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P2C-06: THERMAL CHARACTERIZATION OF GBETIOKUN OIL SHALE VIA ROCK-EVAL PYROLYSIS AND THERMOGRAVIMETRIC ANALYSIS

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Abstract

The pyrolysis characteristics of Gbetiokun oil shale were investigated with rock-eval pyrolysis and thermogravimetry analysis (TGA). The Rock-Eval pyrolysis outlined the hydrocarbon potential of the oil shale sample via total organic carbon (TOC) value, hydrogen Index (HI) and production index (PI). The TGA was investigated at different heating rates of 10, 20 and 30 °C/min in the temperature range of 29-950°C (Fig. 1). From the Rock-eval pyrolysis, it was deduced that the oil shale sample has a total organic carbon (TOC) value of 0.51wt% more than 0.5wt% which is the minimum standard required for the generation of hydrocarbon. The hydrogen index (HI) value of 208 mg HC/gTOC falls within the range of 150-300 mg HC/gTOC indicating that the sample is oil and gas prone. While PI value for the sample is 0.05 which is less 0.1 signifying that the organic matter is immature. The TGA shows the main stage of mass loss at temperature range of 200-620°C and higher corresponding to the release of oil and gas, further weight loss was due to decomposition of carbonate. It was also observed that increasing the heating rate shifted the weight loss to higher temperatures. It can be concluded that Gbetiokun oil shale has high potential to generate hydrogen and both Rock-Eval pyrolysis and TGA show that the sample is oil and gas prone.

Keywords: Rock-Eval pyrolysis, Thermogravimetric Analysis, Total Organic Carbon, Hydrogen Index, Production Index, Differential Thermogravimetric Analysis.

1.0 INTRODUCTION

In this time of global market uncertainty, the world needs energy and in increasing quantities, since the world population is growing rapidly, which is used to support economic and social progress and 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 various production processes. The process of economic development requires the use of various higher levels of energy consumption. Almost everything in the world today can be traced to the use of energy in one form or another. And most of the energy is from the Sun to earth. Apart from direct solar energy, the sun's energy shown in different ways such as in wind power, water power, tidal power, fossil fuels, nuclear energy, coal, 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*). Exploration and production of oil and gas from various 'unconventional' sources (such as methane from coals, shale gas, underground coal gasification, and oil shale) are most likely to have significantly different land-use planning impacts to 'conventional' onshore oil and gas. The alternative sources such as oil shale are available globally which may breach the gap developing between remaining conventional resources and demand (Crown Onshore Oil & Gas, 2011). The inland basins in Nigeria comprises of the following; Anambra Basin, the Dahomey Basin, the Lower, Middle, and Upper Benue Trough, the Chad Basin, the Bida Basin, and the Sokoto Basin (Aizebeokhai, 2012).

is blessed with an abundant 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 (Kok and Ozgur, 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 need to utilized the use of energy sources to meet huge energy demand.

Oil shale is an organic-rich sedimentary rock that can be considered as a source of alternative energy. 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 °C will volatilize from oil, gas and a solid residue of coke (Tissot *et al.*, 1978). The yield of the oil during pyrolysis depends on the quantity or quality of the kerogen contained in the oil shale and its evolution (Tissot *et al.*, 1978). 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 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. However, further treatment to increase the content of desirable compounds in shale oil may be necessary (Akash, 2003; Bai *et al.*, 2015; 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. Moving on to this ground, this study provides insight for the hydrocarbon potential Gbetiokun oil shale sample with Rock-Eval Pyrolysis and TGA.

2.0 EXPERIMENTAL

2.1. Sample

The oil shale used in this study was collected from Gbetiokun Delta South Local Government Delta in the southeastern part of Nigeria. The sample was treated with hydrochloric acid and rinsing with hot water to remove the potential contaminants from drilling mud and evaporative loss. The oil shale samples were grounded to particle size <100 meshes which is a standard procedure according to ASTM (ASTM D 2013-72).

