their distribution (Olajire *et al.*, 2007; Ogala *et al.*, 2010a), composition (Ndiokwere *et al.*,, 1983; Olabanji, 1991; Ewa *et al.*,, 1996; Adedosu *et al.*, 2007;) characteristics (Nwadinigwe, 1992; Sonibare *et al.*, 2005) and association (Ewa, 2004; Ogala *et al.*,2009).With the market for humate expanding and Nigeria having the largest lignite deposit in Africa, this project attempts to appraise the humic acid potential of Nigeria lignite resources and its economic significance in Agriculture using Ohordua and Azagba-Ogwashi lignites as a case study hence, drawing attention to the use of Lignite in Agriculture for soil beneficiation and conditioning.

1.3 AIM AND OBJECTIVES

1.3.1 Aim of Research

The aim of this project is to subject Lignite to analytical study, with a view to determining their humic content and suitability for use in soil beneficiation and conditioning. Humic acid was extracted under alkaline condition, and precipitated using acidic medium of 6M HCl,Hence,this research work gathers information available on characterized Lignites from Ohordua and Azagba-Ogwashi and their humic acid potentials drawing attention to their non-energy use in soil beneficiation and conditioning.

1.3.2 Objectives

1. To Characterize the Lignite on the basis of their humic acid content and potential for soil beneficiation and conditioning.
2. To characterize the extracted portion of the lignite
3. To highlight the chemical properties which make it suitable for soil beneficiation and conditioning

1.4 JUSTIFICATION FOR THE RESEARCH

There have been only a limited number of research works on Nigerian lignite deposits for soil beneficiation and conditioning. At the time of this write up, no visible work had been done previously on the Humic acid potential of Nigeria Lignite for soil remediation because focus on Lignite has been extensively on it's calorific value for source of power generation both industrially and domestically .This research is well recognized by some major lignite Producing countries, examples of such research work include; the work done by Kalaichelvi (2006).

Exploiting the natural resources-Lignite Humic in Agriculture, he found out that Humic acid typically contains heterocyclic compounds with carboxylic, phenolic, alcoholic and carbonyl fractions extracted from lignite with high molecular weight. Humic acid has been extracted from various sources such as lignite, peat, coal, farmyard manure, coir pith besides natural persistence in soil. Humic acid plays a vital role in enhancing the nutrient uptake of crop by acting as a chelate in mobilizing nutrients, prevents losses of degradation and leaching of nutrients and thus reduces the use of inorganic fertilizers besides increasing the efficiency of the applied fertilizers. Presence of growth promoting substances such as auxins and gibberellins had been reported in humic acid and it plays an important role in enhancing the enzymatic activities of the plants. The resistance in the plants found to be increased by the humic acid application. The soil fertility would be improved by mobilizing the unavailable form of nutrients to the available form. The humic acid application at optimal rates has been reported to enhance the yield of various crops (Kalaichelvi et al., 2006).

The terms “humic acid” was first applied in 1826 by Sprengel to that brown amorphous precipitate which is obtained by acidifying the alkali extract of decayed organic matter in soil. Since the inception of the term, humic acids have been extracted not only from artificially obtained in the laboratory by action of inorganic acids or oxidizing agents on carbohydrates, proteins, and phenols.Odin in 1922 redefined humic acids as yellow-brown to black-brown substances of unknown constitution, formed in nature by decomposition of organic materials under atmospheric influence or in the laboratory by chemical action. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually are insoluble in water, soluble in alkali, and re-precipitated by acid. In general, humic acids are not chemically uniform substances, but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000 units. Their micelles carry a negative charge. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl group which account for about 22 percent of the weight of the molecule. Humic acid is an essential part of soil. It is this material, present in good soil that fixes nitrogen, make available to the plant, through base exchange, the soil nutrients, and improve the physical structure of the soil. In recent years, much research has been conducted, particularly in India, Japan, Germany, Russia, and France, on replenishing the depleted humic acid of soils with the so-called “regenerated humic acids” obtained by oxidation of coal. These regenerated acids, which closely resemble the natural humic acids, have either been added directly to the soil or first supplement with plant nutrients. Greenhouse and field tests have shown that these humic acid preparations improve plant yields, decrease loss of moisture from the soil, and increase the workability of the soil. This naturally-oxidized material, which contains up to 86 percent humic acids on a moisture-and-ash-free basis, has been given the name “Leonardite” after A.G. Leonard, first director of the North Dakota Geological survey, who did much of the early studies on these deposit. He further explained that Leonardite (Oxidized Lignite) is a coal like substance similar in structure to lignite, but significantly different in its oxygen and ash contents. He compared the ultimate analyses of lignite, Leonardite (lignite oxidized with air in the laboratory at 150^{o}C), and humic acid extracted from Leonardite with 1M NaOH. The content of Leonardite varies from mine to mine but is usually between 15 and 30 percent on a moisture-free basis. (Asing et al.,2009) worked on Malaysian coal, explained that Humic acid (HA), known as the black gold of agriculture, is increasingly becoming popular for use in agriculture. He extracted humic acid Acid from sub-bituminous coals from Mukah, Sarawak, commercial Humic Acid product (Leonardite), humified peat and various types of compost were extracted and their chemical characteristics compared. Humic Acid yield from various coals ranged from 1.5–11.1%, while composts yielded HA from a low of 4.2% to 16.5%. Humified peat and commercial Leonardite contained 31.6% and 58.5 % humic acid respectively. Functional group analyses of extracted Humic acid from Mukah coals showed a narrow range of carboxylic group from 3.2–3.5 meq g–1 while phenol-OH group was between 6.8–7.3 meq/ g.Functional groups in humic acid from composts were, however, lower than those obtained from coals. The total acidity of HA from composts ranged from5.6–9.5 meq g–1, carboxylic group at 1.9–3.5 meq g–1 and phenol-OH group,3.5–6.2 meq g–1.He concluded that the highest HA recovery from coals and different types of compost were obtained by three successive extractions using0.25 M KOH at 1:10 sample to extractant ratio. The Mukah coals had relatively high CEC with a range of 52.7–88.3 cmol (+) kg–1 and may possibly be used as a cheap source of soil conditioner. Humic acid yield from the various coals ranged from 1.5–11.1% while composts yielded HA from4.2–16.5%. Therefore, highly carbonized coal and composts are unlikely to be rich sources of HA. Oxidized coal such as Leonardite with HA content of about 58% is a rich source of commercial HA. Acidic functional groups in HA from composts were, however lower than those obtained from coals. The HA from composts yielded 1.9–3.5 meq g–1 of carboxylic group and 3.5–6.2 meq g–1 of phenol group. According to International Energy Agency, IEA (Robert,W. 2015),Germany is the world largest producer of Lignite producing 183 Mt of brown coal. But other countries that also have lignite in economical quantity have been able to utilize Lignite as Fertilizer for crop production in Agriculture. Nigeria is the 74thlargest producer of Lignite in the world and so, these lignites should be exploited for their Humic acid contents. inorder to boost the country’s agricultural sector.

1.5 LOCATION OF THE STUDY AREA

The studied area fell within the Anambra Basin section, the study area Ohordua in Esan South East Local Government Area in Edo region with geographical coordinates 6°32' 17" N, 6°24'43"E is a town located in Nigeria about 193miles or 310 km West of Abuja, the country’s capital town. (Lignite exposed at Latitude N6°.32’17N and Longitude E6°.24’ 43”) .The second area Azagba-Ogwashi is located in Delta State located west of the state capital, Asaba and is the headquarter for the local government area Aniocha South, with geographical coordinates 06°10' 59.06" N 06° 31' 27.72" E .Azagba-Ogwashi area (Lignite exposed between Latitude 06° 14' 33"Nand Longitude 006° 35' 48'E'). Fig 1.0 shows the map of the study area with lignite location points.

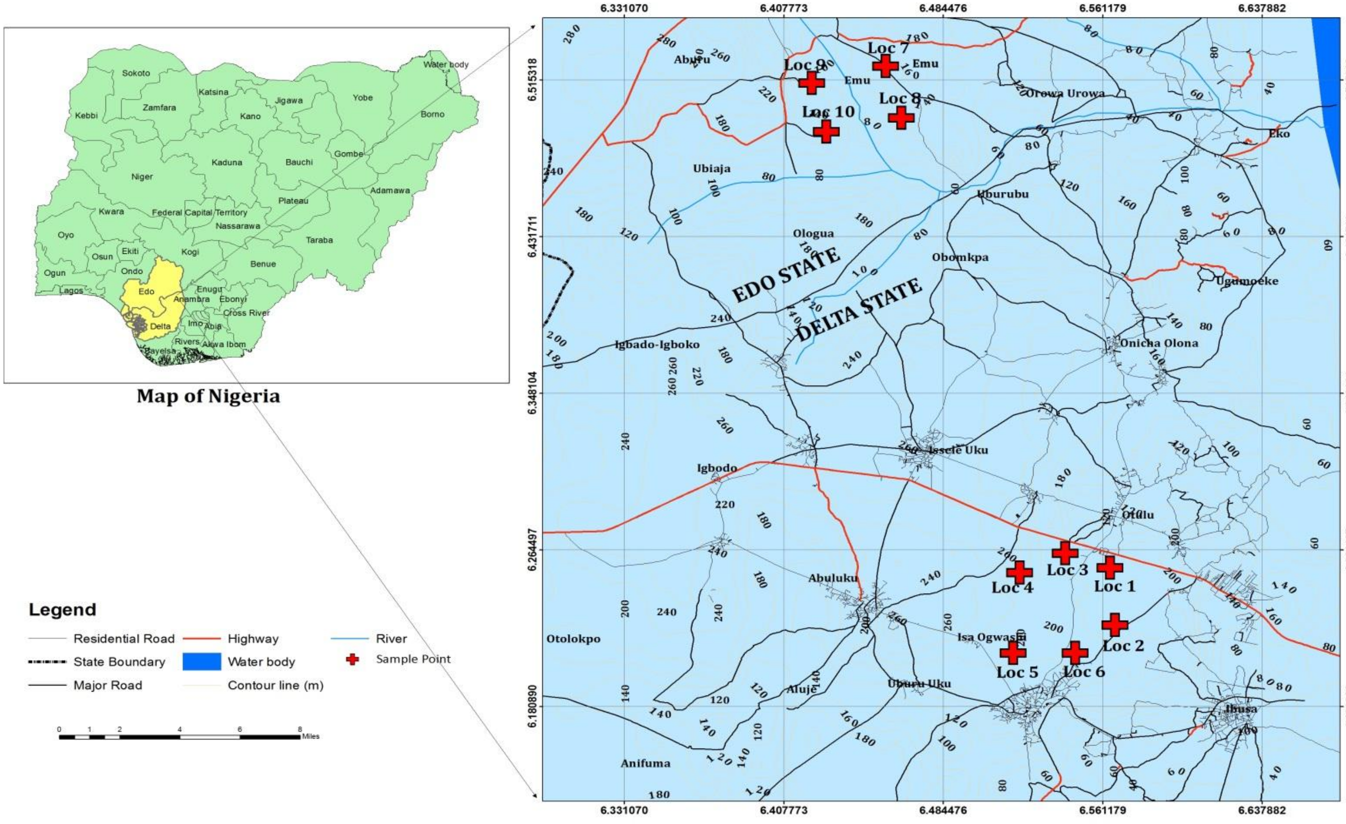


Fig 1.0.Map showing location of study area with sample location of Azagba-Ogwashi and Ohordua.

1.6 CLIMATE AND VEGETATION

Anambra basin falls within the equatorial climate of West Africa and has two distinct seasons They are the rainy season and the dry season which is characterized with the harmattan. The dryness of the climate tends to be discomforting during the hot period of February to May, while the wet period, between June and September is very cold.Rainfall is characterized by the annual double maxima of rainfall with a slight drop in either July or August known as dry spell or (August break). The annual total rainfall is above 1,450mm concentrated mainly in eight months of the year with few months of relative drought.Temperature and Humidity.It has temperature of $27^{o}C$ with daily minimum and maximum temperature ranges are about $22^{0}C$ and $34^{0}C$ respectively. It has a relative humidity of 80% at dawn. (Source: Hydrometeorological department, Awka).

