CHARACTERIZATION OF OIL SHALE FROM THE BIDA BASIN, USING TGA, TOC AND ROCK EVAL PYROLYSIS.

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ABSTRACT
The earth contains large amounts of hydrocarbons that are not contained in what might be called conventional hydrocarbons. With increasing demand for energy both domestically and industrially, a major challenge facing the world, the society is driven to search for alternative energy sources. In this work, oil shale samples were collected from the Bida formation of the Bida Basin, Niger state, Nigeria. Analytical tools such as Rock Eval Pyrolysis, Total Organic Carbon (TOC) and Thermographic Analysis (TGA) were used to characterize the sample. From the Pyrolysis results, the Hydrogen Index (HI) was 45.71 mgHC/gTOC, the Production Index (PI), 0.42 and the Tmax, 342 ^{O}C. The TOC was 1.40 wt%. From the TGA results, the activation energy of the oil shale was calculated using the Arrhenius equation and found to be 48.40 KJ/Mol, while the pre-exponential factor was 884.025 min^{-1}. Consequently, the oil shale is gas-prone and contains migratory hydrocarbons. Also, the content of organic matter in the sample is good.

Keywords: Oil shale, TOC, Rock Eval Pyrolysis, TGA, Hydrocarbons.

INTRODUCTION
Increasing energy demand is one of the most important problems facing the world. In addition to the search for new energy sources, energy demand is driving society to search for more efficient energy conversion systems. Yang et al., 2016. In these times of global market uncertainties and harsh economic realities, the world needs energy in increasing quantity for both industrial and domestic uses. With the world's population growing rapidly, energy will go a long way to support economic and social progress, and also build a better quality

of life especially in developing countries (Imperial Oil Limited, 2019). Energy is the key input in economic growth since it is essential in the process of various production. The process of economic development requires the use of various higher levels of energy consumption. Now, almost everything can be traced to the use of one form of energy or another. Interestingly, more energy reaches the earth from the sun (which is the most important source of energy) in an hour than its use in a year. Aside from direct solar energy, the sun's energy manifests in different ways such as in wind power, tidal power, fossil fuels, nuclear energy, Natural gas and Petroleum, etc.

Petroleum is a naturally occurring liquid located beneath the Earth's surface which can be refined into fuel. Petroleum is a fossil fuel i.e. it has been created by the decomposition of organic matter over millions of years ago. Its formation is in sedimentary rocks under intense heat and pressure for so long. Petroleum may be used as fuel to power vehicles, heating units and machines of all sorts, as well as being converted into plastics and other materials (Tissot et al., 1984). With conventional hydrocarbon reserves being rapidly utilized, a future in which demand for conventional deposits exceed supply is apparently inevitable. Wright et al., (2015). The alternative sources such as oil shale are available globally which may breach the gap developing between remaining conventional resources and demand. There are significant resources of oil shale in Nigeria and the world at large, which if exploited in an environmentally safe manner, would provide secure source of transportation fuels.

Oil shale deposits are found in virtually all world oil provinces because in most cases, they are source rocks for conventional oil reservoirs, although most of them are too deep to be exploited economically. There are more than 600 known oil shale deposits around the world. Although resources of oil shale occur in many countries, only 33 countries possess known deposits of possible economic value (Youngquist, 1998). Nigerian is blessed with an abundance resource of crude oil and its alternatives such oil shale, oil sand, tar, asphaltite, shale gas which can be transformed to increase supply of energy. It has an oil shale deposit of high economic value with the highest concentration in Imo (Okigwe) and Abia states. Other African countries with oil shale include South Africa, Egypt and Madagascar. The oil shale reserve in Nigeria remains untapped because of the large deposit of the conventional oil wells (crude oil). Overland, I. (2016). However, petroleum potentials of Nigeria have not been fully explored, especially hydrocarbon resources in the inland basins. The underutilized basins include Anambra Basin, Benue Trough, Benin Basin, Bida Basin, Borno Basin, Niger Delta Basin and Sokoto Basin (Geologin, 2012). Therefore, there is the need to utilized the use of energy sources in order to meet huge energy demand.