2.2 Rock-Eval Pyrolysis

The Rock-Eval pyrolysis was performed on the Gbetiokun oil shale sample in Getamme Laboratories Nigerian Limited, Port Harcourt. This analysis was done in order to determine the hydrocarbon generative potential of the organic matter (TOC), 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 combustion oven and the amount of carbon is measured as carbon dioxide by Infra-Red Detector. The programmed temperature applied in pyrolysis mode is 300°C (3min) and 650°C (25min) (detected by Final Investment Decision). HI and PI can be deduced from the following expression in equation 1 and 2:

$$HI = S2 \times 100/TOC \quad (1)$$

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

Where S1 represents the quantity of free hydrocarbon present in the source rock sample that can be volatile with kerogen decomposition while S2 represents the number of hydrocarbons obtained through thermal cracking of nonvolatile organic matter.

2.3 Thermogravimetry Analysis

The TGA is an instrument used for measuring mass a sample while heating the it. A sample is heated, it reacts and released mass inform of gas. There are two main types of TGA. The open system and closed systems. An open system is exposes the sample to a sweep substance that constantly replaces the medium around the sample and sweeps the product away while closed systems have to do with isolated sample in a reaction cell and reaction products persist around the sample. Most systems make use of a controlled atmosphere of gases but a unique form of a closed TGA makes use of water as the medium and a magnetic balance commonly mass loss measurement, is made at either isothermal condition or constant heating rate.

3.0 RESULTS AND DISCUSSION

3.1 Rock-Eval analysis

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.

The standard parameters for generative potentials of source rocks are shown in Tables 1 and 2. The total organic carbon (TOC) serves as a measure to determine the amount of organic matter. S1 represents the quantity of free hydrocarbon present in the source rock sample that can be volatilized with kerogen decomposition (S1= 0.05). S2 represents the quantity of hydrocarbons obtained through thermal cracking of nonvolatile organic matter which is 1.04. 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 414°C 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 2, The hydrogen index (HI) of 208 mg HC/gTOC indicates that the sample is prone to oil and gas. The analysis signifies that the source rock contains type II kerogen, since the HI fall within the range of 150 to 300 mg HC/gTOC. Production index defines the thermal maturity of the hydrocarbons. The PI value of 0.05 in this study is below 0.1 which signifies organic matter is immature.

Table 1. Standard geological parameters for generative potentials of immature source rocks (Peters and Cassa 1964)
Table 2. Standard parameters for HI and PI (Peters and Cassa 1964)

Petroleum Potential	TOC (wt%)	S1 mg HC/g rock	S2 mg HC/g rock	Tmax
This study	0.51	0.05	1.04	414^0 C
Poor	<0.5	<0.5	0-2.5	
Fair	0.5-1	0.5-1	2.5-5	
Good	1-2	1-2	5-10	
Very Good	2-4	2-4	10-20	
Excellent	>4	>4	>20	
Standard				

Stage of oil maturity	Production Index	Temp
immature	<0.1	<435
Early mature	0.1-0.15	435-445
Peat mature	0.25-0.40	445-450
Late mature	>0.4	450-470
Post mature	-	>470

HI generative potential	Values (mgHC/gTOC) Standard	This study
No generative potential	<50	
Gas prone	50 to 150	
Oil and gas prone	150-300	208
Oil prone	300	

3.2 Thermogravimetry Analysis

Figure 1 shows the overall profile of weight loss in oil shale. The overall profile can be divided into three stages: water removal (stage I), organic decomposition (stage II) and inorganic decomposition (stage III). Stage II can be further 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 (Al-Harahsheh *et al.*, 2011). This stage produces gas, bitumen, and carbon residue. In the second sub-stage, the produced gas, bitumen and carbon residue are de-volatilized further to produce oil, coke, and gas. This occurs between 350 and 600 °C. (Al-Harahsheh *et al.*, 2009; Fang-Fang, Ze *et al.*, 2010; Qing *et al.*, 2007).

The third stage refers to the inorganic decomposition regime and occurs generally between 600 °C and 800 °C. In this stage, mass loss is observed due to the decomposition of carbonates in the inorganic compounds of oil shale. At higher temperatures the carbon dioxide formed during carbonate decomposition reacts with residual coke and forms carbon monoxide. This process adds to the final weight loss (Qing *et al.*, 2007).