1.7 ACCESSIBILITY

The area could be accessed via footpaths away from the major road which are well connected to the rivers where Lignites are exposed.

CHAPTER TWO

REGIONAL GEOLOGY

2.1 GEOLOGICAL SETTING OF ANAMBRA BASIN

2.1.1 Tectonic Evolution of the Benue Trough

The Anambra Basin came into prominence as a major depocentre in the Southern Nigeria in post-Santonian times following the deformation and uplift of the Abakaliki sector of the Benue Trough. The platform areas boardering the Benue Trough to the west (Anambra platform) and to the east (Afikpo platform) became down warped due to the Santonian Tectonism to the Anambra Basin and the Afikpo syncline respectively (Murat,1972;Petters;1978;Olo;1992).

The emergent Abakaliki anticlinorioum became a positive area that supplied detritus to these new basin-subsequently, the basins were filled with sediments ranging from late Cretaceous to early Tertiary.About 500m of fluvial parallic and marine sediments were deposited in the Anambra Basin (Akande & Mucke 1993)

The present state of knowledge about the tectonic evolution of the Anambra Basin is tied to the genesis and the tectonic of the Benue Trough. The sequence and events leading to the formation of the Benue Trough is well documented (Nwachukwu,1972;Petters,1978).

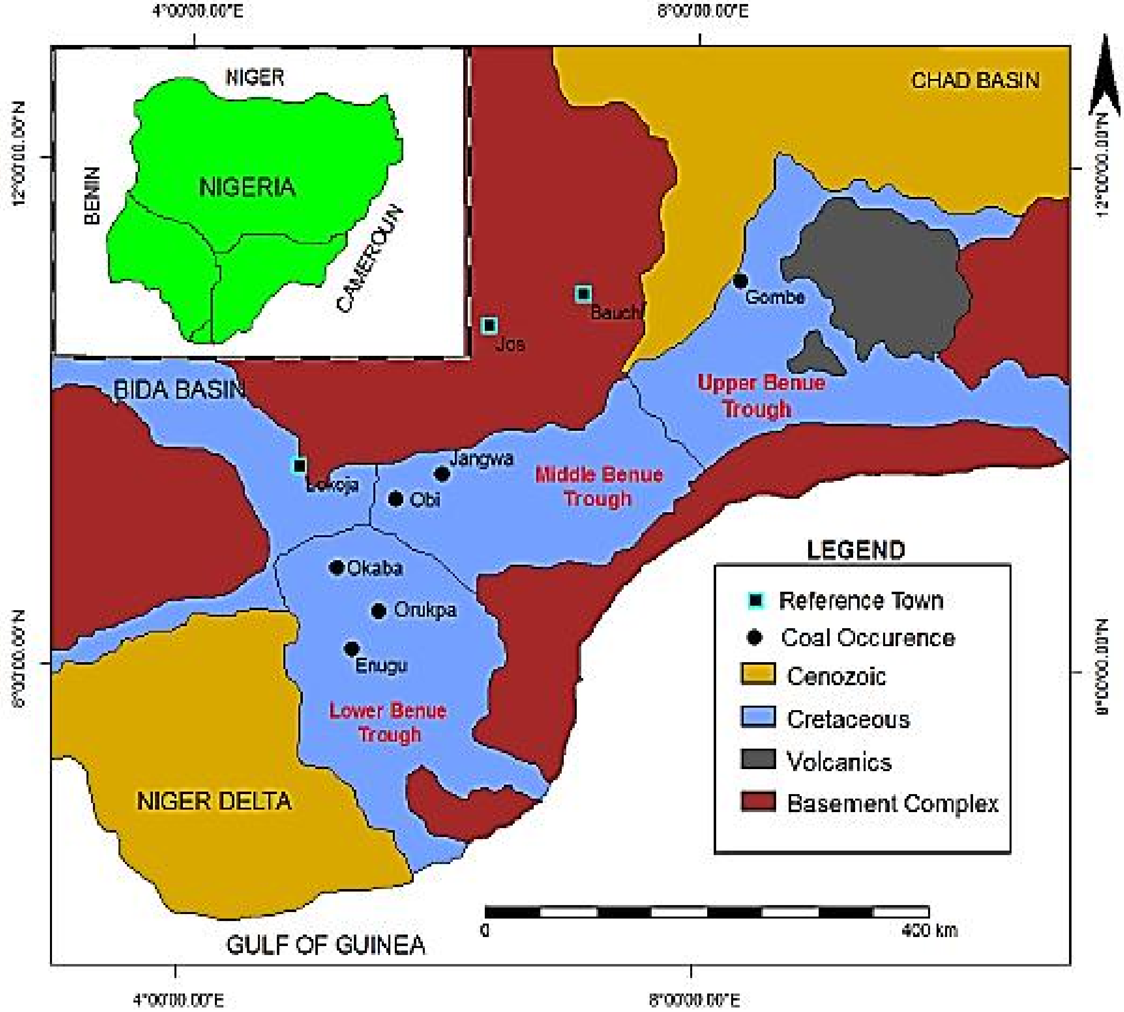


Fig 2.0: *Location of major coal occurrences in the Benue Trough of Nigeria (modified from Obaje et al., 1998).*

Lignites and sub-bituminous coals are distributed within the coal measures of the Maastrichtian Mamu and Nsukka Formations in the Lower Benue Trough (Akande et al.,1992) and in the Campanian – Maastrichtian Gombe Sandstone Formation in the Upper Benue Trough (Figure 2.1). Fig 2.0 shows the major Coal occurrence in the Benue Trough.The coals in the Lower Benue outcrop mainly in Enugu area four mines: Iva Valley, Onyeama, Okpara and Ribadu were being worked by the Nigerian Coal Corporation. Other mines that are being worked in this area include those at Okaba and Orukpa within the Mamu Formation. In the Upper Benue, laterally extensive beds (about 2m thick) of lignites and sub-bituminous coals outcrop along the bank of River Kolmani in Gombe town and along a stream channel behind the village of Hamman Gari about 20km from Gombe on the Gombe – Yola road. Borehole occurrences of coal seams within the Gombe Sandstone have also been reported by (De-Swardt & Casey, 1963; Carter et al., 1963). Not much follow-up studies have been carried out on these coals and consequently they are presently not being worked.

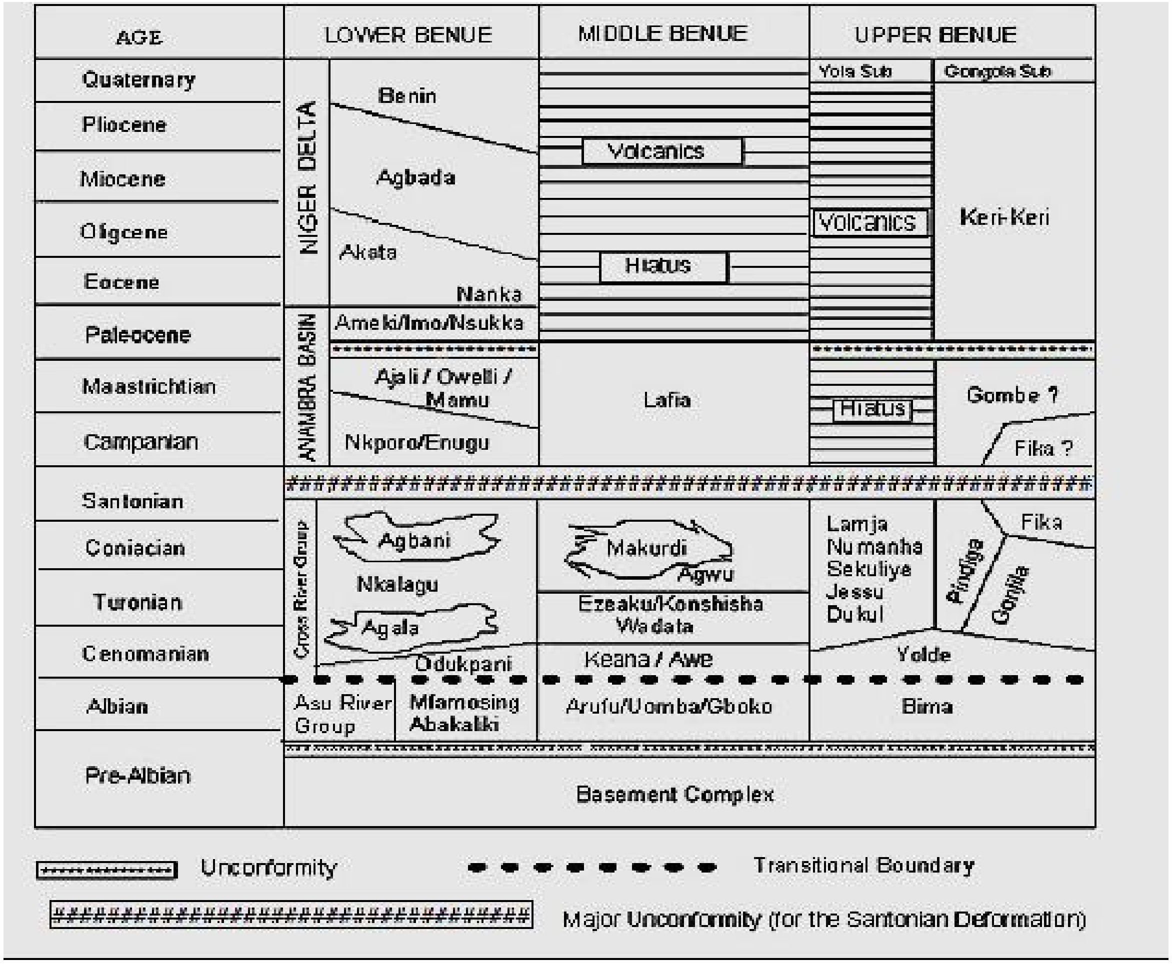


Fig 2.1 *Stratigraphic successions in the Benue Trough of Nigeria (modified from Obaje, 2009).*

2.2 STATIGRAPHY OF ANAMBRA BASIN

The late Cretaceous stratigraphy session in the Anambra Basin begins with the Campanian-Maastrichtian Enugu Formation and its lateral equivalent-Nkporo and Owelli Formations. These basal units are overlain successively by the early Maastrichtian Mamu Formation (lower coal measures) the middle Maastrichtian Ajali sandstone and the Nsukka Formation (upper coal measures), which extends from the late Maastrichtian into Danian. The Tertiary succession consists of the Paleocene Imo shale overlain by the Ameki Formation and its lateral equivalents, the Nanka sand of Eocene age. The Anambra Basin forms a part of the Benue Trough comprising several rift related basins in Nigeria. The trough is about 80 – 90km wide fault-bounded depression containing up to 5000m of deformed Cretaceous – Tertiary sedimentary and volcanic rocks. It is subdivided geographically into the Northern, Central and Southern Benue (Fig 2.4).Basins with the southern consisting of the Abakaliki and the Anambra Basin. The importance of the Benue rift in the evolution of Atlantic mega-tectonic region led to the proposal of numerous tectonics models for it origin and evolution.

The tectonic evolution of the basin was reported by several authors. The author considered the trough as analogous to the Red Sea being a part of the unstable RRR triple plate junction as a result of plate dilation and opening of Gulf of Guinea in the Early Cretaceous. Wrenching was suggested as a dominant tectonic process in Benue Trough evolution.

The first stage of evolution of the Benue Trough was controlled by opening of the Gulf of Guinea during the Early Cretaceous. This stage was marked by the reactivation of inherited fault zones which played a major role in the distribution and geometry of the numerous sub-basins.

These fault zones probably existed throughout the Benue Trough during Aptian times, although there is no direct evidence of their existence. During first Albian transgression, there was deposition of up to 2000m of immature sediments of the Asu River Group12, this was succeeded by the regressive phase during the Cenomanian period restricting sediments to the Calabar flank, leading to the deposition of the Odukpani sequence. The beginning of the second marine transgressive cycle in the Southern and Central Benue Basins led to the deposition of laminated shales and calcareous siltstone of the Eze-Aku Formation which is succeeded by thick black shales and limestone of the Awgu Formation deposited during the transgressive maxima from the Turonian to Coniacian times. Also, the third cycle involving the Upper Turonian-Lower Santonian have been largely removed by erosion as a result of the late Santonian deformation and uplift of the Benue depression. During the Pre-Santonian period, sediments of the first and second depositional cycle were compressionally folded, faulted and uplifted in the Southern Benue and clearly marked by deformational structures at the Abakaliki anticline, the Anambra Basin and Afikpo syncline.