Oil shale is an organic-rich sedimentary rock that can be considered as a viable source of alternative energy to conventional petroleum. The organic matter enclosed in the oil shale is largely an insoluble solid matter referred to as kerogen. Thermal degradation of the kerogen at a temperature in the range of 400-600 ^{o}C will volatilize from oil, gas and a solid residue of coke. The yield of the oil during pyrolysis depends on the quantity or quality of the kerogen contained in the oil shale and its evolution. Understanding the behavior of the thermal degradation of the kerogen in oil shale and its geochemical features are very vital for effective exploitation of this natural resource as alternative source of energy.

Pyrolysis is a general technique used for the decomposition of complex organic material at elevated temperatures in the absence of oxygen (or any halogens); in such a way that low energy kerogen can be transformed into high energy hydrocarbon (shale oil). Shale oil is close to oil crude when its composition is being compared. It can be utilized as a fuel or feedstock for the production of derivatives of oil and chemicals. However, shale oil usually contains olefinic and polar heteroatomic compounds which makes it less attractive than the crude oil. Consequently, further treatment to increase the content of desirable compounds in shale oil may be necessary (Lai et al 2016). The characterization of organic matter for oil shale is a crucial step in the evaluation of hydrocarbon potentials of oil shale. Therefore, this study provides insight into the hydrocarbon potential oil shale sample from the Bida Basin, using TGA, TOC and Rock-Eval Pyrolysis as the analytical tools.

THE MID-NIGER (BIDA) BASIN.

The Mid-Niger Basin otherwise known as the Bida Basin or the Nupe Basin is a NW–SE trending intracratonic sedimentary basin extending from Kontagora in Niger State of Nigeria to areas slightly beyond Lokoja in the south. It is delimited inthe northeast and southwest by the basement complex while it merges with Anambra and Sokoto basins in sedimentary fill comprising post orogenic molasse facies and a few thin unfolded marine sediments (Adeleye, 1974). The orogenic movements of southeastern Nigeria and the Benue valley, nearby. The basin is a NW–SE trending embayment, perpendicular to the main axis of the Benue Trough and the Niger Delta Basin (Fig. 2.1). It is frequently regarded as the northwestern extension of the Anambra Basin, both of which were major depocentres during the third major transgressive cycle of southern Nigeria in Late Cretaceous times. Interpretations of Landsat images, borehole logs, as well as geophysical data across the entire Mid-Niger Basin suggest that the basin is bounded by a system of linear faults trending NW–SE (Kogbe et al., 1983). Gravity studies also confirm central positive anomalies flanked by negative anomalies as shown for the adjacent Benue Trough and typical of rift structures (Ojo, 1984; Ojo and Ajakaiye, 1989).