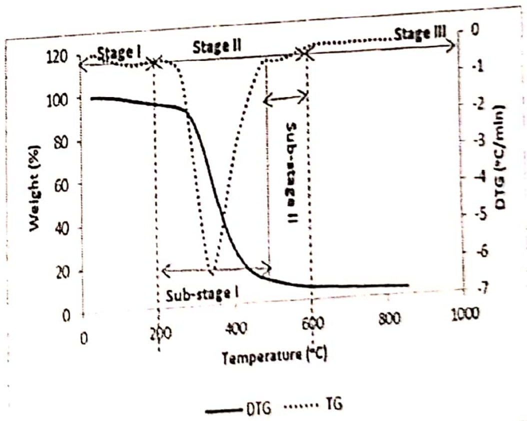

Figure 1: TG/DTG profile for the oil shale sample.

3.3 Effect of Heating Rate on Weight Loss

Figure 2 showed the oil shale thermographs of weight loss (Figure 2) and derivative weight loss (Figure 3) at corresponding different heating rates of 10, 20 and 30 °C/min (Extrapolation of Sedimentary Basin) respectively. At higher heating rate, the curves shift to highest temperatures and maximum weight loss shift to higher temperatures. The heat transfers across the oil shale particles (at a higher heating rate) is more effective but restricted by the heat transfer resistances. However, at a lower heating rate, the time was sufficient enough for heat to infuse steadily into the oil shale particles. These observations are in agreement with what was in the literature (Idris *et al.*, 2010). The corresponding peak temperatures of weight loss were 345, 401 and 430°C for 10, 20 and 30 °C/min heating rate respectively from the derivative weight loss curves in Fig. 3.

Though the oil shale undergone two stages of pyrolysis, the results of the first and second stage weight loss of the oil shale pyrolysis in Table 3 are compatible as in Figure 3. The twin stages of the shale's deferential mass loss at the different temperature ranges showed the complex nature of the oil shale pyrolysis. In stage II, the broad peaks signified the high activity that rapidly pyrolyzed the shale through increased ability to overcome the resistance layer of mass transfer. The scenario can be explained by the chemical reaction that controlled the shale de-volatilization leading to the release of heat energy. Therefore, the stage wise decomposition activities of the shale particles are consistent with the literature (Wu *et al.*, 2014).

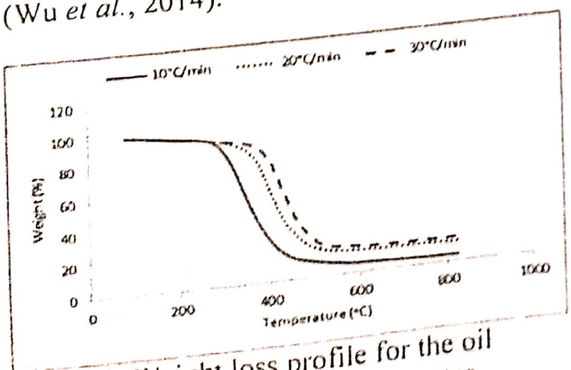

Figure 2. Weight loss profile for the oil shale sample at different heating rates.

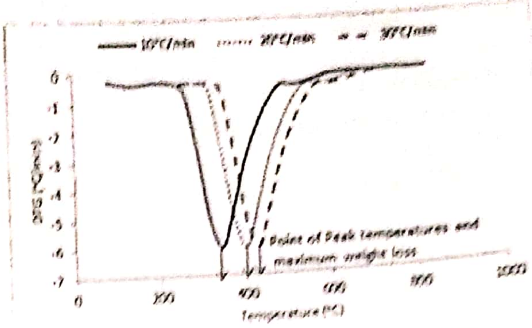

Figure 3:. Derivative weight loss profile for the oil shale sample at different heating rates.

4.0 CONCLUSION

The pyrolysis characteristics of Gbetiokun oil shale was investigated with rock-eval pyrolysis and TGA. It deduces that the oil shale sample has total TOC value more than the minimum standard required for the generation of hydrocarbon. The HI value falls within the standard range indicating that the sample is oil and gas prone. While PI value was below the minimum standard signifying organic matter is immature. The TGA shows the main stage of mass loss corresponding to release bitumen and oil in the temperature range and at higher temperatures, further weight loss was due to decomposition of carbonate. It was also observed that increasing the heating rate shifted the weight loss to higher temperatures.

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