The Post-Santonian collapse of the Anambra platform led to the emergence of several parts of the Southern and Central Benue Basins during the Campanian-Maastrichtian and shift in the depositional axis of sediments for the third transgressive cycle to the Anambra Basin.

(Fig 2.2) and (Fig 2.3) Sediment derived from erosion of the anticlinorium and ancestral Niger River filled the Anambra Basin. The various lithostratigraphic units resulting from these depositional cycles are here presented.

2.2.1 Enugu Formation

The Campanian Enugu and Nkporo shales represent the brakish marsh and fossiliferrous pro-delta facies of the late Campanian-early Maastrichtian depositional Nkporo cycle as proposed by Reigers and Nwajide (1998).The Owelli sandstones is about 600m thick. It is exposed along the Enugu-Portharcourt express way. The shoestring sand body geometry of the formation has been described (Reyment 1965 and Simpson 1954), which suggest a high sinuosity fluvial environment for the Formation. The Enugu Formation is exposed at various locations along the Enugu-Portharcourt express way including location along the Enugu-Onitsha express way.

The Campanian Enugu Formation consists of coarsening upward sequences with thick, dark grey shale at the base, grading upward through siltstones into thin, texturally mature sandstone. The lithologic assemblage suggests deltaic progadation during active delta growth. The carbonaceous shale at the base is interpreted as full marine pro-delta subfacies while the upper part of the section represents shallow water shoreface subfacies. The Campanian Enugu Shale consists of dark grey, fissile shale, brown silty sandy shale, and Mud stone.

2.2.2 Mamu Formation

The Enugu Formation is conformably overlain by the Mamu Formation. The Mamu Formation consists mainly of sand stone/siltstone/shale and coal. The Mamu Formation is composed of two members-white sand stone member and a sandy shale member (Ezwepue and Mogbo, 1993). Mamu lithology is indicative of a fluvio-deltaic or a fluctuating strand plain earth environment of deposition. (Reyment,1965, Agagu et al,1985)**.** The formation is dominantly terrestrial in Origin based on the presence of some brackish water foraminera (Adeleye,1975). The Maastrichtian Mamu Formation consists of rhythmic sequences of sandstones, shales, siltstones, mudstones, sandy shales with interbedded coal seams suggesting deposition under paludal to possibly marginal marine. The coal beds and carbonaceous shales are more concentrated in the basal section of the formation and rare towards the top.

2.2.3 Ajali Sandstone

The Mamu Formation is overlain by the Ajali Formation. The Upper Maastrichtian Ajali Formation is widely referred to in literatures as white false-bedded sandstone and the Eagle rock sandstone (Reyment and Barber,1956).The Ajali sandstone are composed of quartz-arenites, the grains are mostly friable, fine to coarse, in places, pebbly, poorly sorted and sub-angular. Ajali Sandstone consists entirely of cross bedded sandstones with drapes of claystones extending as stacks of sheet like bodies from the Calabar flank northwards towards Enugu. It is a regressive phase conformably overlying the Mamu Formation. The lithology of this formation consists of white, friable, coarse-grained, moderately to poorly sorted, with thin beds of whitish claystone as well as numerous bands of variegated rarely carbonaceous shale19,20. Depositional environment of the Maastritchtian sediments was interpreted to be tidal due to several occurrences of herringbone cross-bedding and bioturbations.

2.2.4 Nsukka Formation

The Ajali Sandstone is succeeded by the Nsukka Formation. A generally parallic deposition environment ranging from estuarine channels, barrier bar, marsh and tidal flats have been interpreted for the Nsukka Formation (Reyment,1965, Agagu et al;1985). Reyment (1965) dated the Nsukka Formation upper Maastrichtian using a lot of fossils among which was Afrobolivian atra.The Danian Nsukka Formation marks the onset of the transgression and a return to paludal conditions. The fluvio-deltaic formation overlies the Ajali Sandstone and consists of variety of sandstones that passes upward into well-bedded blue clays, fine-grained sandstones, and carbonaceous shales with thin bands of limestone.

2.2.5 Imo Shale

The Nsukka Formation is succeeded by the Imo shale. The Imo Shale consists of the dark grey to bluish grey shales with interbeds of thin Sandstones layers. The Formation is richly fossiliferous. The Fossil assemblage is typical of a near-shore marine environment and indicates a Paleocene age. The marine Imo Shale is the outcropping equivalent of the Akata Formation in the subsurface Niger Delta. The shales contain a significant amount of organic matter and may be a potential source for hydrocarbons in the northern part of the Niger delta. The authors assigned a Paleocene age to the Imo Formation and its depositional environment is mainly marine with littoral to neritic environments.

2.2.6 Ameki Formation

Succeeding the Imo shale is the Ameki Formation whose lateral equivalent is the Nanka sandstone. Ameki Formation consists of two lithologic units .The lower unit composed of fine to coarse grained sandstone with interbeds of Cretaceous shale and thin Shelly Limestone. The upper unit consists of coarse, cross bedded sandstone with sandy clay interbeds. Reyment (1965) dated and the Ameki Formation. Eocene based on fossils Planulina Oyae, as well as the other fossils that also gave the same age. The Ameki Group consists of the Nanka Sand, Nsugbe

Formation, and Ameki Formation26. These formations mark the return to transgressive conditions. The outcropping deposits of the Eocene regression, which marked the beginning of the Niger delta progradation, constitute the “Ameki Group” which includes tidal facies and backshore as well as pro-deltaic facies. The Ameki Formation is predominantly alternating shale, sandy shale, clayey sandstone, and fine-grained fossiliferous sandstone with thin limestone bands.

2.2.7 Azagba-Ogwashi Formation

The Oligocene – Miocene Azagba-Ogwashi Formation consist of interbedded successions of lignite, shale, sandstone, siltstone, and claystone facies. It is the outcropping equivalent of the Agbada. Formation in the subsurface Niger Delta. Depositional environment has been interpreted to be continental.

