PYROLYSIS AND CHARACTERIZATION OF GBETIOKUN OIL SHALE

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ABSTRACT

In this work, oil shale sample was collected from Gbetiokun, Delta State, Nigeria. Analytical techniques such as Proximate & Ultimate Analysis, Rock-Eval pyrolysis, Total Organic Carbon (TOC), Fixed Bed Pyrolysis, Gas Chromatography-Mass Spectroscopy (GCMS), and Thermogravimetric Analysis (TGA) were used to characterize the sample. From the results obtained, the TOC of the Gbetiokun oil shale was 0.51 wt%. The Tmax, Hydrogen Index (HI) and Productive Index (PI), were 414 ℃, 203.92 mgHC/g TOC and 0.05 respectively. The GC-MS analysis revealed predominantly paraffinic constituents and a pristane/phytane ratio of 1.21, an indication that the oil shale sample may have been exposed to an oxidizing atmosphere with decreasing salinity. The simulated result of the pyrolysis of Gbetiokun Oil shale using Aspen Plus produced 53.3 % Shale oil, 24.70 % non-condensable gas and 22 % coke. In comparison, the experimental pyrolysis of the oil shale had 50.2 % Shale oil, 25.60 % non-condensable gas and 24.20 % coke. This comparison between the simulated and experimental results showed a good agreement between the two results. Hence, the Gbetiokun oil shale sample has a fair content of organic matter, it is oil and gas prone but thermally immature and primarily composed of kerogen type III.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

In this time of global market uncertainty, the world needs energy and in increasing quantities, because of rapid population (Taylor, 2019). All living organisms need energy to do natural movements, also energy is for domestic purposes, industrial uses, agriculture, and transportation. Providing this energy around the globe comes with high responsibilities and commitments to developing and using available resources responsibly. The human race is committed to protecting both people and the environment, making positive economic contributions. Energy is a key input in economic growth. The process of economic development requires the use of various higher levels of energy consumption. Energy is commonly known to exist in several forms among which are Light and heat (mostly from the sun, which directly or indirectly is the source of all the energy available on Earth) and Electricity. Almost everything can be traced to the use of one form or another. 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. Apart from direct solar energy, the sun's energy shows in different ways such as in wind power, water power, tidal power, fossil fuels, nuclear energy, Coal, Natural gas and Petroleum (Harper, 2007).

Petroleum is a naturally occurring liquid located beneath the Earth's surface that can be refined into fuel. Petroleum is a fossil fuel, that is, it has been created by the decomposition of organic matter several 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 and Welte, 1984). Petroleum is most often associated with crude oil and natural gas in wells dug into the ground to bring that liquid and gas to the surface. The liquid petroleum can vary in colour: from relatively transparent to dark brown or black. Heavier crude oils are often the darkest in colour. The hydrocarbons can be processed in refineries into various types of fuels. Hydrocarbon molecules in petroleum include off-gases, asphalt, paraffin, and naphthene. Petroleum comprises a mixture of various hydrocarbons and can have different chemical and physical properties depending on its location in the world. In general, the denser (heavier) the petroleum the more difficult it is to process and the less valuable it is. "Light" crude is the easiest to refine and is mostly considered as the most valuable, and the viscosity of "heavy" crude makes it more expensive to refine. "Sour" crude contains sulfur and sulfuric compounds (mercaptans), which are regarded as impurities and make the fuel less valuable **(**Chen *et al*., 2018). 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. These energy sources are covered in a separate 'Alternative Fossil Fuels' mineral planning factsheet. Alternative sources such as oil shale are available globally, which may breach the gap between remaining conventional resources and demand (Stacey, 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 and Oyebanjo, 2013).

Oil shale is an organic-rich fine-grained sedimentary rock containing kerogen (a solid mixture of organic chemical compounds) from which liquid and gaseous hydrocarbons can be produced. Oil shale contains a mixture of sand, silt, salt, and an insoluble organic substance called kerogen. Oil shale produces both vapors and gases when heated, which in turn are condensed and turned into oil. Oil shale does require mining and energy-intensive refining processes, as such it is a substantially dirtier energy source than conventional liquid oil. Kerogen is mostly the organic material in sedimentary source rocks. It has variable compositions, consisting of a range of residual materials whose basic molecular structure takes the form of stacked sheets of both aliphatic hydrocarbon chain and aromatic hydrocarbon rings in which atoms of sulfur, oxygen, and nitrogen also occur (Vandenbroucke and Largeau, 2007).

Oil shale retorting is the process, which involves the application of heat to break down the kerogen followed by removal and quenching of the volatile products. According to Ringer *et al*. (2006), pyrolysis may be defined as the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogens). It is an irreversible process that involves either the simultaneous change of chemical composition and physical phase, hydrogenation (a chemical reaction between molecular hydrogen and another compound or element, usually in the presence of a catalyst), or thermal dissolution (a chemical decomposition caused by heat). The organic matter in the rock (kerogen) is converted into synthetic oil and gas during these processes. These processes produce an unconventional oil that can be readily used as a fuel or can also be improved to achieve feedstock specifications by conducting additional purification methods. This could be achieved by adding hydrogen and removing other impurities such as nitrogen and sulfur. The resultant product can be used for the same applications as derived from crude oil (Carrie *et al*., 2012).

Crude oil is an unrefined petroleum product that is composed of hydrocarbon deposits and other organic materials. It occurs naturally. As a type of fossil fuel, it can be refined to produce usable products such as gasoline, diesel, and various forms of petrochemicals which are used in automobiles and various industries. Crude oil cannot be replaced naturally (a nonrenewable resource). It can be obtained typically through drilling, where it is usually found with other resources, such as natural gas (which is less dense, and as such, sits above the crude oil) and saline water (which is denser, and sinks below in the ground). After exploration, the Crude oil is then refined and processed into a variety of forms, such as gasoline, kerosene, and asphalt, which are sold to consumers. Crude oil (also known as Black Gold) has ranging viscosity and can vary in color from yellow and black depending on its hydrocarbon composition. Distillation, the process by which oil is heated and separated into different components, is the first and main stage of refining.

The main difference between crude oil and shale oil is in the process of generation of each. Oil production is separated into three distinct phases: primary, secondary, and tertiary (which is also known as Enhanced Oil Recovery or EOR). Primary oil recovery is limited to only hydrocarbons that naturally rise to the surface or those that use artificial lift devices, such as pump jacks (nodding donkey). Secondary recovery employs the use of water and gas injection to displace the oil and driving it to the surface. The way to further increase the oil production is through the tertiary recovery method that is, EOR. Although more expensive to employ on a field, EOR can increase production from a well to as high and above 75 % recovery. Used in oil fields that exhibit heavy oil, poor permeability, and irregular fault lines, EOR entails changing the actual properties of the hydrocarbons, which further distinguishes this phase of recovery from the secondary recovery method. While the secondary recovery method uses water-flooding and gas injection to push the oil through the well, EOR applies the use of steam or gas to change the makeup of the reservoir. EOR does restore formation pressure and enhances oil displacement in the reservoir. There are three main types of EOR, which are chemical flooding, gas injection, and thermal recovery (Alto, 1999).

According to Sarathi (1999), in-situ combustion (fire flooding) is an injection of an oxidizing gas (air or oxygen-enriched air) to generate heat by burning a portion of resident oil. Most of the oil is produced by a combination of the Gas drive (from the combustion gases), Steam, and Water drive. Based on the respective directions of front propagation and airflow, the process can be either forward (when the combustion front advances in the same direction as the airflow) or reverse (when the front moves against the airflow). In-situ combustion is the only thermal method that can presently be applied to deep reservoirs, though deep downhole steam generation is being tested. It can be used at any stage of reservoir depletion and in special situations such as offshore or in Arctic regions. Due to the lack of heat losses at the surface and in the injection wells, it is the most thermally efficient recovery method. The injectant (air) is very much available. Combustion allows wider well spacing than steam and the economic results are comparable to those of steam injection (Gorlov, 2007).

1.2 Statement of the Research Problem

Increase in population has brought about an increasing need for energy both domestically and industrially. The task of meeting the shortfall is a continuous challenge. Despite the great deal of work done on oil shale, the pyrolysis of Gbetiokun oil shale has not been reported (Obaje, 2009).

1.3 Aim and Objectives of the Study

The aim of this research work is to Pyrolyse and characterize Gbetiokun oil shale. The research objectives include the following:

i. Rock-Eval pyrolysis of the oil shale to determine the hydrocarbon generative potential of the sample.
ii. Thermogravimetric Analysis (TGA) of the oil shale to know its thermal stability.
iii. Pyrolysis of oil shale using Fixed-Bed reactor.
iv. Characterization of the liquid product (shale oil) via Gas Chromatography-Mass Spectrometry **(**GC-MS).
v. Validation of the experimental results using Aspen Plus simulation software.

1.4 Justification of the Study

Oil shale, an unconventional source of energy could complement crude oil in meeting up the energy demand of the growing population. The study of the Gbetiokun oil shale will provide useful information on the energy potential of the sample

1.5 Scope of the Study

This study is limited to pyrolysis and characterization of Gbetiokun oil shale using Rock-Eval pyrolysis method, TGA method, Fixed-bed pyrolysis method, GC-MS, and validation of experimental results using Aspen Plus simulation software.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Oil Shale in Nigeria

Oil shales are compact rocks of sedimentary origin with an ash content of more than 33 % and containing organic matter that yields oil when destructively distilled but not appreciably when extracted with petroleum solvents. The shales contain large quantities of insoluble organic matter, kerogen, which yields oil upon pyrolysis at temperatures of about 500 ^{o}C (Osuji, 2015).

The United States has the largest oil shale resources in the world - a total of 3340 billion tons, constituting 62 % of the world's known recoverable oil-shale potential. Other countries such as Brazil, Canada, Egypt, Germany, Israel, Jordan, Morocco, Nigeria, and Romania have significant oil shale deposits. Moreover, previous studies (Okon *et al*., 2017) reported the abundance of oil shale deposits in Nigeria, especially in Adamawa, Benue, Borno, and Ebonyi States. There are also potentials for shale gas in the Niger Delta region. Mid-Cretaceous oil shale deposits are found to be the richest, existing in the Lokpanta area of the Abakiliki anticlinorium (a depocentre in the Lower Benue trough). The estimate for oil shale in the Lokpanta area is 5.76 billion tonnes; having a recoverable hydrocarbon reserve of about 1.7 billion barrels of oil (Sonibare *et al*., 2005).

Presently, conventional crude oil is a major source of energy. The increasing need for petroleum products (due to increasing demand for energy) results in the challenges of meeting the energy demands of those countries concerned. One of the ways of contributing towards addressing the challenges is through developing the oil shale research, which have enormous deposits around the world. In Nigeria, much is yet to be done for the development of oil shale.

2.2 Oil Minning Lease (OML) 40

The OML 40 license lies onshore within the Niger Delta, approximately 65 km northwest of Warri, and covers an area of 498 square kilometres. The acquisition of a 45 % equity stake in OML 40 was completed in September 2012 and has been producing oil from the Opuama field since 2014. OML 40 is operated by Nigerian Petroleum Development Company (NPDC), a subsidiary of Nigerian National Petroleum Corporation (NNPC).

OML 40 contains the producing Opuama field; the Gbetiokun field, which commenced production in 2019; the large, low risk, Amobe prospect (Prospective Resources of 78 MMstb) on which an exploration well will be drilled; the potentially large Abiala discovery (Contingent Resources of 26 Million Barrels) which was appraised in 2020; four other discoveries (Adagbassa, Polobo, Ugbo, and Tongarafa) and about 20 other prospects and leads, including the Abiala North and South prospects, which lie adjacent to the Abiala-1 discovery (Seplat, 2020).

Table 2.1: OML 40 Information (Seplat, 2020)

Operator	NPDC
Working interest	45 %
Partners	NPDC, Starcrest
Main fields	Opuama (producing), Gbetiokun (producing), Amobe, Abiala
Average	498 km^2
Available export route	Forcados, Barging
Concession expiry date	October, 2038
2019 working interest liquids production	8,963
2019 working interest gas production	n/a
Working interest remaining 2P oil reserves	29 MMbbls
Working interest remaining 2P gas reserves	n/a
2020 activities	Production and development

2.2.1 Gbetiokun oil field

Gbetiokun oil field offshore Nigeria according to Zweidick (2020) has come on stream through an early production facility, reports Eland Oil & Gas, Aberdeen. Initial production will rise to 12,000 barrels/day from the Gbetiokun-1 and Gbetiokun-3 wells in the southwestern area of OML 40. The early production facility has a nominal capacity of 22,000 barrels/day. Shuttle tankers carry the crude to the main OML export pipeline. The first development phase focuses on three of the deepest of 19 oil-bearing reservoirs in what Eland describes as a relatively simple dip-closed structure. The depths of all the reservoirs range from 5,000 ft to 10,000 ft. The second phase will target less well-defined shallower reservoirs. Eland holds a 45 % interest in OML 40 while Nigerian National Petroleum Corporation (NNPC) the operator, holds 55 %.

2.3 Basins

A basin is essentially a depression, or dip, in the Earth's surface. Usually, Basins are shape-like bowls, with sides higher than the bottom. They can be circular or oval, similar to a sink or tub that you might have in your bathroom. Some are filled with water. Others are empty. Basins are formed by forces above the ground (like erosion) or below the ground (like earthquakes). They are created over thousands of years or almost overnight (Obaje, 2009). The major types of basins are river drainage, structural and ocean basins.

2.3.1 River drainage basins

A river drainage basin is an area drained by a river and all of its tributaries. A river basin is made up of many different watersheds.

A watershed is a small version of a river basin. Every stream and tributary has its watershed, which drains to a larger stream or wetland. These streams, ponds, wetlands, and lakes are part of a river basin. The Mississippi River basin in the U.S., for instance, is made up of six major watersheds: Missouri, Upper Mississippi, Ohio, Tennessee, Lower Mississippi, and Arkansas-Red-White Rivers (Peters and Cassa, 1994).