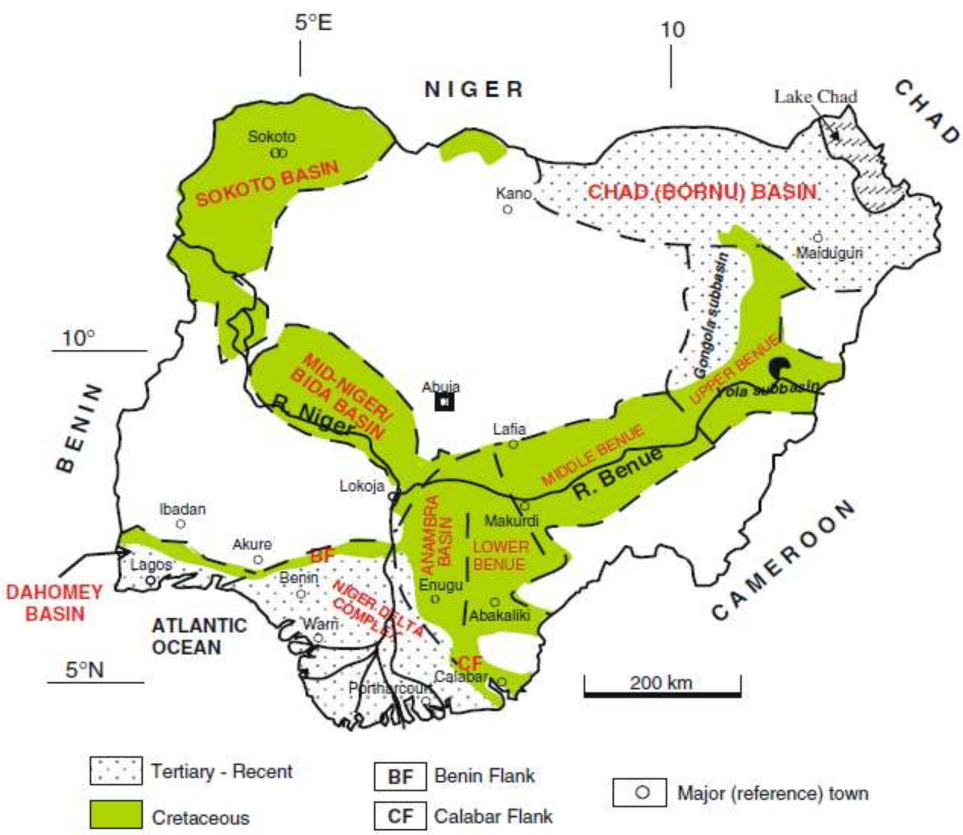


Figure 1 Sedimentary Basins of Nigeria.

Previous studies on the geology of the Bida Basin were reported in Adeleye (1973) and the micropaleontological studies of Jan du Chene et al. (1979) which documented the palynomorph-foraminiferal associations including the interpretation of the paleoenvironments of the Lokoja and Patti Formations. Akande et al. (2005) interpreted the paleoenvironments of the sedimentary successions in the southern Bida Basin as ranging from continental to marginal marine and marsh environments for the Cretaceous lithofacies. Whereas, the origin of the oolitic ironstones in the Bida Basin has been a principal subject of several workers (e.g. Adeleye,1973; Ladipo et al., 1994; Abimbola, 1997), only few investigations have been made on the hydrocarbon prospectivity of the basin.

Stratigraphic Framework

The stratigraphic succession of the Mid-Niger Basin, collectively referred to as the Nupe Group (Adeleye, 1973) comprises a two fold Northern Bida Basin (Sub-Basin) and Southern Bida Sub-Basin or Lokoja Sub-Basin. The Bida Basin is assumed to be a northwesterly extension of the Anambra Basin (Akande et al.,2005). The basin fill comprises a north west trending belt of Upper Cretaceous sedimentary rocks that were deposited as a result of block faulting, basement fragmentation, subsidence, rifting and drifting consequent to the Cretaceous opening of the South Atlantic Ocean. Major horizontal (sinistral) movements along the northeast–southwest axis of the adjacent Benue Trough appear to have been translated to the norths-south and northwesterly trending shear zones to form the Mid-Niger Basin perpendicular to the Benue Trough (Benkhelil, 1989). Although the sedimentary fill of the Benue Trough consists of three unconformity-bounded depositional successions (Petters, 1978), the Bida and Anambra geographical regions were platforms until the Santonian. Pre-Santonian sediments are recorded principally in the older Benue Trough and parts of the southern Anambra Basin. The collapse of the Mid-Niger and Anambra platforms led to the sedimentation of the Upper Cretaceous depositional cycle commencing with the fully marine shales of the Campanian Nkporo and Enugu Formations which may have some lateral equivalents in the Lokoja Formation of the Bida Basin. Overlying the Nkporo Formation is the sedimentary units of the Mamu Formation. These consist of shales, siltstones, sandstones and coals of fluvio-deltaic to fluvio-estuarine environments whose lateral equivalents are the conglomerates, cross-bedded and poorly sorted sandstones and claystones of the Lokoja and Bida Formations in the Bida Basin.

The Mamu Formation is succeeded by sandstones of the Lower Maastrichtian Ajali Formation laterally equivalent to the Patti, Sakpe and Enagi Formations of the Bida Basin. These sandstones are well sorted, quartz arenite that are commonly interbedded with siltstones and clay stones and similar in part to the lithologies of the Patti and Enagi Formations. The Patti and Enagi Formations are overlain by the Agbaja and Batati Formations (lateral equivalents) of Upper Maastrichtian age
(Fig. 2.2).

