

**EVALUATION AND CHARACTERISATION OF OIL PRODUCTION FROM
KEROGEN IN BIDA BASIN**

BY

**MOHAMMED, Iiyasu Kudu
MEng/SEET/2016/6156**

**DEPARTMENT OF CHEMICAL ENGINEERING
FEDERAL UNIVERSITY OF TECHNOLOGY
MINNA**

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ABSTRACT

Production and Characterization of oil from kerogen obtained from Bida Basin. In this study, kerogen from Bida Basin was used as a source of hydrocarbon for the production of oil and gas. Different thermal characterization such as Thermogravimetric Analysis (TGA) and Rock Eval (R.E) pyrolysis were employed. TGA was studied for the purpose of determining the thermal decomposition of kerogen. The decomposition of kerogen occurs at temperature of 308.28-471.68 °C. Thermal breakdown of the kerogen content using TGA and R.E takes place mainly at the temperature of 300 to 600 °C. The analysed kerogen sample from R.E have Total Organic Carbon (TOC) content of 0.68 wt % and constitute of oil and gas prone kerogen type II. The maximum temperature (Tmax) is 418 °C. Thermal characteristics of analyzed sample obtained by TGA is in conformity with R.E parameters. The results obtained from R.E pyrolysis reveal that the shale oil contains good quality kerogen to generate oil and gas during pyrolysis. Fixed bed pyrolysis was performed in order to obtain shale oil, gas and coke. Temperature of 500 °C gave an optimum yield of 50.20 wt %.GCMS analysis shows the organic compounds present in the shale oil. Physical properties such as viscosity, density, pour point, flash point, calorific value, pH and moisture content were studied and compared with standard shale oil. The BET analysis shows that the specific surface area of the kerogen was 171.95 m² / g, pore size was 2.97 nm and pore volume was 0.068 cm³ / g which enhance the flow of oil within the kerogen sample.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Energy is a very important resource of any nation all over the world. It can be observed that increase of industrial growth of any nation is a function of the quantity of energy available in that nation and the extent it is utilized (Osueke and Ezugwu, 2011). Conventional energy source are petroleum, coal and natural gas. Nigeria is the world's tenth biggest reserve of crude oil estimated to be about 36 billion barrels. Onshore drilling refers to drilling deep holes under the earth surface whereas offshore drilling refers to drilling underneath the seabed. These drilling methods are used in order to extract natural resources usually oil and gas (Oyedepo, 2012). The most exploited natural resource in Nigeria is petroleum. However recent findings suggest that petroleum potentials of Nigeria have not been fully realized, particularly with emphasis to its inland basins. Nigeria's inland basins have been highly under explored basically as a result of abundance of oil in the Niger Delta. Examples of inland basin in Nigeria are Anambra Basin, Benue Trough, Benin Basin, Bida Basin, Borno Basin, Niger Delta Basin and Sokoto Basin (Geologin, 2012).

The technology of exploring inland Basin is Seismic, which is technology employed by oil and gas companies to find-out the rock where there is potential for hydrocarbons. Seismic technology operates with sound waves to predict what lies in the ground. Therefore, there is a need to utilize the use of energy sources to meet huge energy demand. Similarly, alternatives fossil fuels such as oil shale, oil sand, tar, asphaltite, shale gas and so on can be

transformed to increase supply of energy (Kok and Ozgur, 2016). Kerogen (Petroleum Source Rock) can simply be defined as the organic matter content of the oil shale with sufficient amount of hydrocarbon to form a commercial quantity of oil or gas (Al-Areeq, 2018). The elemental contents of kerogen are Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S) and Oxygen (O) (Adegoke *et al.*, 2015).

Pyrolysis is one of the new alternative methods used to produce fossil fuels (oil and gas). The major methods of pyrolysis are combustion (presence of oxygen), thermal / cracking, catalysis / cracking (catalyst), hydrocracking (hydrogenation), gray-king pyrolysis (fixed bed pyrolysis) and micro wave pyrolysis (Olufemi, 2016).

In the study of thermal and geochemical characterization of Lokpanta oil shales conducted by (Sonibare *et al.*, 2005) stated that kerogen sample was characterized using Thermogravimetric Analysis (TGA) and Rock Eval (R.E) pyrolysis. Thermogravimetry Analysis (TGA) was the instrument that gave information about thermal behavior of the kerogen with respect to the composition of organic matter and heating rate and the Rock Eval (R.E) pyrolysis was used extensively in analyzing the organic matter contained in the oil shale with respect to quantity, quality or type and thermal maturity. The sample was heated in oxygen free environment to a particular temperature range using a special temperature program. The first peak (S1) stand for hydrocarbon already present in the sample at about temperature of 300 °C. The second peak (S2) stand for hydrocarbon gotten from thermal cracking of kerogen at about temperature of 300 – 550 °C and the third peak (S3) stand for the CO₂ which is generated from kerogen during thermal cracking. The

analysis also provides information about maximum S2 peak (Tmax) and the Total Organic Content (TOC) of the oil shale.

(Obaje *et al.*, 2013) studied the geological surveying, mapping and characterization of the kerogen from Bida Basin using Rock Eval pyrolysis instrument. (Liu *et al.*, 2017) study kinetics characterization of kerogen from Mudanjiang using Rock Eval pyrolysis instrument. The results of heating rate obtained are 10, 15, 20, 25 and 30 °C/min while temperature range of 200 - 600 °C. However they are limited to kinetics, Thermogravimetric Analysis (TGA) and Rock Eval (R. E) Pyrolysis. This research is going further by carrying out fixed bed pyrolysis experiment on the kerogen to obtained liquid, solid and gas. The shale oil from fixed bed pyrolysis was characterized with Gas Chromatography Mass Spectrometer (GCMS) in order to know the organic compounds present in the kerogen (Stanshenko and Martinez, 2014). The kerogen sample was analyzed in Brunauer Emmitt Teller (BET) in order to know the pore size, pore volume and specific surface area of the kerogen. The aim of this research work is to evaluate and characterize oil production from kerogen in Bida Basin.

1.2 Aim and Objectives of the Study

The aim of this research work is to evaluate and characterise oil production from kerogen in Bida Basin area in Niger State, Nigeria. The aims can be achieved through the following objectives.

- I. To evaluate the composition and chemical content of the kerogen and shale oil through ultimate and proximate analysis.
- II. Rock Eval pyrolysis of the carbonaceous kerogen in order to evaluate the Total Organic Carbon (TOC) and hydrocarbon generative potential of the sample.
- III. Thermogravimetric analysis (TGA) of the carbonaceous kerogen in order to evaluate thermal and chemical contents and Brunauer Emmett Teller (BET) analysis in order to obtain the specific surface area, surface pore size and pore volume of the kerogen.
- IV. Fixed bed pyrolysis experiment of carbonaceous kerogen to obtain shale oil, shale gas and coke.
- V. Determinations of physical properties such as viscosity, density, calorific value, pour point, flash point, moisture content and pH of the shale oil.

VI. Characterisation of the shale oil via GCMS.

1.3 Scope of the study

The scope of this research is limited to evaluation and characterization of oil production from kerogen in Bida Basin in Niger State, Nigeria and characterization of the shale oil with GCMS, characterization of kerogen using TGA, Rock Eval pyrolysis and BET analysis.

1.4 Statement of the Research Problem

This study has become very important because of the need for energy as a result of population growth, dependence on fossil fuel and depletion of already existing oil reserves such as Niger Delta Basins. The commonest methods of extracting crude oil are thermal dissolution, hydrogen treatment (hydrogenation), and pyrolysis. Consequently, the need for a viable energy sources have become imperative. Pyrolysis is one of the new alternative methods used to produce fossil fuels (oil and gas). This research is aimed at studying the evaluation and characterisation of oil production from kerogen in Kudu Bida Basin area in Niger State and characterisation of the shale oil obtained from fixed bed pyrolysis with GCMS, Characterisation of kerogen using TGA, Rock Eval pyrolysis and BET analysis.

1.5 Justification of the Study

This is justified for the following reasons, kerogen as an indicator to presence of hydrocarbon deposit in Bida Basin will go a long way to provide more oil reserve which

will therefore solve the problem associated with demand for energy. This will in turn provide more sources of energy from fossil fuel for the teaming population.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Energy

The increased rate of industrial growth of a nation is a function of the quantity of energy available and the extent to which it is utilized (Osueke and Ezugwu, 2011). Crude oil remained the world leading fuel that is accounting for 32.9 % of the world energy consumption. However, as a result of the increase in economics activities, there is a high demand for energy most especially crude oil all over the world. The record of production levels are on the increase in OPEC which states that there is increase in consumption rate from 1.6million barrel per day to 38.2 million barrel per day . Internal Energy Agency (IEA) defined oil as a mixture of hydrocarbons that exist in liquid phase under normal

surface conditions. Therefore, there is need to differentiate between conventional and unconventional oil. Conventional oils are hydrogen rich compounds relatively short hydrocarbon chains, fewer carbon atoms C₁ to C₆₀ and lower molecular weight whereas unconventional oils are defined as those obtained by unconventional production means because they cannot be recovered through pumping in their natural state from an ordinary production well without being heated or diluted (Gordon, 2012). In order to have sustainable energy development, there is need for rational use of energy resources as well as technologies and development of appropriate Government policies. There is a large insufficient supply of energy and it has become a major challenge to growth and quality of life (Saifuddin *et al.*, 2016). Energy is important today and will still be important in the future. Energy connects many communities and nation together through energy initiative interaction. It is very imperative to know many countries depend on harnessing energy supply (Edomah *et al.*, 2016). Energy demand is a growing issue in various nations of the world both developed and developing nation. To be precise, energy must be adequate, reliable and affordable. A nation cannot be considered as developed if it has inadequate, balanced, reliable and sufficient energy mix because it is very important for human needs (Oluwatoni, 2017). Energy is an essential tool for socio economic development and growth. The aim of energy is to give energy services and energy services are the needed for almost all human endeavours. Source of useful services of energy includes lighting, provision of air conditioned indoor climate, refrigerated storage, transportation, appropriate temperatures for cooking and so on. It can be seen clearly that energy is the basic necessity for modern life. However, oil rich nation like Nigeria recorded significant economic gains where as

those developing nations that did not have crude oil are more faced with serious economic challenges. Presently a large amount of the global energy output is gotten from fossil fuels such as oil and coal (Sambo, 2005).

2.1.1 Energy in Nigeria

Nigeria is a developing nation in Africa where application of renewable energy technology is situated. However, it is largely remain untapped as a result of insufficient knowledge skills about energy resources. Therefore, there is need to look at the energy deficiency and find an everlasting solution to it (Saifuddin *et al.*, 2016). Nigeria has high potential resources such as fossil fuels and renewable energy resources. It is important to motivate the participation of an energy mix program that leads to transformation of petroleum resources and continued exportation will serve as foreign exchange earnings for the country for many years (Sambo, 2005). Energy to be specific oil and gas has continued to contribute more than 70 % of Nigeria's national income and securities agency relied mainly on these revenue earnings. 25 % of Gross Domestic Product (GDP) has been on crude oil for many years ago. Nigeria has high potential of crude oil as its primary sources of energy. Nigeria is the world's tenth biggest reserve of crude oil estimated to be 36 billion barrels. The country also has more potential for Natural Resources Island than oil with an estimated value of 166trillion standard cubic feet (Oyedepo, 2012). The oil industry reforms brought into existence the Nigerian National Petroleum Corporation (NNPC) in 1975, the Petroleum Products Pricing Regulatory Authority (PPPRA) in the early 2000's, the Nigerian Local Content Development Initiative and Greenfield Refinery Projects. Furthermore, as a result of the environmental problems and poor infrastructure of the oil producing areas, this led to

the introduction of the Petroleum Industry Bill (PIB) in 2008. This PIB is an executive bill that seeks for an act to provide for the establishment of a legal, fiscal and regulatory framework to address the environmental and other related matters in the oil sub sector. The gas sector is also very important in transforming the Nigeria economy through areas like electricity, petro-chemicals, cement, iron and residential. The Gas sector received attention from Federal Government of Nigeria in the area of Gas Master Plan. This is aimed at providing a network that would make sure the realization of maximum value from the nation gas resources. The Nigerian Liquefied Natural Gas (NLNG) company Limited and other Nigeria Gas companies has gas processing facilities. According to American Petroleum Institute (API) stated that the energy sector supports more than 9.0miliion jobs opportunities directly or indirectly which is more than 5.0 % of the world total employment (Rapu *et al.*, 2015).

2.2 Exploration Technology Drilling and Reservoir Technologies

Seismic technology has been used by oil and gas companies to find out the rock where there is potential for hydrocarbons. Seismic technology operates with sound waves to predict what lies deep in the ground. Other technologies are magnetic geophysical methods,

gravitational, passive, magnetic, electric, sonic and radioactive processing, aerial and satellite remote sensing (LAND SAT), 2-dimensional, 3-dimensional and 4-dimensional are used to carried out detailed evaluation of the nature and distribution of rock units as well as frequency, orientation and geological history of folds that will serve as trap for the migrating hydrocarbons. After the exploration process has been carried out within the acceptable standard, the next process is to drill for oil and gas. The major types of drilling are horizontal, directional, slant rotary, electro and turbo drilling (Akinwale, 2016).

2.3 Fossil Fuel

The age fossil fuels were formed is known as the Carboniferous period which approximately about 286 – 360 million years ago. The environment where they were formed was swampy and full of green vegetation including algae. When these plants died and decomposed, they sank all the way to the rock bottom to form spongy materials referred to as peat. The peat got covered by clay, sand particles and many mineral and hardened to form a sedimentary rock. As more rock piled on it, the peat squeezed out as a fluid that changed out to be fossil fuel. After all, it is this fossil fuel human being use as coal, natural gas and oil (Rice, 2013). Alternatively the formation of fossil fuel is that, fossil fuel is a fuel that formed from the remains of living organisms (plants and animals). It includes natural gas, oil and coal (Beatty *et al.*, 2018). Fossil fuel is one of the primary sources of energy that is to say without fossil fuel most people cannot drive a car, turn on light and heat their homes. This is attributed to the fact that majority of the energy required to performed these activities comes from fossil fuels (Rice, 2013). Fossil fuels presently meet 80% of world energy demand. There is high demand for energy in world in countries such as China,

Indian and so on. The use of coal, gas and oil to fuel power, industries, buildings and transportation sector is set to increase. However, as a result of environmental challenges has led to reduction in lower carbon options which are not utilized wisely to meet the present or future demand for energy. Fossil fuels will continue to give most of the world energy needs for future but this cannot be achieved as a result of inadequate resources to meet the demand for fossil fuels. Fossil fuels are classified as resources and not yet as reserves. Resources are those volumes that have yet to be fully characterized or technical difficulties or costly to extract. For example, in a situation where technologies that permit extraction in an environmentally sound and cost effective way are still to be developed whereas reserves are those volumes that are expected to be produced economically using current technology. They are usually linked with a project that is already well defined or ongoing. As the available supplies are exhausted, more technical demanding resources will need to be exploited. Fossil fuels are mainly referred to as hydrocarbon such as oil, gas and coal. Any source of oil and gas that requires production technologies different from those used to produce from conventional reservoir is known as unconventional. The unconventional oil sources include kerogen shale, oil sands, light tight oil, oil derived from coal to liquids and various technologies used to convert biomass to liquids (International Energy Agency, 2013). Some of the areas where fossil fuels are applied are transportation (use of vehicles powered by gasoline, diesel or other fossil fuel), electricity (use electricity generated by burning (coal, oil or natural gas), heating (heat your home appliances that burn coal, oil or natural gas or electricity), products (products made from petroleum such as polyester clothing, ball-point pens, printer cartridges and so on) (Rice, 2013).

2.4 History of Pyrolysis

Reports have shown that pyrolysis has been employed as far back as the early period of mankind when materials were burned to provide heat. Charcoal, a byproduct of wood burning, was used by early man as far back as about 4000 years ago for drawing purposes (Brownsort, 2009). For several centuries, charcoal was widely used to provide heat for cooking as well as melting metals during the bronze age. Reports have also revealed that prior to the discovery of hydrocarbons, pyrolysis of woody biomass provided the source of useful organic chemicals that were used industrially (Brownsort, 2009).

2.4.1 Types of pyrolysis

Process operating environment which is characterized by operating temperature, degree of heating, purging rate and configuration setup all are critical in determining products yield and distribution during pyrolysis. Based on this, pyrolysis has been categorized into three (3) types namely: slow or dull, rapid or fast and flash pyrolysis (Jahirul *et al.*, 2015).

2.4.2 Slow pyrolysis

This is the oldest form of pyrolysis that has existed as far back as the period of early man when wood burning was practiced (Sadana and Boateng, 2009). Slow pyrolysis usually optimizes the yield of solid products (charcoal or biochar or shale char) when compared to other types of pyrolysis and hence it is mostly employed for char production (Bridgewater *et al.*, 2007). It is usually carried out at a low heating rate of less than or 10°C/min and long residence time (Dewangan, 2014).

2.4.3 Fast pyrolysis

This kind of pyrolysis is an enhancement of slow pyrolysis and it is usually employed to maximize liquid yield (Kabir and Hameed, 2016). It normally entails subjecting a substance to high heating rate (usually above 20 °C / min), high temperature (450 – 650 °C), vapor time of residence (< 2 seconds) and quick condensation of vapor to liquid (Bridgewater *et al.*, 2007). In fast pyrolysis, liquid products yield could reach as high as 75 % while non condensable gas and char share the rest (Dewangan, 2014).