Every river is part of a network of watersheds that make up a river system's entire drainage basin. All the water in the drainage basin flows downhill toward bigger rivers. The Pease River, in northern Texas, is part of the Arkansas-Red-White watershed. It is a tributary of the Red River. The Red River is a major tributary of the Mississippi River, which flows into the Gulf of Mexico.

The Amazon Basin, in northern South America, is the largest in the world (Maaten *et al*., 2016). The Amazon River and all of its tributaries drain an area of more than 7 million square kilometers (about 3 million square miles).

2.3.2 Structural basins

Structural basins are formed by tectonic activity. Tectonic activity is the movement of large pieces of the Earth's crust, called tectonic plates. This activity is responsible for such phenomena as earthquakes and volcanoes (Harb *et al*., 2003). The natural processes of weathering and erosion also contribute to forming structural basins.

Structural basins form as tectonic plates shift. Rocks and other materials on the floor of the basin are forced downward, while materials on the sides of the basin are pushed up.

Sedimentary basins are a type of structural basin that are not shaped like typical basins, sometimes forming long troughs. Sedimentary basins have been filled with layers of rock and organic material over millions of years. Materials that fill up the basin are called sediment fill. Sedimentary basins are key sources of petroleum and other fossil fuels. Millions of years ago, tiny sea creatures called diatoms lived and died in ocean basins. Eventually, these ancient oceans dried up, leaving dry basins. The remains of the diatoms were at the bottom of these basins (Speight, 2020). The remains were crushed under billions of tons of sediment fill. In the right conditions, the pressure of the sediment fill turns the diatom remains into petroleum.

The Niger Delta sedimentary basin, in the countries of Nigeria, Cameroon, and Equatorial Guinea, is one of the most productive petroleum fields in Africa. In North America, the Western Canadian Sedimentary Basin is one of the continent's largest suppliers of gas and coal (Osuji, 2015).

2.3.3 Ocean basins

Ocean basins are the largest depressions on Earth. Edges of the continents, called continental shelves, form the sides of ocean basins. There are five major ocean basins, coordinating with the major oceans of the world, they are the Pacific basin, the Atlantic basin, the Indian basin, the Arctic basin, and the Southern basin (Taylor, 2019). Many smaller basins are often considered oceanic basins, such as the North Aleutian Basin, between the Pacific and Arctic Oceans.

Seafloor spreading happens along the boundaries of tectonic plates that are moving apart from each other. These areas are called mid-ocean ridges. New seafloor is created at the bottom, or rift, of a mid-ocean ridge. Ocean basins that have mid-ocean ridges are expanding. The Atlantic basin, for instance, is expanding because of seafloor spreading (Tchapda *et al*., 2017).

Subduction happens along the boundaries of tectonic plates that are crashing into each other. In these subduction zones, the heavier plate moves underneath or subducts the lighter one. Ocean basins that experience subduction, such as the Pacific basin, are shrinking.

Even though ocean basins make up more than 70 percent of the total land on Earth, scientists know relatively little about them (Stacey, 2011). Some oceanographers (and some astronomers) say that we know more about the surface of the moon than we do about the surface of the ocean floor. It is very difficult to get information about landforms of the ocean basin, such as trenches and mid-ocean ridges. These landforms are thousands of feet below the surface of the water. Few instruments can endure the intense pressure, cold, and dark at the bottom of ocean basins.

2.4 Basins in Nigeria

According to the Troutner (1996), Nigeria is situated entirely within the tropical zone and is located between latitudes 4° and 14° N of the Equator and longitudes 3° and 15° E. It is bounded on the west by the Republic of Benin, to the north by the Republic of Niger, to the east by the Republic of Cameroon and to the south is bathed by the Atlantic Ocean. In Nigeria, there are eight main sedimentary basins as seen in Figure 2.1, which include the Benue Trough, Delta and Cross Rivers, the Imo-Anambra, Hadejia-Chad, Sokoto-Rima, Niger-Bida, Owena and Ogun, and Osun Basins.

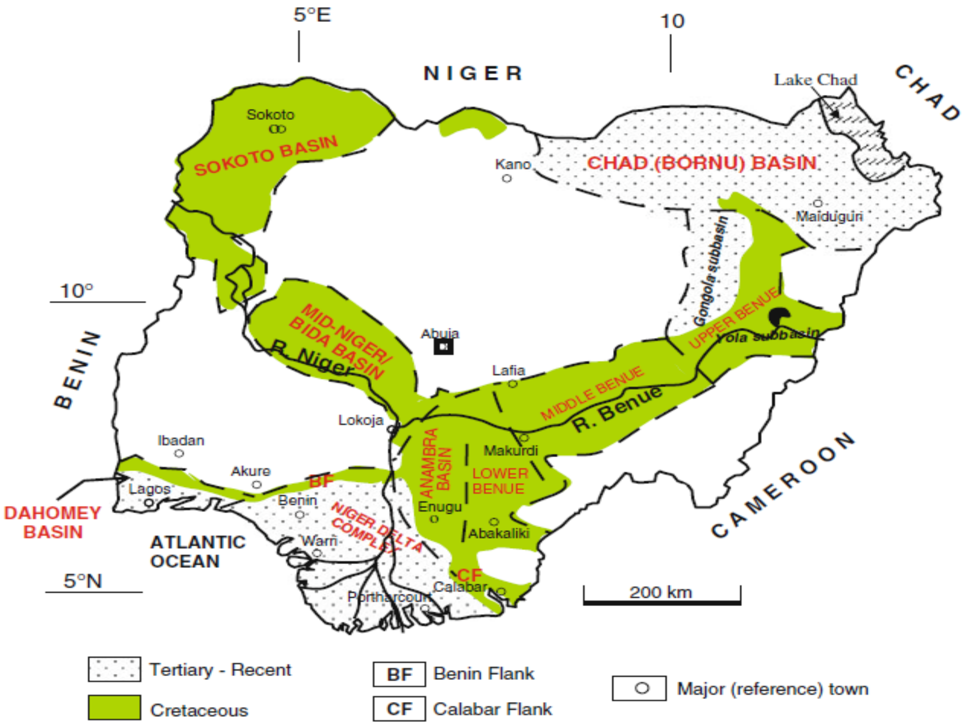


Figure 2.1: Sedimentary Basins of Nigeria (Obaje, 2009)

2.4.1 Niger delta basin

Figures 2.2 and 2.3 show the geology of Niger Delta Basin also referred to as the Niger Delta province is an extensional rift basin located in the Niger Delta and the Gulf of Guinea on the passive continental margin near the western coast of Nigeria with suspected access to Cameroon, Equatorial Guinea, and São Tomé and Príncipe. This basin is quite complex, and it carries high economic value as it contains a very productive petroleum system. (Ohakwere-Eze and Adizua, 2014). The Niger Delta basin is one of the largest subaerial basins in Africa. It has a subaerial area of about 75,000 km^2, a total area of 300,000 km^2, and a sediment fill of 500,000 km^3. The sediment fill has a depth between 9 - 12 km. It is composed of several different geologic formations that indicate how this basin could have formed, as well as the regional and large-scale tectonics of the area. The Niger Delta Basin is an extensional basin surrounded by many other basins in the area that all formed from similar processes. The Niger Delta Basin lies in the south westernmost part of a larger tectonic structure, the Benue Trough. The other side of the basin is bounded by the Cameroon volcanic line and the transformed passive continental margin (Oluwajana *et al*., 2017).

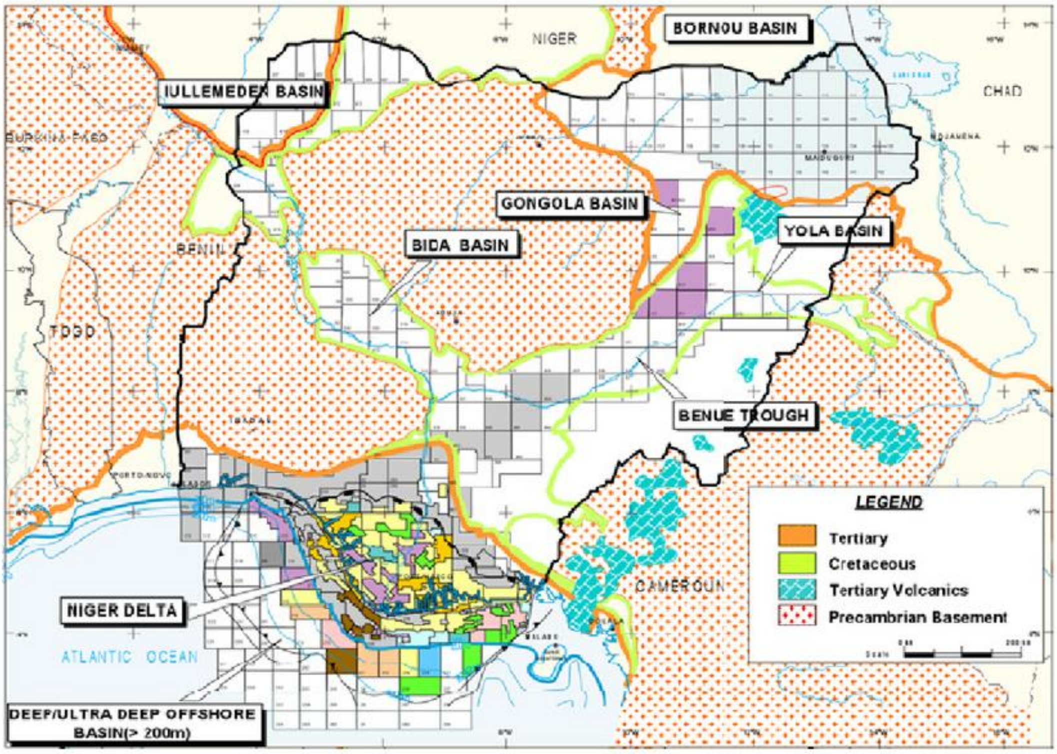


Figure 2.2: Geological Map of the Niger Delta Basin in Nigeria

(Ohakwere-Eze and Adizua, 2014)

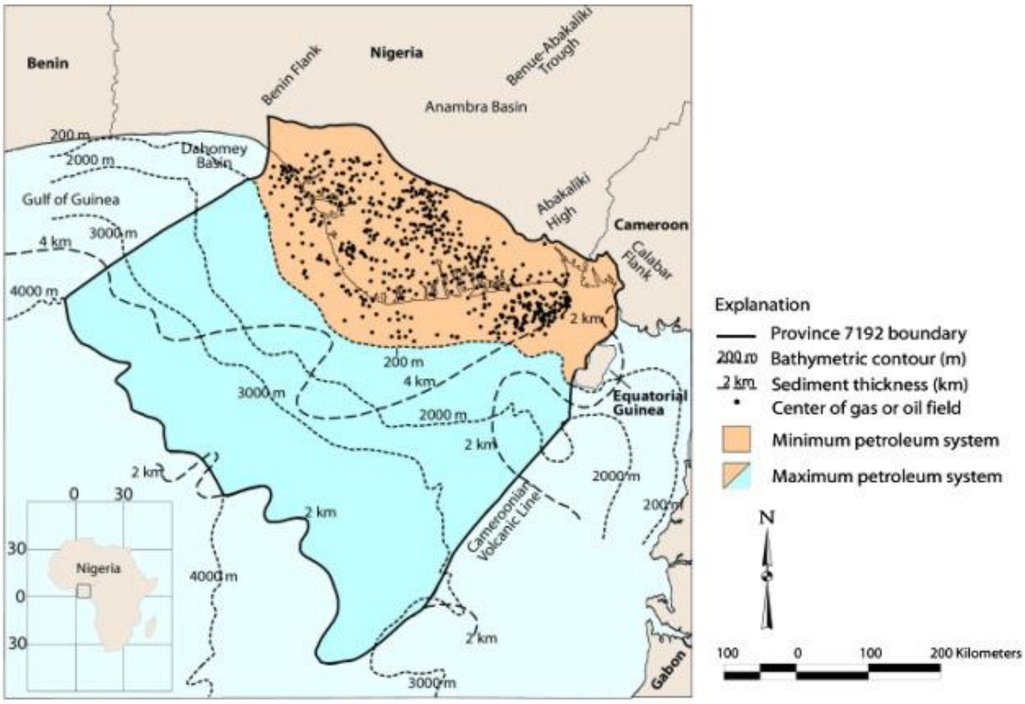


Figure 2.3: Geology of the Niger Delta Basin (Oluwajana, 2017)

2.5 Pyrolysis

According to Ringer *et al*. (2006), pyrolysis may be defined as the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogens). It is an irreversible process that involves either the simultaneous change of chemical composition and physical phase, hydrogenation (a chemical reaction between molecular hydrogen and another compound or element, usually in the presence of a catalyst), or thermal dissolution (a chemical decomposition caused by heat). The organic matter in the rock (kerogen) is converted into synthetic oil and gas during these processes. These processes produce an unconventional oil that can be readily used as a fuel or can also be improved to achieve feedstock specifications by conducting additional purification methods (Speight, 2020). This could be achieved by adding hydrogen and removing other impurities such as nitrogen and sulfur.

The resultant product can be used for the same applications as derived from crude oil. Pyrolysis can be categorized as slow, fast, and flash. Fast pyrolysis (also known as fixed-bed pyrolysis) techniques are Rock-Eval pyrolysis and TGA. In Rock-Eval pyrolysis according to Law (1999), a sample is placed in a vessel and is progressively heated up to 550 °C under an inert atmosphere. During the process, the hydrocarbons already present in the sample are volatized at a moderate temperature. The amounts of hydrocarbon are measured and recorded as a peak. Next, that is pyrolyzed is the kerogen present in the sample, which generates hydrocarbons and hydrocarbon-like compounds, CO_2, and water. Residual carbon is also measured. According to Saadatkhah *et al.,* (2020), Thermogravimetric analysis (TGA) is a method of thermal analysis in which the mass of a particular sample is measured over time as the temperature changes. The basic principle of the TGA is that as a sample is heated, its mass changes. This change can be used to obtain the composition of the material or its thermal stability, up to 1000 ^{o}C. Usually, a sample loses weight as it is heated up due to decomposition, reduction, or evaporation. A plot of weight % vs. temperature (thermogravimetric curve) is drawn which usually consists of a series of steps, obtained by measuring the mass of a sample during heating.