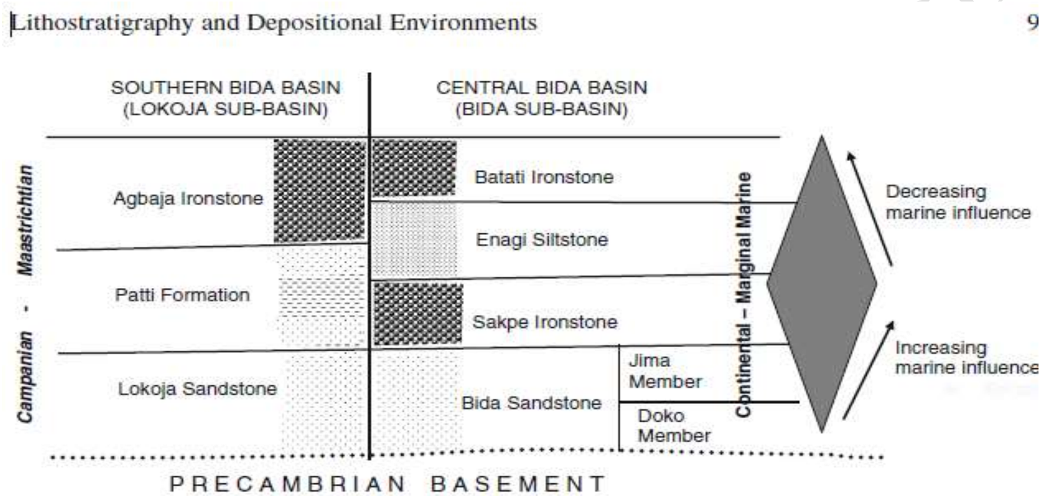


Figure 2 Stratigraphic successions in the Mid-Niger Basin (Also known as Bida or Nupe Basin).

MATERIALS AND METHODS

Sample

The oil shale used in this study was collected from Lapai Local Government Area of Niger State, Middle Belt, Nigeria. The sample was treated with hydrochloric acid and rinsing with hot water to remove the potential contamination from drilling mud and evaporative loss. The oil shale samples were grounded to particle size <100 meshes and prepared following standard procedure according to ASTM (ASTM D 2013-72).

Total Organic Carbon (TOC)

In every organic compound there is always the presence of carbon and the composition of this carbon are usually kerogen, bitumen, and hydrocarbon

(HC). Total Organic Carbon (TOC) content, is a very important parameter to determine the quality of any source rock in a reservoir. Hence, TOC is a measure of the organic carbon present in a unit weight of any source rock (Espitale et. al.1980). determination of TOC is a rapid and inexpensive method of screening for source rocks. The total organic carbon (TOC), was determined using Walkley Method of organic Carbon in soil; conducted at the School of Agriculture, Federal University of Technology, Minna, Nigeria.

Rock Eval Pyrolysis

The Rock Eval Pyrolysis involves the use of heat break down complex chemical substances into simpler ones. It is a screening technique that gives indication of generated or migratory hydrocarbons, source rock maturity, hydrocarbon source potential and quality. This analysis was done in order to determine the hydrocarbon generative potential of the organic matter, to determine the maturity of the source rock (PI) and to evaluate the relative proportion of the hydrocarbon (HI) in the samples. The samples are then introduced into the LECO combustion oven and the amount of carbon is measured as carbon(IV)oxide by Infra-Red Detector. The temperature-programmed applied in pyrolysis mode is 300^0C (3min) and 650^0C (25min). HI and PI can be deduced from the following expression in equation 1 and 2:

$$HI=S2\times100/TOC \qquad 1$$

$$PI=S1/(S1+S2) \qquad 2$$

Where S1 represents the free or mobile hydrocarbons present in the source rock sample that can be volatile with kerogen decomposition while S2 represents bonded hydrocarbons that indicate the potential of the source rock.

Thermogravimetric Analysis

Thermal techniques are used to measure physical property as a function of temperature program (heating, cooling or isothermal). Differential Thermal Analysis (DTA) helps to find out the temperature at reactions take place in a given sample while TGA essentially, measures mass loss. Thermal properties and kinetics parameters such as activation energy and pre-exponential factor of kerogen decomposition can be identified by the use of TGA. It is a useful tool to obtain thermal characteristics of compounds by microscopic weight loss in few milligrams of the sample at varied atmospheres and temperature conditions.

The unit is often coupled with Mass spectrometer to determine the off gases from the sample decomposition or oxidation which is measured as a function of temperature.