2.4.4 Flash pyrolysis

This is aimed at obtaining high liquid products by decreasing char formation. Liquid yield in flash pyrolysis could range between 70 – 75 % (Dewangan, 2014). Reaction condition during flash pyrolysis usually involves a reaction time of up to about 150 minutes, short vapor residence time, high heating rate and temperature.

Method	Operating Condition	Temperature	Residence time	Liquid	Gas	Solid
				(%)	(%)	(%)
Fast	Moderate	Temperature	Short hot vapor	75	13	12
	Around 500 °C		residence time ~ 1s			
Intermediate	Moderate	Temperature	Moderate hot vapor	50	30	20
	around 500 °C		residence times			
			~ 10 – 20 s			
Slow	Low Temperature		long residence	30	35	35
	(Carbonization)	around 400 °C	time			
Gasification	High Temperature		Long residence time	5	85	10
	Around 800 °C					

Table 2.1: Product distribution by various dry wood pyrolysis techniques (Wijayapala *et al.*, 2006)

2.4.5 Products of pyrolysis

The degradation of solid substance through the process of pyrolysis usually results in the formation of three main products which are solid, liquid and gas.

2.4.6 Pyrolysis solid

This is commonly known as char, which is the solid residue that is obtained after decomposition process is completed. Depending on the type of feedstock and process parameters employed, the quantity and quality of the char could vary. Slow pyrolysis is usually applied to maximize char production.

2.4.7 Pyrolysis liquid

This is often called bio oil or shale oil or any liquid product. The pyrolysis liquid depends on the type of feedstock used. When biomass is employed, it is referred to as bio – oil. When oil shale (kerogen) is used, it is referred to as shale oil. It is also called pyrolysis oil when polymeric materials are used. Fast and flash pyrolysis are widely used when the interest is to produce more liquid products.

2.4.8 Pyrolysis gas

This is known as syngas or biogas or shale gas depending on the feedstock's used. High temperature usually above 600 °C and long residence time usually favors the formation of more gaseous yield during pyrolysis (Abnisa *et al.*, 2014). Long vapor time of residence in the reactor causes secondary reaction of condensable vapor that result in increasing the yield of non-condensable gases.

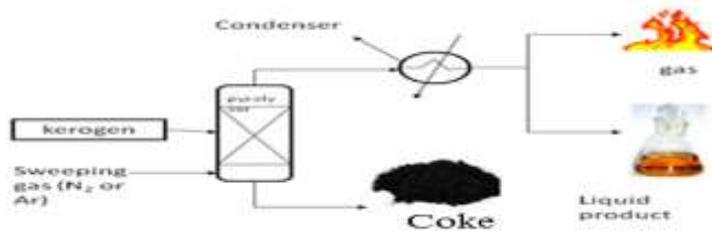


Figure 2.1: Configuration of pyrolysis process and products

2.5 Oil Shale

The world energy problem has increased the prices of oil products which caused renewed interest in carbonaceous material as an energy source. They include coal, oil shale, biomass and organic wastes (Wang, 2013). Oil shale is simply a composite of tightly bond organic and inorganic materials such as quartz, field spar, clay, carbonates, pyrites and other minerals. The organic matter composed of less than 20 % of the shale mass and may be subcategorized into segments either soluble (bitumen) or insoluble (kerogen) in an organic solvent. However, during pyrolysis process both bitumen and kerogen breakdown form gaseous and liquid products. The liquid is usually upgraded and refined to give synthetic liquid fuels (Gordon, 2012). Oil shale can be defined as a sedimentary rocks containing large potential of organic matter (kerogen) which can be converted into a material same as petroleum by heating (Borghi *et al.*, 2006). Oil shale is a sedimentary rock found in many part of the world which is mainly used as a fossil to generate electrical energy or higher value fuels (Maaten *et al.*, 2016). Presently oil shale resources are majorly shared around the world and more than 600 deposits are known in more than 30 countries on all continents

with a conservatively estimated 4.8 trillion barrels of oil shale in place is almost 4 times more than proven crude oil resources of 1.3 trillion barrels (Wang, 2013). Large deposits of oil are found in U.S.A, China, Brazil and Estonia. Oil shale serves as a reasonable substitute to conventional energy sources such as crude oil, coal and natural gas. Oil shale components are quartz, calcite, and dolomite. Oil shale pyrolysis is made up of 3 stages, water evaporation at lower temperature (below 200 °C), pyrolysis (200 to 600 °C) and decomposition of carbonates (at temperature above 700 °C) in an oxygen free environment (Maaten *et al.*, 2016). During oil shale pyrolysis, numerous physical and chemical processes occurs such as heat transfer, chemical reaction kinetics, multi-phase flow, phase change, mineral alteration and interaction and physical properties changes (Tiwari *et al.*, 2011).

2.5.1 Kerogen

Kerogen can simply be defined as the fined grained organic matter content of the oil shale with sufficient amount of hydrocarbons to produce oil or gas upon pyrolysis. The source rock is mainly shales and lime mudstones which contains significant amount of organic matter (Al Areeq, 2018). Kerogen sample consist of carbon (C), hydrogen (H) nitrogen (N), sulphur (S) and oxygen (O) (Adegoke *et al.*, 2015). The average molecular weight of kerogen is about 3000 and the approximate empirical formula is $C_{200}H_{300}SN_5O_{11}$ (American Chemistry Society, 2012).

2.5.2 Kerogen origin and formation

Kerogen is a physical- chemical structure which emanate from sediments buried underground over a millions of years ago. Kerogen is sediments that contain organic matter.

The organic matter is gotten mainly from two distinct sources, the primary producer that is algae and terrestrial sources. The organisms such as fungi and bacteria (heterotrophic) escape complete mineralization during the carbon cycle processes and the remains are deposited in marine environment. The photoautotrophic organisms is the first stage of carbon cycle that involves the primary producers which transform CO₂ dissolved in water using photosynthesis into metabolites. However, after series of physiochemical processes and reactions, the organic matter that happens to be buried below 1 meter will subsequently be kept at high sedimentation. The place that has large deposition of terrestrial organic input material has a imperative relationship with high sedimentation. Bacterial works such as degradation of minerals usually initiate the formation the Total Organic Carbon (TOC) during sedimentation and cementation processes. It is very important to note that in marine environments 70 and 30 % of the accumulated sediments material will be particulate organic matter which initiates for the formation of kerogen (Yeboah, 2015).

2.5.3 Kerogen types

The following are the major types of kerogen samples

- **Type I Kerogen:** is mainly gotten from algae material preserved in an anaerobic environment. It is composed of lacustrine and it is gotten sometimes from a marine source. It is rich in hydrogen and deficient of oxygen and also it has aliphatic characteristics.
- **Type II Kerogen:** It is made up of degraded phytoplankton debris preserved in an anaerobic or aerobic environment. It is second most rich hydrogen kerogen which is

aliphatic in nature with a bias towards cyclic compounds in comparison to the Type I kerogen.

- **Type III Kerogen:** It is relatively hydrogen poor and polyromatic in nature in comparison with Type I and II. It is gotten from higher plant debris sources. The oxygen carbon ratio is high as a result of oxidation reaction associated with the detrital sedimentation.
- **Type IV Kerogen:** It has small or no potential to produce hydrocarbons with hydrogen carbon ratio less than 0.5. It contains organic matter in the form of polycyclic aromatic hydrocarbons. It is a highly oxidized kerogen (Olufemi, 2016).

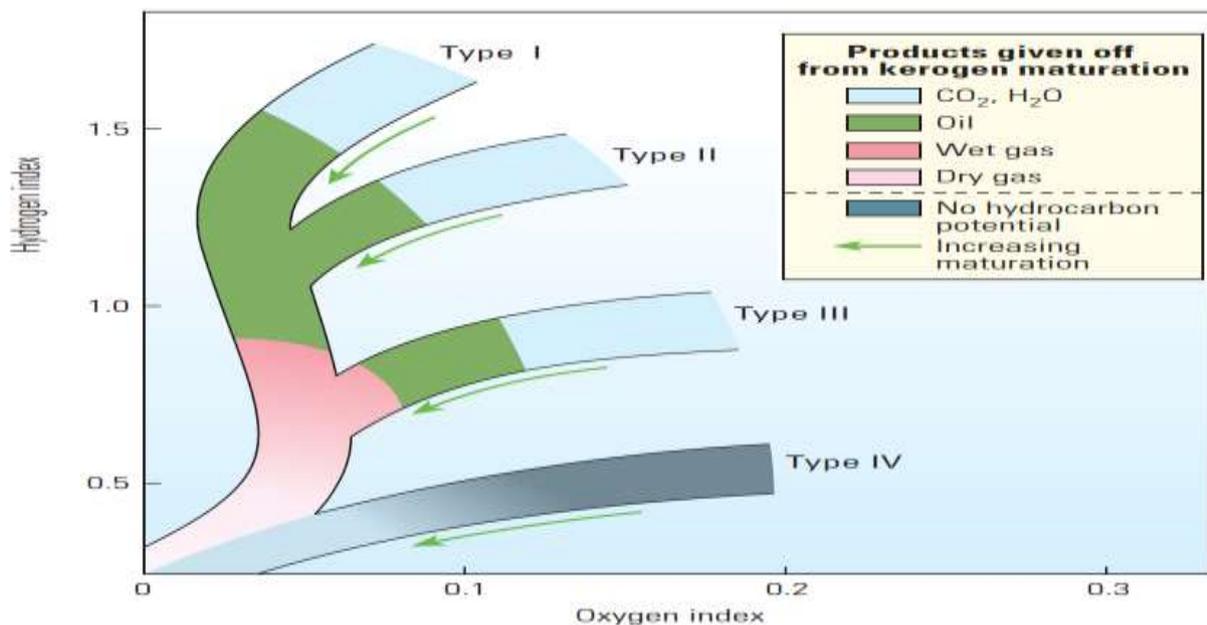


Figure 2.2: Van krevelen Diagram showing maturation paths for the four types of kerogen (Sorensen, 2016).

Kerogen	H/C	O/C	Petroleum
Type I, algae	1.65	0.06	Oil
Type II, liptinic	1.28	0.1	Oil and Gas
Type III, humic	0.84	0.13 – 0.2	Gas

Table 2.2: Kerogen Types Showing H/C, O/C and Petroleum Generation (Adegoke *et al.*, 2015)

2.5.4 Kerogen pyrolysis

Pyrolysis is a principal method used to convert kerogen to liquid fuels and solid matter. During the process of heating the kerogen sample up to the thermal destruction. The organic matter pass through degradation, followed with breaking of chemical bonds and formation of reactive products most likely free radicals which could form more complex molecules (Budinova *et al.*, 2014). Kerogen pyrolysis can also be defined as an endothermic process also referred to as cracking, involving the use of heat to thermally breakdown carbon based material in oxygen free environment. Its main product is a gaseous mixture of CO and H₂ called syngas that can be used for steam and electricity generation (American Chemistry Council, 2012). The major operating conditions on pyrolysis are temperature, heating rate and vapor residence time. Vapor residence time seems to be the most important parameter to differentiate between pyrolysis processes (Reyhanitash, 2013). Kerogen sample is usually insoluble in normal petroleum solvents. Kerogen is differentiated from bitumen because it is insoluble in normal petroleum solvent whereas bitumen is soluble (Al-mashramah, 2011). The volatile pyrolysis products obtained from kerogen are formed according to the same principles of thermal cleavage reaction and can be used to predict the composition of petroleum nature. Kerogen and asphaltenes due to their structural closeness break upon pyrolysis to give many compound types including hydrocarbons, ketones, alcohols, nitriles and thiols which are represented by saturated and unsaturated, cyclic and acyclic carbon structures. The most regularly and identifiable compounds in the pyrolysis are aliphatic hydrocarbons (alkanes), aromatic compounds (alkyl benzene) and Sulphur containing

compounds (alkylthiophenes). The kerogen constituents relayed on the source of the organic matter and evolutionary process (Geologin *et al.*, 2012).

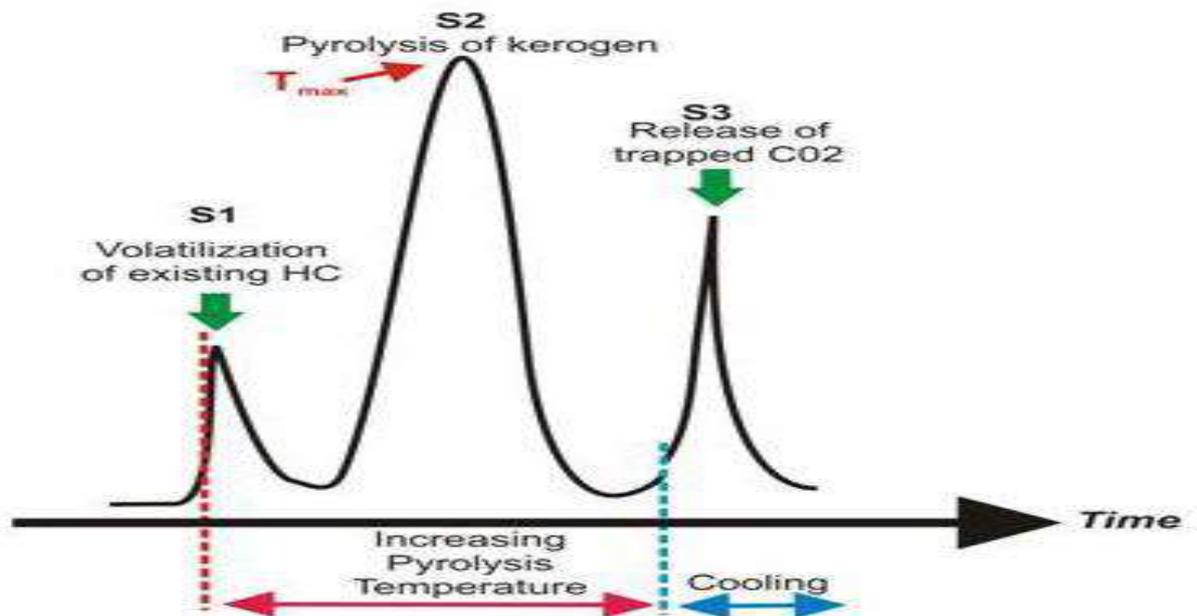


Figure 2.3: Schematic diagram of Rock Eval pyrolysis (Yeboah, 2011)

2.5.5 Classifications of pyrolysis

The following are major pyrolysis techniques

- **Thermally/Cracking Pyrolysis:** The feedstock is heated at high temperatures (350 – 900 °C) in the absence of a catalyst. For example, thermal cracking yields low octane liquid products and a gas product that require refining to be upgraded to useable fuel products.
- **Catalysis Pyrolysis/Cracking:** The feedstock is processed using a catalyst. The presence of a catalyst reduced the required reaction temperature and time compared

to thermal pyrolysis. The catalyst used in this process can include acidic materials (silica- alumina), zeolites (HY, HZSM-5, mordenite) or alkaline compounds (zinc oxide). Research has shown that is method can be used to process a variety of plastic feedstocks.

- **Hydrocracking (sometimes referred to as hydrogenation):** The feedstock is reacted with hydrogen and catalysts. The process occurs under moderate temperature and pressures (150 - 400 °C and 30 - 100 bars hydrogen). Most research on this method has involved generating gasoline fuels from various waste feedstock's (American Chemistry Council, 2012).
- **Gray- King Pyrolysis:** This is a fixed bed pyrolysis technology that has been used for coal pyrolysis for many years. It is a destructive technique and could result in the thermal breakdown of coal composition. Gray-King pyrolysis thermally decomposes coal into coke, liquids and gaseous state.
- **Microwave Pyrolysis:** Temperature and thermally diffusivity are processes coordinated by the conductivity, radiation and convection properties of the materials determines the rate of heat transfer in materials from the surface of a material to the internal region .The rate of flow from the surface of a material to the internal region is a function of the thermal conductivity, density and specific heat capacity of the material (Olufemi, 2016).

2.6 Petroleum and Reservoir Statistics

Petroleum has a complex chemical environment with intricate mixture of hydrocarbons and small amount of heteroatom compounds. To evaluate the behavior of any petroleum

product, it is imperative to understand the chemical composition, corrosion, density, emulsion stability, interfacial tension and viscosity are all significant to physiochemical characteristics that have impact on how crude oil behave and how it should be handled (Sorbo, 2016). Virtually every oil or gas emanate from a source rock in a petroleum reservoir. The potentiality of each source rock plays a significant role in the formation of crude oil. In the absence of the source rock all other constituents and techniques needed to exploit become insignificant. A source rock can be defined as any fined grained organic rich rock that has the capacity of forming petroleum at elevated condition of temperature and pressure. The petroleum formation means is directly related and connected to its volume, organic richness and thermal maturity (Carthy *et al.*, 2011).