2.5.1 Types of pyrolysis

There are three types of pyrolysis: 1) conventional or slow pyrolysis, 2) fast pyrolysis, and 3) ultra-fast or flash pyrolysis. Table 2.2 and Figure 2.4 summarize how each method differs in temperature, residence time, heating rate, and products made.

2.5.1.1 ***Slow pyrolysis*** is normally used to modify the solid material, minimizing the oil produced. Fast pyrolysis and ultra-fast (flash) pyrolysis, on the other hand, maximizes the gases and oil produced respectively.

2.5.1.2 ***Fast pyrolysis*** uses moderate to high heating rates to rapidly decompose carbonaceous materials thermally in the absence of oxygen. It is the most common of the methods, both in research and in practical use because the major product is bio-oil. The typical yields of the products are liquid condensates – 30-60 %; gases (CO, H_2, CH_4, CO_2, and light hydrocarbons) – 15-35 %; and char – 10-15 %.

2.5.1.3 ***Ultra-fast or flash pyrolysis***, on the other hand, is an extremely rapid thermal decomposition pyrolysis, with a very high heating rate. The main products obtained are gases (higher) and bio-oil (lower). Heating rates can vary from 100-10,000 °C/min and residence times are short in duration. The yields of the products are liquid condensate ~10-20 %; gases – 60-80 %; and char 10-15 % (Boyt, 2003).

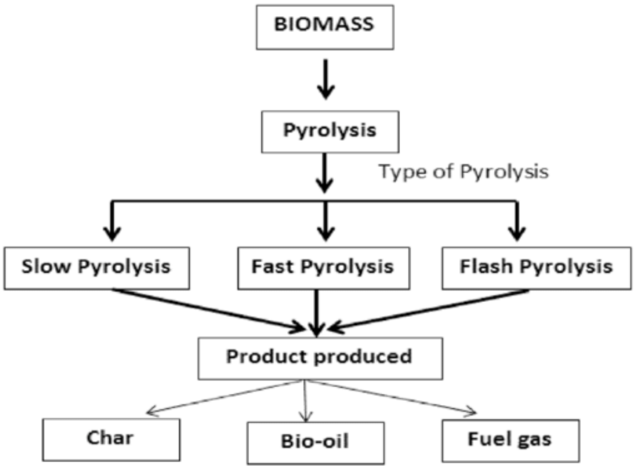


Figure 2.4: Types of pyrolysis (Artyushkova, 2014)

Table 2.2: Types of pyrolysis (Boyt, 2003)

Method	Temperature (°C)	Residence Time	Heating rate (°C/s)	Major products
Conventional/slow pyrolysis	Med-high 400-500	Long 5-30 min	Low 10	Gases Char Bio-oil (tar)
Fast pyrolysis	Med-high 400-650	Short 0.5-2 s	High 100	Bio-oil (thinner) Gases Char
Ultra-fast/flash pyrolysis	High 700-1000	Very short < 0.5 s	Very high >500	Gases Bio-oil

2.5.2 Pyrolysis of oil shale

The organic matter of oil shale is kerogen, which is not easily obtained by extraction but through pyrolysis. Moreover, pyrolysis is an essential means of converting kerogen to oil and gas. Understanding this reaction helps to efficiently control the pyrolysis process of oil shale (Raja *et al.*, 2017).

Generally, pyrolysis entails heating in an inert atmosphere (absence of oxygen); it causes the breaking down of several bonds in kerogen leading to multiple reactions. Thus pyrolysis functions to break large molecules into simpler ones that can be analyzed by many other analytical techniques. Hillier (2011) reported that it is thermodynamically impossible to synthesize long-chain alkanes from other hydrocarbon configurations by purely thermal means.

In terms of product formation, kerogen is first converted into bitumen (a viscous mixture of hydrocarbons), and then finally into shale oil (a mixture of short-chain hydrocarbons) (Yongjiang *et al.*, 2011; Torrente and Galan, 2001). In addition, oil shale semicoke is a solid byproduct of the process which is rich in carbon (Loo *et al.*, 2017).

Three main processes make up the oil shale pyrolysis, they are:

1) Evaporation of water at low temperatures (< 200 ^{o}C)

2) Pyrolysis of kerogen (from 200 up to 600 ^{o}C)

3) Decomposition of carbonates (at temperatures above 700 ^{o}C) (Maaten *et al.*, 2016).

The understanding of kerogen grew together with the growth of analytical techniques. Despite the development in analytical techniques, pyrolysis has remained a major tool in studying kerogen structure. It is partly because pyrolysis can be used to analyze macromolecules (Hillier, 2011).

Early works in the pyrolysis of kerogen were based on simplified mechanisms for decomposition. These reaction schemes consider kerogen as made of two components: an oil forming component and a coke forming component.

2.6 Pyrolysis Techniques

The pyrolysis techniques are:

2.6.1 Rock-eval pyrolysis

In Rock-Eval pyrolysis, a sample is placed in a vessel and is progressively heated up to 550 °C under an inert atmosphere. During the process, the hydrocarbons already present in the sample are volatized at a moderate temperature. The amounts of hydrocarbon are measured and recorded as a peak. Next, that is pyrolyzed is the kerogen present in the sample, which generates hydrocarbons and hydrocarbon-like compounds, CO_2, and water. Residual carbon is also measured (Law, 1999).

2.6.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method of thermal analysis in which the mass of a particular sample is measured over time as the temperature changes. This measurement provides information about its physical phenomena, such as phase transitions, absorption, adsorption, and desorption; as well as its chemical phenomena including chemisorptions, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction). The basic principle of the TGA is that as a sample is heated, its mass changes. This change can be used to obtain the composition of the material or its thermal stability, up to 1000 ^{o}C. Usually, a sample loses weight as it is heated up due to decomposition, reduction, or evaporation. A plot of weight % vs. temperature (thermogravimetric curve) is drawn which usually consists of a series of steps, obtained by measuring the mass of a sample during heating (Saadatkhah *et al.*, 2020).

2.6.3 Fixed bed pyrolysis of oil shale

Stainless-steel fixed-bed retort is a setup of equipment used to produce bio-oil by progressively increasing the temperature of a sample in an inert atmosphere. Other products are gases and solids (Char in case of Kerogen sample). The oil shale sample of a known mass is electrically heated in an 800 cm^3 cylindrical retort. Reactor and furnace temperatures need to be controlled to obtain the desired retorting temperature (200 - 600 ^{0}C in this case). Type K thermocouple is then inserted from the top side of the retort to the middle point of the oil shale sample for monitoring purposes, while the other thermocouple is situated between the external body of the retort and the inner side of the ceramic cylinder for controlling the retort temperature. Sweep gas is introduced from the top of the retort in an 8 mm pipe for preheating while passing down to the bottom of the retort and then is allowed to disperse to sweep the generated products toward the retort topside outlet. Oven temperature is controlled and monitored by a digital temperature controller indicated as oven T ^{o}C in Figure 2.5.

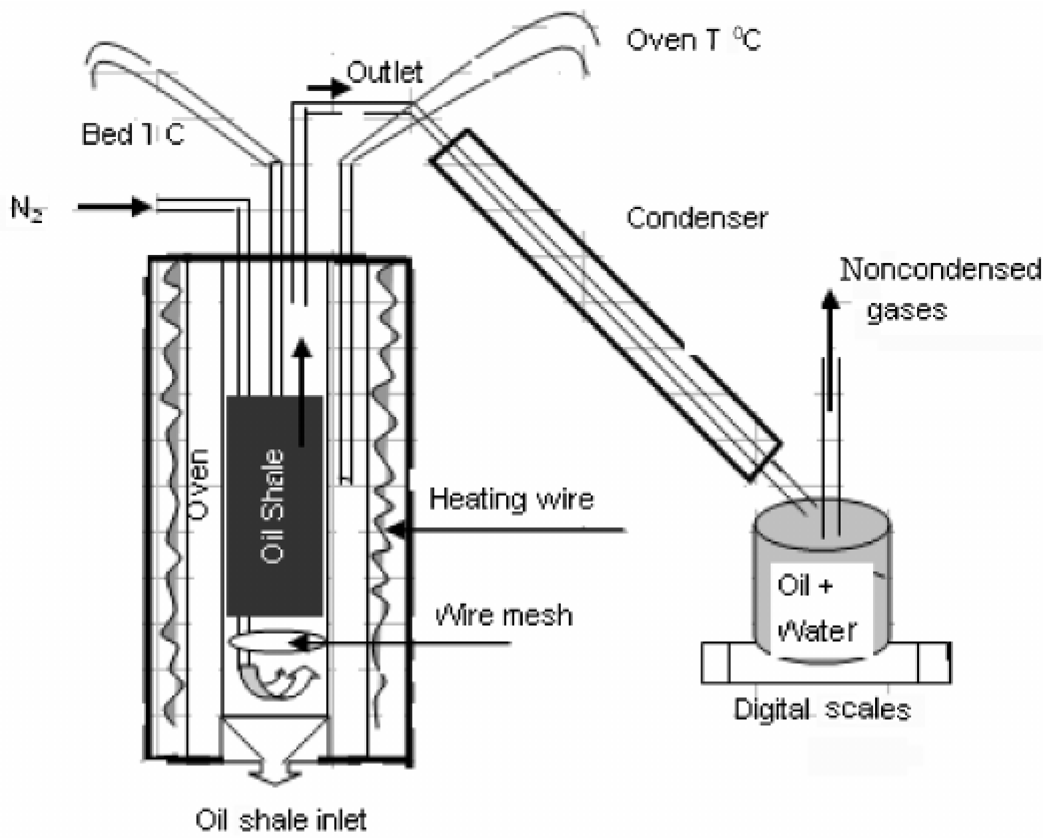


Figure 2.5: Oil Shale Pyrolysis in Fixed-Bed Retort (Al-Harahsheh, 2009)

The generated hydrocarbons will then sweep from the reaction zone by gaseous nitrogen. The circulating coolant will be maintained at 2 ± 2 °C to condense liquid hydrocarbons and water carried by nitrogen gas. Condensable hydrocarbons and water will then be collected while the non-condensable light organics and other non-condensable gases will be vented into the atmosphere. The weight of the condensed liquid shale oil and water will be recorded continuously as a function of time and retort temperature as the digital scales indicate the increase of the accumulated weight on its digital panel. Finally, water will be separated for oil yield. At the end of each run, the retort will be emptied and the spent shale weighed for the total weight loss measurement (Al-Ayed *et al.,* 2009).

2.7 Gas Chromatography-Mass Spectometry (GC-MS)

The technique in which Gas Chromatography (GC) is combined with Mass Spectrometry (MS) is referred to as Gas Chromatography-Mass Spectometry (GM-MS). The GC separates a mixture into individual compounds and as each compound elutes out of the GC column, it passes into the mass spectrometer where the molecules are ionised (usually by electron impact). Some of the primary ions so generated may further undergo fragmentation thereby generating secondary ions the kind of which are dependent on the structure of the compound.

In the furnace are GC oven, column and MS. The oil shale undergoes pyrolysis in a temperature program in the furnace and the volatile molecules are carried by the carrier gas into the GC column in an oven for separation into various components while the ion source in the MS ionizes the molecules into ions to be detected by the MS. It is detected based on scan programme such as 29 - 600 mass/charge number of ions ratio and represented by total ion chromatogram (TIC) as reported by (Yeboah, 2015).

Gas Chromatography has played a fundamental role in determining how many components and in what proportion they exist in a mixture. However, the ability to establish the nature and chemical structures of these separated and quantified compounds is ambiguous and reduced, and requires a Spectroscope Detection System. The often used, is the Mass Spectrometric Detector (MSD) which allows obtaining the mass spectrum of the molecule. Mass Spectra provide information on the molecular weight and elemental composition.

2.8 Process Simulation

Process simulation predicts the behaviour of a process by using basic engineering relationships, such as mass and energy balances as well as phase and chemical equilibrium (Mehta *et al*., 2009). We can simulate actual plant behaviour when given realistic operating conditions, reliable thermodynamic data, rigorous equipment models, and realistic operating conditions. Process simulation enabled us to conduct "what if" analyses, performed sensitivity studies, run many cases, and optimize runs. Better plants can be designed with simulation and increase profitability on existing plants. Process simulation is useful throughout the entire lifecycle of a process, from research and development through process design to production. It is also use for troubleshooting and safety in the process plant. Aspen Plus does make it easy to build and run a process model by providing hypertext help, a comprehensive system of online prompts, and expert system guidance on a stepwise basis.

CHAPTER THREE

3.0 MATERIALS AND METHODS

Oil shale sample contains hydrocarbons (bitumen) and kerogen; thus, it is a potential raw material for petroleum production (Yeboah, 2015). This chapter comprises the various techniques of experiment and characterization done in this study.