RESULTS AND DISCUSSION

TOC/Rock Eval Pyrolysis

The TOC and Rock-Eval pyrolysis are applied to classify the organic matter in a source rock into S1, S2 and S3 peaks. Table 4 represents the results from the oil shale sample. Source Rock Analysis (SRA) also known as Rock Eval Analysis is a quick and conventional technique used in the field of petroleum exploration to assess different source rocks, their petroleum potential, maturity and to characterize the degree of evolution of gas/oil, type of kerogen and depositional environment.

Table 1 Rock-Eval Pyrolysis data of oil shale (hydrocarbon) from the Bida Basin.

S1(mg/g)	S2(mg/g)	S3(mg/g)	HI(mgHC/gTOC)	Tmax(^{O}C)	PI	TOC(wt %)
0.47	0.64	3.55	45.71	342	0.42	1.40

The Total Organic Carbon (TOC) obtained was 1.40 wt %. S1 represents the quantity of free hydrocarbon present in the source rock sample that can be volatile with kerogen decomposition which is 0.47. S2 represents the quantity of hydrocarbons obtained through thermal cracking of nonvolatile organic matter which is 0.64. S2, therefore, represents the existing potential of rock to generate petroleum. The Tmax is the measure of the organic matter potential and maturity. Tmax is equivalent to the temperature of the maximum production of hydrocarbon during pyrolysis (S2 peak maximum). Tmax value relies on the kerogen type. Tmax result of 342^{O}C. It signifies immature to early mature stage. Tmax further gives detail explanations of where does the maturity fall in relation to oil generation window. It can either be immature for oil generation, mature for oil generation or overmatured for oil generation.

HI: is the normalized hydrogen content. From the standard parameters for generative potentials listed in Table 5, The hydrogen index (HI) of 45.71 mg HC/gTOC indicates that the sample is prone to gas. Production index

(PI=S1/(S1+S2) which defined the thermal maturity of the hydrocarbons. The PI value of 0.42 in this study is above which signifies organic matter is matured.

Table 2 Petroleum potential (quantity) of an immature source rock (Peters and Cassa, 1994)

Source Rock	Petroleum potential (quantity) of immature		
Petroleum potential	Organic matter		
	TOC	Rock-Eval pyrolysis	
	(Wt %)	S1	S2
Poor	0-0.5	0-0.5	0-2.5
Fair	0.5-1	0.5-1	2.5-5
Good	1-4	1-2	5-10
Very good	2-4	2-4	10-20
Excellent	>4	>4	>20