Countries	1995	2005	2014	2015
U.S	29.8	29.9	55.0	55.0
Canada	48.4	180.0	172.2	172.0
Italy	0.8	0.5	0.6	0.6
Russia	1.0	0.5	0.6	0.6
Iran	93.7	137.5	157.8	157.8
Iraq	100.0	115.0	143.1	143.1
Kuwait	96.5	101.5	101.5	101.5
Saudi Arabia	261.7	264.2	267.0	266.7

United Arab Emirate	98.1	97.8	97.8	97.8
Algeria	10.0	12.3	12.2	12.2
Egypt	3.8	3.7	3.7	3.5
Libya	29.5	41.5	48.4	48.4
Nigeria	20.8	36.2	37.1	37.1
China	16.4	15.6	18.5	18.5

Table 2.3: Total Proved Oil Reserves (Thousand Million Barrel) (James, 2016)

Countries	995	2005	2014	2015
U.S	4.7	5.8	10.4	10.4
Canada	1.9	1.6	2.0	2.0
Venezuela	4.1	4.3	5.6	5.6
Russia	31.1	31.2	32.4	32.3
Iran	19.4	27.6	34.0	34.0
Iraq	3.4	3.2	3.7	3.7
Saudi Arabia	5.5	6.8	8.3	8.3
United Arab Emirates	5.9	6.1	6.1	6.1

Algeria	3.7	4.5	4.5	4.5
Egypt	0.6	.9	1.8	1.8
Libya	1.3	1.3	1.5	1.5
Nigeria	3.5	5.2	5.1	5.1
Australia	1.2	2.2	3.5	3.5
Brunei	0.4	0.3	0.3	0.3
China	1.7	1.6	3.7	3.8

Table 2.4: Natural Gas Total Proved Reserves (Trillion Cubic Metres) (James, 2016).

Countries	Crude oil	API	Sulfur% w/w
Abu Dhabi (UAE)	Abu Al Bu Khoosh	31.6	2.00
Algeria	Zarzaitine	43.0	0.07
Australia	Airlie	44.7	0.01
Brazil	Garoupa	30.0	0.68
China	Daqing (Taching)	32.6	0.09
India	Bombay High	39.2	0.15

Iran	Aboozar (Ardeshir)	26.2	2.480
Iraq	Basrah Heavy	24.7	3.50
Nigeria	Antan	32.1	0.32
(UK)	Alba	20.0	1.33
Russia	Siberian Light	37.8	0.42
Saudi Arabia	Arab Extra Light (Berri)	37.8	1.15
USA (Alaska)	Alaska North Slope	27.5	1.11
Venezeula	Lago Medio	32.2	1.01

Table 2.5: API Gravity and Sulfur Content of Selected Crude Oils (James, 2016).

Country	Crude oil	API	Sulfur% w/w
Nigeria	Antan	32.1	0.32
	Bonny Light	33.9	0.14
	Bonny Medium	25.2	0.23

Brass River	42.8	0.06
Escravos	36.4	0.12
Forcados	29.6	0.18
Pennington	36.6	0.07
Qua Iboe	35.8	0.12

Table 2.6: API Gravity and Sulfur Content of Nigeria (James, 2016).

Region	2014	2015	from 14-15	2016	from 15-16	2017	from 16-17	2018	from 17 -18
America	24.1	24.2	0.004%	24.3	0.004%	24.4	0.004%	24.5	0.004%
Asia Ocean	8.1	8.0	-0.012%	7.9	-0.012%	7.9	0%	7.9	0%
Europe	13.4	13.3	-0.007%	13.3	0%	13.2	-0.07%	13.1	-0.07%
China	10.4	10.6	0.0196%	10.9	0.0028%	11.2	0.027%	11.5	0.026%
Africa	3.9	4.1	0.051%	4.2	0.024%	4.4	0.047%	4.5	0.22%
World	92.4	93.3	0.009%	94.5	0.012%	95.7	0.012%	96.9	0.012%

Table 2.7: Global Oil Demand by Region from 2014 - 2018 (Wer, 2016)

2.6.1 Origin of petroleum

Crude oil comes into existence when there is incomplete decay of organic matter. The starting materials in marine sediments consist of aquatic plants and animals such as algae

and plankton. Over a longer period of time, the sediments are subjected to more temperature and pressure. The first process is known as Diagenesis which is the first phase of transformation and refers to the biological, chemical and physical changes of the organic matter. In this process, heat is not yet necessary and hydrolysis is the main chemical reaction which resulted into high molecular weight polymer called Kerogen that represents the halfway point generation of petroleum products. During the process when the sediments is seriously buried, temperature increases and at a depth equivalent to 60 °C .The second process is known as Catagenesis which is the opening of the oil window, the big kerogen structures are reduced by thermal cracking. The large possible products in petroleum are made possible by the production of radicals and their propagation reaction. The oil window is neared at a depth equivalent to 170 °C and gas is the only product produced to a depth equivalent to 225 °C. At this depth Metagenesis begins and represents the final carbonaceous product graphite (Sorbo, 2016).

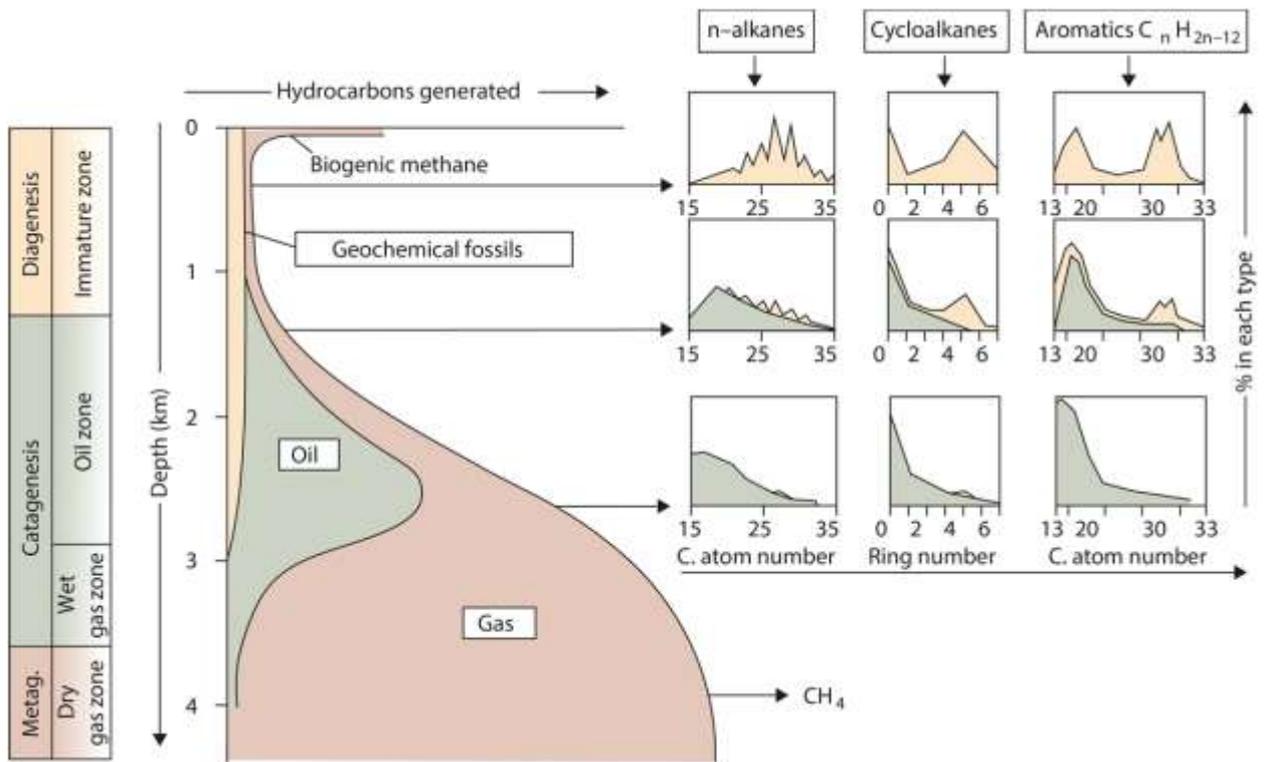


Figure 2.4: The transformation of organic matter to kerogen and oil and gas (Abay, 2017)

2.6.2 Reservoir rock properties

Porosity: can be defined as the percentage of pore volume compared to the total bulk volume of a rock. A high porosity implies that the rock can contain more oil per volume unit. The pores that are linked in order to allow movement of the hydrocarbons within the reservoir was studied by French engineer Henry Darcy in 1805's who investigated fluids flow through a bed packed sand. Darcy's law is similar to Fourier's heat conduction law or Fick's law of diffusion. Darcy's law can be derived from the Navier-Stokes equation

$$Q = \frac{KADp}{\mu Dl} \quad (2.1)$$

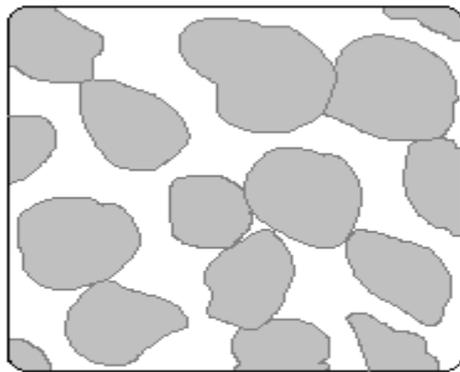
Where q = volumetric flowrate

k = permeability

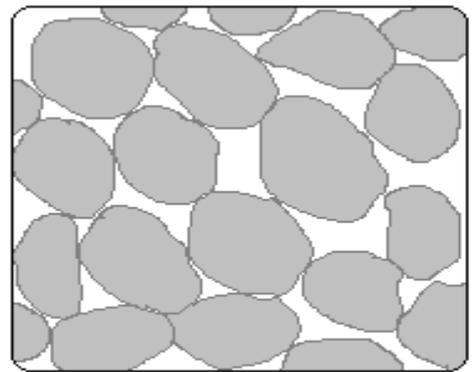
μ = fluid viscosity

dp = change in pressure

dl = change in length



a) High porosity



b) Low porosity

Figure 2.5: Simplified examples of material with high and low porosities (hook, 2009)

Permeability: can be defined as the ability of a rock to permit fluid movement when only one fluid is present in the rock defined from Darcy's equation (Hook, 2009).

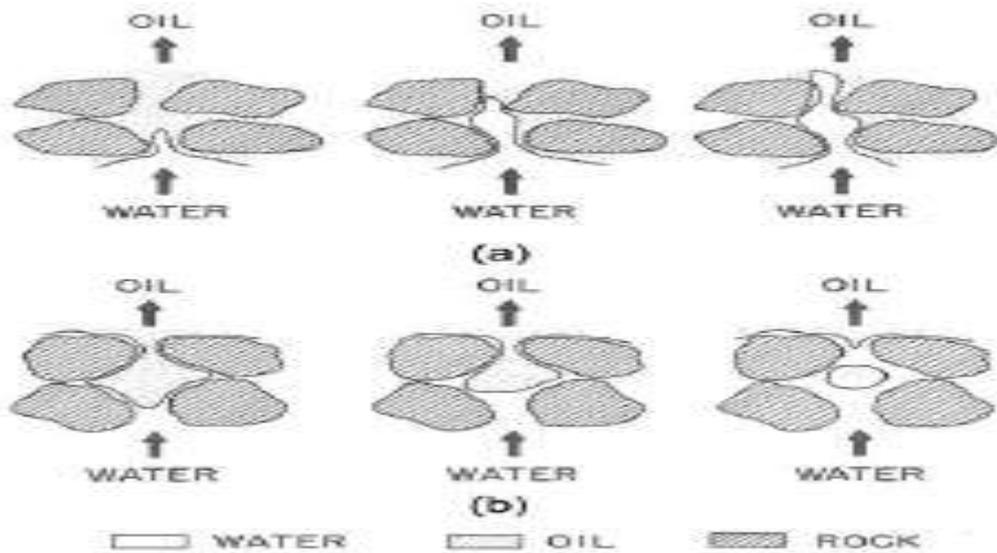


Figure 2.6: Displacement of oil by water (a) oil-wet rock and (b) water-oil rock (Melberg, 2010)

Wettability: can be defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. When two immiscible phases are in contact with a solid surface, one phase usually is attracted to the solid surface. One phase usually is attached to the solid more strongly than the other. The more strongly attracted phase is called the wetting phase (Melberg, 2010).

2.7 Geological History of Nigeria

2.7.1 Niger delta

Petroleum exploration in Nigeria started as far as 1908. In 1956 the first commercial oil discovery was made at oloibiri in the onshore Niger delta and production of the crude oil began in 1958. Since that time petroleum has played a significant role in the social and

economic development of Nigeria. As a result of this landmark achievement, petroleum resources account for about 99 % of the national income. In the globe, Nigeria is positioned as the 6th in OPEC and 14th in the world in terms of oil production. The Niger Delta Basin to date is the most important and economic sedimentary basins in Nigeria by virtue of the impact size petroleum accumulation, discovered and produced as well as spatial distribution of the petroleum resources to the onshore, continental shelf through deep water terrains. Most of the prominent basins we have in Nigeria are Anambra Basin, Benue Trough, Benin Basin, Bida Basin, Borno Basin, Niger Delta Basin and Sokoto Basin (Geologin, 2012).

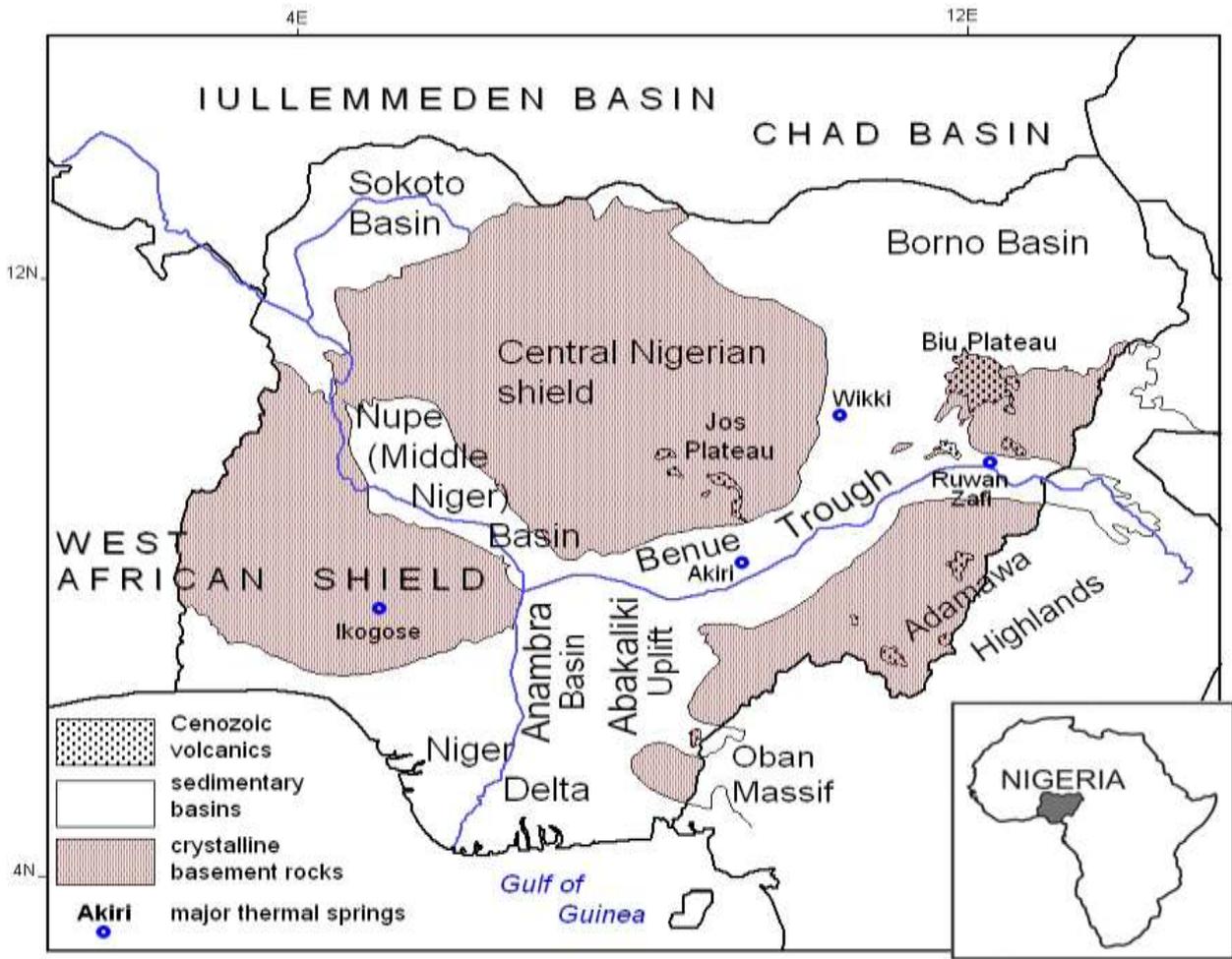


Figure 2.7: Geological setting and location of major structural units in Nigeria (Kurowska and Schoeneich, 2010)

The Niger Delta is located in the Gulf of Guinea in a rift triple junction similar to the southern Atlantic started in the late Jurassic to the Cretaceous. Niger Delta is located in Nigeria West Africa latitude 3 °N and 6 °N and longitude 5 °E and 8 °E respectively. The Niger Delta is the biggest delta in the whole of Africa with a sub-aerial exposure area of approximately 75,000 km² and a clastic fill of about 9,000 to 12,000 m (30,000 to 40,000 ft). Several studies have been carried out on the Niger Delta basin (Ahiarakwem and Opara, 2012). Niger Delta is positioned among the world's main hydrocarbon areas in the world. Oil and gas in the Niger Delta are majorly trapped in sandstones and unconsolidated sands in the Agbada formation. The traps, structure and stratigraphy are very difficult to map correctly because they are very slight, not obvious and very complicated. The extent and precision of the mapping can be greatly influenced by introducing seismic data with well logs usually used freely in hydrocarbon exploration and exploitation studies (Nyantakyi *et al.*, 2013). Oil and gas windows are subsurface level intervals where oil and gas are formed. Hydrocarbon formation processes are co-ordinated by temperature and level. Oil windows are usually found in the 60 – 120 °C range at 2- 4 km level where gas windows are found at the 120 – 150 °C intervals at approximately 3-6 km level. The major ingredients for hydrocarbon generation are source rock, a porous and permeable reservoir rock, non-permeable cap rock and organic rich rock (shale) subjected to elevated temperature and pressure. At the stage of geothermal gradient of about 60 °C / km, oil starts to form by

means of geomogenic breakdown of organic matter. The oil already formed is removed from the source rock and migrates upwards through porous and permeable rocks to be stopped by an impermeable layer of rock called the cap rock. Shales are a good source rock inside a petroleum reservoir (Adedapo *et al.*, 2014).