3.1 Experimental Diagram for the Analysis of Gbetiokun Oil Shale Pyrolysis

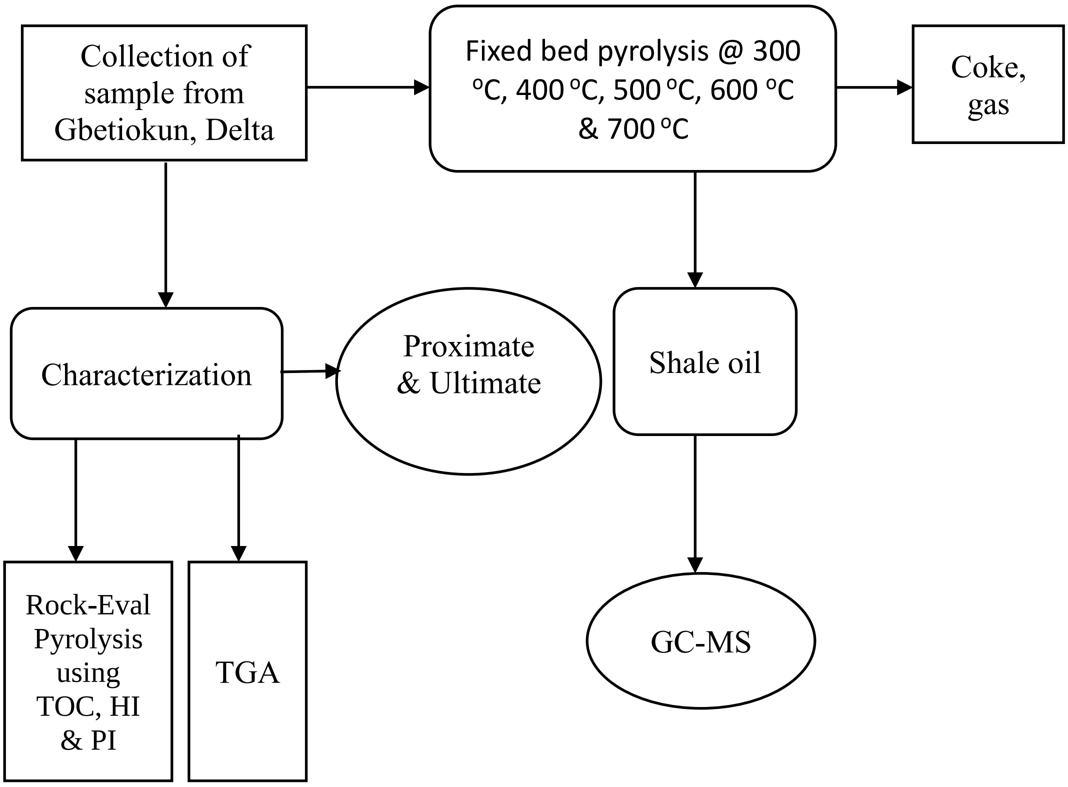


Figure 3.1: Experimental Procedure for the Analysis of Gbetiokun Oil Shale pyrolysis

The diagram in Figure 3.1 shows the methodology for the experiment of Gbetiokun oil shale. The sample was collected from Gbetiokun in Delta state of Nigeria. After passing through the pre-treatment stage (section 3.2), it was characterized using proximate and ultimate analyses, Rock-Eval pyrolysis and Thermogravimetric analysis methods. The proximate was done to determine the fuel-like properties such as Moisture content, Volatile content, Fixed carbon and Ash content while the ultimate gave the elemental compositions of the sample such as Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur.

In the Rock-Eval pyrolysis, the sample is placed in a vessel and is progressively heated up to 550 °C under an inert (Nitrogen) atmosphere. During the process, the hydrocarbons already present in the sample are volatized at a moderate temperature. The amounts of hydrocarbon are measured and recorded as a peak. Next, that is pyrolyzed is the kerogen present in the sample, which generates hydrocarbons and hydrocarbon-like compounds, CO_2, and water. During the process, amount of carbon present is measured as the total organic carbon (TOC), the free hydrocarbons present in the sample was measured as S1 and the amount of hydrocarbon during the cracking of the kerogen is measured as S2. TOC, S1 and S2 using equations 3.1, 3.2 and 3.3 were used to calculate the Hydrogen Index (HI), Production index (PI) and Oxygen Index (OI).

Thermogravimetric Analysis (TGA) was done on the oil shale to know its thermal stability. This was also achieved using heating rates of 10, 20, and 30 ^{o}C/ min with Nitrogen (as the sweep gas) to know the weight loss profile of the oil shale. Details of the procedure can be found in section 3.5. Fixed-Bed pyrolysis was carried out to produce the oil, gas and recover the spent oil shale (char). The oil produced was then characterized using GC-MS through detecting, separating and quantifying the hydrocarbon constituents into smaller organic compounds. The molecules are also ionised (usually by electron impact). Some of the primary ions so generated may further undergo fragmentation thereby generating secondary ions.

3.2 Pretreatment of Oil Shale Sample

The oil shale sample, Plate I was obtained from the Niger Delta basin, precisely from Gbetiokun in Delta State, Nigeria (located at Longitude 6.0 ^{o}E and Latitude 5.5 ^{o}N). The specimen was then charged into the machine (containing steel balls) for crushing, milling into powder, and then sieving. The milled oil shale sample was used for further analyses.

Plate I: Gbetiokun oil shale sample

The procedure for the extraction of kerogen was based on the method reported by Oluseyi *et al.,* (2011). 10 g each of the oil shale samples were weighed into extraction thimbles. The extraction was done using the soxhlet extractor with 250 ml dichloromethane (DCM) for 16 h. The residue (kerogen) was washed several times with de-ionized water until its pH reached 6.8. Based on the method reported by Han *et al.,* (2013), the residue and the extract (bitumen) were dried at room temperature for one day and then at 70 ºC for 2 h.

The removal of carbonates was done based on the method described in Han *et al.,* (2013) on the kerogen. 100 ml of 6 M HCl acid was poured into 2 g of the powdered sample and was left for 24 h. After that, the setup was decanted, and the product was washed repeatedly in the centrifuge with hot de-ionized water until it reached a pH of 6.7. The residue was dried for 1.5 h at 70 ºC in a vacuum oven. Table 3.1 shows the list of equipment and apparatus used to carry out the experimental analyses.

Table 3.1: List of Equipment and Apparatus

S/No	Equipment/Apparatus	Model
1	GC-MS	Agilent 6890/5973N
2	Rock-Eval Pyrolyser	LECOSC-632Carbon/ Sulphur Analyser
3	Weighing balance	MF100/1108596
4	Thermal Gravimetric Analyser	PerkinElmer TGA 4000

3.3 Proximate and Ultimate Analyses

To know the composition and fuel-like properties of the sample, proximate and ultimate analyses were done. The proximate analysis measures moisture, ash, and volatile oil shale content; it was done based on the ASTM D 7582 reported by Ibrahim *et al.,* (2019). Ultimate analysis shows the elemental compositions such as carbon, hydrogen, sulphur, nitrogen, and oxygen content which are important factors that influence product yield and quality during the pyrolysis process. This analysis was done according to procedures produced from standard test methods used for coal standards (ASTM D5373) in the report of Ibrahim *et al.*, (2019).

3.4 Rock-Eval and TOC Analyses

The oil shale contains organic matter (OM), which is the source of petroleum; OM is made of bitumen and kerogen (Yang *et al.*, 2017; Yeboah, 2015). To determine the crude oil potential of the oil shale sample, Rock-Eval analysis was done on the milled sample at the Getamme Laboratories Nigerian Limited, Port Harcourt, according to the method described by Zheng (2013). The sample was introduced into the LECO combustion oven with model indicated in Table 3.1, and the Infra-Red detector measures the amount of carbon as carbon dioxide. First, the sample was heated at a rate of 25 °C/min at 300 °C for 3 min and then to 650 °C in an inert atmosphere of helium. During the pyrolysis process, the quantity of the volatile hydrocarbons present in the sample (S1 peak, mg hydrocarbons per g of sample) and the number of hydrocarbons released by the thermal cracking of the kerogen (S2; mg hydrocarbons per g of sample) were detected by a flame ionization detector (FID).

The organic matter present in the sample was also established through Total Organic Carbon (TOC) using the LECO SC-632 carbon/sulfur analyzer. The analyzer followed NIGOGA, 4th Edition protocol. Jet-Rock 1 (a standard) was performed as every tenth sample and then inspected to see if it falls within the acceptable range given in the Norwegian Industry Guide to Organic Geochemical Analyses (NIGOGA).

The following were parameters determined from Rock-Eval pyrolysis:

1. S1- The quantity of free hydrocarbon present in the oil shale.
2. S2- The amount of hydrocarbon generated during thermal cracking of non-volatile organic matter.
3. S3- The amount of CO_2 produced during pyrolysis.

4. Tmax- It is the maximum temperature through which hydrocarbon are release from the cracking of kerogen.

   The above mentioned parameters were used to obtain the following:

   a. HI (Hydrogen Index); this is the ratio of hydrogen to carbon available in the source rock. It is given by;

      $$HI = \frac{(S2\times100)}{TOC} \tag{3.1}$$

   b. PI (Production Index); this is the amount of hydrocarbon produced during first and second stages of pyrolysis. It is given by;

      $$PI = \frac{S1}{(S1+S2)} \tag{3.2}$$

   c. OI (Oxygen Index); this is the ratio of oxygen to carbon ratio of the source rock. It is given by;

      $$OI = \frac{(S3\times100)}{TOC} \tag{3.3}$$

3.5 Thermogravimetric Analysis (TGA)

The TGA involved using a tiny sample (< 1 g) of the milled sample to measure its mass loss as a function of temperature over a predefined heating rate. The machine also makes a provision for an electronic differentiation of the mass-loss signal into a rate of mass loss (DTG). The analysis (TGA) of the shale sample was done using a Perkin Elmer TGA 4000 thermogravimetric analyzer as indicated in Table 3.1. The sample was heated from room temperature 28 ^{o}C to 824 ^{o}C at various heating rates of 10, 20, and 30 ^{o}C/ min using nitrogen as the sweep gas.

3.6 Experimental Fixed-Bed Pyrolysis

The setup in Figure 3.2 is comprised of a semi-batch reactor made of stainless steel tube 145 mm long, outer diameter 41 mm, and internal diameter of 37 mm. it was sealed at one end and had an outlet tube. The oil shale sample (30 g) was kept in a stainless-steel cylindrical retort. An external electric furnace uniformly heated the apparatus; a proportional–integral–derivative (PID) controller was mounted to control the temperature. A thermocouple was used to determine the temperature of the reactor. N_2 gas was introduced into the reactor, at a fixed metered flow rate, to create an inert atmosphere during the reaction. The gas also flowed through the reactor during the pyrolysis to sweep out the gaseous products. The liquid products were collected by the condenser unit. The gaseous products were carried into the online gas analyzer. After the experiment, masses of the liquid product and the spent shale (char) were collected and measured.

The above procedure was done at a constant time of 45 min at 300, 400, 500, 600, and 700 °C. After completing each experimental run, the yield liquid, solid and gaseous products were calculated in terms of percentages.

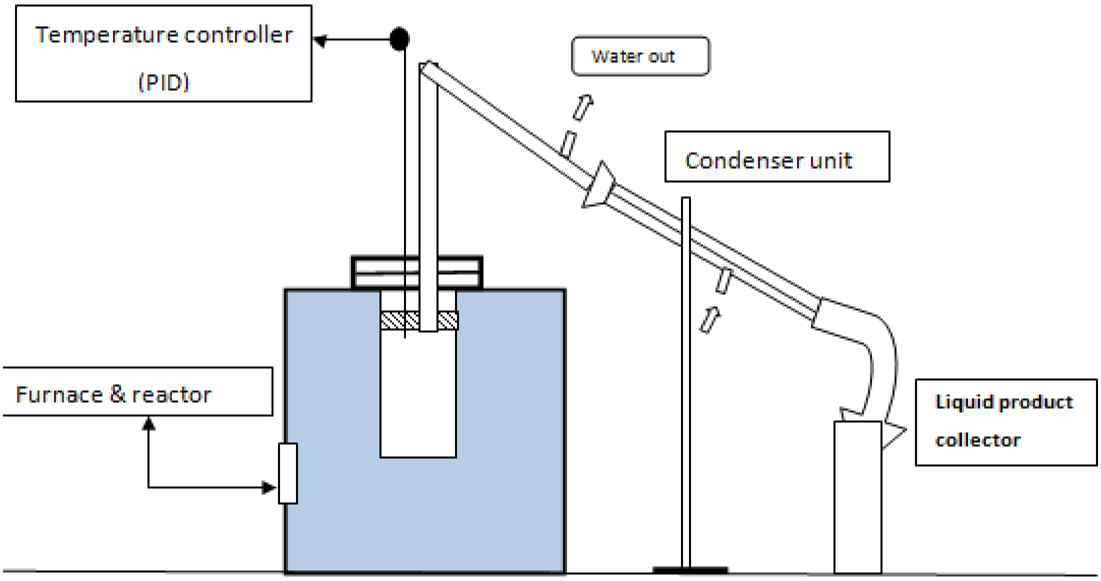


Figure 3.2: Setup for the pyrolysis of Gbetiokun oil shale

3.7 Gas Chromatography-Mass Spectrophotometry (GC-MS)

Tchapda (2017) reported that the GC-MS is an efficient technique to identify and analyze the pyrolysis products. GC-MS detects, separates, and quantifies small volatile compounds in the gas phase. In Gas Chromatography (GC), liquid samples are vaporized, then carried by an inert gas through a long, thin column.

Agilent 6890/5973N represented pictorially in Plate II was used to perform the GC-MS technique on the sample. The GC has a fused silica capillary column (30 m x 250 um x 0.25 um) through which the carrier gas (helium) flowed at 1.5 ml/min. The oven temperature of the GC was held at 320 ºC for 10 min.