Thermogravimetric Analysis

Figure 3 TGA for oil shale

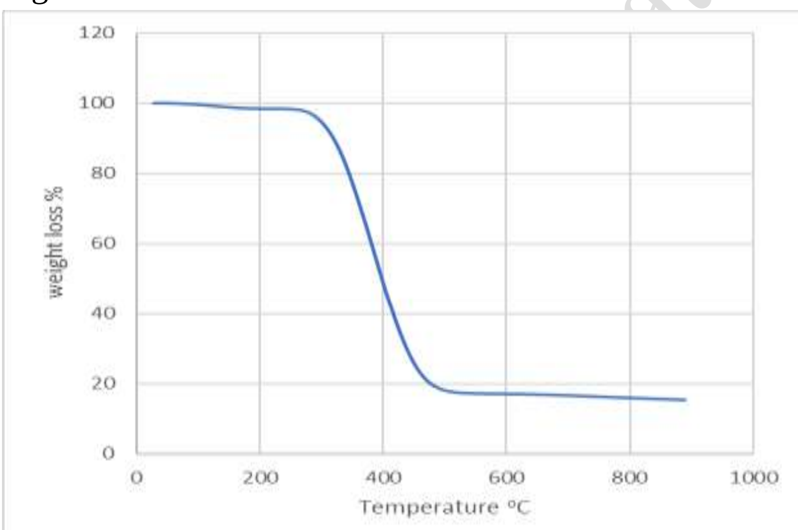
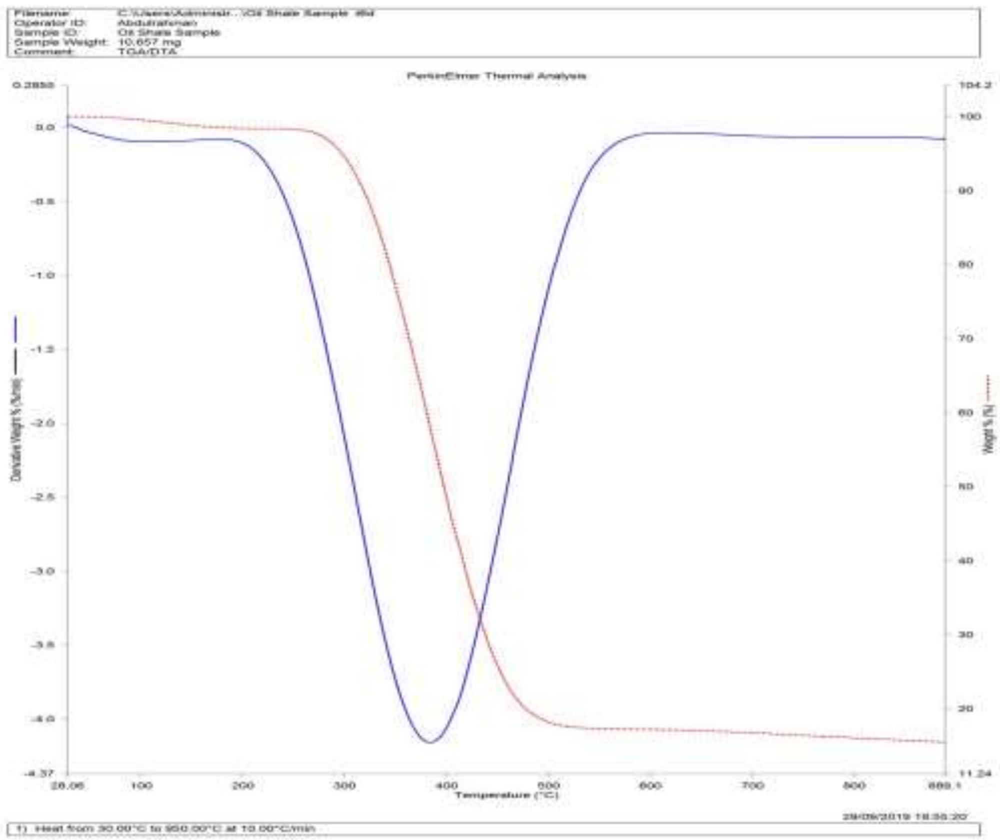


Figure 3 shows the overall profile of weight loss in oil shale. The overall profile can be divided into three stages: Weight loss due to moisture content/water removal (stage I); Decomposition due to the presence of organic matter (stage II); and Inorganic decomposition/weight loss due to minerals present (stage III). The second stage, which is the most important of the three, takes place between (280 & 520) ^{O}C. Furthermore, Stage II can be divided into two sub-stages i and ii of weight loss. These two sub-stages occurring during pyrolysis process can be identified as bitumen and oil regimes. The first sub-stage decomposition occurs generally until 350 °C and represents organic decomposition; where degradation of kerogen produces bitumen. This stage produces gas, bitumen, and carbon residue. In the second sub-stage the produced gas, bitumen, and carbon residue de-volatilized further to produce oil, coke, and gas. This occurs between 350 and 520 °C. Wei-Gang, & Wen-Li, 2010; Aijuan, Jingru, & Shaohua, 2007.

Figure 4 TGA/DTA for oil shale



Using the Arrhenius equation, the Activation Energy (Ea), of the oil shale sample was calculated to be 48.40 KJ/Mol, while the preexponential factor (A), was 884.025 min^{-1}.

CONCLUSION

In this study, characterizations and experiments of oil shale from Bida Basin were carried out. On the basis of the qualitative and/or quantitative analyses, a better understanding on the properties of the oil shale has been obtained. Some of the main findings are summarized as follows.

The oil shale sample has a TOC value of 1.40 wt %. It has a Tmax of 342^{O}C, which gives an indication that the kerogen type is gas prone and shows a good maturity.

The apparent activation energy and pre-exponential factor were determined to be 48.40 KJ/mol and 884,025 min^{-1}.

The TGA shows the temperature range where the products of the shale can be obtained, between 280^{O}C and 520^{O}C.

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