2.7.2 Bida basin

The Bida Basin is a straight line co-ordinate of NW-SE. To the east, it is adjacent to Anambra basin. To the northwest, it is adjacent to the Sokoto basin. It is divided into northern and southern Bida Basin due to wide difference of the facies across the basin. Many Geologists has performed various researches on Bida basin for almost forty decades. They include Adeleye (1973, 1974), Brade (1992), Olaniyan and Olabaniyi (1996). They put more emphasis on the sedimentary and stratigraphy of the northern Bida Basin. More attention was also given to southern Bida basin. Some researchers have also studied some parts of the petroleum potential of the Bida basin as part of the ongoing research of the petroleum potential assessment of the Nigeria inland basin, they include Idowu and Enu (1992), Brade (1992), Ojo (1992), Obaje *et al.*, (2004), Akande et al, (2005) and (Ojo *et al.*, 2012).The Bida basin referred to as Mid Niger or Nupe Basin is located in west central Nigeria.

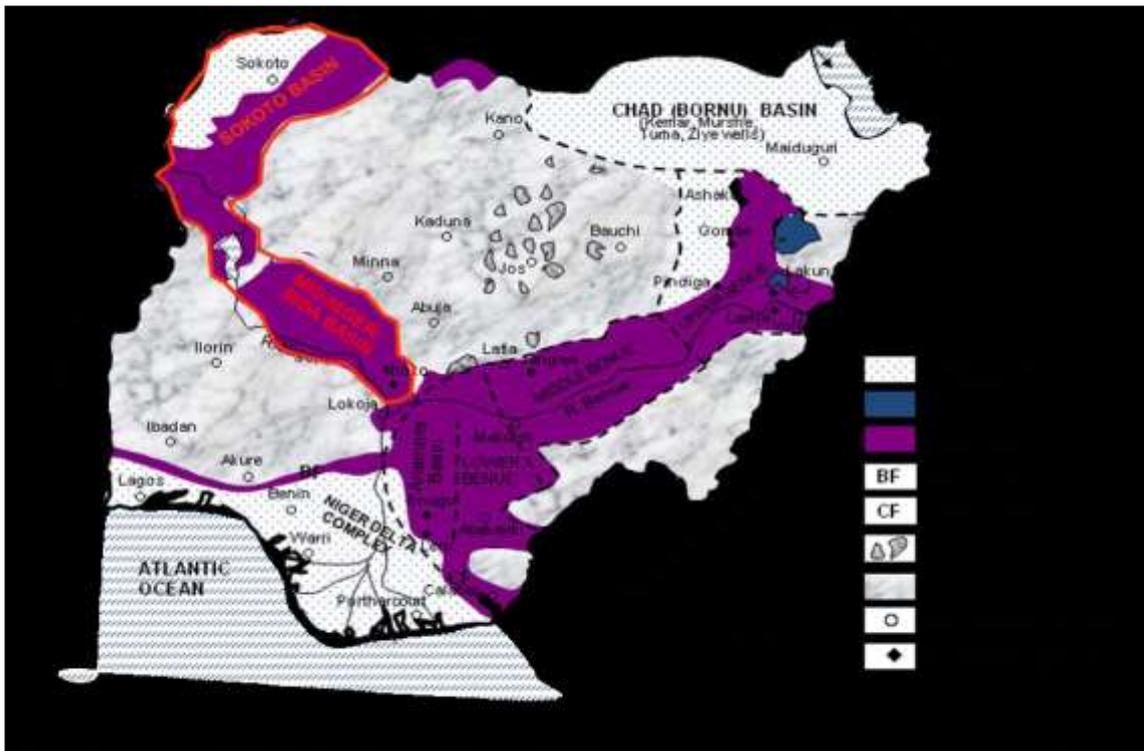


Figure 2.8: Generalized Geological map of Nigeria showing the location of Bida and Sokoto Basins (Obaje *et al.*, 2013)

Nigeria present proven petroleum reserves are about 38 billion barrel of oil and about 190 trillion standard cubic feet of gas gotten from the Niger delta on and off shore. Explorations of the inland basin have not been commercially accepted to date because of the inadequate knowledge of their geology and actual distance from the existing infrastructure. Geological studies revealed that most of the potential source rock in the Bida basin is gas prone (Obaje *et al.*, 2011).

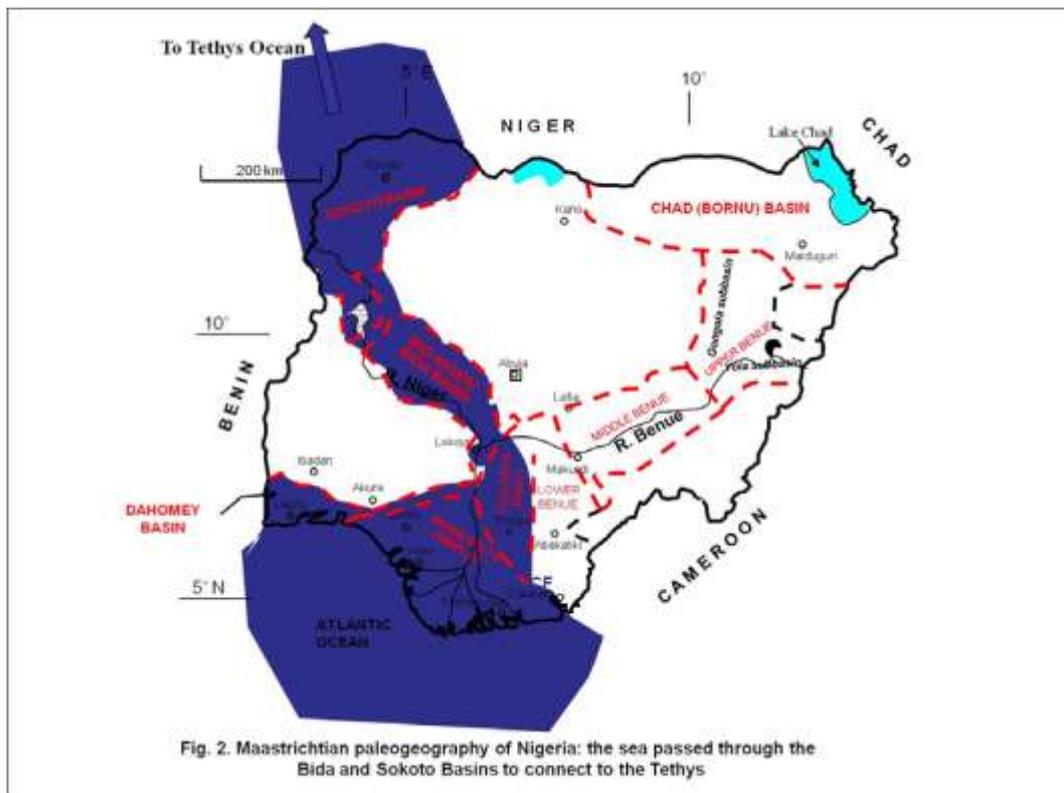


Figure 2.9: Maastrichtian paleogeography of Nigeria: the sea passed through the Bida and Sokoto Basins to connect to the Tethys (Obaje *et al.*, 2013)

The Bida Basin is made up of Bida and Lokoja formations which were gotten during the Comanian. The Sakpe, Enagi, Batati, Patti and Agbaja formations were gotten during the Maastrichtian. The Bida formation is divided into Doko and Jima situated 16km south of Bida and having a basal unit of 80 m massive and flat bedded arkoses and coarse sandstone with breccias horizons. The jima sandstone are usually quartzose, non-arkosic and brownish. The lithologic parts in Lokoja formation are conglomerates coarse to fine grained sandstones, siltstones and claystone's. The Sakpe formation is made up of oolitic and pisolitic ironstones with claystones. The Enagi formation is made up of siltstones which is

similar to Patti formation in the Lokoja sub-basin. The Batati formation is made up of the uppermost parts in the sedimentary sequence of the Bida basin which includes argillaceous, oolitic and goethitic ironstones. The Patti formation lies between koton-karfi and abaji and it is made up of sandstones, siltstones, claystone's and shales. The agbaja formation lies in the southern Bida basin while Batatiformation lies in the northern Bida Basin (Tsepav and Mallam, 2017).

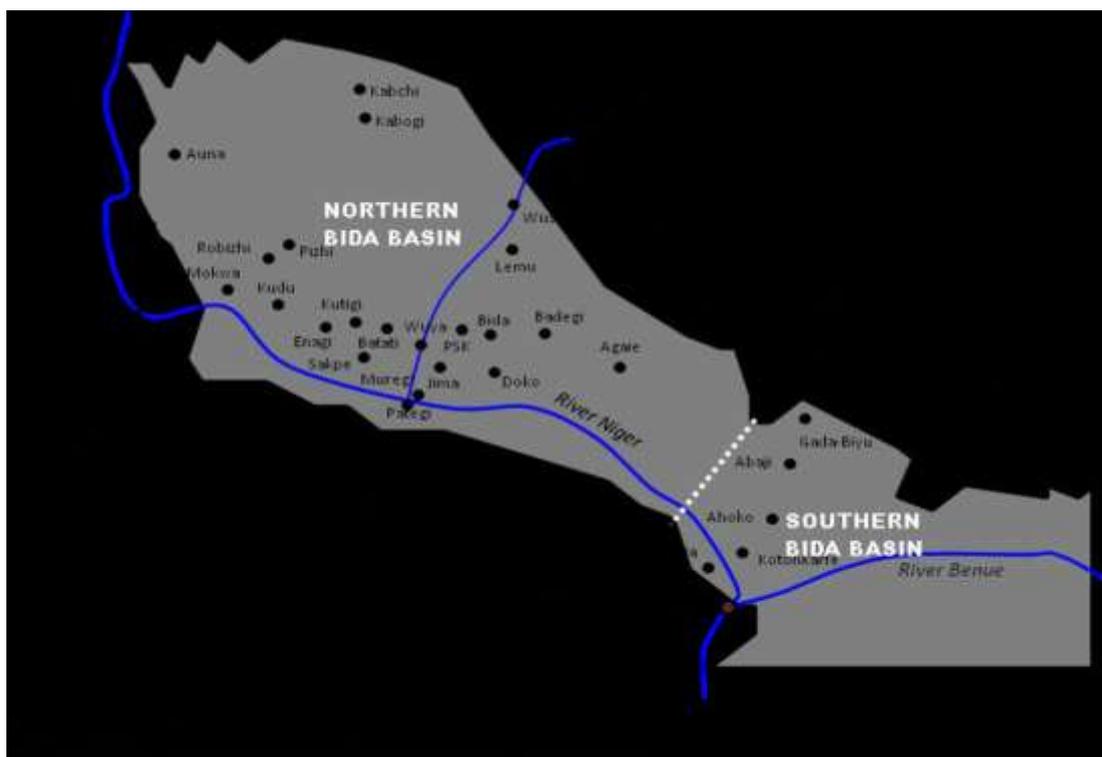


Figure 2.10: Approximate boundary indications between Northern and Southern Bida Basin (Obaje *et al.*, 2011)

Bida Basin consists of places such as Bida, Agaie, Badegi, Jima, Doko, Dabban, Batati, Enagi, Kudu, Kabogi, Sakpe, Mokwa, Agho, Dakina and Lokoja respectively. The Bida

Basin is a North West- South East moving sedimentary basin in Niger State linking from Kontagora in the north to areas partially below beyond Lokoja in the south. The layer arrangement studied succession in the Basin comprise of Bida sandstone at the base in the northern Bida Basin followed successively upward by the Sakpe, Enagi, Dabban and Batati formation. In the southern Bida Basin the Lokoja formation lies at the base and it is followed upward by the Patti and Agbaja formation. The Geology revealed that there is possibility of the buildup of potential petroleum systems which normally as a result the generation, migration and accumulation of hydrocarbons in commercial quantities (Obaje *et al.*, 2011).

2.8 Characterisation

The characterisation of the physiochemical properties of the oil shale and kerogen was study using Rock Eval pyrolysis, Thermogravimetry analysis (TGA), Fixed Bed pyrolysis, Gas Chromatography Mass Spectrometer (GCMS), Fourier Transform Infrared Spectroscopy (FTIR) and CHNS Analyzer.

2.8.1 Physiochemical characterisation of kerogen and shale oil

Some important analysis such as ultimate and proximate analysis is required to be conducted over the kerogen and shale oil sample in order to determine its pyrolysis characteristics.

2.8.1.1 Proximate analysis

Proximate analysis gives information about fixed carbon, moisture, volatile component and ash component of kerogen. It can be carried out using standard procedure described by ASTM D3170 - 07 methods. The ash content and volatile components of the sample gives insight on the recoverable potential of liquid product after pyrolysis. High volatile and low ash content Favour more shale oil and vice versa (Dewangan *et al.*, 2016).

2.8.1.2 Ultimate analysis

Carbon, hydrogen, nitrogen, oxygen and sulphur content of the kerogen can be analyzed through ultimate analysis which is of great importance in determining the constituents' chemical species of the pyrolysis liquid synthesized after degradation. Standard procedures also exist for conducting ultimate analysis using appropriate equipment.

2.8.2 Rock Eval (R . E) pyrolysis

(Gajica *et al.*, 2017) determined the hydrocarbon generative potential of kerogen using Rock Eval pyrolysis and the stage of formation realized was immature source rock type to the matured type of kerogen. However, Rock Eval pyrolysis was developed primary for ancient sedimentary rocks and kerogens and became a standard analytical technique in the petroleum industry. The Rock 6, marketed by Vinci Technologies, is the most recent version and is widely used. Obviously analysis and interpretation of Rock Eval data should be considered by each interpreter depending on the particular device in use. The Rock Eval 6 techniques provide many measurements from the concluded pyrolysis and oxidation of a sample. Firstly, the splitting of the pyrolysis effluent (under N₂) into two halves at the outlet of the pyrolysis oven, allows the progress detection and quantitation of hydro carbonaceous

effluents with flame ionization detection (FID) and CO and CO₂ with infra-red (IR) detection respectively. The S₁ and S₂ signals successively determined with FID, similar firsts to the quantity of hydrocarbons (S₁ gas and oil) volatilized for 3 min at 300 °C, the second peak (S₂) stand for the hydrocarbons generated from kerogen cracking between 300 and 650 °C, with heating rate of 25 °C / min. The quantity of CO₂ and CO represents the S₃ and S₃ peaks respectively. All these basic parameters are expressed either in milligram of hydrocarbon or CO₂ / CO per gram of rock. The temperature at which hydrocarbons maximum resulting from kerogen cracking occurs is called Tmax. The residual organic and inorganic carbon content (in wt %) of the pyrolysed sample is obtained by combustion in air from 300 to 850 °C with heating rate of 20 °C / min. The CO₂ and CO gotten from this combustion are also known with an IR cell and similar to peaks S₄ and S₅ for CO₂ and peak S₄ CO for CO from these basic parameters, the Total Organic Carbon content (TOC, wt %) is calculated as the sum of pyrolysed OC and residual OC. The hydrogen index (HI, mg HC / g TOC) similar to the amount of pyrolysable organic compounds (S₂ peak) comparative to TOC. The oxygen index (OI, mg CO₂ / g TOC) similar to the amount of CO₂ (S₃ peak) comparative to TOC. The Rock Eval 6 device measures CO₂ and CO separately, allows three OI's to be defined. One for CO₂, one for CO and additional one for CO₂ + CO called OI_{RE}. The latter is expressed in mg O₂ / g TOC. Finally, the mineral carbon (MinC) is also calculated as S₃ + S₃'CO + S₅ peaks. It is very necessary to note that only Rock- Eval 6 allows selective detection of residual OC and inorganic Carbon. MinC is not a parameter provided by earlier Rock Eval devices (Baudin *et al.*, 2015).