Plate II: A Gas Chromatograph Setup for the Analysis of Gbetiokun Oil Shale Pyrolysis Product (Agilent 6890/5973N)

3.8 Simulated Fixed-Bed Pyrolysis

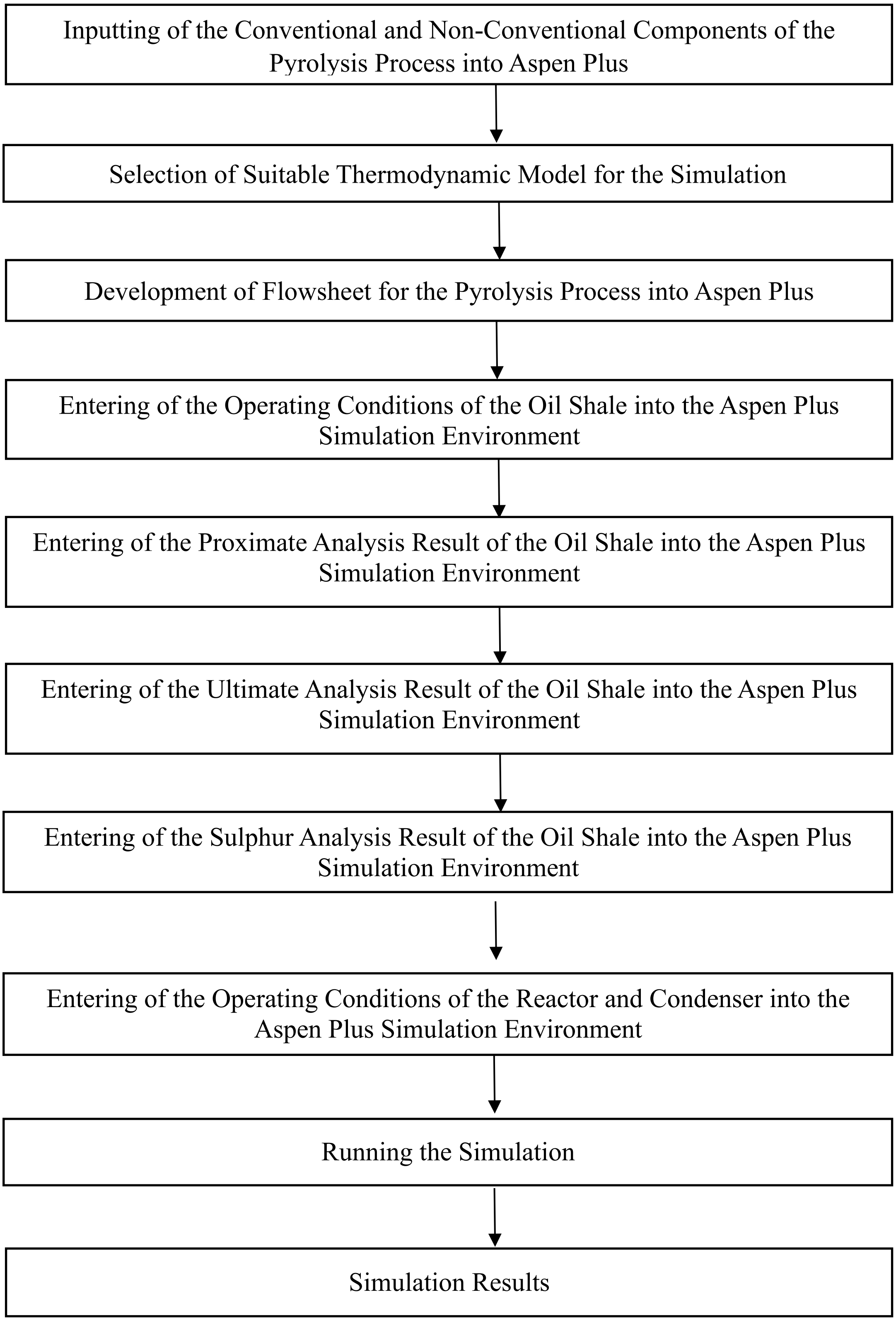


Figure 3.3: Simulation Procedure of the Fixed-Bed Pyrolysis of Oil Shale using Aspen Plus

Aspen Plus simulation software was used to validate the experimental results obtained. Figure 3.3 shows the procedure used to carry out the simulation of the oil shale from Gbetiokun. First, the Conventional and Non-Conventional Components of the Pyrolysis was inputted into Aspen Plus. After which Selection of Suitable Thermodynamic Model for the Simulation was done (Redlich-Kwong-Soave cubic equation of state was selected for its good nature in oil, gas and petrochemical operations, (Redlich and Otto, 1949)). The Flowsheet for the Pyrolysis process was developed in the simulation environment and the operating conditions for the oil shale, 500 °C at 4 KPa (from experimental results) were entered. The compositions, which are proximate, ultimate and Sulphur results were entered into the simulation environment. Finally, the yields and operating conditions for the pyrolysis reactor (500 °C at 4 KPa) and operating conditions for condenser (70 °C at 4 KPa) were inputted. Upon convergence, the simulation was ran and results recorded.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The results and discussion of the methods of experiment conducted in Chapter three are reported in this chapter.

4.1 Proximate and Ultimate Analyses Results of Gbetiokun Oil Shale

Table 4.1 shows the results of the proximate and ultimate analyses of the Gbetiokun oil shale sample. The sulfur content of Gbetiokun oil shale is low at 0.03 %, which is environmentally friendly. But it has a very high carbon content of 89.25 wt. %.

Table 4.1: Compositions of Gbetiokun Oil Shale

Proximate	Value (wt. %)	Value (wt. %) (Loo, 2018)	Ultimate	Value (wt. %)	Value (wt. %) (Loo, 2018)
Moisture content	6.93	0.5	Carbon	89.25	27.4
Volatile content	45.73	47.5	Hydrogen	9.06	2.7
Fixed carbon	33.62	1.3	Oxygen	0.44	-
Ash content	9.33	50.7	Nitrogen	1.11	0.07
TOC	2.23	21.8	Sulphur	0.03	1.6
			Hydrogen/ Carbon	0.1	-

According to Caillat and Vakkilainen, (2013), the quantity of carbon increases the heating value of the sample. Some of the carbon will form part of the volatile matter, and the other will form most of the char. The hydrogen/carbon (H/C) ratio of the sample is 0.1 %. A Low H/C ratio is not favorable for producing high-quality shale oil. The sample's hydrogen content is 9.06 wt %, which contributes to the heating value of the fuel (Caillat and Vakkilainen, 2013). The sample has a moisture content of 6.93 wt %. According to Dewangan (2014), the high moisture content is usually unfavorable for oil shale conversion, which tends to reduce the combustion properties of the products. The volatile matter composition is 45.73 wt %. Abnisa and Daud, (2014) reported that a high volatile matter favors more extraction/pyrolysis oil production and consequently reduces coke and gas yield. High ash content has a negative impact on the yield but tends to promote a solid-coke and gaseous product (Abnisa and Daud, 2014). The Table shows that the Gbetiokun sample has a TOC value of 0.51 wt %. This implies a source of rock with fair potential for oil. However, the high organic carbon content in sediments does not necessarily indicate a potential oil source (Sari *et al.*, 2015).

4.2 Rock-Eval and TOC Results of Gbetiokun Oil Shale

Rock-Eval results obtained from Getamme Laboratories, Nigeria, are hereby presented. Table 4.2 shows that the Gbetiokun oil shale sample has a Total Organic Carbon (TOC) content of 0.51. It is fair in the composition of Organic Matter (OM) (Dembicki, 2017). The S_1 and S_2 peaks are 0.05 and 1.04, respectively. Based on the TOC value obtained, the sample has a fair potential for generating hydrocarbons. As already defined, the S_3 value represents the yield of carbon dioxide (CO_2) produced during the thermal breakdown of kerogen; Table 4.2 shows that it is a 0.57 mg CO_2/g rock sample.

Table 4.2 Rock-Eval Analysis Results of Gbetiokun Oil Shale

TOC	S_1 (mg Hc/g rock)	S_2 (mg Hc/g rock)	S_3 (mg CO_2/g rock)	S_2/S_3	T_{max} (°C) thermally	HI (mg HC/g TOC)	PI	OI (mg HC/g TOC)
0.51	0.05	1.04	0.57	1.82	414	203.92	0.05	111.76

The Hydrogen index (HI), Production Index (PI), Oxygen Index (OI), and S_2/S_3 value of the organic matter were computed using equations 3.1, 3.2 and 3.3 as 203.92 mg HC/g TOC, 0.05, 111.76 mg HC/g TOC, and 1.82, respectively (Table 4.2). Peters and Cassa (1994) reported that an HI range of 50-200 indicates type III kerogen and 200-300 indicates type II/III (kerogen with intermediate HI between types II and III). S_2/S_3 value range of 1-5 indicates type III kerogen. Examining all these values leads to the conclusion that the oil shale sample has a type III kerogen. A T_{max} value of 414 °C (T_{max}< 435 °C) and Production Index value of 0.05 classify the sample as being thermally immature (Peters and Cassa, 1994).

4.3 Thermogravimetric Analysis (TGA) of Gbetiokun Oil Shale

Figure 4.1 shows the decomposition profile of kerogen derived from the Gbetiokun oil shale sample. Its decomposition profile can be divided into three stages: stage I (water removal), stage II (organic decomposition), and stage III (inorganic decomposition).

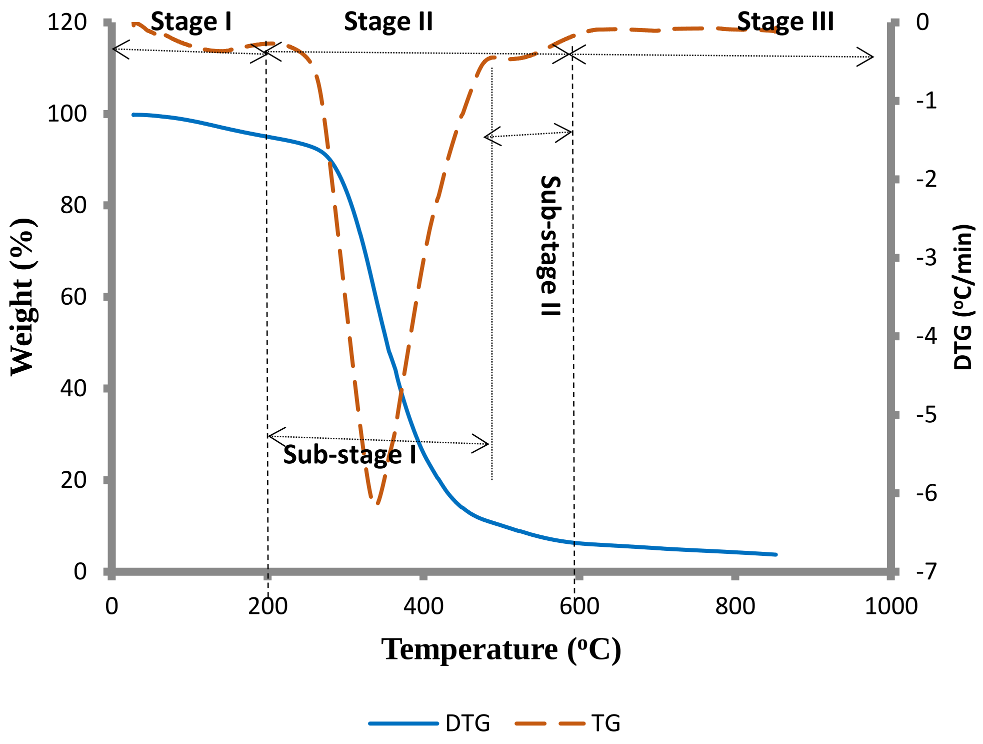


Figure 4.1: General TGA/DTG Profile for the Kerogen Sample

Stage II can be further divided into two sub-stages I and II of weight loss. These two sub-stages occurring during the pyrolysis process can be identified as bitumen and oil regimes. The first sub-stage decomposition generally occurs until 350 °C and represents organic decomposition where degradation of kerogen produces bitumen (Al-Harahsheh *et al.*, 2011). This stage produced gas, bitumen, and carbon residue. In the second sub-stage, the produced gas, bitumen, and carbon residue devolatilize further to produce oil, coke, and gas. This occurs between 350 and 600 °C (Al-Harahsheh *et al.*, 2010).

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

Figures 4.2 and 4.3 show the mass loss profile due to pyrolysis of the kerogen sample at heating rates of 10, 20, and 30 °C/min, up to a temperature of 800 °C.

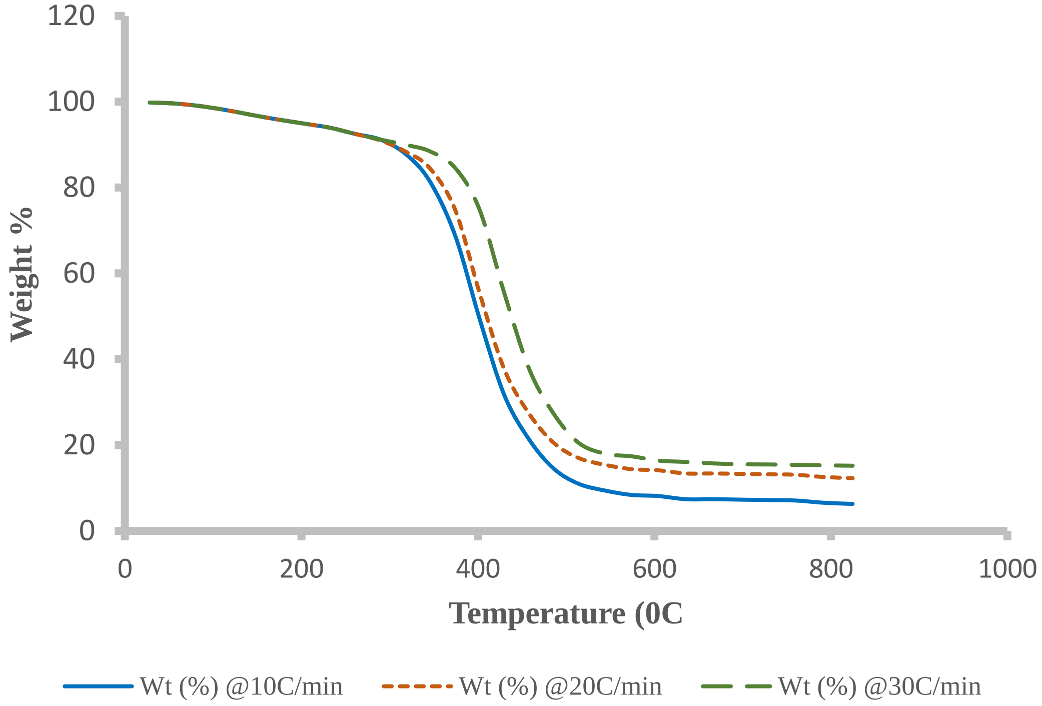


Figure 4.2: Weight Loss Profile for the Kerogen Sample at Different Heating Rates

The thermogram in Figure 4.2 clearly show that the mass loss below the temperature range of 280–370 °C can be attributed to moisture evaporation during heating. Most of the mass loss occurs in the temperature range of 320-510 °C, and it is the pyrolysis of OM and kerogen to release hydrocarbons. At this point, the kerogen begins to release hydrocarbons when the temperature is high enough to decompose it. The Figure also shows that the total mass loss of oil shale samples decreased with the increase of heating rate. This result is in good agreement with the work of Al-Harahsheh *et al.* (2011). However, the temperatures at which the reaction starts and ends increase with an increased heating rate. For instance, at a heating rate of 10

^{o}C/min, the mass loss starts at a temperature of 320 ^{o}C and stops at 480 ^{o}C. At a heating rate of 20 ^{o}C/min, the mass loss starts at a temperature of 380 ^{o}C and ends at 500 ^{o}C/min. Mass loss starts at 380 ^{o}C and stops at 560 ^{o}C for a heating rate of 30 ^{o}C/min.