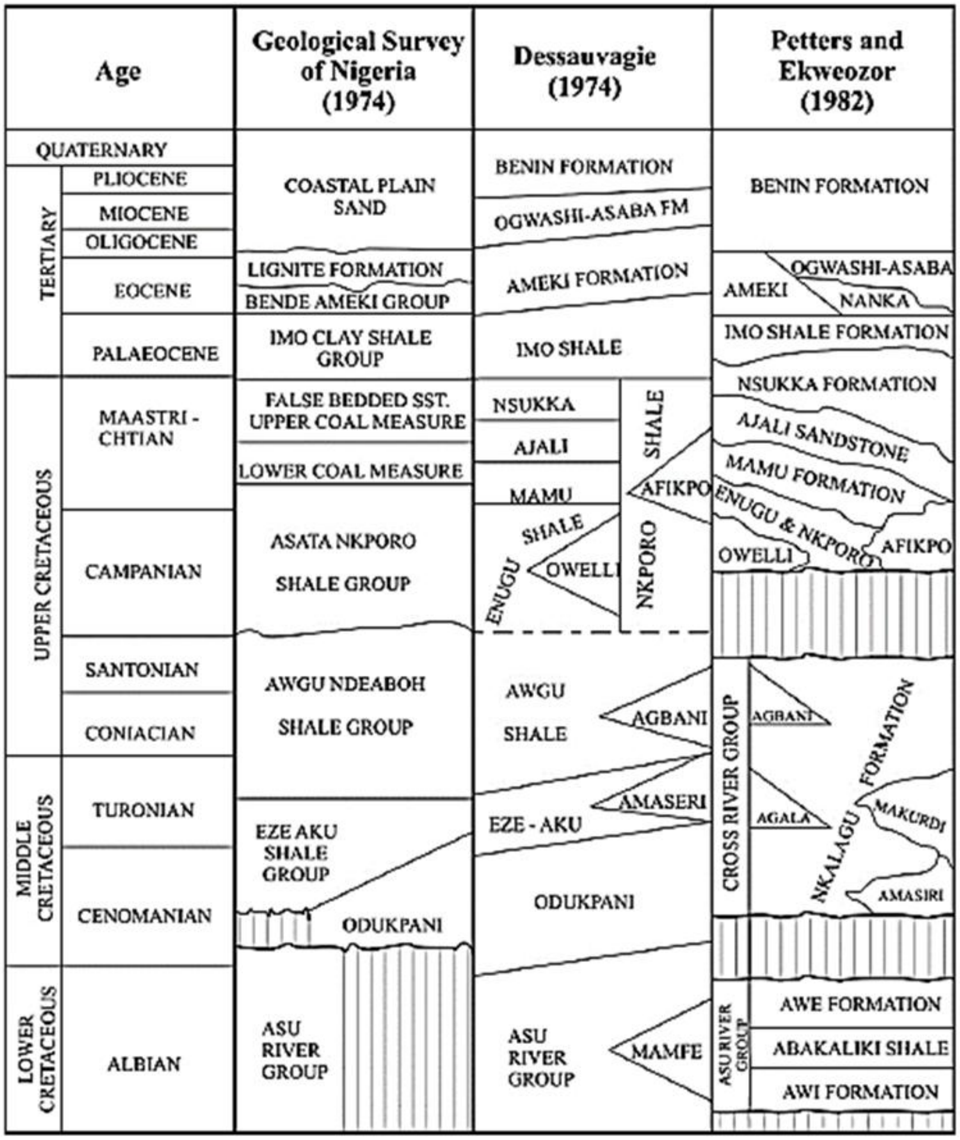


***Fig 2.2** Stratigraphic subdvision of the Lower Benue Trough.*

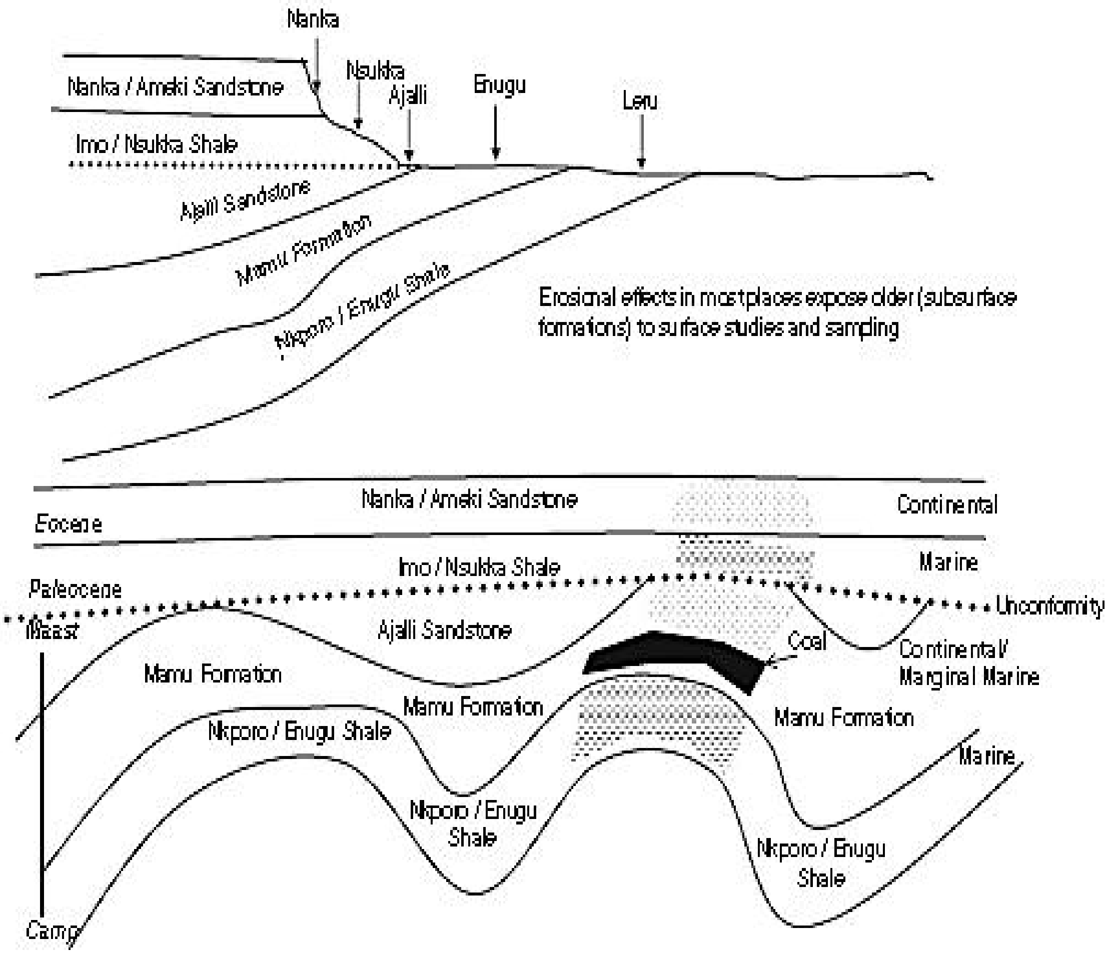


Fig 2.3 *Stratigraphic successions in the Anambra Basin*

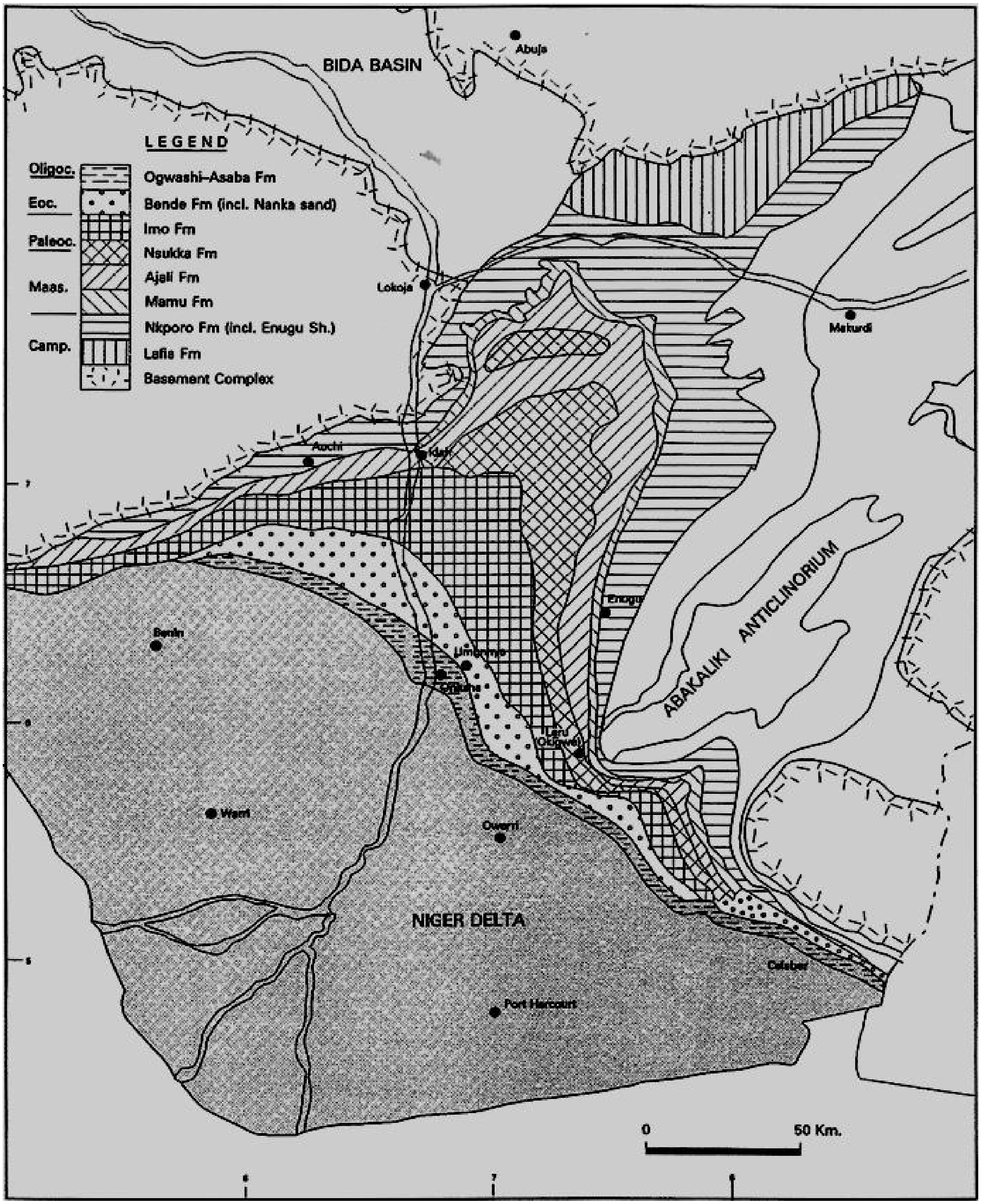
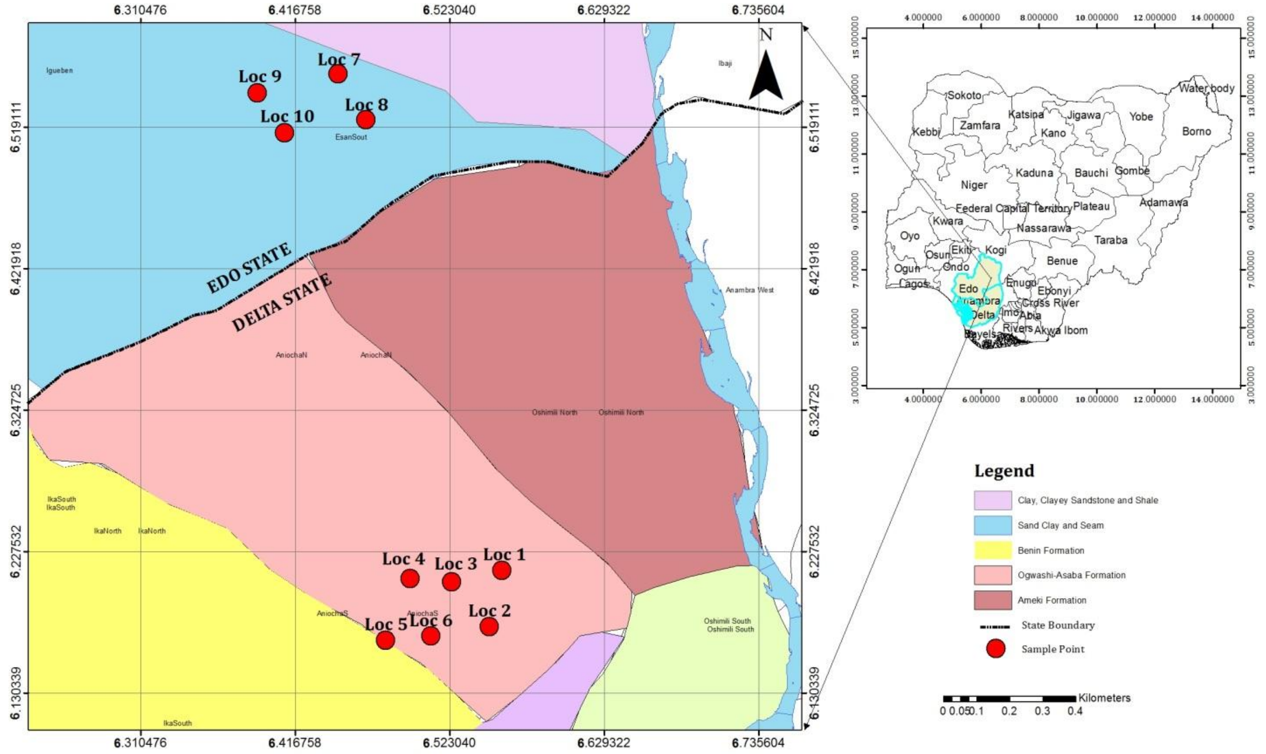


Fig 2.4 *Regional Sketch map of the Anambra Basin*

2.3 LOCAL GEOLOGY OF THE STUDIED AREA

The lignite series, also called the Azagba-Ogwashi Formation (Reyment, 1965) is located on the continental margin of southern Nigeria in a 16–20 km wide strip, covering a distance of about 240 km (Fig.2.0). Lignite layers have also been encountered in the lowermost strata of the Ameki Group (Fig 2.2) and the uppermost strata of the Benin Formation in drill holes, streams/river banks and road-cut outcrops (Okezie and Onuogu, 1985). The sedimentary basin in southern Nigeria formed in early Cretaceous.The Benue–Abakaliki Trough constitutes a failed arm of the rift junction associated with the separation of the African andSouth American continents and the subsequent opening of the South Atlantic Ocean (Murat, 1972). During the filling of the Benue–Abakaliki sector of the Trough in Albian–Santonian times, the proto-Anambra Basin was a platform. The east–west Coniacian–Santonian compressional forces uplifted the Abakaliki segment of the Trough, causing a westward translation of the depositional axis. The platform areas bordering the Benue Trough to the west (Anambra Platform) and to the east (Afikpo Platform)became downwarped due to the Santonian tectonism to form the Anambra Basin and the Afikpo Syncline, respectively (Fig 2.2) (Benkhelil, 1989; Murat, 1972). The Anambra Basin contains a 6-km thick sedimentary sequence of Cretaceous/Tertiary age and is the structural link between the Cretaceous Benue Trough and the Tertiary Niger Delta (Mohammed, 2005). The lithic fill took place during three major cycles (Reyment and Morner, 1977), corresponding to the major marine transgressions during Campanian, Palaeocene, and Eocene. The Campanian transgression into the basin resulted in the deposition mainly of shale (prodelta) with subordinate sand (Nkporo Group). Slow subsidence was followed by a regression in Maastrichtian times, during which deltaic forestsand floodplain were developed resulting in the coal measures ofthe Mamu, Ajali and Nsukka Formations. The outbuilding of the modern Niger Delta lithofacies began with a large-scale Palaeocene transgression that led to the Imo Shale formation. Marine regression during the Eocene resulted in the deposition of the Ameki Group strata comprising the Nanka Sand, which is overlain by the Oligocene–Miocene lignite-bearing Azagba-Ogwashi Formation. Reyment (1965) suggested an Oligocene–Miocene age for the latter formation, whereas Jan du Chêne et al. (1978) based on palynological data proposed a Middle Eocene age for the basal part. The Benin Formation is the topmost unit of the delta (Fig.2.1). The Azagba-Ogwashi Formation consists of a sequence of coarse grained sandstone, light coloured clay and carbonaceous shale with lignite intercalations. The lignite seam comprises two main thick layers: the lower and the upper one, averaging 6 m and 3 m in thickness, respectively, and being separated by a 4-m-thick shale layer. The Azagba-Ogwashi lignite outcrops along river valleys, streams/springs at least at seven localities between Obomkpa and Isele-Uku in the northwest and Nnewi in the southeast . The average ratio of overburden to lignite is 6:1, which appears to rule out open-casting (De Swardt and Piper, 1957).



Geological Map of the Study Area (Adapted from NGSA, 2004).