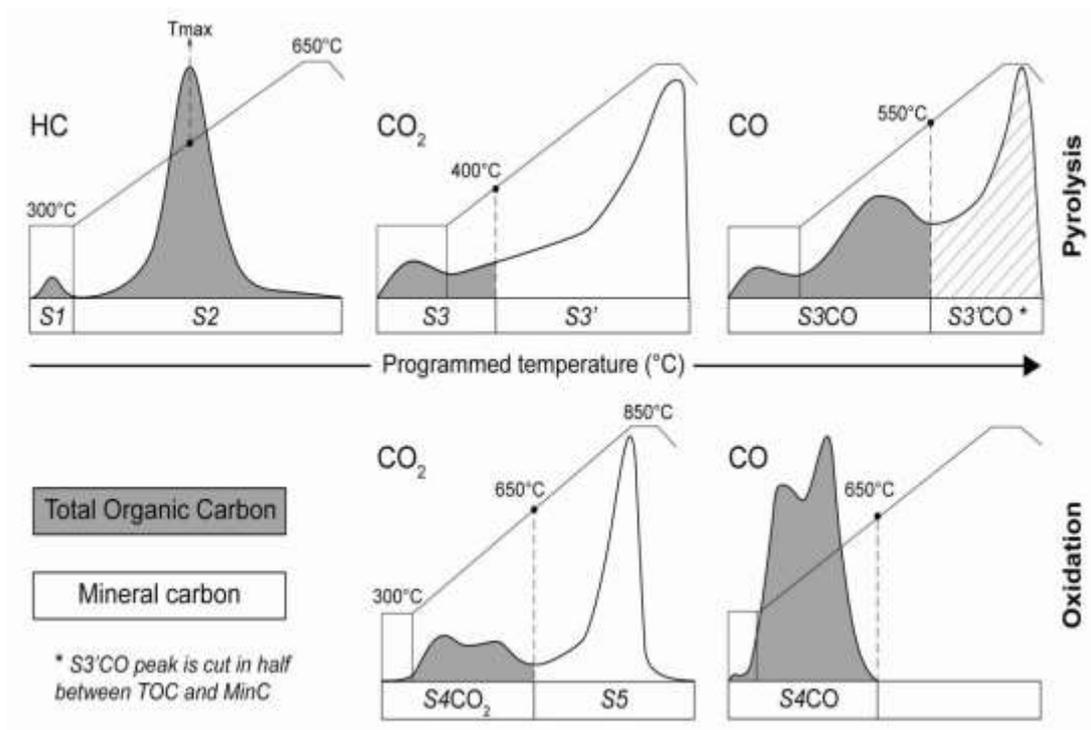


Figure 2.11 Rock Eval Pyrolysis Processes (Baudin *et al.*, 2015)

2.8.3 The thermogravimetric analysis

Thermogravimetric analysis (TGA) is a commonly used instrument to analyse the kinetics of thermal breakdown of many solids and liquids because of its capacity to set a unique atmosphere and apply a wide range of heating rates (Maaten *et al.*, 2016).

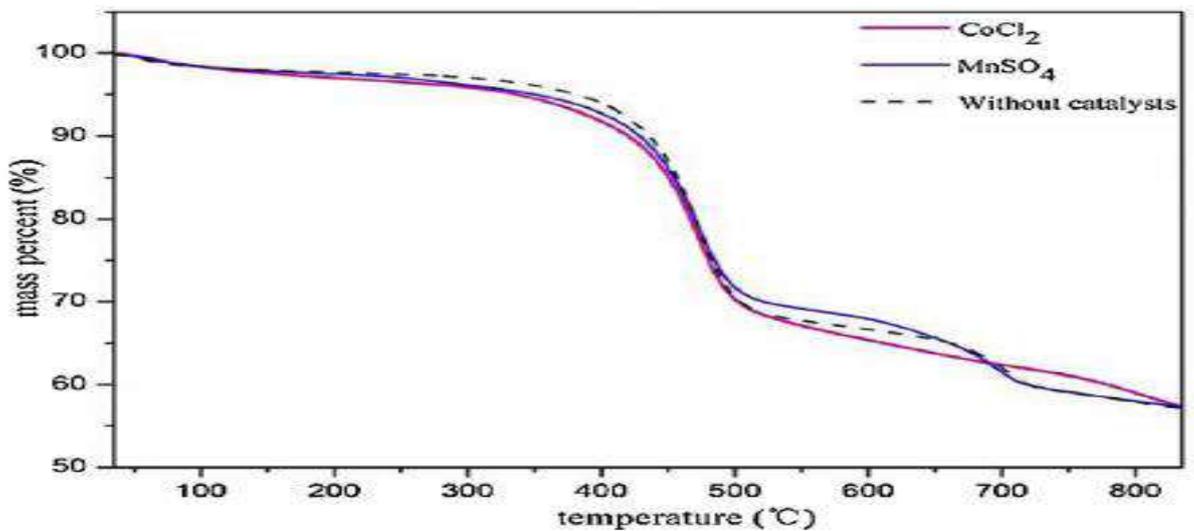


Figure 2.12 TGA curves for the oil shale (Yeboah, 2015)

2.8.4 Gas chromatography mass spectrometer

GCMS is widely applied techniques in many branches of science and technology for over half a century. 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 spectroscopy detection system. The most used, is the mass spectrometric detector (MSD) which allows obtaining the fingerprint of the molecule (its mass spectrum). Mass Spectra provide information on the molecular weight, elemental composition. If a high resolution mass spectrometer is used, functional groups presents and in some cases, the geometry and spatial isomerism of the molecule (Stashenko *et al.*, 2014). GC/MS is a combination of two separate analytical procedures, Gas Chromatography (GC) and Mass Spectrometry (MS) is used to analyze complex organic and biochemical mixtures. GC can separate volatile and semi volatile compounds with great resolution, but cannot

identify them. MS can give detailed structural information on most compounds such that they can be exactly identified and quantified but cannot readily separate them. Therefore, it was not surprising that combination of the two techniques was suggested shortly after the development of GC in the mid 1950's. Gas Chromatography and Mass Spectrometry are in numerous ways highly compatible techniques. In both procedures, the sample is in the vapor phase and both techniques deal with about the same amount of sample (typically less than 1 ng) (Hussain *et al.*, 2014).

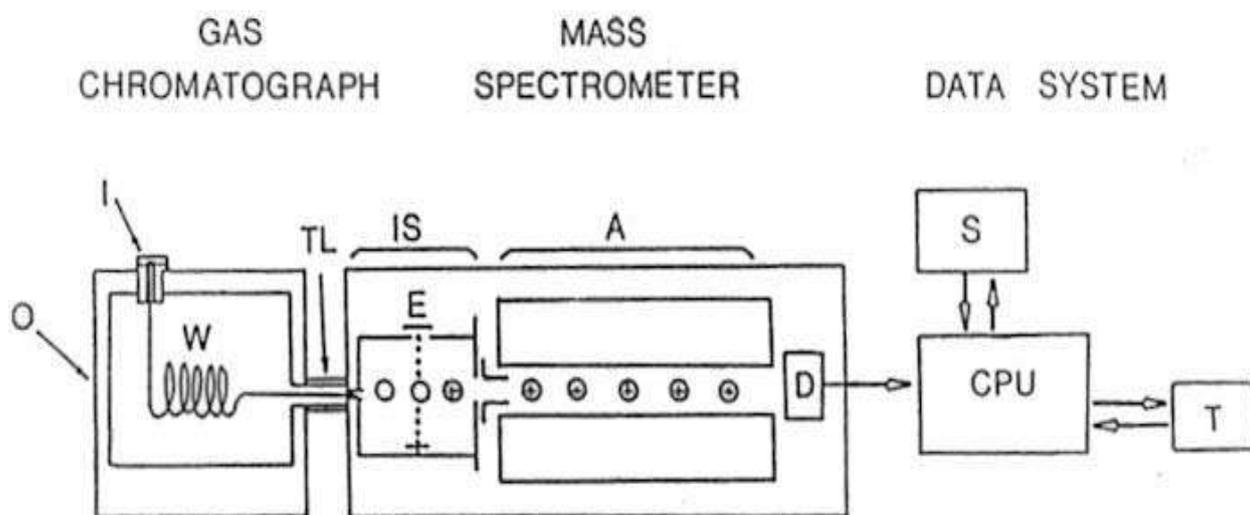


Figure 2.13: Schematic of GCMS system (Clement and Taguchi, 2012)

2.8.5 Fourier transform infrared spectroscopy analysis

FTIR analysis is carried out to establish or know the chemical functional groups present in the liquid oil. This is one of the chemical analysis that is carried out on liquid products from kerogen in order to determine possible groups of compound that are present in the sample.

2.8.6 CHNS analyzer

This analysis is carried out to establish the quantities and percentages of Carbon, Hydrogen, Nitrogen and Sulphur content of the kerogen. It is of great importance in determining the constituent's chemical species of the pyrolysis liquid after degradation process.

2.8.7 The Brunauer Emmett Teller (BET)

The pore system in the oil shale is primarily associated with organic matter. The BET analysis is used in knowing pore volumes and sizes and also specific surface area. The nitrogen sorption experiment and BET work hand to hand. The principle of nitrogen sorption experiment is based on the gas pressure forcing the gas molecules absorbed to the surface of pores. When the gas pressure begins to increase the gas molecules form a monolayer (one molecule thick).As the pressure increases, the gas molecules fill the small pores and finally fill all the pore volume, which is defined as the adsorption process and the inverse phenomenon occurs with pressure decreasing in the desorption process (Mal, 2016).

2.9 Extraction

Since liquid products from kerogen are a mixture of several compounds, there are numerous useful substances which can be extracted from it. Chemicals such as pyridine, phenols, organic acids, alcohols and so on which are useful in industries like resin, food, cosmetic and fertilizer can be extracted using appropriate technology. However, complexity and cost associated with separating these chemicals is an impediment that must be overcome in order for liquid products from kerogen to be utilized for this purpose.

2.10 Relationship between Oil, Sand and Water

Sandstone reservoir happens to be the main source of the world hydrocarbons. Approximately 70% of oil and gas reservoirs worldwide are unconsolidated sandstones. This signifies that a good number of oil and gas discipline are face with the problem of sand and fine production issues worldwide. The production of formation sand along with reservoir fluids is one of the oldest challenges faced by oil companies and it is very difficult to solve. Sand production can be defined as the migration of formation sand caused by the flow of reservoir fluids. It starts when rock around the perforations fails and the fluids can push the loose grains into the wellbore. Sand production is processes that develop simultaneously in three phases. Incapacity of rocks surrounding an open hole or perforation from which free sand grains are generated, disaggregation of sand particles from failed materials and transport of those free grains by the effluents into the wellbore and up to the surface. It is clear that sand particles have to be breakdown from its parent rock before it can flow along the reservoir fluids in the wellbore. This occurs when the reservoir rock has low formation strength and fails under the in situ stress condition and the imposed stress transformation due to hydrocarbon production. Studying the principal of fluid dynamics, two main categories of interaction is said to happen in multiphase flow. Interphase interaction is a process where the fluid phase interacts with particulate phase. Drag force is expressed on the particles by the fluid stream and momentum is move from one stage to another while interphase interaction where solids particles in the particulate phase interacts with one another. It is characterized mainly by the frequency of particle collision. The presents methods that are used to know the sand production and fines from reservoir

formation, transport of sand fines in multiphase flow of oil, gas and water from bottom hole to well head in the reservoir (Richard, 2013).

2.10.1 How to measure the quantity of crude oil

Viscosity is one of the important and useful parameter used to measure the quantity of crude oil in mixture. Viscosity is a measure of a liquid resistance to flow, the viscosity of a liquid relates directly to intermolecular interactions and molecular structures. Large molecules increase to viscosity of oils, as a result of both molecular enticements and increase force interactions. Heterogeneous atoms produce permanent dipoles in molecules which increase intermolecular interactions and progressively increase viscosity. Liquids with high viscosities tend to have high density viscosity is mostly relayed on temperature and reduces with increasing temperature. Conventional crude oils are characterized as Newtonian fluids which mean that the viscosity is relayed on shear rate. The Total Acid Number (TAN) is a measure of crude oils acidity. TAN is expressed in milligrams of potassium hydroxide needed to neutralize the acid in gram of oil while Total Base Number (TBN) is a measure of crude oils basicity (Kolltveit, 2016).

2.11 Relevance Literatures to the Research

Tiwari and Deo (2012). Studied the behavior of oil shale from green river oil using thermogravimetric analysis combined with online mass spectrometry (TGA- MS). The activation energies were determined between the ranges of 90 – 230 kj / mol in relation to conversion. (Han *et al.*, 2015) used TGA to study oil shale and kinetics at 10, 20, 30 and 40 °C / min heating rate on two oil shales from Huadian and Fushun in northeast China.

Characterizes the hydrocarbon released during pyrolysis. However, weight loss at 400 – 550 °C using TGA and hydrocarbon generation 400 – 475 °C. The activation energy obtained is 10 kj / mol (Huadian) and 1 kj /mol (Fushun). It was reported by (Gai *et al.*, 2014) studied the influence of inherent and additional pyrite on oil shale pyrolysis in a fixed bed reactor with heating rate of 460 – 580 °C. The oil and gas produced on the shale pyrolysis at 500 °C with addition of 8 wt % pyrite are 41.7 wt % and 14.4 wt %. According to (Sonibare *et al.*, 2005) studied thermal decomposition of Lokpanta oil shale from Nigeria using Thermogravimetry (TG) and Differential Thermal Analysis (DTA) within a temperature range of 25 – 600 °C. Rock Eval pyrolysis was used to study the geochemical characteristics of oil shale within a temperature range of 300 – 570 °C. The activation energy is evaluated within a range of 73.2 – 75.0 kj / mol. The results of Rock Eval indicate that oil shale contains adequate amount of good quality kerogen to produce both oil and gas. (Al-Ayed *et al.*, 2010) studied a modified first order kinetics equation with changes activation energy is used to model the total weight loss of Ellajjun oil shale samples with temperature 350 – 550 °C and heating rate of 2.6 – 5.0 °C / min. The value obtained for activation energy is within the range of 98 – 120 kj / mol whereas corresponding frequency factor changed is within the of 9.51×10^5 – 1.16×10^6 . It was reported by (Tian *et al.*, 2018) studied the rapid pyrolysis of oil shale coupled with in situ upgrading volatiles over oil shale char was investigated in a laboratory two – stage fluidized bed (TSFB) gotten shale yield at temperatures range of 500 – 600 °C. The biggest yield was 12.7 wt % at 500 °C and was about 1.3 times of the Fischer oil yield. (Liu *et al.*, 2017) stated that the pyrolysis kinetics characteristics of oil shale gotten from Mudanjiang using Rock Eval analysis. The

heating (10, 15, 20, 25 and 30 °C / min) and temperature range of 200 – 600 °C. Kinetics model was used to evaluate the activation energy and frequency factor. (Lin *et al.*, 2015) studied the pyrolysis of a coal in a fixed bed reactor. This was achieved through the application of pyrolysis to mitigate the problem of low oil shale yield and low heating performances of oil shale particles in conventional fixed beds. It was operated within the temperature range of 600 – 1000 °C and oil shale yield obtained are within the range of 9.5 – 84.9 wt % with the aid of Fischer assay. The 12.49 wt % was in dry base and there is reduction in the yield of oil shale from 9.53 to 4.60 wt % respectively.

CHAPTER THREE

3.0 MATERIALS AND METHODS

Table 3.1: List of Materials

Materials	Source
Carbonaceous Kerogen	Kudu Mokwa LGA
Nitrogen gas	Getame Lab Portharcourt
HCl	Minna
Hot water	Minna

Table 3.2: List of Equipments

Equipment's	Model	Source
Weighing balance	MF100/1108596	FUT Minna Chemical
Eng.Dept.		
Proximate and Ultimate Analysis		FUT Minna WAFT Laboratory
Thermogravimetry analysis (TGA)	Pelkin Elmer Analyzer	Step B Fut Minna
Brunauer Emmett Teller (BET)	NOVA2400e	Step B Fut Minna
Rock Eval Pyrolysis Instrument	LECO SC-632/Sulfur Analyzer	Getame Lab porthcourt
Fixed Bed Pyrolysis Experiment		Central Lab N.C.R.I Badegi

Gas Chromatography Mass Spectrometer (GCMS) GC/MS/77780 Uni of Ilorin Lab

Stainless Steel Reactor (100mm) AZ blacksmith

Electric Furnace (MRI200AA1) Goodman

Beakers (250ml) Pyrex

Water Cooling Condenser Pyrex

Oven (AX30) Carbolite Gero

Thermocouple Cr-A1: K type

Stop Watch

Water Hose

This chapter will outline the various experimental and characterization techniques used to produce and characterize of oil production of carbonaceous kerogen sample from Kudu Basin Area in Niger State, Nigeria. The detailed procedures and analysis is further discussed as follows.

3.1 Samples Collection

The dark black carbonaceous kerogen was geologically map, survey and drilled at Kudu Bida Basin Area in Niger State, Nigeria.



Plate 3.1: Carbonaceous kerogen sample from Kudu Mokwa LGA in Niger State

3.2 Pre - Treatment

Plate 3.1 shows the pictures of carbonaceous kerogen samples obtained from Kudu Area of Bida Basin in Niger State. The samples were treated with hydrochloric acid and rinsed with hot water to remove the potentially contamination from drilling mud and evaporative loss during sample storage and preparation before laboratory analysis.

3.3 Characterisation of Kerogen Sample

3.3.1 Proximate analysis

This analysis was carried out using standard procedures described by ASTM D3170-07 for the purpose of determining the fixed carbon, volatile matter component, moisture and ash component of the kerogen (Kumar and Singh, 2011).