Al-Harahsheh *et al.* (2011) reported that this phenomenon could relate to the effects of heat flux on the sample and the initiation of the secondary cracking reaction. While very high heating rates provide enough heat to initiate multiple expelling hydrocarbon responses from the sample, low temperatures support oil shale particles to heat uniformly and for slow reactions to occur.

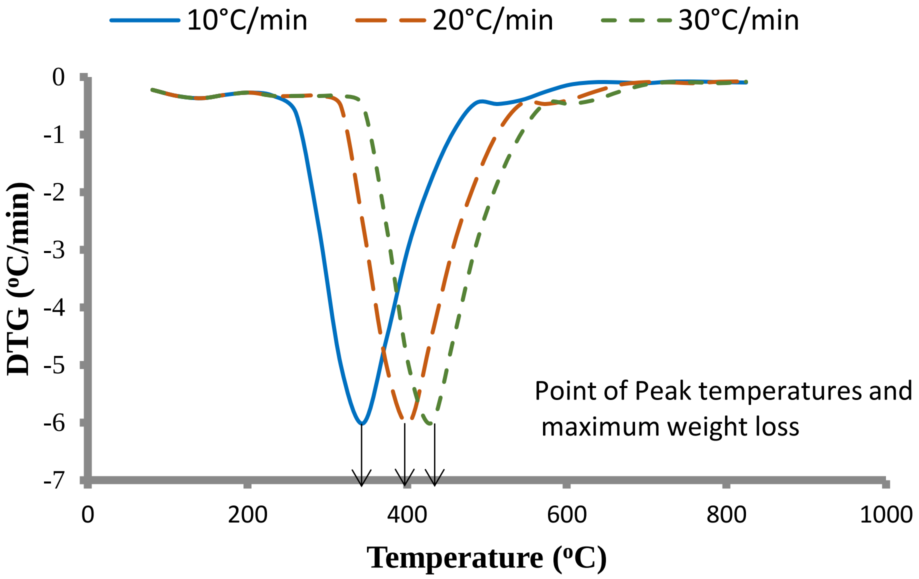


Figure 4.3: Derivative Weight Loss Profile for the Oil Shale at Different Heating Rates

The TG and DTG curves of kerogen (Figures 4.2 and 4.3) show that the oil shale sample's total mass loss decreased with increased heating rate. For the three heating rates tested, 10 ^{o}C/min caused the quickest decomposition, followed by 20 ^{o}C/min and then 30 ^{o}C/min.

4.4 Fixed-Bed Pyrolysis Yields of Gbetiokun Oil Shale

Figure 4.4 shows the Gbetiokun shale oil, non-condensable gas, and char yields in the pyrolysis reactor, heating from 200 °C to 700 °C. Figure 4.5 shows the yields of oil, gas and coke as 50.2, 25.6 and 24.2 % respectively. The oil yield increased up to 50.2 %, from 200 – 500 °C. However, raising the furnace temperature beyond 500 °C dropped shale oil yield from 50.2 % to 42.1 %. The non-condensable gas yield increases consecutively from 200 – 700 °C. Wang *et al.* (2014) suggested that pyrolysis becomes more active as the temperature increases and large amounts of kerogen are directly converted into non - condensable gases. The yield of char decreases from 54 % to 18.4 % with the Figure's increasing furnace temperature. Wang *et al.* (2014) and Lin *et al.* (2015) reported that shale oil yields and non-condensable gas increased with increasing temperature while the yield of char decreases. The declining yield of shale oil beyond 500 ^{o}C could be attributed to shale oil's coking reactions. Moreover, Wang *et al.* (2014) reported that the maximum yield of oil is obtained at an optimal temperature. Exceeding the optimal temperature could reduce the yield of shale oil, probably because of secondary coking and cracking of the oil vapor to improve gases yield.

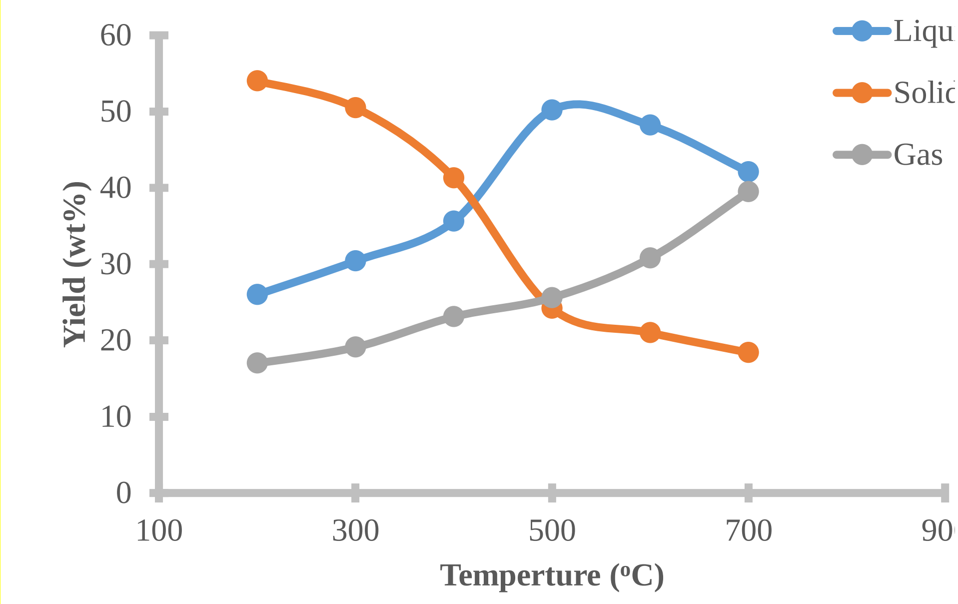


Figure 4.4: The Yields from Pyrolyzing Gbetiokun Oil Shale

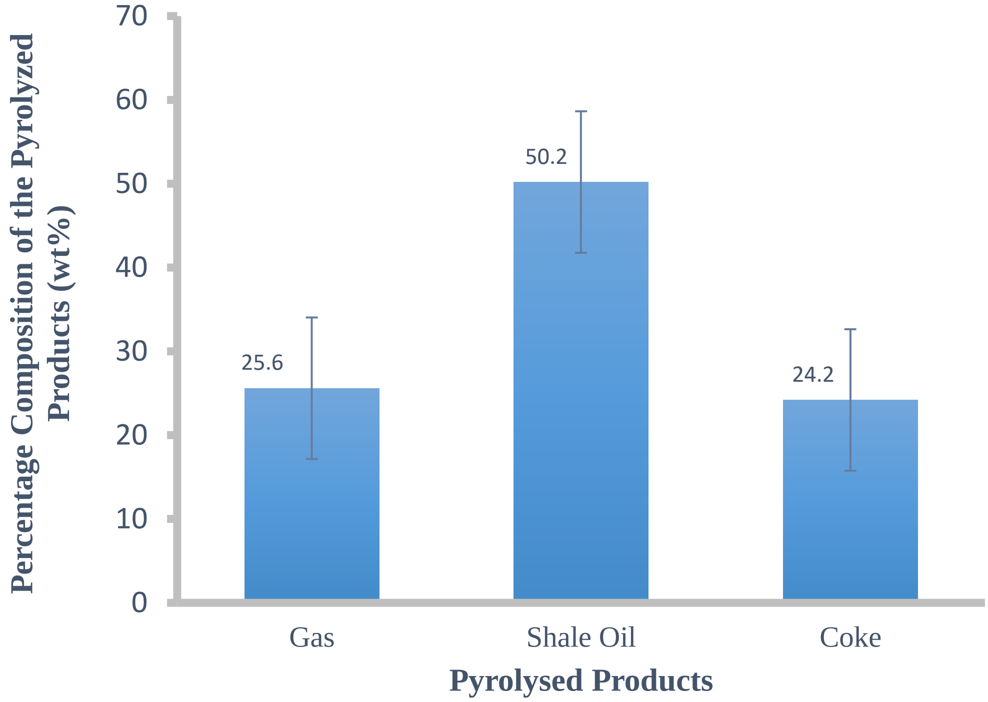


Figure 4.5: Experimental Results of Fixed Bed Pyrolysis of the Oil Shale to Obtain Shale Oil, Gas, and Coke

4.5 GC-MS Analysis Results of Gbetiokun Oil Shale

The result of the GC-MS analysis is presented in Figure 4.6. It shows a pristane/phytane ratio of 1:21. According to (Harb *et al.*, 2003), this ratio is useful as correlation parameters because it is believed to be sensitive to diagenetic conditions. Pr/ph ratios substantially below unity could be taken as an indicator of highly reducing depositional environments. Very high pr/ph ratios (more than 3) are associated with terrestrial sediments, including coals. Pr/ph ratios ranging between 1 and 3 reflect oxidizing depositional environments. Thus the value of 1:21 shown in the Figure indicates that the oil shale sample could be of the oxidizing atmosphere with decreasing salinity.

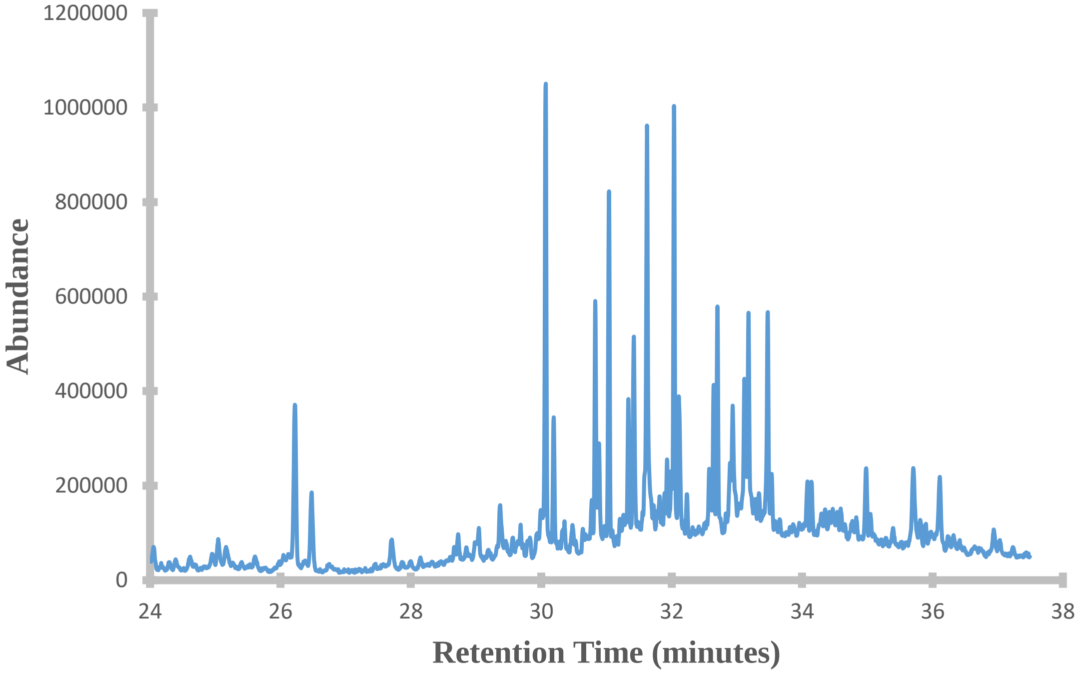


Figure 4.6: GC-MS Profile for the kerogen sample

4.6 Fixed-Bed Pyrolysis Simulation Results of Gbetiokun Oil Shale using Aspen Plus

Figure 4.7 shows the simulated result of the pyrolysis of Gbetiokun Oil shale using Aspen Plus. As shown in Figure 4.7, the result of the simulation depicts that 53.3 % Shale oil, 24.70 % non-condensable gas, and 22 % coke were obtained from pyrolysis of Gbetiokun Oil shale. Also, Figure 4.8 shows that the experimental and simulated pyrolysis of the Gbetiokun oil shale which produced 50.2 % and 53.3 % Shale oil, respectively. The result of the experimental and simulated pyrolysis of the Gbetiokun oil shale also had 25.6 % and 24.7 % non-condensable gas, respectively, shown in Figure 4.8. The coke content of experimental and simulated pyrolysis of Gbetiokun oil shale obtained from Figure 4.8 is 24.2 % and 22 %, respectively. These results show that there is a good agreement between the experimental and simulated results. The flow sheet of the simulation of Gbetiokun oil shale is shown in Figure 4.9.