Fig 2.5 *Geological Map of the Study Area.*

2.4 REVIEW OF RELEVANT LITERATURE

Many research works had been done on Nigeria coals by numerous scholars with much attention on its energy usage (Gasification, Liquefaction Electric Power Generation and Coke Manufacture)(Felix Bamidele et al, 2013)Such Research workinclude:Integrated Geochemical and Organic Petrographic Characterization of the Campano-Maastrichtian, (AkaegbobiI. M.,2009) where he attempts to re-evaluate the discrepancies in past investigations based on the prospective value and Characterization of the Campano-Maastrichtian source rocks and their hydrocarbon potential taking cognizance of the interactions between source rocks and their prevailing pale depositional environment. According to (Akande et al, 1998), the rank and petrographic composition of selected upper Cretaceous and tertiary coal of southern Nigeria

(Enugu, Orukpa, Okaba, Ihioma and Azagba-Ogwashi) where determined by reflectance measurements. The result reflectance measurements indicates a range from sub-bituminous A Coalification grade for the Lower Maastrichtian coals of the Mamu Formation, whereas the Oligocene-Miocene Coals in Azagba-Ogwashi Formation are predominantly of Lignite rank. The highest grade of sub-bituminous A was attained in Enugu area (Onyeama mine) in the South and decrease towards the Okaba mine where the ranks are within the sub-bituminous C coalification grade..Chukwu et al, (2016), characterized some Nigerian Coals for Power Generation, where Five coal samples from Odagbo (Kogi State), Owukpa (Benue State), Ezimo (Enugu State), Amansiodo (Enugu State), and Inyi (Enugu State) of Nigerian coal deposits were subjected to proximate analysis, ultimate analysis, calorific value determination, and petrographic and thermo gravimetric analysis to determine their suitability for power generation. Based on results of tests carried out, Amansiodo coal is a bituminous, low sulphur, and medium ash coal, while Owukpa coal is a sub bituminous A, low sulphur, low ash coal rich in huminites, Odagbo coal is a subbituminous B, medium sulphur, low ash coal rich in huminites, Ezimo coal is a subbituminous C, low sulphur, high ash coal, and Inyi coal is a subbituminous C, low sulphur, high ash coal. Between Odagbo and Owukpa subbituminous coals, Owukpa has a lower ignition temperature (283.63∘C) due to its higher volatile matter content (39.1%).However, Ezimo sub-bituminous coal, which has a lower volatile matter (31.1%), unexpectedly has the same ignition temperature as Owukpa (283.63∘C) due to its higher liptinite content (7.2%) when compared with that of Owukpa (2.9%).The ease of combustion of the coal samples in decreasing order is Odagbo <Owukpa <Inyi <Ezimo <Amansiodo.Akande et al,2011 study has investigated the petroleum potentials of the outcrop samples exposed at Azagba-Ogwashi, Oba and Ihioma areas from the organic petrologic and geochemical viewpoints, where he concluded that The relatively

large proportion of liptinites (Type II oil prone Kerogen) in the lignite especially in Azagba Ogwashi suggests the potential for oil generation, while the predominance of huminites (Type III gas prone Kerogen) in Oba and Ihioma suggest the potential for gas generation. Source rock facies including the Shales and coals investigated have good to excellent organic matter content and can therefore be considered as potential petroleum source rocks which upon maturity will generate oil and gas.(De Swardt and Piper (1957) described the lignite deposits of Azagba-Ogwashi Formation, while (Okezie and Onuogu (1985) published a summary of available information on the lignite seams of southeastern Nigeria. They noted that the lignite seams are products of Tertiary tropical and semitropical coal-forming forests. Nwadinigwe (1992) described the wax and resin characteristics of Nigeria's low-rank coals and concluded that the lower the coal rank the higher the total amount of wax and resin extracted from them. Adedosu et al. (2007) applied energy dispersive X-ray fluorescence spectrophotometry (EDXRF) to determine eight trace metals in sub-bituminous coals from five coal fields (Ribadu, Okaba, Okpara, Orukpa and Ogboyoga) and lignite seams from Ogwashi–Asaba Formation. Olobaniyiand Ogala (2011) applied Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) in order to determine 21 major, trace and rare earth element contents in samples obtained from these five Nigerian lignite deposits. The low silica (<10 wt. %) and alumina contents (<7 wt. %) are explained by a very limited detrital input during coal formation. Also the low MgO (0.02–0.11 wt. %) and CaO contents (0.05–0.15 wt. %) imply a continental origin for the coal. This is in consonance with the continental setting of the Azagba-Ogwashi Formation (Kogbe, 1976).Reflected light oil immersion techniques was used in an attempt to characterize and differentiate optical properties of coal (Asuen G. O et al ,2013) using samples from north-eastern England and Scottish Fife field coal observed that lower rank values manifested in the

Westfield is a reflection of both clean/homogeneous surface and the heavy bitumen staining of the vitrinite particles.

2.4.1 Extraction and Characterization of Lignites

Various methods had been employed in the extraction and Characterization of Lignite, Mona Zara (2017) deals with the extraction and characterization of humic acids from low rank coals of Thar, Chakwal, and Quetta. Three respective coal samples were initially oxidized with 2% HNO3 and then treated with 2.5, 3, and 3.5% KOH solutions for the extraction of humic acid. The 3.5% concentration of KOH was found to be the optimum for the extraction of humic acid. The extracted humic acid was investigated for its quantitative assessment through gravimetric and UV spectrophotometer procedures. The gravimetric method showed 24.6, 13.6, and 18.0% of humic acid extraction from Thar, Chakwal, and Quetta coals, respectively, whereas the humic acid determined by UV spectrophotometry was 29.67, 20.1, and 22.6% for the same sample sequence. FTIR analyses of extracted humic acid samples have shown the presence of carboxylic, phenols, alcoholic, and amines functional groups. The 13C NMR spectra of three humic acids have exhibited the broad diversity of aliphatic and aromatic compounds such as carboxylates, carbohydrates, ethylene, phenols, and amines. The results of the study could be useful for selection of suitable coals for humic acid extraction.Deborah P. D (2002) Humic acids (HA) extracted from two coals of different ranks, from their regenerated samples and from a nitrated sample, were characterized by elemental analysis and by infra-red (FTIR), solid state 13C nuclear magnetic resonance (NMR) and eletronic paramagnetic resonance (EPR) spectroscopies. The low rank coal HA presented higher C and lower O contents, higher C/N and lower H/C and O/C ratios than high rank coal HA. NMR results showed that both samples were more aromatic and less carboxylic than common soil HA. Those characteristics may limit the coal HA efficiency as an appropriate soil conditioner and fertilizer. The regeneration process did not produce major alterations in the coal HA, except a decrease of the free radical content as determined by EPR spectroscopy. Probably, the regeneration conditions and time were not adequate to oxidize the samples. The obtained FTIR spectra were much alike, except that from the nitrated sample, where the absorption band at 1533 cm-1 confirms the presence of nitrated groups. The nitration process increased the N content and reduced the C/N ratio to values comparable to those reported for soil HA, but the aromaticity still remained high and the carboxylic content was lowered after the procedure.

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CHAPTER THREE

METHODOLOGY

3.1 MATERIALS AND METHODS

The study of the area was carried out in three phases:

(1) Preliminary review of literature.

(2) Visits to outcrops and field studies.

(3) Laboratory analyses and interpretation of results from collected samples.

3.1.1 Preliminary studies:

Reviews of the relevant literature concerning the study area both on regional and local scales were carried out to get acquainted with the area. The terrain, regional stratigraphic succession and accessibility of the area were depicted in geologic maps and table.

3.1.2 Visit to outcrop and Field studies:

The area was traversed using the Global Positioning System (GPS) to get the coordinates and elevation of outcrop locations. Other instruments used include digital camera, field hammer. Outcrops were studied and lithological characteristics recorded and samples taken. Lithologic sections and sketches of notable features were jotted down. Collected samples were appropriately packaged, labelled and sealed using sample bags and masking tapes.

3.1.3 Laboratory Analyses

Lignites samples were subjected to analytical study, with the view to characterizing its humic content and properties for use in soil beneficiation and conditioning. XRD and XRF analytical methods were employed to determine the mineralogical and elemental composition of the samples, respectively. Proximate and Ultimate analytical techniques were used to characterize the lignite from which humic acid was extracted under alkaline condition, and precipitated using acidic medium of 6M HCl. The humic acid was characterized using Ultimate analysis and Uv-Vis analytical technique.

3.2 SAMPLE LOCATION

Two locations regarded as different sources of lignite: outcrop exposed at Mgbiligba River, Delta State and Ohordua in Esan Edo respectively, were surveyed and selected for this study. Grab Lignite samples were picked up randomly from outcrops of the two locations at the banks of streams and rivers. Composite samples of the various spots where taken into six representative samples for further analysis. The samples were stored in appropriately labeled airtight polythene to retain their as-received conditions.

PLATE 3.1a;*Rock exposure of Azagba-Ogwash Lignite(Yellow layer shows layers of Clay gritted with sands;Dark layers shows Lignite Layers 3m thick with Conchoidal fracture and dull lustre)*

PLATE 3.1b;*Rock exposure of Azagba-Ogwash Lignite(highly indurated yellowish stained dark lignite rock 6m thick)*

PLATE 3.2a*;Rocke exposure of Ohordua Lignite (dark-brownish layers shows highly indurated lignite rock exposed at Ohordua river)*

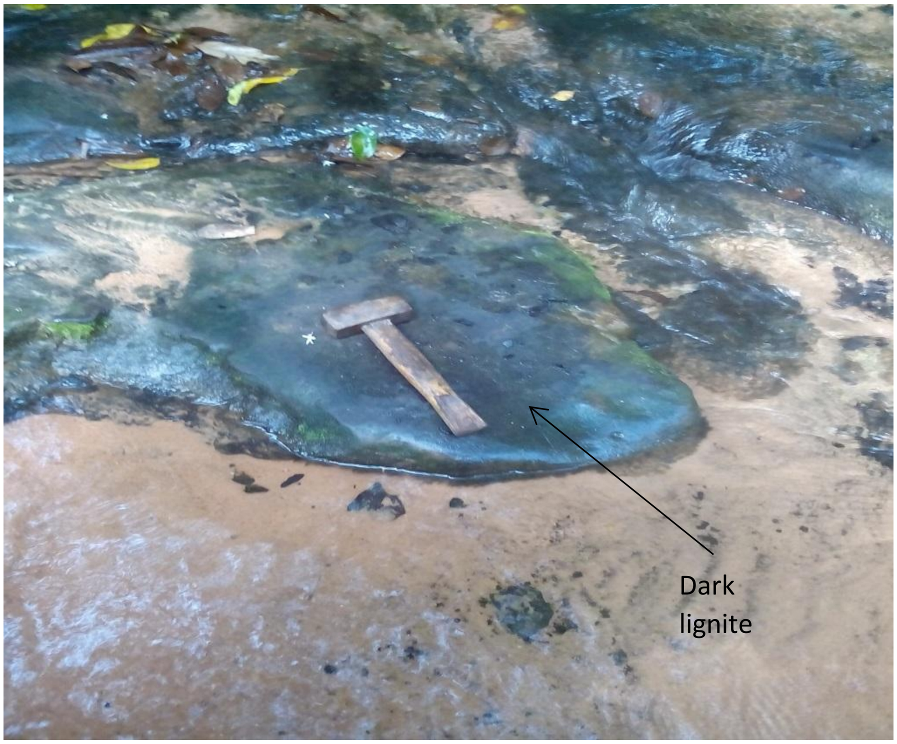

PLATE 3.2b *Lignite exposure of Ohordua Lignite.(dark lignite rocks exposed on Ohordua river)*

PLATE 3.3 *Sample collection of Lignite sample(Azagba-Ogwash)*

3.3 GENERAL SAMPLE PREPARATION.

Lignite samples were washed and dried at 105 °C for 24 hours before pulverizing into powder. The principle of mixing and then dividing, using manual methods as described in the International Organization for Standardisation (ISO) 13909-4:2001 specifications, was used to generate a representative pulverised sample of each Lignite and then used to prepare each sample to the desired analytical specifications using wooden mortar and pestle.The sample was reduce from a top size of 150mm to a suitable size distribution range of 150–212 μm. A manual sieve shaker was used for sieving the samples to the desired size distribution required for each test, while a hand rifle was used to split the samples into representative subsamples.

3.4 QUALITATIVE ANALYSIS OF LIGNITE (PROXIMATE ANALYSIS)

The qualitative analysis involves Proximate and Ultimate analytical method.1g of each Lignite sample passing a 212 μm test sieve was used for proximate analysis. Moisture content was analysed using the air oven method based on South African National Standards (SANS) 5925:2007 specifications with a LABCON air oven .Ash content was analysed based on ISO 1171:1997 using a LENTON programmable furnace.

Procedures:

In order to assess the quality of Lignite the proximate analysis was conducted.

Proximate analysis of the Lignite was done with respect to it's use as soil conditioner and not on the basis of it's calorific value. Hence, two parameters which have been analysed under this particular method as (a) Moisture content and (b) Ash content were observed.

3.4.1 Moisture Content Analysis:

It is the loss of weight of Lignite when heated at about 105°C in a crucible. A known amount of finely powdered Lignite sample, in silica crucible is heated in an electrical hot air oven at 105°C-110°C for about an hour, later cooled in a dessicator and weighed. This process of heating cooling and weighing is repeated till the weight of the crucible containing anhydrous Lignite becomes constant. Loss in weight is reported as percentile moisture.