3.3.2 Ultimate analysis

This analysis determines the component element of kerogen. The CHNSO Elemental Analyzer was used to evaluate the percentage composition of Carbon, Hydrogen, Nitrogen, and Sulphur while the residual is the percentage of oxygen.

3.4 Rock Eval Pyrolysis of Carbonaceous Kerogen Samples

The Rock Eval 6 pyrolysis was performed on the kerogen samples, kerogen mixture and kerogen soil samples in order to estimate the quantity of organic matter in the sample, to determine the hydrocarbon generative potential of the organic matter, to determine the maturity of the source rock and to evaluate the relative proportion of the hydrocarbon in the samples respectively. The Total Organic Carbon (TOC) was determined using a LECO SC – 632 / Sulfur Analyzer. The samples are then introduced into the LECO combustion oven and the amount of carbon is measured as carbon dioxide by Infra-Red Detector. The temperature programmed applied in pyrolysis mode is 300 °C (3min) and 650 °C (25min).

3.5 The Thermogravimetry Analysis of Carbonaceous Kerogen

The TGA is an instrument used for the measurement of mass sample while heating the sample at elevated temperature. A sample is heated, it reacts and released mass in form of vapor or gas.

3.6 The Brunauer Emmett Teller (BET)

The nitrogen sorption experiments and BET methods, kerogen sample was crushed into powder (< 0.4 mm) for nitrogen sorption measurements which are measured with the aid of surface area analyzer. The pore surface area is measured using BET theory and the pore

volume and sizes are measured using Barret Joyner Halenda (BJH) method. The BET equation and BJH theory are used to calculate the surface area and pore volume during the process.

3.7 Fixed Bed Pyrolysis

Fixed Bed pyrolysis experiment was performed at constant time 45 min at 300,400,500,600 and 700 °C. After the completion of each experimental run, the yield liquid, solid and gaseous products were calculated in terms of percentage and tabulated using the following formulae below.

$$\% \text{ yield of shale oil} = \frac{\text{Volume of liquid product (in ml)}}{\text{Starting weight of sample (g)}} \quad (3.1)$$

$$\% \text{ yield of shale char} = \frac{\text{Weight of solid product (g)}}{\text{Starting weight of sample (g)}} \quad (3.2)$$

$$\% \text{ yield of shale gas} = 100 - (\% \text{ liquid} + \% \text{ solid}) \quad (3.3)$$

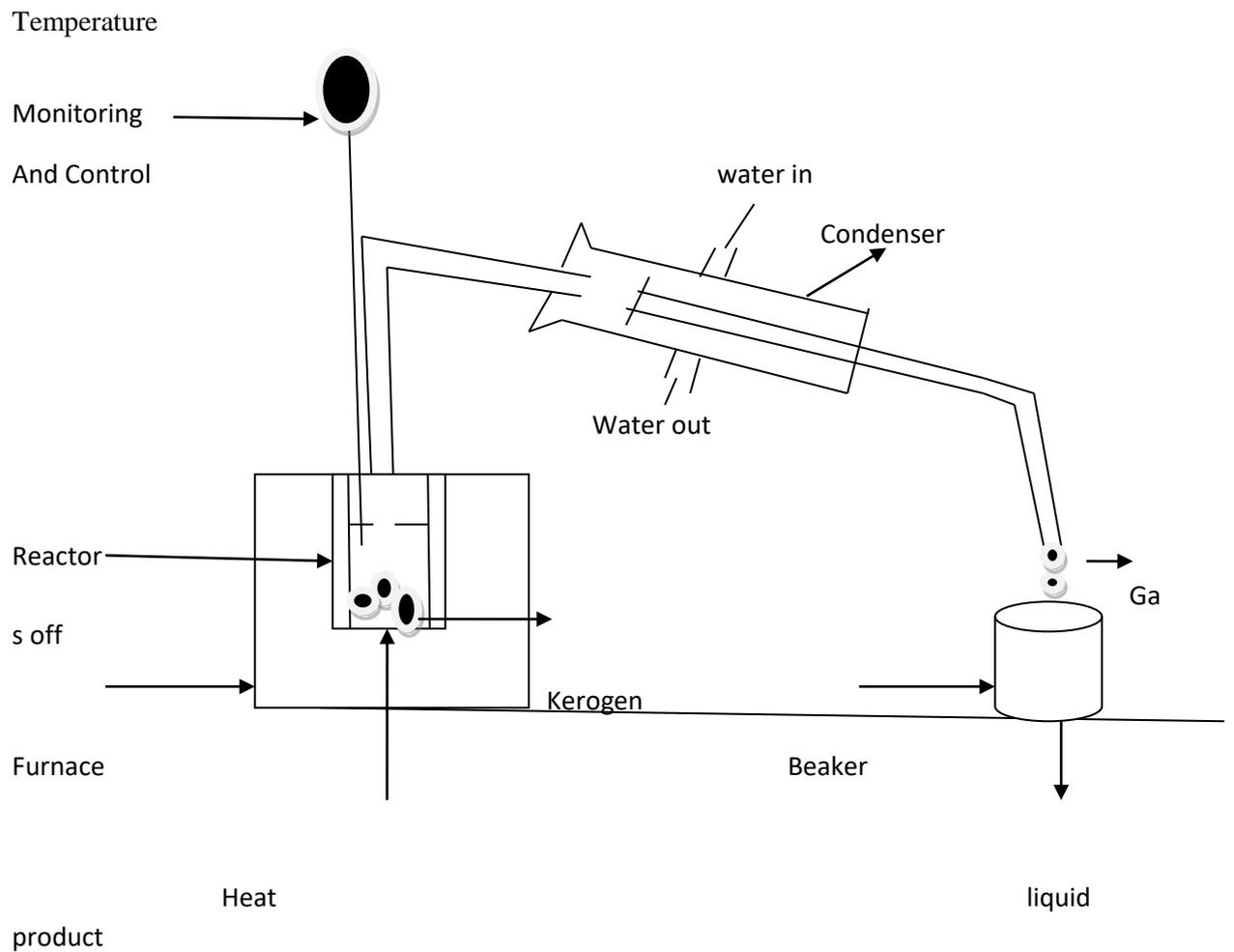


Figure 3.1: pyrolysis reaction setup

3.8 Physiochemical Characterisation of Shale Oil

3.8.1 Viscosity

The viscosity was measured according to standard test method ASTM 445. The sample was inserted and held in a capillary glass viscometer tube and the temperature maintained at 35 °C. The needed time for the sample specific volume to move through the capillary tube was noted. The time has a proportional relationship to the kinematic viscosity of the feedstock.

3.8.2 Calorific value

The heat content of the pyrolysis liquid was measured with a Parr 6100 calorimeter. 1ml of the sample was measured into a crucible and placed inside the calorimeter, the vessel was filled with oxygen and ignited. The resulting temperature increased was measured from which the calorific value was calculated.

3.8.3 Density

The density was measured using digital densitometer by measuring 1g of the sample into the flexible hose of the device.

3.8.4 Moisture content of pyrolysis liquid

The moisture quantity of the shale oil was evaluated by means of a Karl Fischer Moisture Titrator MKS - 500. The oil sample was measured into a titration vial and dispersed in a solvent medium containing chloroform and chloro-ethanol. An iodine reagent is then used to titrate the solution continuously until water is completely removed. Water and iodine

interact on the basis of mole to mole and hence, the fraction of moisture in the oil is deduced from the starting weight of the sample.

3.8.5 Flash point

Flash point was analyzed using closed cup flash point method (ASTM D93).75 milliliters of the sample was measured into a closed cup. It was agitated and heated at a fixed rate. At periodic intervals, the cup is opened and a source of ignition is brought over the apex of the cup. The flash point represents smallest temperature that the vapors above the liquid ignite when an ignition source is brought into contact.

3.8.6 Pour point

The pour point was measured according to ASTM D97 Standard Procedure. An oil sample was warmed at first and subsequently cooled at constant rate. It motion was observe at temperature of 3⁰C.The least temperature that the flow of the sample is noticed when the container is shifted denotes the pour point.

3.8.7 pH

This measure the degree of acidity or alkalinity of the shale oil, pH value from 0 to 7 is acidic, 7 is neutral and 7 to 14 is alkaline or basic in nature.

3.9 The Gas Chromatography Mass Spectrometer (GCMS)

The GCMS was performed in EGA 3030D with a pyrolyser temperature of 550 °C agilent GS / MS / 77780 was used at GC injection temperature of 300 °C and oven temperature of 340 °C (20 °C / min, 13 min hold). It is also used for biomarker assessment of the n-alkane distribution.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Characterization of Kerogen

4.1.1 Proximate and Ultimate Analysis of Kerogen and Shale oil

Table 4.1 Proximate and Ultimate Analysis of Kerogen

Proximate	Value (wt %)	Ultimate	Value (wt %)
Moisture Content	4.430	Carbons	88.741
Volatile Content	54.817	Hydrogen	10.570
Fixed Carbon	30.984	Oxygen	0.250
Ash Content	9.330	Nitrogen	0.439
TOC	0.658	Sulphur	0.000

Table 4.1 shows the proximate and ultimate analysis of kerogen. Proximate and ultimate analysis of kerogen is a simple means of showing its composition and fuel like properties. Proximate analysis measures the moisture, volatile matter, fixed carbon and ash content of the kerogen whereas 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 pyrolysis process (Abnisa and Daud, 2014). From literature it has been reported that a high volatile matter is needed to favor production of more pyrolysis oil and consequently reducing coke and gas yield while high ash content has a negative impact on the yield but tends to promote formation of solid-coke and gaseous products (Abnisa and Daud, 2014). Similarly, high moisture content is usually unfavorable for kerogen conversion and tends to lead to a reduction in the combustion properties of the products (Dewangan, 2014). The elemental composition of the kerogen shows the possible chemical components of products after pyrolysis process. Table 4.1, it can be seen that

moisture, volatile, ash and fixed carbon content of kerogen were 4.430, 54.817, 9.330 and 30.984 wt % respectively. This shows that the kerogen has the potential to be converted into shale oil, shale-coke and shale gas with appreciable yield. Similarly, Carbon and Hydrogen contents 88.741 and 10.570 wt % respectively which shows its potential as a possible source of hydrocarbon.

Table 4.2 Proximate and Ultimate Analysis of Shale Oil

Proximate	Value (wt %)	Ultimate	Value (wt %)
Moisture Content	0.50	Carbon	80.80
Volatile Content	40.76	Hydrogen	17.76
Fixed Carbon	0.000	Oxygen	0.45
Ash Content	0.000	Nitrogen	1.05
Carbonites	58.75	Sulphir	0.00

Results from Table 4.2, shows the compositional properties of shale oil. It can be seen that shale oil has a very high volatile matter of almost 100 weight percent and a high carbon, hydrogen content of about 80.80 and 17.76 wt % respectively. This is indicative of the excellent fuel like quality of the shale oil and also a very potent material that can be used to improve the yield and quality of products through pyrolysis with kerogen sample.

4.2 Analysis of Rock-Eval Pyrolysis

The kerogen sample was obtained from well drilled from kudu Northern Bida Basin Niger State Nigeria. The kudu source rock is believed to be major source rock in the northern Bida Basin which lies deep down of about 2 km depth.

The organic geochemical analysis was performed on kerogen sample to obtain detail results on organic richness, kerogen type and maturity of potential source rocks. The analysis is explained as follows as presented in Table 4.3.

Table 4.3 Rock Eval Pyrolysis Results

TOC	S1	S2	S3	Tmax	HI	OI	S2/S3	S1/TOC×100	PI
0.68	0.05	1.04	0.57	418	152.94	83.82	1.827	7.35	0.05

4.3.1 Quantity of organic matter

The total organic carbon (TOC) is 0.68 wt % as shown in Table 4.3. The TOC value indicates that the source rock has high generative capacity compare with standard. S1 represent the quantity of free hydrocarbon present in the source rock sample which signifies that the quantity of hydrocarbon present in the source rock is 0.05 mg HC/ g rock. S2 represents the quantity of hydrocarbons obtained through thermal cracking of nonvolatile organic matter which is 1.04 mg / HC g rock. S3 represents the quantity of CO₂ generated during pyrolysis of source rock sample which is 0.57 mg /HC g rock. The S1 value is as result of low maturity of source rock sample not to poor generative capacity. 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 rely on the kerogen type. Tmax result of 418 °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 over matured for oil generation. The Rock Eval pyrolysis was carried out at Getamme Laboratory in Port Harcourt.

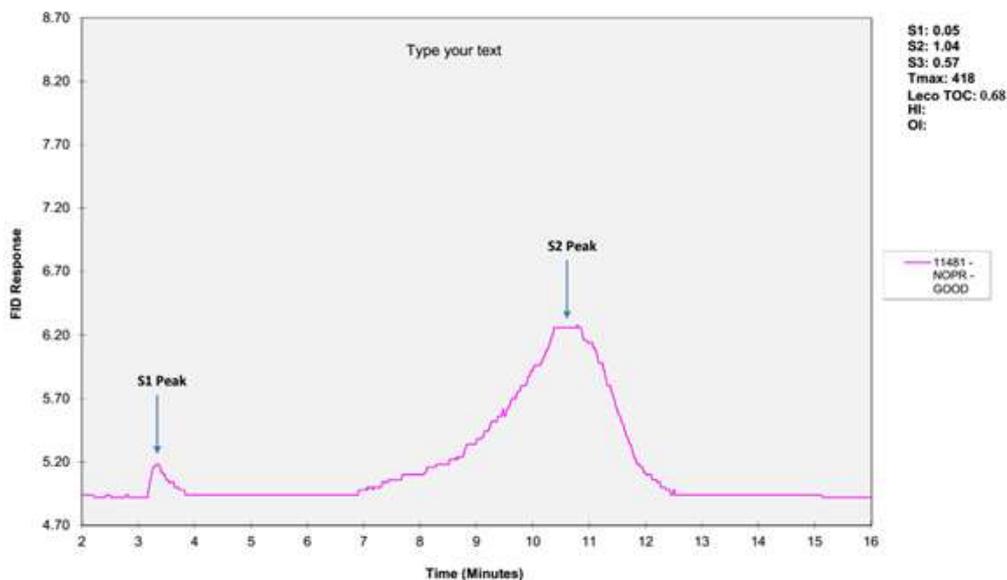


Figure 4.1 Relationship between flame ionization detection (FID) Response and Time

Figure 4.1 shows the relationship between flame ionization detection (FID) responses with Time. It can be seen that FID and Time increases progressively until it reaches its optimal conditions. The S1 and S2 signals successively determined with FID equivalent to first quantity of hydrocarbons and second peak representing the hydrocarbons produced from thermal cracking of source rock sample.

4.3.2 Quality of organic matter

The result of hydrogen index (HI) is 152.94 mg HC / g TOC, oxygen index (OI) is 83.82 mg HC / g TOC, S2 / S3 is 1.80, S1 / TOC×100 is 2 and PI is 0.05 respectively. The hydrogen index (HI) of 152.94 indicates that 69.12 % oil and gas and 30.88 % gas. HI 300mg and above HC / g TOC will generate Oil, HI 150 to 300 mg HC / g TOC will generate oil and gas, HI 50 to 150mgHC/g TOC will generate gas, HI less than 50 mg HC / g TOC have no hydrocarbon generative potential. The analysis signifies that the source rock contains type II kerogen, since the HI fall within the range of 150 to 300 mg HC / g TOC.

4.3.3 Maturity of organic matter

Production index (PI) is 0.05, which implies that the hydrocarbons quantity has been produced naturally in relation to the total quantity of hydrocarbons which the source rock sample can produce. The PI value of 0.05 signifies that it is immature organic matter in conformity with low S1 value of 0.05 resulted from low thermal maturity.

4.3.4 Hydrocarbon generative potential

The results from Table 4.3 significantly shows that organic matter of sample is immature to early mature. Hydrocarbon production capacity depends on organic matter type and quantity. TOC, HI, OI, S2 / S3 reveal that sample has potential for organic matter represented by oil and gas prone kerogen II. In Rock –Eval terminology, the TOC consists of pyrolysable (PC) and residual (RC) carbon. PC equivalents to the carbon content in the HCs (S1+S2). $100PC / TOC > 30 \%$ are typical for an oil prone source rock while $100PC /$

TOC < 30 % shows a gas prone source rock. Most of the samples have 100 PC / TOC is range from 55 to 65% (Carthy *et al.*, 2011,Obaje *et al.*, 2013,Zhao *et al.*, 2016, Gajicaet *al.*, 2017).