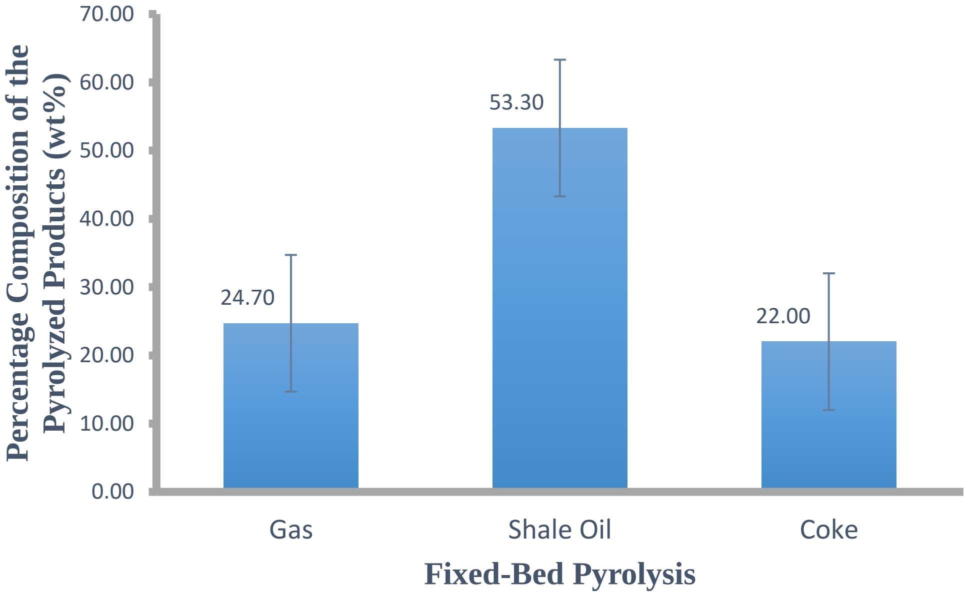


Figure 4.7: Simulated Results of Fixed Bed Pyrolysis of the Oil Shale to Obtain Shale Oil, Gas, and Coke

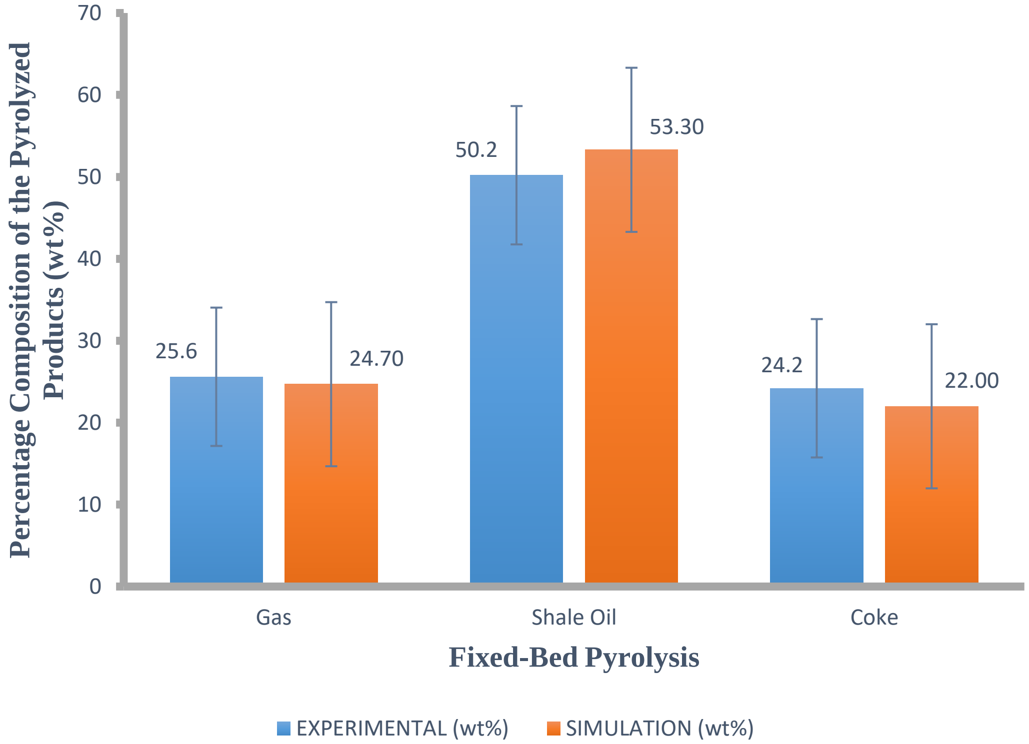


Figure 4.8: Experimental and Simulated Results of Fixed Bed Pyrolysis of the Oil Shale to Obtain Liquid, Gas, and Coke

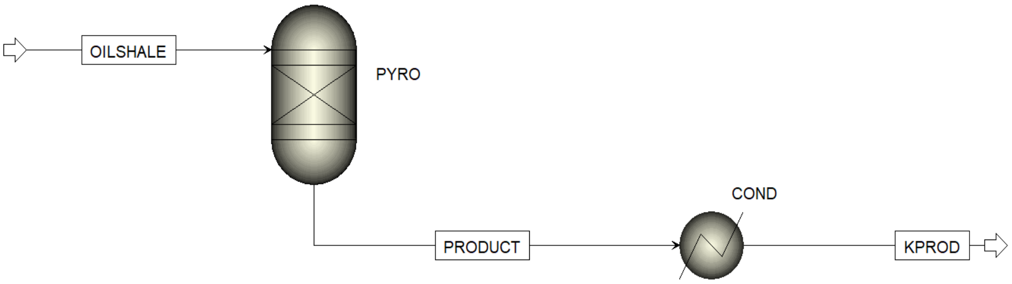


Figure 4.9: Flowsheet Simulation of Gbetiokun Oil Shale to obtain Shale Oil, Gas, and Coke

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In line with the objectives of this study, the following conclusions are made.

The Rock-Eval pyrolysis results of the Gbetiokun oil shale based on the TOC, Hydrogen Index and Production Index were 0.51 wt%, 203.92 mg HC/g TOC and 0.05 respectively revealed that the sample has good hydrocarbon potential due to its fair content of organic matter; it is oil and gas prone and in its immature stage.

The TGA shows the main stage of mass loss corresponding to release bitumen and oil in the temperature range (250 – 600) ^{o}C and at higher temperatures, further weight loss was due to decomposition of carbonate.

Fixed Bed Pyrolysis results showed that as temperature increased to 500 ^{0}C, the shale oil produced reach optimum yield for both experimental and simulated results. Temperature higher than 500 ^{0}C shows reduction in oil yield.

From the GC-MS results, the Gbetiokun shale oil is predominantly Paraffinic (C_{18} to C_{36}) in nature, which is best used for Asphalt, Wax and Base oils production. Also, the Pristane/Phytane ratio of the GC-MS analysis indicates the value of 1.21, thus showing that the oil shale sample could be of the oxidizing environment with decreasing salinity.

5.2 Recommendations

The following recommendations are made in order to have a more detailed understanding and to further appreciate the potential of the oil shale sample used in this research:

Study on the mineral content of the Gbetiokun oil shale can be done. Also, the TOC of the sample could be determined from Walkey-Black method and the result compared to LECO method. Lastly, the functional groups in the oil shale sample can also be studied. Validation of the Fixed-bed experimental results using Aspen plus simulation can also be carried out under unsteady (dynamic) state condition and the difference compared with that of the steady state condition.

5.3 Contribution to Knowledge

1. Based on my Rock-Eval results, the Hydrogen Index (HI) of the Gbetiokun Oil Shale 203.92 mg HC / g TOC indicating that it is oil and gas prone.
2. The GC-MS results show that the oil shale is predominantly paraffinic in nature and the Pristane-Phytane ratio was 1.21 indicating that it is of the oxidizing atmosphere with decreasing salinity.
3. The sample, based on the Production Index (PI) of 0.05 and Tmax value of 414 ^{o}C, is in its thermal immature stage.
4. Both the experimental and simulated results of the Fixed-Bed pyrolysis agrees that the oil shale has an optimum yield of Shale oil at 500 ^{o}C.

REFERENCES

Abnisa, F., & Daud, W. M. A. W. (2014). A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management*, *87*, 71-85.

Aizebeokhai, A. P., & Oyebanjo, O. A. (2013). Application of vertical electrical soundings to characterize aquifer potential in Ota, Southwestern Nigeria. *International Journal of Physical Sciences, 8*(46), 2077-2085.

Al-Ayed, O. S., Al-Harahsheh, A., Khaleel, A. M., & Al-Harahsheh, M. (2009). *Oil Shale Pyrolysis in Fixed-Bed Retort with Different Heating Rates*, *26*(2), 140-146

Al-Harahsheh, A., Al-Ayed, O., & Abu-El-Halawah, R. (2010). Heating rate effect on fractional yield and composition of oil retorted from El-lajjun oil shale. *Journal of Analytical and Applied Pyrolysis*, *89*(2), 239-243.

Al-Harahsheh, M., Al-Ayed, O., Robinson, J., Kingman, S., Al-Harahsheh, A., Tarawneh, K., & Barranco, R. (2011). Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales. *Fuel Processing Technology, 92*(9), 1805-1811.

Alto P., C. A. (1999). Enhanced Oil Recovery Scoping Study. *Electric Power Research Institute, Washington, D.C, USA. Final Report,* 113-136.

Boyt, R. (2003). Wood Pyrolysis. *Retrieved from Bioenergylists Organization, Oregon, United States of America*, 40-45.

Caillat, S., & Vakkilainen, E. (2013). Biomass combustion science, technology and engineering, 9-30

Carrie, J., Sanei, H., & Stern, G. (2012). Standardisation of Rock–Eval pyrolysis for the analysis of recent sediments and soils. *Organic Geochemistry*, *46*, 38-53.

Chen, G., Lin, J., Hu, W., Cheng, C., Gu, X., Du, W., & Qu, C. (2018). Characteristics of a crude oil composition and its in situ waxing inhibition behavior. *Fuel*, *218*, 213-217.

Dembicki, H. From Satellite Images to Reservoired Hydrocarbons (2017): The In-Depth Investigations of the Marco Polo Seeps, Green Canyon, Gulf of Mexico. In *AAPG Annual Convention and Exhibition*, 607-608.

Dewangan, P., Mandal, R., Jaiswal, P., Ramprasad, T., & Sriram, G. (2014). Estimation of seismic attenuation of gas hydrate bearing sediments from multi-channel seismic data: A case study from Krishna–Godavari offshore basin, India. *Marine and Petroleum Geology*, *58*, 356-367.

Gorlov, E. G. (2007). Thermal dissolution of solid fossil fuels. *Solid Fuel Chemistry*, *41*(5), 290-298.

Han, E. M., Sampei, Y., & Roser, B. P. (2014). Characterization of kerogen using combined pyrolysis-GC-MS and FT-IR in weathered and unweathered coals and coaly shales from the Central Myanmar Basin, Myanmar, Burma in Southeast Asia. *Researches in Organic Geochemistry*, *29,* 49-59.

Harb, F. S., El Nady, M. M., & Basta, J. S. (2003). Oil: oil correlation for some oil fields in the north western part of the Western Desert, Egypt. *Petroleum science and technology*, *21*(9-10), 1583-1600.

Harper, R. T. (2007). Determination of the proton affinities of gas phase peptides by mass spectrometry and computational chemistry, Stockton, USA, 24-50

Hillier, J. L. (2011). *Pyrolysis kinetics and chemical structure considerations of a Green River oil shale and its derivatives*. Brigham Young University, USA, 143-132

Ibrahim, A. F., Dandamudi, K. P. R., Deng, S., & Lin, J. Y. (2020). Pyrolysis of hydrothermal liquefaction algal biochar for hydrogen production in a membrane reactor. *Fuel*, *265,* 116-135.

Law, C. A. (1999). Treatise of Petroleum Geology/Handbook of Petroleum Geology: Exploring for Oil and Gas Traps. Chapter 6: Evaluating Source Rocks, 36-79.

Lin, L., Zhang, C., Li, H., Lai, D., & Xu, G. (2015). Pyrolysis in indirectly heated fixed bed with internals: The first application to oil shale. *Fuel Processing Technology*, *138,* 147-155.

Loo, L., Maaten, B., Neshumayev, D., & Konist, A. (2017). Oxygen influence on Estonian kukersite oil shale devolatilization and char combustion. *Oil Shale*, *34*(3), 219-231.

Loo, L., Konist, A., Neshumayev, D., Pihu, T., Maaten, B., & Siirde, A. (2018). Ash and flue gas from oil shale oxy-fuel circulating fluidized bed combustion. *Energies, 11*(5), 1218-1300.

Maaten, B., Loo, L., Konist, A., Nesumajev, D., Pihu, T., & Külaots, I. (2016). Decomposition kinetics of American, Chinese and Estonian oil shales kerogen. *Oil shale*, *33*(2), 167-180.

Mehta, N. M., Compher, C., & ASPEN Board of Directors. (2009). ASPEN Clinical Guidelines: nutrition support of the critically ill child. *Journal of Parenteral and Enteral Nutrition*, *33*(3), 260-276.

Obaje, N. G. (2009). *Geology and mineral resources of Nigeria* (Vol. 120). 145-155

Ohakwere-Eze, M. C., & Adizua, O. F. (2014). Qualitative Delineation of Hydrocarbon bearing Reservoir from Preliminary study of Well Log Data over an Offshore Niger Delta Field". *Pacific Journal of Science and Technology (PJST), 15*(2), 293-297.

Okon, A. (2017). *Combustion dynamics in a lean premixed combustor with swirl forcing and fuel conditions* (Doctoral dissertation, Cardiff University), England, 121-123.

Okon, A. N., Appah, D., & Akpabio, J. U. (2017). Water coning prediction review and control: developing an integrated approach. *Journal of Scientific Research and Reports*, 1-24.

Oluseyi, T., Olayinka, K., Alo, B., & Smith, R. M. (2011). Comparison of extraction and clean-up techniques for the determination of polycyclic aromatic hydrocarbons in contaminated soil samples. *African Journal of Environmental Science and Technology*, *5*(7), 482-493.

Oluwajana, O. A., Ehinola, O. A., Okeugo, C. G., & Adegoke, O. (2017). Modeling hydrocarbon generation potentials of eocene source rocks in the agbada formation, Northern Delta Depobelt, Niger Delta Basin, Nigeria. *Journal of Petroleum Exploration and Production Technology*, *7*(2), 379-388.

Osuji, L. C. (2015). The future of petroleum in Nigeria and prospects of shale oil as an alternative energy supplier. *Journal of Chemical Society of Nigeria*, *40*(1), 52-128.

Peters, K. E., & Cassa, M. R. (1994). Applied source rock geochemistry, *Essential elements*, 5-12.