The loss in weight is expressed in percentage as % of moisture =(Loss of weight due to removal of moisture/ ×100)W1 − W2/W1× 100.

$$\% \, of \, Moisture = \frac{Loss \, of \, weight \, due \, to \, removal \, of \, moisture}{weight \, of \, coal \, sample \, taken} X100$$

$$\% \, of \, Moisture = \frac{(W1 - W2)}{W1} X100 \ldots\ldots\ldots. (1)$$

3.4.2 Determination of Ash content:

It is weight of residue obtained after burning a known amount of dry Lignite in an open crucible. The sample is heated at 700-750°Cfor about half an hour in a muffle furnace. Heating, cooling and weighing is repeated till a constant weight is obtained. The solid residue (ash) is cooled and weighed.

$$\text{Ash content} = \frac{Weight \, of \, the \, solid \, residue}{Weight \, of \, dry \, lignite \, taken} X \, 100 \ldots . \ldots (2)$$

3.5 CHEMICAL AND MINERALOGICAL ANALYSIS

3.5.1 Principle of Diffraction

The XRD analysis is based on passing X-ray beam through a lignite sample. The X-ray identifies the structural layers which is dependent on the d-spacing of the lignite minerals. The d-spacing is the exact spacing of the staking of the crystal lattices which indicates the arrangement of the atoms in a mineral. The X-ray on passing through the lignite samples gives peaks that is typical of each type of diffracted along a group of planes and the way they are diffracted is characteristics of the arrangement of the atoms within the mineral.

3.5.2 Diffractometer Technique

The less than 2 micron lignite fraction was grouped and the powder was pressed into an aluminum sample holder and rim through a wide angle Phillips P.W. 1011 goniometer connected to a PM 8220 recorder. The scanning was done from 2' to 40' under the following instrumental setting conditions. Nickel filtered Fek and radiation .Recording/scanning rate = 1' 20cm/min.

3.5.3 Extraction of Humic Acid

Extraction Studies on the sample to extractant ratio and their concentrations on HA recovery were carried out under ambient temperature. The following HA extraction procedure was adopted from Asing et al. (2004). Sample to extractant ratio:1:5, 1:10 and 1:20 with 0.25 M KOH KOH concentration (M) : 0.1, 0.25 and 0.5, Extracting agents : 0.25 M KOH, 0.25 M NaOH and 0.03 M Na4P2O7 + 0.175 M NaOH. Lignite samples weighing 10 g each were shaken up with 50 ml of 0.1, 0.25 and 0.5 M KOH respectively for 24 h in an orbital shaker. This was repeated for the 1:10 and 1:20 sample to extraction ratio. Residue in solution was separated by centrifuging at 10,000 rpm for 20 minutes before filtering. The residue was further subjected to two similar successive extractions. The combined supernatants from the three successive extractions were acidified to pH 1 by adding 6 M HCl to precipitate HA. The precipitate was allowed to coagulate for 24 h before centrifuging to recover the HA. The recovered HA was again solubilized by adding the desired alkali to be followed by the acidification and coagulation procedure for purification purpose. Inorganic impurities in the recovered HA were removed by adding 20 ml of 0.5% hydrochloric-hydrofluoric acids (HCL-HF) solution. This was placed in an orbiter shaker for 24hours after which HA was separated by centrifuging and filtering. The recovered HA was washed repeatedly with distilled water until no trace of Cl- was detected to remove soluble salts, chiefly KCl, from the HA. The yield of HA was calculated after drying the purified HA at 105 °C for 24 h. All determinations were carried out in triplicates.

3.6 ELEMENTAL ANALYSIS

UV-SPECTROMETER was used to carry out ultimate analysis and characterization of the Lignite and it's extract (HA). Ultimate analysis involves determining the Carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and Oxygen (O) of the Lignite. While organic characterization of the Humic Acid was done to determine it's potential for soil beneficiation and conditioning .

3.6.1 Acidic functional groups

Total acidity and carboxylic groups were determined according to the Schnitzer and Gupta (1965); and Wright and Schnitzer (1959). In order to measurement of total acidity, the IL-HA was treated with a barium hydroxide solution under N2 atmosphere for 24 h. The $Ba(OH)_2$ remaining in the solution after the reaction is then back titrated with a standard acid solution. For the titration of carboxylic groups, the HA was handled for 24 h with calcium acetate solution in excess which causes the release of acetic acid. The CH_3COOH released is then titrated with a standard base solution. Phenolic OH group was calculated by difference between total acidity and the acidity of the carboxylic groups.

3.6.2 Analysis of Lignite and humic acid properties

Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen concentrations in the lignite and humic acid samples (Elemental analysis of C, H, N, S,O) were determined by using UV-VIS. Ash content was measured after heating 50 mg of each peat sample at 750°C for 8 hours. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference.

3.6.3 Total acidity and Carboxylic Groups

For estimation of carboxylic groups and total acidity, an automatic titrator TitroLine easy (Schott-Geräte GmbH) was used. The known Ca-acetate method (Tan, 2005), based on the formation of acetic acid, was used for determining the total number of carboxylic groups. To estimate the total acidity, Ba(OH)2 method was used (Tan, 2005). Humification degree according to (Blackford and Chambers, 1993) and modified by (Borgmark, 2005)) was estimated as absorption at 540 nm after treatment of 1.00 g of peat sample for1½ hrs with 25 ml of 8 % NaOH in 25 ml plastic tube in a boiling water bath (95 ºC) and filtration.

3.6.4 Organic characteriazation of Humic Acid using UV spectroscopy.

UV–Vis follows the Beer-Lambart Law .This law states that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is actually proportional to the concentration of the solution and the incident radiation.

A=Log (IO/I)=ECI (A stands for the absorbance, IO refers to the intensity of light upon a sample cell, I refers to the intensity of light departing the sample cell, C stands for the concentration of the solute, L stands for the length of the sample cell and E refers to the molar absorptivity.)

The absorption of visible light or ultraviolet light by a chemical compound will produce a distinct spectrum. UV-Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermoelectron Co)spectrophotometer in a 1-cm quartz cuvette. The UV-Vis spectral ratios E2/E3 (Peuravuori et al.,1997) and E4/E6 ratio (Chen et al., 1977), i.e. the ratio of absorbance at 280 and 360, and 465 and 665nm respectively, was determined for humic acid solutions 10 mg/l diluted in 0.05 *M* NaOH.

Absorbance ratios E280/472, E280/664, E472/664 were calculated from UV-Vis absorbance at 280,472 and 664 nm (Albrecht, 2011). Absorbance ratio E270/400 were calculated from UV-Vis absorbanceat 270 and 400 nm (Uyguner and Bekbolet, 2005). Absorbance ratio E254/436 were calculated from UV-Visabsorbance at 254 and 436 nm (Shirshova et al., 2006).

Specific absorbance A280 (Chin et al. 1994), (Scotta et al., 2001) were calculated based on UV-Vis absorbance at 280, 254, 436 and 340 nm, where values were normalized per mol C with units L mol C-1 cm-1 of organic matter in solution (Chin et al. 1994). The value of Δ log K coefficient, Δ log K = log A400 – log A600, was calculated to determinedegree of humification (Fong et al., 2006).

3.7 INORGANIC GEOCHEMISTRY OF LIGNITE USING X-RAY FLUORESCENCE (XRF)

The XRF method depends on the fundamental principles that are common to several other instrumental methods involving interactions between electron beams and x-rays with samples. The analysis of major and trace elements in the Lignite sample is made possible by the behavior of atoms when they interact with x-ray radiation, they become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and it is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the Lignite sample.

CHAPTER 4

PRESENTATION AND DISCUSSION OF RESULTS

4.1 PRESENTATION OF RESULTS

Table 4.1.1 Inorganic geochemistry of the lignites in wt.%

Shows the geochemistry and major oxides of lignites from Ohordua and Azagba–Ogwashi

RESULT SAMPLE	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**P_2O_5**	**K_2O**	**MnO**	**MgO**	**Na_2O**	**LOI**
OH 1	55.38	30.21	2.34	1.26	6.54	0.76	0.95	0.01	1.42	0.76	12.44
OH 2	55.40	30.40	1.78	1.21	5.87	0.60	0.86	0.0I	1.32	0.66	12.20
OH 3	54.30	31.30	2.3O	1.19	6.45	0.60	0.99	0.01	1.31	0.65	11.80
AO 1	55.91	27.78	1.87	1.42	8.26	0.53	1.02	-	2.04	1.03	12.32
AO 2	52.32	26.77	1.88	1.32	7.50	0.64	1.07	-	2.00	1.40	12.47
AO 3	54.86	27.90	1.66	1.11	8.30	0.55	0.85	0.01	1.98	1.06	12.50

Table 4.1.2: Trace elements in lignite in ppm.

Trace elements detected in the lignites showing Barium having a higher concentrations.

RESULT SAMPLE	Ba	Cu	Cr	Ni	Zn
OH1	714.85	23.26	110.22	30.55	211.40
OH2	770.62	23.33	112.40	32.55	210.44
OH3	699.61	24.33	100.30	31.60	210.45
AO1	705.52	22.18	110.14	30.70	210.45
AO2	672.67	22.36	111.20	31.65	210.45
AO3	686.53	21.80	109.10	30.80	210.38

Table 4.1.3 Proximate and Ultimate analysis (%) of average of Lignite samples from Ohordua and Azagba-Ogwashi respectively.

Carbon content increased while H, N and O decreases,the values range depict a typical lignite rank .

RESULT SAMPLE	C	H	N	S	O	H/C	O/C	Ash	Moisture
OH	65.22	6.60	1.34	0.77	26.07	0.10	4.0	5.02	26
AO	67.16	6.22	1.19	0.7	24.73	0.01	0.37	4.5	25.4

Table 4.1.4 Chemical analysis of Humic acid in Ohordua and Azagba-Ogwash Lignite in wt.%

The table shows content of C, H, O, N, and S which provides essential information on the origin of the sample. The H/C, O/C and C/N atomic ratios indicate the structure and the molecular shape of the Humic acid.

RESULT SAMPLE	C	H	N	S	O	O/C	H/C	N/C	C/N	C/H	O/H	Ash
OH	57.5	5.1	2.5	-	34.9	0.66	0.09	0.04	23.00	10.88	7.24	2.8
AO	55.8	3.9	1.1	0.3	38.9	0.70	0.07	0.03	50.53	14.31	9.97	1.5

Table 4.1.5 UV-Vis absorbance ratios, specific absorbance A_{280} and Δ log K of Humic acid.

This ratio shows the relationship between the molecular weight and degree of condensation.which helps to depict Aromatic or Aliphatic condensation.

Humic Acid	A_{280}	E_4/E_6	E_2/E_3	E_{280}/E_{472}	E_{280}/E_{664}	E_{270}/E_{400}	E_{472}/E_{664}	Δ log K
OH	21.69	4.5	2.75	6.2	25.83	4.17	3.54	o.66
AO	19.39	4.6	2.72	6.23	27.4	4.4	3.51	o.66

Table 4.1.6 UV-Vis absorbance ratio and Aromaticity.

Shows aromaticity values of AO and OH,slightly higher value of 34.06 was recorded in AO humic fraction, while OH recorded a value of 33.90,showing that AO humic substance is slightly richer in aromatic molecules than OH humic substance.

RESULT SAMPLE	E_4/E_6	E_2/E_3	**Aromaticity**
OH	**4.5**	**2.75**	**33.90**
AO	**4.6**	**2.72**	**34.06**

Table 4.1.7 Total acidity, carboxylic and phenolic group content of Humic acid (meq g-1) from Lignites.

The table shows the total acidity of both lignites , with Ohordua Lignite slightly higher than Azagba-Ogwash.