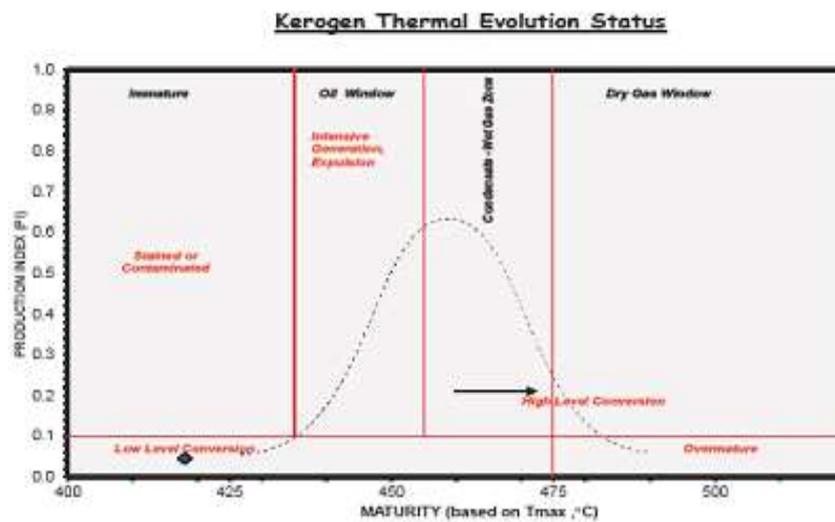


Figure 4.2: Relationship between Production index (PI) and Maturity (based on Tmax)

The source rock can either be immature, mature or over mature. The production index and maturity increases significantly. The immature source rock is made up of heterogeneous mix of large molecules that are reaching their stability at low temperature. It is also regarded to be the reference point from which thermal maturation changes the solid kerogen to other forms. The source rock serve as load bearing matrix which elongate particles. The source rock that has vitrine reflectance (R_0 %) less than 0.5 equivalent to hydrocarbon production which is referred to as oil shale. The mature source rock involves changes to oil, the remaining sample is likely to be more aromatic as solids shape become more ordered and denser with stack aromatic pattern. As the temperature rises the rocks become more

mature and thereby converting oil to gas through process called thermal cracking. During this conversion, the quantity of pore fluid rises and resulted in over pressure in organic shales as a result of very small permeability. The source rock is similar to pores production through thermal maturation as inclusion in the solid sample. The source rock has a vitrine reflectance of ($0.5 < R_o (\%) < 1.3$) equivalent to the major stage of hydrocarbon production and primary migration. This stage usually composes of oil window and it is called shale oil. At the overmature stage, the organic matters behave like a spongy texture and are dispersed in the inclusion space of organic shale. The organic matter is highly inclusion filling and the matrix is more supported by inorganic grains at over mature stages. As a result of continuous maturation resulted to a rearrangement of the polyaromatic network and in turn an sequential graphitization of remaining sample can successively stiffen the organic matter. The geochemical attributes of sample transform with maturation because it releases volatiles such as CH_4 , CO_2 and H_2O during thermal decomposition. The source rock has a vitrine reflectance of ($R_o (\%) > 1.3$) (Zhao *et al.*, 2016).

4.4 Thermogravimetric Analysis (TGA)

TGA was used to measure changes in physio-chemical characteristics of the temperature was elevated with constant heating rate. It is used to study the thermal attributes of samples due to degradation. It was done using a TGA analyzer Perkin Elmer with a sample measurement of 10mg at a degree of heating of $10\ ^\circ C / min$. Derivative Thermogravimetry (DTG) is also determined from TGA data, to elevate the degree of weight loss when temperature is elevated. The TGA and DTG data is often applied in the study of chemical kinetics of the degradation process and also the decomposition of behaviour of samples.

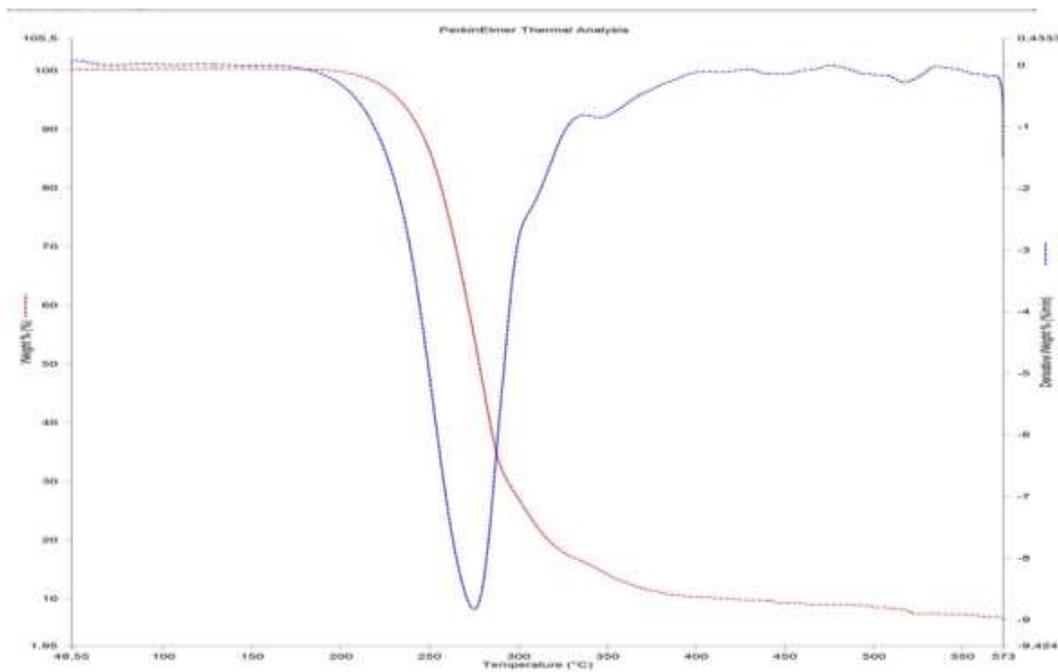


Figure 4.3 TGA and DTG Curves of kerogen

Thermogravimetric Analysis (TGA) is a technique that is used to study the thermal decomposition behaviour of oil shale sample. It gives a measure of the weight loss of a sample material as a function of temperature or time. The decomposition characteristic of oil shale sample is given in Figure 4.3 from the TGA curve. It can be seen that weight loss increased with the increase in pyrolysis temperature. It has been reported from literature that the degradation of oil shale involves three main stages, which are moisture content

elimination, decomposition of sample and continues slight valorization (White *et al.*, 2011). The TGA curve of oil shale shows that the decomposition is divided into 3 stages which is due to the varying composition of oil shale. In the initial stage of the decomposition which began at room temperature up to 200 °C, there was a gradual weight loss about 10.0 wt % which can be attributed to the release of moisture and partial hydrolysis of some extractives. In the second stage it is observed that an accelerated decomposition of oil shale sample which constituted organic matter is observed within a temperature range of 200 to 500 °C with an approximate weight loss of about 100%. The last stage which is observed above 550 °C shows a constant residue ratio which can be attributed to complete loss of the decomposable fractions. The maximum yield usually occurs between the temperature ranges of 280 to 500 °C (Almeida *et al.*, 2008, White *et al.*, 2011 and Dewangan, 2014). Furthermore, representatives of TG/DTG curve of Bida Basin Kerogen shown in figure 4.3 above. The DTG curves of the sample show the same trend of attributes, having two major peaks. The first peak involves weight loss or removal of moisture from kerogen. The second peak, occurring at the temperature range of 320 °C and 573 °C is attributed to the thermal breakdown of the oil shale content to give oil, gas and residual carbon content. The estimated total decomposable oil shale constituted in the sample varies. The quantity stands for the total weight loss subtracted from the weight loss as a result of moisture. The major attributes point on the DTG curve is the peak temperature and burn out temperature. The peak temperature stands for the measure of weight loss at a maximum. The burn out temperature stand for the temperature where thermal decomposition is complete. The attributes temperature values are listed. The peak and burn out temperature range from 450

to 520 °C and 550 to 570 °C respectively. The DTA curves of oil shale shown in Figure 4.3. All the DTA traces show the same behaviour, having a small endothermic peak up to 270 °C, followed by an exothermic peak that moved to the end of the pyrolysis process. This observation signifies that the thermal decomposition of the oil shale is an exothermic reaction process (Sonibare *et al.*, 2005).

4.5 BET Analysis

The BET analysis was performed on kerogen for the purpose of obtaining specific surface area, pore size, and pore volume as shown in Table 4.4.

The pore size was studied to reveal the capacity for hydrocarbon storage within the kerogen sample as follows.

Table 4.4: Analysis of Kerogen by Brunauer Emmett Teller (BET)

Surface Area:	171.95m ² / g
Pore Size:	2.97 nm
Pore Volume:	0.07 cm ³ / g
Sample weight:	0.05 g
Outgas time:	3.00 hrs
Analysis time:	33.70 minute

Sample volume:	1.00 cm ³
Outgas temperature:	250 °C
Bath temperature:	273 °k

In the case adsorbate the nitrogen molecular weight is 28.013, temperature is 77.35 °k, cross section is 16.200Å and liquid density is 0.808g / cm³. The size distribution and interconnectivity of pores in any reservoir are in relation to knowing permeability. Pores usually occupy the intergranular volume with a smaller porosity portion in the interior grains resulting from dissolution process. Pore throat decrease in size and specific surface area increases as grain size decreases resulting to the well-known relationship between porosity, permeability and grain size.

In the case of multi point BET the slope is 20.173, intercept is 8.012×10^{-2} , correlation coefficient, $r = 0.999489$ and surface area is 171.951m²/g. In carbonate reservoirs, porosity is usually the product of recrystallization and dissolution of primary components which is normally relied on particle size.

In the case of langmuir data, slope is 13.07470, intercept is 0.53143, correlation coefficient, $r = 0.997$ and surface density is 171.951m²/g. The analysis of porosity in shale reservoir is considered most challenging than sand stone or carbonate reservoirs. Complications usually occurs as a result of small pores.

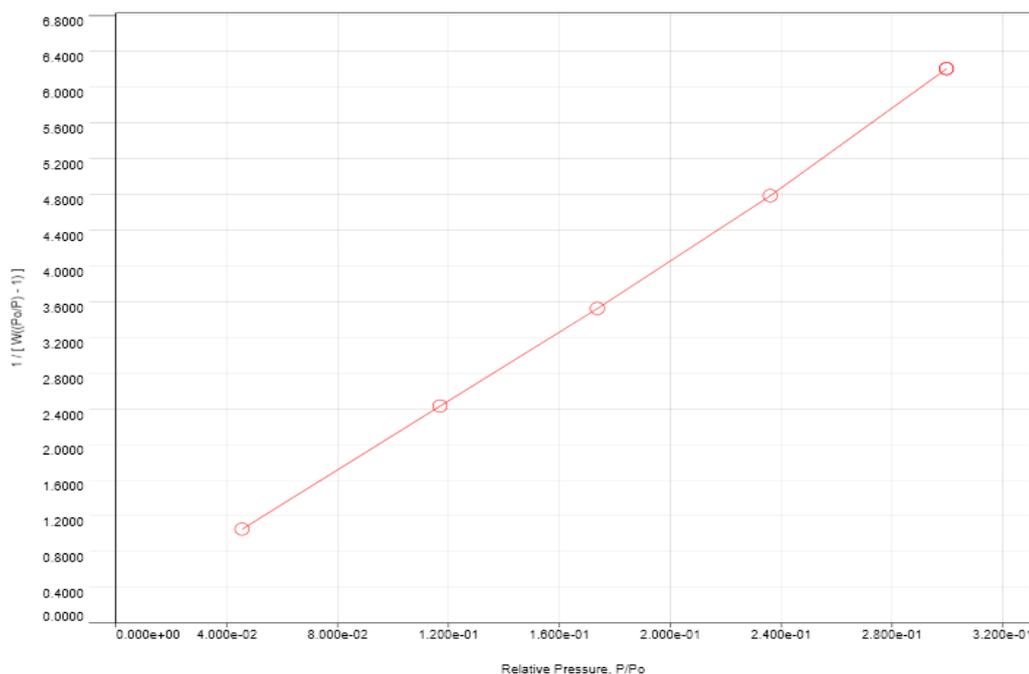
In the case of DR method data slope is -1.138×10^{-1} , intercept is 3.562×10^{-3} , correlation coefficient is 0.9802, average pore width 2.965 nm, adsorption energy 8.768 kj / mol,

microspore volume is $0.068\text{cm}^3/\text{g}$ and microspore surface area is $248.085\text{ m}^2/\text{g}$ (Harns and Dong 2013)

In the case DA method, the best E is 2.916 kJ/mol , Best n is 1.000, D A microspore volume is 0.110cm^3 , pore diameter is 1.820nm . More detailed evaluation of the porosity reveal that four pore types can be known with respect to the geometry and relationship with mineral or organic matter pores. The pores are as follows intra-organic ($<0.2\mu\text{m}$ diameter), organic matter (0.2 to $2\mu\text{m}$ diameter), inter mineral pores (0.2 to $1\mu\text{m}$ diameter) and intra mineral pores, elliptical or angular pores (0.05 to $0.3\mu\text{m}$) which are usually spherical pores bounded in organic matter particles (Mal, 2016).

In the case of DFT method, pore volume is $0.079\text{cm}^3/\text{g}$, surface is $115.814\text{m}^2/\text{g}$, lower confidence limit is 1.614 nm , fitting error is 0.611% , pore width (mode) is 1.688 nm and moving point average is off. The pore system of the kerogen is principally within the organic matter. The kerogen sample has a small volume which resulted to extremely low connectivity

In the case of Area volume summary, BJH / DH method moving point average is off, DR



method; Affinity coefficient (β) is 0.3300, HK method; tabulated data:1,SF method; tabulated interval.

Figure 4.4: BET Plot of Kerogen

The pore size distribution can be demonstrated as an incremental pore versus relative pressure. It can be seen that its increases progressively. The pore size distribution shown in this way depends on the experimental point spacing. It can also be seen that the plot is linear with ordinate and abscissa, the area under the curve is proportional to the partial pore volume for the specific difference. The relative pressure range (P/P_0) in which a monolayer is expected to form is between a specific range. The monolayer capacity can be evaluated by inverting the adsorption isotherm (Godinez, 2014).

In the case of surface area data, single point BET is $1.682+10^{-2} \text{ m}^2/\text{g}$, multi point BET is $1.720+10^{-2} \text{ m}^2 / \text{g}$, Langmur surface area is $2.664+10^{-2} \text{ m}^2 / \text{g}$, BJH method cumulative adsorption surface area is $1.559+0.2 \text{ m}^2 / \text{g}$, DH method cumulative adsorption surface area is $1.708+0.2 \text{ m}^2/ \text{g}$. 1- method external surface area is $1.608+0.2 \text{ m}^2/\text{g}$, 1-method microspore surface area is $1.112+0.2 \text{ m}^2 / \text{g}$, DR method microspore area is $2.481+0.2 \text{ m}^2 / \text{g}$ and DFT cumulative surface area is $1.158+0.2 \text{ m}^2 / \text{g}$. Nitrogen gas adsorption to determine surface area can use nitrogen, ethane, water, CO_2 , ammonia and other gases as probe molecular BET. BET derived an equation from multimolecular adsorption theory that would determine the number adsorbate molecules in a monolayer which is referred to as monolayer capacity. Specific surface area is similar to the monolayer capacity of a sample. The monolayer capacity of a sample is defined as the amount of adsorbate needed to cover

the surface of the sample with a monolayer molecule. Surface area can be deduced from the monolayer capacity v_m of a sample (Godinez, 2014).

In the case of pore volume data, BJH method cumulative adsorption pore volume is $6.979+0.2 \text{ cm}^3/\text{g}$, DH method cumulative adsorption pore volume is $7.313+0.2 \text{ cm}^3/\text{g}$, 1-method microspore volume is $5.648+0.3 \text{ cm}^3/\text{g}$, DR method microspore volume is $8.816+0.2 \text{ cm}^3/\text{g}$, HK method microspore volume is $7.148+0.2 \text{ cm}^3/\text{g}$, SF method microspore is $5.211+0.2 \text{ cm}^3/\text{g}$ and DFT method cumulative pore volume is $7.930+0.2 \text{ cm}^3/\text{g}$. The nitrogen isotherms are inverted to know the pore size distribution of the kerogen sample. There are basically two unique kinds of inversions techniques that determine pore size distribution from raw isotherm data. They are Barret Joyner Halenda (BJH) and Density Functional Theory (DFT). The BJH model depend on the kelvin model whereas DFT model depend on a statistical thermodynamic foundation (Mal, 2016).

In the case of pore size data, BJH method adsorption pore diameter (mode $D_v(d)$) is $1.453+00 \text{ nm}$, DH method adsorption pore diameter (mode $D_v(y)$) is $1.453+00 \text{ nm}$, DR method microspore pore width is $2.965+00 \text{ nm}$, DA method pore diameter (mode) is $1.820+00 \text{ nm}$, HK method diameter (mode) is $3.675 - 0.1 \text{ nm}$, SF method pore diameter (mode) is $4.523 - 0.1 \text{ nm}$ and DFT pore diameter (mode) is $1.688+00 \text{ nm}$ respectively. Although the DFT model is very known as result of its capacity to fit experimental data. It is very important to take note that broad range organic content cannot be used to model DFT data. The BJH model is recommended by Kuila (2013), for the inversion of isotherms to gotten the pore size distribution in kerogen as a result of the sample analyzed in this study are usually mesoporous. Therefore, BJH model is one of the model used in this study

to study the pore structure effectively. The specific surface area and specific pore volume are unambiguously defined as total surface area and total pore volume normalized by sample mass. The pore size distribution can be defined and represented in many forms. There are four kinds of plots that can be gotten from the inversion of the isotherm. They are cumulative specific pore, volume against pore size, incremental specific pore volume against pore size, differential pore volume against pore size and log differential pore volume against pore size (Mal, 2016).

4.6 Fixed Bed Pyrolysis

A fixed bed pyrolysis system has been used for production of shale oil. The major components of the system are fixed bed reactor, liquid condenser and liquid collector. Nitrogen gas was used to maintain the inert atmosphere in the reactor where pyrolysis reaction takes place.