Qing, W., Baizhong, S., Aijuan, H., Jingru, B., & Shaohua, L. (2007). Pyrolysis Characteristics of Huadian Oil Shales. *24*(2), 47-74.

Raja, M. A., Chen, H., Wang, H., Zhao, Y., Shi, C., Zhang, S., & Zhang, X. (2017). Process Analysis for the Production of Hydrogen and Liquid Fuels from Oil Shale. *Energy Technology*, *5*(11), 1963-1978.

Redlich, O., & Kwong, J. N. (1949). On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chemical reviews*, *44*(1), 233-244.

Ringer, M., Putsche, V., & Scahill, J. (2006). *Large-scale pyrolysis oil production: a technology assessment and economic analysis* (No. NREL/TP-510-37779). National Renewable Energy Lab. (NREL), Golden, CO (United States), pp. 543-576.

Saadatkhah, N., Carillo Garcia, A., Ackermann, S., Leclerc, P., Latifi, M., Samih, S., & Chaouki, J. (2020). Experimental methods in chemical engineering: Thermogravimetric analysis—TGA. *The Canadian Journal of Chemical Engineering*, *98*(1), 34-43.

Sarathi, P. S. (1999). *In-situ combustion handbook--principles and practices* (No. DOE/PC/91008-0374). National Petroleum Technology Office, Tulsa, USA, 67-70.

Sari, T. P., Mann, B., Kumar, R., Singh, R. R. B., Sharma, R., Bhardwaj, M., & Athira, S. (2015). Preparation and characterization of nanoemulsion encapsulating curcumin. *Food Hydrocolloids*, *43*, 540-546.

Seplat, (2020). *Seplat Energy Company of Nigeria*. (2020 Activities) Production and Development, 82-91.

Sonibare, O. O., Ehinola, O. A., & Egashira, R. (2005). Thermal and geochemical characterization of Lokpanta oil shales, Nigeria. *Energy conversion and management*, *46*(15-16), 2335-2344.

Speight, J. G. (2020). *Synthetic fuels handbook: properties, process, and performance*. McGraw-Hill Education, USA, 65-86.

Stacey, C. (2011). Bocardo SA v Star Energy UK Onshore Ltd and Another. *Aberdeen Student L. Rev.*, *2*, 124-157.

Taylor, G. D. (2019). *Imperial standard: Imperial Oil, Exxon, and the Canadian oil industry from 1880*. Calgary: University of Calgary Press, Alberta, Canada, 765-811.

Tchapda, A. H., Krishnamoorthy, V., Yeboah, Y. D., & Pisupati, S. V. (2017). Analysis of tars formed during co-pyrolysis of coal and biomass at high temperature in carbon dioxide atmosphere. *Journal of Analytical and Applied Pyrolysis*, *128,* 379-396.

Tissot, B. P., & Welte, D. H. (1984). From kerogen to petroleum. In *Petroleum formation and occurrence*. Springer, Berlin, Heidelberg, Germany, 160-198.

Torrente, M. C., & Galan, M. A. (2001). Kinetics of the thermal decomposition of oil shale from Puertollano (Spain). *Fuel*, *80*(3), 327-334.

Troutner, J. (1996). National Geographic. *Teacher Librarian*, *24*(2), 38.

Vandenbroucke, M., & Largeau, C. (2007). Kerogen origin, evolution and structure. *Organic Geochemistry*, *38*(5), 719-833.

Wang, K., Kim, K. H., & Brown, R. C. (2014). Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chemistry*, *16*(2), 727-735.

Wang, Q., Ye, J. B., Yang, H. Y., & Liu, Q. (2016). Chemical composition and structural characteristics of oil shales and their kerogens using Fourier Transform Infrared (FTIR) spectroscopy and solid-state 13C Nuclear Magnetic Resonance (NMR). *Energy & Fuels, 30*(8), 6271-6280.

Yang, Y., Lu, X., & Wang, Q. (2017). Investigation on the co-combustion of low calorific oil shale and its semi-coke by using thermogravimetric analysis. *Energy Conversion and Management*, *136*, 99-107.

Yeboah, I. (2015). *Characterization and Thermal/Catalytic Upgrading of Kerogen in a Green River Oil Shale* (Master's thesis, NTNU), Trondheim, Norway, 32-98.

Yongjiang, X., Huaqing, X., Hongyan, W., Zhiping, L., & Chaohe, F. (2011). Kinetics of isothermal and non-isothermal pyrolysis of oil shale. *Oil shale*, *28*(3), 35-60.

Zheng, A., Zhao, Z., Chang, S., Huang, Z., Wang, X., He, F., & Li, H. (2013). Effect of torrefaction on structure and fast pyrolysis behavior of corncobs. *Bioresource technology*, *128*, 370-377.

Zweidick, O. G. J. (2020). *Macroinvertebrate Communities of Perennial and Intermittent Streams in Bioregion 14 (“Grazer Feld und Grabenland “, Austria: Styria) with a Special Focus on Caddisflies*, University of Natural Resources and Life Sciences, Vienna, 116-118.

APPENDICES

APPENDIX A

A.1: The Shale Oil results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale

The Shale Oil results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale is shown in Table A.1

Table A.1: Fixed Bed Pyrolysis Results for Shale Oil

S/N	Yield (wt%)	Temperature (°C)
1	26	200
2	30.4	300
3	35.6	400
4	50.2	500
5	48.2	600
6	42.1	700

A.2: The Non-Condensable Gas results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale

The Non-Condensable Gas results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale is shown in Table A.2

Table A.2: Fixed Bed Pyrolysis Results for Non-Condensable Gas

S/N	Yield (wt%)	Temperature (°C)
1	17	200
2	19.1	300
3	23.1	400
4	25.6	500
5	30.8	600
6	39.5	700

A.3: The Coke results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale

The Coke results for the Fixed Bed Pyrolysis of the Gbetiokun Oil shale is shown in Table A.3

Table A.3: Fixed Bed Pyrolysis Results for Coke

S/N	Yield (wt%)	Temperature (°C)
1	54	200
2	50.5	300
3	41.3	400
4	24.2	500
5	21	600
6	18.4	700

A.4: Experimental and Simulated Results of Fixed Bed Pyrolysis of the Oil Shale to Obtain Liquid, Gas, and Coke

The experimental and simulated results of fixed bed pyrolysis of the oil shale to obtain liquid, gas, and coke are shown in Table A.4.

Table A.4: Experimental and Simulated Results of Fixed Bed Pyrolysis of the Oil Shale to Obtain Liquid, Gas, and Coke

S/N	Pyrolyzed Product	Experimental (wt%)	Simulation (wt%)
1	Gas	25.6	24.70
2	Shale Oil	50.2	53.30
3	Coke	24.2	22.00
	Total	100	100

APPENDIX B

B.1: The GC-MS analysis of Gbetiokun shale oil

The results of GC-MS of the Gbetiokun shale oil is shown in Table B.1

Table B.1: GC-MS results of the Gbetiokun shale oil

S/No.	Retention time	Compound name	Molecular formula	Molecular weight (g/mol)
1	10.61	Cyclohexene	C_6H_{10}	82
2	24.39	Cyclopentane, 1,1,3-trimethyl-	C_8H_{16}	112
3	26.57	D – Limonene	$C_{10}H_{16}$	136
4	29.90	Cyclohexane, butyl-	$C_{10}H_{20}$	140
5	31.63	Decane	$C_{10}H_{22}$	142
6	34.15	Cyclohexane, pentyl-	$C_{11}H_{22}$	154
7	30.78	Cyclohexane, 1-(cyclohexylmethyl-3methyl-, trans	$C_{14}H_{28}$	194
8	28.85	Cyclotetradecane	$C_{14}H_{28}$	196
9	21.39	Tetradecane	$C_{14}H_{30}$	198
10	35.90	Decane, 3-cyclohexyl-	$C_{16}H_{32}$	224
11	26.48	Hexadecane	$C_{16}H_{34}$	226
12	34.47	1-Heptadecane	$C_{17}H_{34}$	239
13	28.73	Heptadecane	$C_{17}H_{36}$	241
14	29.94	1-Octadecane	$C_{18}H_{36}$	253
15	30.19	Octadecane	$C_{18}H_{38}$	255
16	32.58	1,19-Eicosane	$C_{20}H_{38}$	279
17	32.11	Eicosane	$C_{20}H_{40}$	281
18	30.89	Hexadecylcyclopentane	$C_{21}H_{42}$	295
19	32.83	Heneicosane	$C_{21}H_{44}$	297
20	26.05	1-Docosene	$C_{22}H_{44}$	309
21	28.24	Tricosane	$C_{23}H_{48}$	325
22	35.05	Tricosane, 2-methyl-	$C_{24}H_{50}$	339
23	34.42	Octadecane, 9-ethyl-9-heptyl-	$C_{27}H_{56}$	381
24	29.04	Octacosane	$C_{28}H_{58}$	395
25	32.27	Nonacosane	$C_{29}H_{60}$	409
26	30.97	Triacontane	$C_{30}H_{62}$	423
27	31.83	Cyclodotriacontane	$C_{32}H_{64}$	449
28	32.90	17-Pentatriacontene	$C_{35}H_{70}$	491
29	29.68	Heptotriacontane	$C_{37}H_{76}$	521
30	32.55	Tetracontane	$C_{40}H_{82}$	563
31	29.53	Tetratetracontane	$C_{44}H_{90}$	619
32	35.46	Nonatetracontane	$C_{49}H_{100}$	689

APPENDIX C

C.1: Standard geological parameters for generative potentials of immature source rocks (Peters and Cassa 1994)

The standard geological parameters for generative potentials of immature source rocks are shown in Table C.1.

Table C.1: Standard geological parameters for generative potentials of immature source rocks (Peters and Cassa, 1994) modified by (Yeboah, 2015)

Potential Petroleum	Poor	Fair	Good	Very Good	Excellent	This Study
TOC (wt%)	<0.5	0.5-1	1-2	2-4	>4	0.51
S1 mgHC/g rock	<0.5	0.5-1	1-2	2-4	>4	0.05
S2 mgHC/g rock	0-2.5	2.5-5	5-10	10-20	>20	1.04

C.2: Standard parameters for Productive Index (Peters and Cassa 1994)

The Standard parameters for the Productive Index are shown in Table C.2.

Table C.2: Standard parameters for Productive Index (Peters and Cassa 1994) modified by (Yeboah, 2015)

Stages of oil Maturity	Immature	Early Mature	Peat Mature	Late Mature	This Study
Production Index	<0.1	0.1-0.15	0.25-0.40	>0.4	0.05
Temp (ºC)	<435	435-445	445-450	450-470	414

C.3: Standard parameters for Hydrogen Index *(Peters and Cassa 1994)*

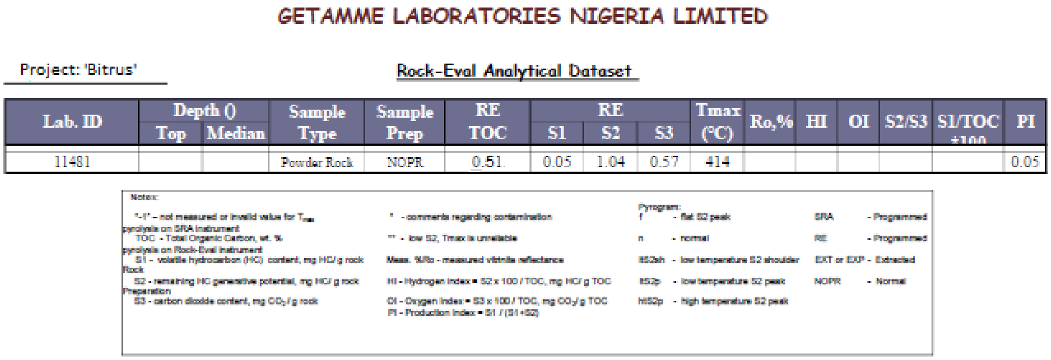
The Standard parameters for Hydrogen Index are shown in Table C.3.

Table C.3: Standard parameters for Hydrogen Index (Peters and Cassa, 1994) modified by (Yeboah, 2015)

HI Generative Potential	Standard Values (mgHC/gTOC)	This Study
No generative potential	<50	
Gas prone	50 to 150	
Oil and gas prone	150-300	203.92
Oil prone	300	

C.4: The Rock-Eval Analytical Dataset of Gbetiokun Oil shale.

The Rock-Eval Analytical Dataset of the Gbetiokun Oil shale is shown in Figure C.4



GETAMME LABORATORIES NIGERIA LIMITED

Project: 'Bitrus'

Rock-Eval Analytical Dataset

Lab. ID	Depth ()		Sample Type	Sample Prep	RE TOC	RE			Tmax (°C)	Ro,%	HI	OI	S2/S3	S1/TOC *100	PI
	Top	Median				S1	S2	S3							
11481			Powder Rock	NOPR	0.51	0.05	1.04	0.57	414						0.05

Notes:

"-1" – not measured or invalid value for T_{max}
TOC - Total Organic Carbon, wt. %
S1 - volatile hydrocarbon (HC) content, mg HC/ g rock
S2 - remaining HC generative potential, mg HC/ g rock
S3 - carbon dioxide content, mg CO_2/ g rock

* - comments regarding contamination
** - low S2, Tmax is unreliable
Meas. %Ro - measured vitrinite reflectance
HI - Hydrogen Index = S2 x 100 / TOC, mg HC/ g TOC
OI - Oxygen Index = S3 x 100 / TOC, mg CO_2/ g TOC
PI - Production Index = S1 / (S1+S2)

Pyrogram:
f - flat S2 peak
n - normal
lS2sh - low temperature S2 shoulder
lS2p - low temperature S2 peak
hS2p - high temperature S2 peak

SRA - Programmed pyrolysis on SRA instrument
RE - Programmed pyrolysis on Rock-Eval instrument
EXT or EXP - Extracted Rock
NOPR - Normal Preparation

Figure C.4: Rock-Eval Analytical Dataset