Humic acid	**Total acidity**	**COOH**	**Phenolic**	**Acidity ratio**
OH	10.4	3.4	7.0	0.49
AO	10.1	3.3	6.8	0.48

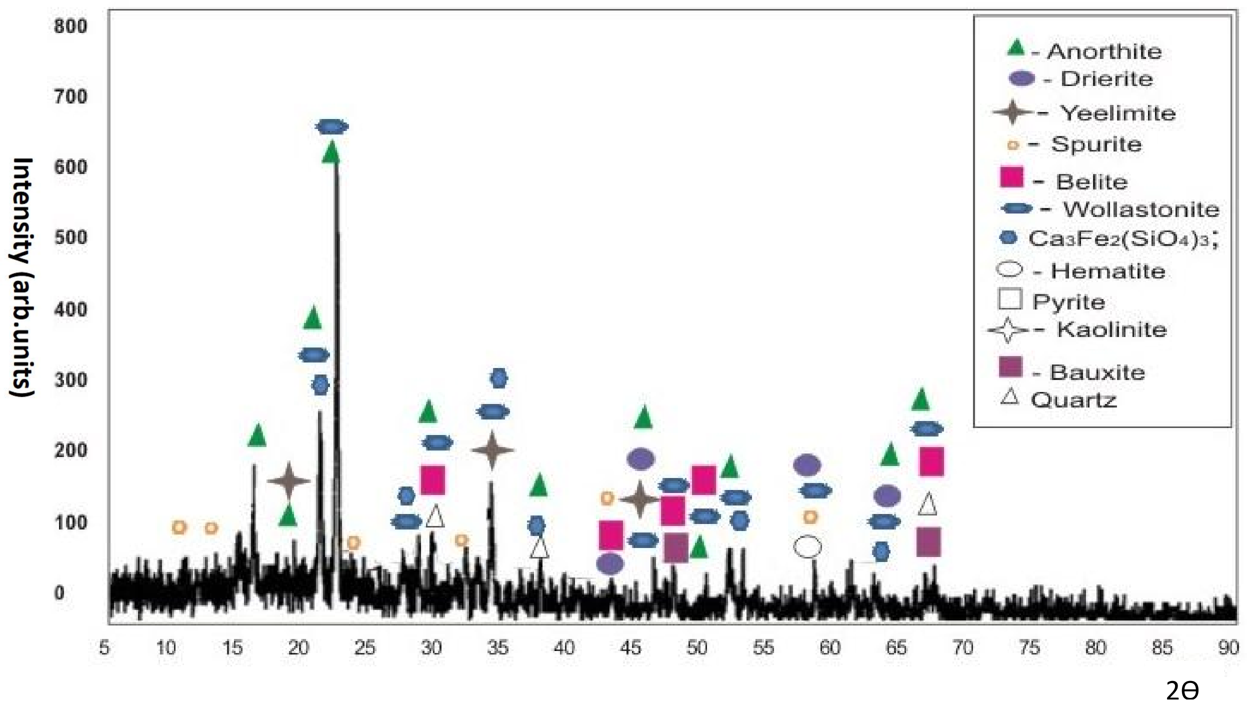

Fig4.1:Ohordua Lignite diffractogram.

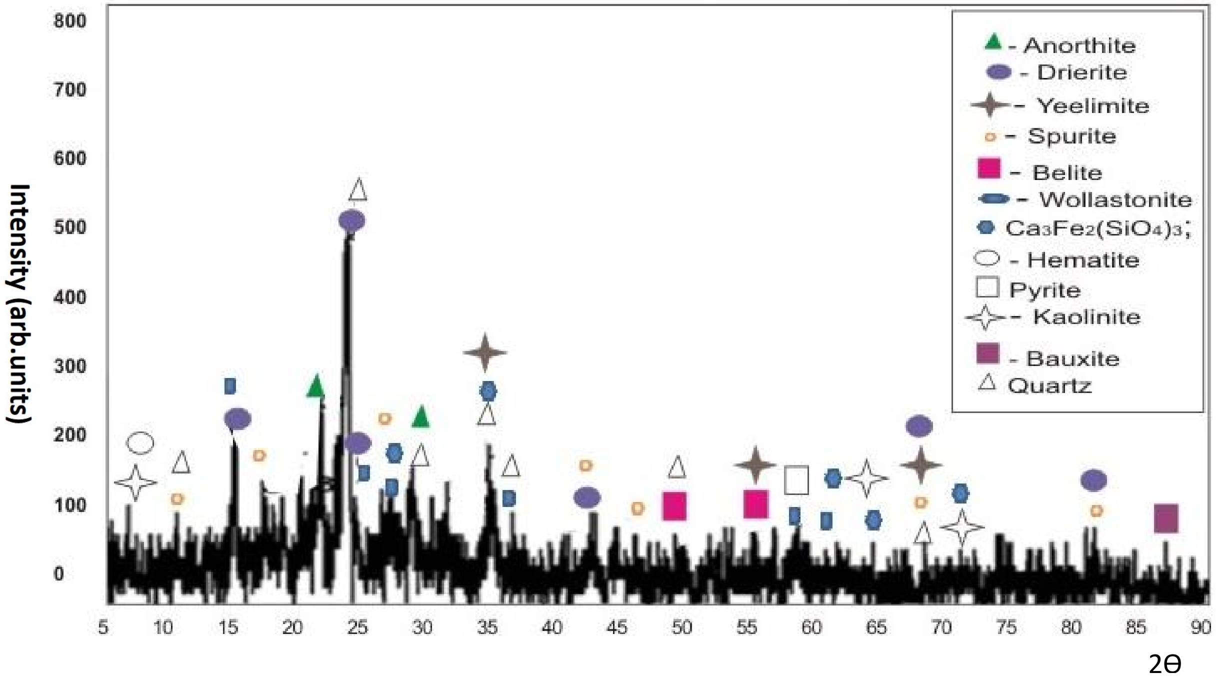

Fig4.2: Azagba-Ogwashi Lignite diffractogram.

4.2 DISCUSSION OF RESULTS

4.2.1 Inorganic Geochemistry

Table 4.1.1 shows the geochemistry/major oxides of lignites from Ohordua and Azagba – Ogwashi. The trace element of samples is also recorded in Table 4.1.2. Results from both tables shows that the samples are rich in silica (54.30-55.40 %) for Ohordua and (52.32-55.91%) for Azagba-Ogwashi, as well as alumina (30.21-31.30%) for Ohordua and Azagba-Ogwashi (26.77-27.90%) They are the dominant oxides in the samples. This may be due to the inter bedding/association of the lignite samples with sand stones and clays. The relatively high Silica (SiO_2) and Alumina (Al_2O_3) content suggested very high detrital input during coal formation. Concentrations of these oxides are lesser in the Azagba-Ogwashi samples compared to that of the Ohordua samples except in the alkaline and alkaline earth oxides. Other oxides recorded are; Fe_2O_3(1.78-2.34%), TiO_2(1.19-1.26%), CaO(5.87-6.54%), P_2O_5(0.60-0.76%), K_2O (0.86-0.99%), MnO(0.01%), MgO(1.31-1.42%), Na_2O(0.65-0.76%) and LOI (11.80-12.44%) for Ohordua lignites and Fe_2O_3(1.66-1.88%), TiO_2(1.11-1.42%), CaO(7.50-8.30%), P_2O_5(0.53-0.64%), K_2O(0.86-1.07%), MnO(0.01%), MgO(1.98-2.04%), Na_2O(1.03-1.40%) and LOI (12.32-12.50%) for Azagba-Ogwashi lignites. The relatively low CaO (5.87-6.54%) and MgO (1.98-2.04%) content implied a continental origin for the Lignite. The Azagba-Ogwashi lignites are richer in CaO more than the Ohordua lignites. The moderate to high SiO_2, Al_2O_3 and Fe_2O_3 concentration was due to quartz, feldspar and pyrite in the lignite samples.XRF analyses revealed the main constituents of the electric precipitated fly ash samples to be SiO_2, Fe_2O_3 and Al_2O_3 indicates the abundance of quartz and aluminosilicate minerals in the lignite sample.

4.2.2 Trace elements

Trace elements detected in the lignites (Table 4.1.2) are Ba (699.61-714.85ppm), Cu (23.26-24.33ppm), Cr (100.30-112.40ppm), Ni(30.55-31.60ppm) and Zn(210.44-211.40ppm) for the Ohordua lignite and Ba (686.53-705.5ppm), Cu (21.80-22.36ppm), Cr (109.10-111.20ppm), Ni(30.70-31.65ppm) and Zn(210.38-210.45ppm) for the Azagba-Ogwashi lignite. Ba, Zn and Cr have higher values than Cu and Ni in all the samples.They may not be inherent but allochtonous.Ba is toxic and source can be from successive sewage sludge,Ba cation has been shown to accummulate in acidic condition,this depicts the environment of deposition must have been acidic to enhance the accummulation of Ba in such quantity.

4.2.3 Mineralogy

The XRD diffractograms as shown in Figures 4.1 and 4.2 shows that in the lignite samples, Kaolinite was the main clay mineral identified. Non clay minerals such as anorthite,drierite,yeelimite, spurite, belite, wollastonite, hematite, pyrite, bauxite and quartz were also identified in both samples. These minerals could be epigenetic in nature as they may not be part of inherent mineral matter of the lignites.

4.2.4 Chemical characteristics of Lignites

The measurement of Carbon concentration is still the leading and most accurate parameter among other chemical characteristics for evaluation of coal rank. Generally, coal contains high amount of carbon (70–95%), 3–5% hydrogen, 2–22% oxygen and 1–2% of sulphur and nitrogen Lawson & Stewart, 1989), Coal with high Carbon and low Oxygen content has low Humic acid content. Lignites from Ohordua and Azagba-Ogwashi showed Carbon content ranging from 65.22–67.16% and Oxygen from 26.07–24.73% (Table 4.1.3). The Carbon content was slightly higher in Azagba-Ogwashi than Ohordua, while Oxygen is the reverse 26.07 and 24.73%. These values are within the fixed carbon range of 60 to 75% for lignite deposits (Martin et al.,1983). As coal rank increased, the Carbon content increased while H, N and O decreases,the values range decreased from Azagba-Ogwashi 6.22-6.60%, 1.19-1.34% and 24.73-26.07% to Ohordua respectively. This is attributed to more intensive aromatization as coal rank increases (Francioso et al.,2003). This is shown in Table 4.2.1 below. Comparing these lignite values with other lignites and sub-bituminous coal of Nigeria, the Ohordua lignite is the lowest in rank amongst them all.Result from the Proximate analysis shows that the samples are of lignite rank with lower carbon content depicting that it has not been buried very long(meaning it is more recent than bituminous and anthracite coals.), with low energy density. Since Azagba Ogwashi Lignite has a higher carbon content and lower Oxygen content,this indicates that the Azagba-Ogwashi lignite is a little more matured and purer than Ohordua and Ohordua Lignite is more recent in burial than Azagba-Ogwashi.

Table 4.2.1: Comparison with other lignites and sub-bituminous coals in Nigeria

LOC RESULT	**OH**	**AO**	**IB[1]**	**OK[2]**	**OB[3]**	**IH[4] (Imo)**	**UB[5] (Imo)**	**NW[6]**	**ON[7]**	**OBI[8]**	**OA[9]**
C	65.22	67.16	65.6	67.0	65.0	71.33	72.28	63.7	75.40	87.6	80.50
H	6.60	6.22	6.15	6.5	7.6	6.43	7.17	7.7	5.4	5.6	6.0
N	1.34	1.19	1.05	1.0	0.96	1.33	0.73	0.9			
S	0.77	0.70	4.3	-	7.7	0.83	0.90	-	0.7	0.9	0.37
O	26.07	24.73	25	25.6	24.0	4.5	5.67	27.8	-	-	-
MC	26.00	25.40	37.6	39.0	33.6	7.57	6.19	43.6	5.8	3.58	3.45
Ash	5.02	4.5	5.4	8.0	32.1	7.33	6.50	8.4	6.0	5.3	5.8

1) Ibussa (Delta) 2) Okpanam (Delta) 3) Obomkpa (Delta) 4) Ihioma (Orlu) 5) Ubaha (Orlu) 6) Nnewi (Delta) 7) Onyeama (Enugu) 8) Obi (Benue) 9) Okaba (Benue).

1, 2, 3 and 6 (Ogala et al., 2012)

4 and 5 (Ahiarakwem and Opara, 2012**).**

OH-Ohordua (Edo) and Azagba –Ogwashi (AO)

4.2.5 Hydrogen, Oxygen Nitrogen and Sulfur

The average hydrogen contents of Ohordua and Azagba-Ogwashi lignite deposits are 6.60 and 6.22% respectively, while the oxygen values are 26.07 and 24.73% respectively. The average nitrogen concentrations are 1.34 and 1.19% respectively. The average sulfur contents are 0.77

and 0.70% respectively. These values are relatively higher than those of bituminous coal (Table 4.1.3), as expected. The coalification process results in loss of moisture (dehydration) and decarboxylation (loss of carboxylic acid as CO2); as the coalification process progresses; the carbon (rank) increase while the oxygen and hydrogen contents decreases. The increased Oxygen concentration is in accordance with greater contents of moisture and hydrated minerals or as a result of advanced coal weathering, while the loss of Oxygen occurs in later stages of development of coal due to well known decrease in oxy-containing functional groups as carboxylate and increase in aromaticity (Rasheed, et al.,2015).The lignite samples have lower carbon and high hydrogen contents when compared with those of sub-bituminous coals in other parts of Nigeria and lower than lignite of Orlu area. The lignite deposits also have higher moisture and low ash content when compared with the sub-bituminous coal (Table 4.2.1). Generally, the sulphur content of the lignite deposits are low usually less than 1% and this makes them environmentally friendly in terms of industrial utilization. The low Nitrogen is a character ristics of low-ranking coal which the sample concentration falls within.

4.2.6 Ash Content of Lignites:

In the case of heterogeneous and complex substances, such as Lignite, the ash content is generally used as an indicator of the amount of inorganic compounds present in the sample or purity of the sample. It represents the bulk mineral matter after Carbon, Oxygen, Sulphur and water are given off during combustion indicating the quality of coal. The low ash contents of both lignite differ from each other. Ohordua recorded a value of 2.8 %, while that of Azagba-Ogwashi is 1.5%. This is an indication that the Ohordua humic acid is less purer than Azagba-Ogwashi.

4.2.7 Moisture Content of Lignites

The average value of the moisture at Ihioma Umuhu-Okabia and Ubaha are 6.76, 6.23 and 6.79% respectively (Table 4.2.1). It is quite imperative to note that moisture content decreases as the coalification process progresses. A comparison of the average moisture contents of the three lignite deposits in the study area with those of sub-bituminous coals in some parts of Nigeria indicates that lignite are gradually tending towards sub-bituminous coal; the moisture content decreases as the fixed carbon increases . The moisture is an important factor of Lignite as all coals are mined wet. The groundwater and other extraneous moisture known as adventitious moisture is readily evaporated while the moisture held within the coal itself is inherent moisture that is analysed quantitatively. Generally,the moisture content of Lignites ranges from 5% to nearly 70%.The fluid matter of Lignite comprises moisture,gas and gas-liquid inclusions associated with both solid organic matter (OM) and inorganic matter (IM).The increased contents of this physically and chemically adsorbed water are characteristic of lower-rank coals, while the decreased values of this parameter are typical of high-rank coals. In the present study the moisture. In the present study the moisture content for OH is 26%wt and OA 25.4%wt indicating the existence of lignite. The total moisture content is important in assessing and controlling the commercial processing of lignite.

4.3 Analysis of Humic Acid

For this study, UV-Vis method was used for the characterization of the humic fraction of the lignites. The various parameters used are shown in Tables 4.1.4.The content of C, H, O, N, and S provides essential information on the origin of the sample. The H/C, O/C and C/N atomic ratios indicate the structure and the molecular shape of the Humic acid. The heating value of coal generally increases as the proportion of H/C ratio increases due to higher heating value than carbon. The lower H/C ratio of Ohordua Lignite (0.09%wt) and Azagba-Ogwashi Lignite (0.07%wt) indicates a larger amount of unsaturated structures. In other words, an increase in the hydrogen content indicates a greater number of aliphatic carbons (CH_2) than aromatic carbons (C=C) (Traina, et al.,1990). Although the H/C ratio are almost the same, that of Ohordua is slightly higher, hence more aliphatic carbons while Azagba-Ogwashi with lower H/C atomic ratios, has more aromatic fractions.

The O/C atomic ratio is related to the carbohydrate and carboxylic acid contents (both aromatic and aliphatic) and degree of oxidation of the Humic acid. The lower values of this ratio in the humic acid of these samples indicate a higher degree of humification due to the reduction in the carbohydrate content in the Oxygen-bearing structures (polysaccharides).

The C/N atomic ratio indicates a seasonal influence on the degree of humification. The C/N ratios of fractions in Azagba-Ogwashi (50.53%wt) is greater than Ohordua (23.00%wt), indicating that the largest contribution to the humification of Azagba-Ogwashi Humic fraction resulted from the decomposition of vascular plants (Rocha, et al., 2007).

In general, the elemental analysis results (Table 4.1.4) indicate that smaller molecular size fractions contain a larger aliphatic proportion than aromatic carbon atoms and a relatively high percentage of oxygen atoms bound to alkyl groups and carboxylic acid.

Sulfur was not detected in the Ohordua fraction but Azagba-Ogwashi recorded a low value of 0.3%wtHS samples investigated.

4.3.1 Uv-Vis Absorbance Ratios

The E2/E3is inversely related to molecular .The E2/E3 size ratio was between 2.75 for OH and 2.72 for AO and compared well with other reported values of both natural and synthesized humic substances .Decrease in this order is proportional to the degree of condensation or the molecular weight, such that a high ratio would reflect a low degree of aromatic condensation and the presence of relatively large proportions of aliphatic structures. (Peuravuori et al.,1997),the ratio is usually < 5 for Humic Acid.This ratio is independent of Humic acid attributed to the lesser oxygen content in Ohordua fraction than Azagba-Ogwashi. Absorbance ratios E2/E3 and E4/E6 measured at (250/365nm) and (465/665nm) respectively were calculated for each Humic acid fractions. The values are shown in (Table 4.1.6). According to prior studies, E4/E6 ratio is inversely concentration and in general <5. Low E4/E6 ratio gives a better humification of Humic Acid .Although the E4/E6 ratio of Ohordua (4.5) and Azagba-Ogwashi (4.6)are low Ohordua ratio is slightly lower than Azagba-Ogwashi, this suggest that more chromophore molecules are concentrated; i.e., carboxylic and ketonic C=O and aromatic C=C in Azagba-Ogwash fraction than Ohordua fraction. Based on these results, it may be interpreted that Azagba-ogwash fractions has slightly higher aromaticity compared to Ohordua fraction.

The specific absorbance at 280 nm (A_{280}) has been used as an indicator of carbohydrate presence in the samples. The E_{280} values of humic acid shows a decrease from Ohordua (21.69) fraction to

Azagba-Ogwashi (19.39). This means that the presence of carbohydrate in Ohordua fraction is higher than Azagba-Ogwashi fraction and elucidate the increasing presence of carbohydrate in the samples.

This technique is used to evaluate the aromaticity and humification degree of HS (Silverstein et al., 1994). Table 4.1.5 summarizes the E4/E6 (absorbance at 465 and 665 nm) and E2/E3 (absorbance at 250 and 365 nm) atomic ratios of the OH and AO humic acid fractions. Higher E4/E6 ratios reflect the prominence of aliphatic structures, whereas lower E4/E6 ratios indicate the dominance of aromatic constituents (McDonald et al., 2004). Higher E2/E3 ratios are usually associated with lower molecular weight and lower degree of aromaticity (Vergnoux et al., 2011a). The E4/E6 ratio is influenced by the molecular size, environmental pH, oxygen content, carbon, carboxylic groups, origin and age of the humic material (Stevenson, 1994).Table 4.1.6 shows that the E4/E6 ratios of the humic fractions of both lignites were similar.

Also, the E2/E3 ratio values for both OH (2.75) and AO (2.72) fractions are similar (Tables 4.1.5 and 4.1.6). In larger fractions, the number of condensed rings is higher in comparison to the aliphatic structures, due to the high humification degree. When the values of E4/E6 and E2/E3 ratios are compared, the same tendency is observed, that is, the larger the molar mass, the higher its condensation degree and aromaticity. The E4/E6 ratio values for Ohordua Humic acidfraction (4.5) is slightly lower than Azagba-Ogwashi humic acid fraction(4.6).

To indicate the aromaticity of the molecule, an equation suggested by Peuravuori and Pihlaja (1997) was used, in which **Aromaticity = 52.5 - 6.78 E2/E3**. The aromaticity values are shown in Table 4.8. From the Table, slightly higher value of 34.06 was recorded in AO humic fraction, while OH recorded a value of 33.90. This shows that AO humic substance is slightly richer in aromatic molecules than OH humic substance.

4.3.2 Acidic Functional Groups of Extracted Humic Acid

Total acidity consisting of carboxylic acid and phenol groups has strong affinity for chelating metals such as Fe, Cu, Mn and Zn (Helena Chemical Company 2003). Humic acid from Ohordua and Azagba-Ogwashi lignites have a narrow range between10.4 and 10.1 meq/g(Table 4.1.7)and also in the ratio of COOH to OH groups (acidity ratio) of 0.49 and 0.48meq/g. Although the values for both lignites are similar, the value for Ohordua is still slightly higher than Azagba-Ogwash.E4/E6 ratio is inversely related to the Acidic functional group of the Humic Acid. The implication is that humic substance derived from degradable lignite material produces humic substances having more COOH than those containing higher content of lignin which is more resistant to degradation. This also means that coal of higher ranks will produce less COOH molecule than lower rank coals (lignites and peats) because of their high lignin contents.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The present study aimed to characterize the coal in the areas under study through chemical composition utilizing the parameters through proximate and ultimate analyses. The analytical results show that the Carbon content ranges between 65.22 and 67.16 wt%, Oxygen content varies from 26.07 and 24.73 wt%, the hydrogen content ranges from 5.1 and 3.9 wt%, the sulphur ranges between 0.00 and 0.3 wt%, the Nitrogen content ranges between 2.5 and 1.1wt%. for Ohordua and Azagba Ogwashi sample respectively. The analytical results suggest the existing coal is of lignite rank..The interpretation of laboratory data shows that there exists predominantly lignite, with Lignite from Azagba-Ogwashi slightly purer in constituent as a result of its higher fixed Carbon. The geochemical characteristics of the Lignite samples from the Azagba-Ogwashi and Ohordua were investigated; the main mineral phases contained in the lignite were Kaolinite ,anorthite, drierite, yeelimite, spurite, belite, wollastonite, hematite, pyrite, bauxide and quartz .The relatively high to moderate silica (SiO_2) and alumina (Al_2O_3) content suggested a high detrital input during Lignite formation. Extracted HA of Ohordua and Azagba-Ogwash Lignte respectively had narrow range of acidic functional groups with carboxylic group varied from 0.49–0.48 meq g–1 while phenolic group ranged from 10.4–10.1 meq g–1.Uv-Vis Absorbance-Ratio of the extracted humic acid from lignite revealed that typical major structural elements of HA such as H bonded OH and C=O (both carboxyl and ketonic) functional groups, C=C in aromatic rings and aliphatic CH2and CH3 groups were present indicating that the extracted HA were authentic and of high humification. it is this abundance of carboxyl groups and weakly acidic phenolic groups, which contribute to their complexation and ion-exchange properties. They exhibit both hydrophobic and hydrophilic characteristics and can bind topsoil mineral surfaces.. (ratio of Acidic functional groups, is lower in Azagba-Ogwashi HA and degree of Aromacity higher)For the above reasons HA from the studied are very good substance suitable for soil beneficiation and conditioning. Results from this research indicate that the Lignite from both locations are similar in geochemistry, mineralogy and organic properties. Although,humification is high in both samples, Ohordua Lignite with lesser aromaticity and E4/E6 ratio, higher E2/E3 ratio and higher acidity ratio is more suitable for soil beneficiation and conditioning than that Azagba-Ogwashi.

5.2 RECOMMENDATION

1. Appropriate economic appraisal of the deposits within the area should be done to fully ascertain the quality and quantity of the Lignite deposits; this will help in employing the most appropriate methods of extraction and processing and also the best use for the Lignite.
2. Further study on how humic acid from Lignite significantly affected plant height and shoots growth compared to organic fertilizers should be carried out as way of verifying the effectiveness of the extracted humic acid.

CHAPTER SIX

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