Table 4.5 Percentage Yield of Various Temperatures during Pyrolysis

Process Description	Yield (wt %)
---------------------	--------------

S/N	Temperature ($^{\circ}$ C)	Time (Minute)	Liquid	Solid	Gas
1	300	45	30.40	50.50	19.10
2	400	45	35.60	41.30	23.10
3	500	45	50.20	24.20	25.60
4	600	45	48.20	21.00	30.80
5	700	45	42.10	18.40	39.50

Table 4.5 showed that pyrolysis reaction parameters like temperature and time. It can be seen that that time is constant throughout at various temperatures. The pyrolysis parameters have an influence on the quantity of various products such as liquid crude oil, solid char and gas formed during the pyrolysis process.

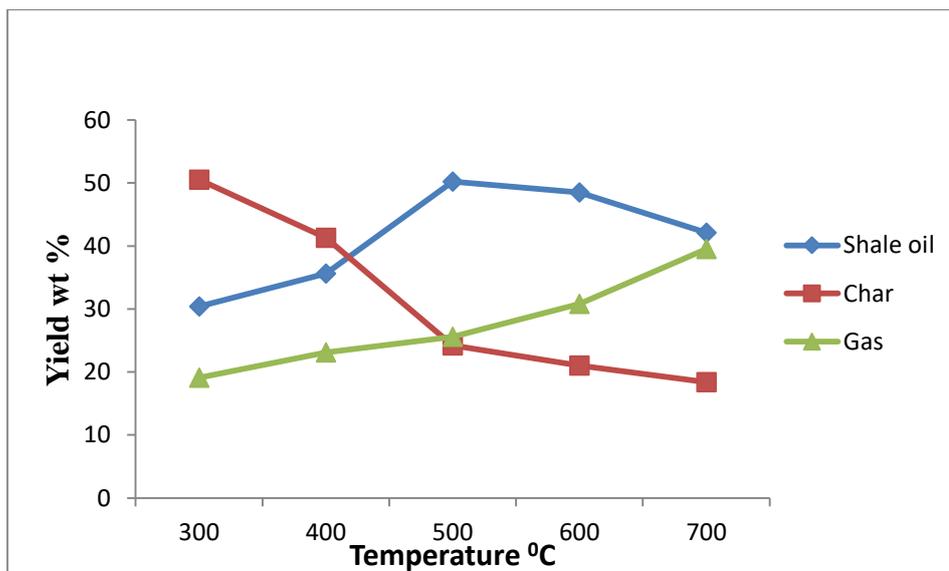


Figure 4.5: Effects of Temperature on Yield

Figure 4.5 is a plot of the yield of the liquid, gaseous and solid product obtained during the pyrolysis of kerogen against various pyrolysis temperatures at a constant reaction of 45 minute and heating rate of 10 °C / minute. The plot shows that for the liquid, as the temperature is increased from 30.40 wt % to 50.20 wt % at 500 °C.

Table 4.6 Physical Properties of Shale Oil Obtained from Kerogen

Viscosity:	4.60 cst
Calorific Value:	6.00 mj / kg
Moisture Content:	2.40
Flash Point:	23.00 °C
Pour Point:	-8 .00°C
Density:	1.71 g / cm ³
pH:	3 .60

4.7 Physical Properties of Shale Oil Obtained from Kerogen

The results of the physical properties of shale oil are shown in Table 4.6. Comparison of the physical properties of the shale oil was made to that of the petroleum light fuel for the purpose of determining the suitability of the shale oil produced as a possible replacement for petroleum fuel. It can be seen that in-terms of viscosity, the liquid product had a value

4.6 cst and from literature minimum value for viscosity of shale oil from kerogen is 2.0 to 100 cst and this clearly shows that the viscosity of the shale oil from kerogen is much closer. Similarly, the calorific value is an important property that shows its combustion efficiency was tested for the liquid product, the result show that shale oil from kerogen had a value of 6.0 mj/kg and from literature minimum value for calorific value is 5 - 20 mj/kg. Furthermore, for the moisture content, which is an undesirable property in the shale oil is 2.4 and from literature minimum value for moisture content is 2 to 15. A similar trend was observed for the density as well. The shale oil from kerogen had value of 1.71g/cm³ and from literature the minimum density is 1.60 to 1.80g/ cm³ which gave the closest value to that of the petroleum fuel value. The pH value of a good fuel is expected to be neutral in order not to cause engine problems. Shale oil is acidic nature with a value of 3.6 from Table 4.4. The major contributory factor to the high pH of shale oil is the presence of organic acid such as carboxylic acid. The result from the GCMS analysis showed that about 20 % of the chemical compound making up the liquid product was organic acid. The flash and pour point of liquid fuel is another important property that demonstrate its combustion behaviour. The flash and pour point of light fuel oil is reported to be < 60 and 16 to 52 °C. Comparing these values to those of shale oil, it can be seen shale oil from kerogen is 23°C and -8 °C and from literature the minimum value for flash and pour point is 23 °C and 0 to -10 °C was closest to values of liquid fuel oil. The improvement observed in these properties can be seen as a result in of the increase in organic content inside kerogen as shown in the result of GCMS analysis (Daud, 2014., Onal *et al.*, 2014, Martinez *et al.*, 2014, Abina and Daud, 2014).

4.8 Chemical Properties

4.8.1 GCMS of the shale oil

The GCMS analysis of the shale oil sample obtained from kerogen was carried out to know exact composition of the oil. The analysis was carried out for liquid pyrolysis oil obtained at pyrolysis temperature of 500 °C for kerogen sample. The component mostly presents in kerogen sample are aliphatic and aromatic compounds with carbon number C₄ – C₈. It can be observed from results as presented in table 4.2 that there 9 compounds in the liquid oil sample from the kerogen. The compounds present in shale oil are pyridine 2,6 dimethyl, pyridine, 2 ethyl, butyrolacetone, pyridine 2,5 dimethyl, pyridine, 2 ethyl-6- methyl, phenol, phenol, 2- methyl, phenol, 2 methoxy and phenol 2,6-dimethoxy. It can be seen that the shale oil from kerogen is mainly constituted by oxygenated compounds such as phenols, butyrolacetone and nitrogenous compounds such as pyridine. Pyridine was derived from pyrite, which is the components found inside kerogen sample at early stage of maturity (Pradhan, 2012).

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the evaluation and characterisation of oil production from kerogen in Bida Basin was investigated as follows. Rock Eval (R.E) 6 instruments was used to know the hydrocarbon potentials of the kerogen, the maximum temperature T_{max} is 418 °C and the instrument also reveal information about the Total Organic Content (TOC) which is 0.68 wt % and the kerogen type II that contain adequate quantity of hydrocarbon that can generate oil and gas upon pyrolysis process. The kerogen sample was analyzed with Thermogravimetric analysis (TGA) in order to know the thermal decomposition of the kerogen (308.28 – 471.68 °C). The BET analysis on kerogen reveal that specific surface area is 171.951m²/g, pore size is 2.965 nm and pore volume is 0.068 cm³/ g which enhance

flow of oil. Fixed bed pyrolysis experiment was also performed in order to obtain shale oil, gas and coke. Increased reaction temperature showed a corresponding increase in the liquid product quantity, until a temperature of 500 °C which gave an optimum yield of 50.20 wt %. Further increase in temperature led to a reduction in the liquid yield and an increase in the gaseous product at an optimum time of 45 minutes. The physical properties analysis of liquid revealed that it contains properties similar to petroleum light fuel. GCMS analysis showed the organic compounds present in the shale oil.

5.2 Recommendations

In a bid to further improve on the quality and quantity of shale oil obtained through fixed bed pyrolysis of kerogen. The following recommendations are suggested for future scope of research work.

1. Upgrade of shale oil to meet refinery feedstock specifications by hydrogenation (addition of hydrogen) and removing sulphur (S) and nitrogen (N) impurities.
2. Kinetics studies of the kerogen in order to obtain the activation energy (E) of the reaction, Pre exponential factor (A) and Correlation Coefficient (R).
3. Production of catalyst to speed up the rate of conversion of kerogen to shale oil and also increase the quality and yield of the shale oil obtained.

4. Modification of reaction set-up such as the use of a fluidized bed reactor to achieve continuous operation.
5. Environmental Impact Assessment (EIA) of Bida Basin.
6. More sample need to the analyzed from Bida Basin in order to have best hydrocarbon generative potentials.

REFERENCES

- Abay, T. B. (2017). Diversity of Petroleum in terms of source rock properties and secondary alteration process Norwegian Continental Shelf, 4(3),13 -14.
- Abnisa, A., and Daud, W. M. A. (2014). A review on co-pyrolysis of biomass:an optional technique to obtain high grade pyrolysis oil.Journal of Energy Conversion and Management, 87, 71- 85,
- Adedapo, J. O., Ikpokonte, A. E.,Schoeneich, K., and Kurowska, E. (2014).An estimate of oil window in Niger Delta Basin from recent studies .*American International Journal of contemporary research*, 4(9), 114 – 115.
- Adegoke , A. D., Abdullahi, W. H., Yandako,B. M. S., and Abubakar, M. B. (2015). Kerogen Characterisation and Petroleum Potential of late Cretaceous Sediments Chad (Borno).Basin, northeastern Nigeria.*Bulletin of the Geological Society of Malaysia*, 6(1), 30 - 33.
- Ahiarakweni., and Opara. (2012).Application of Brine Concentrations as a Reconnaissance Geochemical tool for hydrocarbon Exploration.Case Study of Field ”X”,OML63,Coastal Swamp 1 Depobelt,Niger Delta Basin,Nigeria, 6(4), 46-48.
- Akinwale, Y. O. (2016).Harnessing science Technology and innovation for enhancing marginal oil and gas field development in Nigeria, A comparative analysis.*International journal of ebusiness and egovernment studies*,8(2), 2146 – 0744.
- Al- Ayedi, O. S. (2010).Study of the kinetics and mechanisms of thermal decomposition of Ellajjun oil shale, 3(2),1 -2.
- Almashramah, Y. A. (2011).Maturity of Kerogen, petroleum generation and the application of fossils and organic matter for paleo temperature measurement.Masters thesis in Geology at Lund University, 2(7), 6 – 8.
- American Chemistry Council.(2012).Environmental and Economic analysis of emerging plastics conversions technologies final project report.700 2nd street,NE,Washington DC 20002, 5(4), 6 -8.
- Al – Areeq, N. M. (2018). Petroleum sourcr rock characterization and hydrocarbon generation.Recent insight in petroleum science and engineering, 4(2), 12-14.
- Baudin F, Disnar J. R., Abousson, A., and Savignae, F. (2015).Guidelines for Rock –Eval analysis of recent marine sediments.Organic geochemisrtyelsevier halid:insu - 01170142, 5 - 34.

- Beatty, C., Barbara. L., James, M. B., Amy,C. S.,Nina ,C.,Shannon,D., and Linda, F.(2018).Fossil fuels to product, 2(3), 13 – 14.
- Bridgewater, A. V. (2012). Review of fast pyrolysis of Biomass and product Upgrading.Biomass and Energy 38, 68 – 94.
- Budinova, T., Huang, W. L., Racheva, I.,Tsyntsarski, B ., Petrova, B., and Yardim, M .F., (2014). Investigation of kerogen transformation during pyrolysis by applying a diamond anvil cell.Estonian Academy Publisher, 31(2), 122 - 123.
- Carthy, K. M., Niemann. M., Palmowski, D., Peters, K., and Stankiewicz A. (2011). Basic Petroleum Geochemistry For Source Rock Evaluation, 3(4), 38.
- Daud, W. M .A. (2014).Pyrolysis of mixtures of palm shell and polystyrene:an optional method to produce a high grade pyrolysis oil.Environmental progress and sustainable energy 33,1026.
- Edomah , N., Foulds,C., and Jones, A. (2016).The role of policy makers and institutes in the energy sector.The case of energy infrastructure governance in Nigeria.Global sustainability institutew,Anglia Ruskin University,Cambridge CBI IPT,UK information systems academy pan atlantic University lagos Nigeria, 4(3),1 – 2.
- James, S.G (2016). Introduction to enhanced recovery methods for heavy oil, 7-11. Elsevier.,
- Gai, R., Jin, L., Zhang, J.,Wang, J. and Hu, H. (2014).Effect of inherent and additional Pyrite on the pyrolysis behaviour of oil shale.*Journal of Analytical and Applied Pyrolysis*,5(2), 342 - 343.
- Gajica, G. D., Sajnovic, A. M., and Stojanovic, K. A. (2017).The influence of pyrolysis type on shale oil shale generation and its composition (Upper layer of Aleksinac oil shale).*Journal of Serbian Chemical Society*,82(12),1468 – 1471.
- Geologin, D. (2012).Geology and petroleum potentials of Nigeria sedimentary Basins, 6 (4), 12 -13.
- Godinez, L. J. (2014).Important Mineralogical Factors for liquids saturation,specific surface area and pore size distributions based on gas adsorption,cation exchange capacity and 2D dielectric microscopy.A case study of Quartz phase porcelanites in the miocene monetary formation, 3(2), 49 - 68.
- Gordon, D. (2012).Understanding unconventional oil energy and climate.carnegie endowment for international peace Washington D.C, 2(3), 6 - 8.
- Han, H., Zhong ,N, N.,Huang, C, X., and Zhang,W.(2015).Pyrolysis Kinetics of oil shale from Northeast China.Implications from Thermogravimetric and Rock Eval Experiments,159,776 - 777.

- Harns., and Dong. (2013).Characterizing porosity in the horn river shale,North Eastern British Columbia, 4(3), 33 - 38.
- Hillier, J .L .(2011).pyrolysis kinetics and chemical structure considerations of a green river oil shale and its derivatives.Brigham young University.BYU scholars archieve ,5(2), 3 – 4.
- Hook, M. (2009).Depletion and decline curve analysis in crude oil production.Licentiate thesis.Global energy system, 3(2), 20 - 32.
- Hussain, S.Z., and Maqbool, K. (2014).GCMS principle, technique and its application in food science.Division of post harvest technology,she –e –kashmir.University of Agricultural science and technology of kashmir india Int J curr sci 13, 2250 – 1770,1 – 2.
- Internatiional Energy Agency (IEA). (2013).Resources to reserves.Oil, gas and coal technologies for the energy markets of the future, 3(1), 17 -18.
- Jahirul, M. I, Rasul, M. G., Chowhurry, A. A., and Ashwath, N.(2015).Biofuels production through Biomass pyrolysis.A Technology Review.Energies, 5, 4952 – 5001.
- Kabir, G., and Hameed, B. H. (2016).Recent progress on catalytic pyrolysis of ligno cellulose Biomass to High Grade Bio-oil and Bio-chemicals.Renewable and Sustainable Energy Review, 21-23.
- Kok, M.V., and Ozgur .E. (2016).Combustion Performance and Kinetics of oil shales.Energy sources,part A:Recovery utilization and environmental effects, 38(8),1039 – 1047.
- Kolltveit, Y. (2016).Relationship between crude oil composition and physical chemical properties, 3 (3), 2 -3.
- Kurowska, E., and Schoeneich.K. (2010).Geothermal exploration in Nigeria.Proceeding world geothermal congress Bali.Indonesia, 3(4), 1 -2.
- Li & Yue. (2003). Study of Pyrolysis Kinetics of oil shale State Key lab of Heavy oil Processing,school of Chemical Engineering.University of Petroleum,Changping,Beijing 102200.People Republic of China,779-780.
- Lin, H., Tian, H and Wang, J.(2017).Pyrolysis Mechanism and Kinetics Model of Mudanjiang oil shale in the Songhow Basin.China.Energy Exploration and Exploitation,34(4), 504 -505.
- Maaten, B., Loo, L., Konist, A., Nesunajev, D., Pihu, T., and Kulaots, I. (2016).Decomposition kinetics of American,Chinese and Estonian oil shales kerogen Estonian Academy Publishers ,33(2),168 – 169.

- Mal. (2016). Multi-scale 3D imaging of the micro-structure in organic-rich shales.3 (2),98.
- Martinez, J. D., Vesses, A., Mastral, A. M., Murillo, R., Navarro, M. V., and Puy, N. (2014). Co-pyrolysis of Biomass with waste tyres: upgrading of liquid *Biofuel*. *Fuel Process Technology*, 119, 263-71.
- Melberg, H. (2010). Experimental study of low salinity EOR effects from the vary field. University of Stavanger faculty of science and technology. Masters thesis. 2 (1):12 -13.
- Nyantakyn, A. A. (2013). Structural and Stratigraphic Mapping of Delta Field, Agbada formation, off shore Niger Delta, Nigeria, 4(2), 34-38.
- Obaje, N. G., Balogu, D .O., Nda, A.I, Goro, I.A, Ibrahim, S.I, Musa, M. K., Dantata, S.H., Yusuf ,I., Dadi, N.M., and Kolo, I.A. (2013). *Preliminary Integrated Hydrocarbon Prospectivity Evaluation of the Bida Basin in north central petroleum Technology journal .An international journal ,3(2),37–42.*
- Obaje, N.G., Moumouni, A., Goki, N.G., and Chaada. (2011). Stratigraphy paleogeography and hydrocarbon resource potentials of the Bida Basin in north central Nigeria. *Journal of Mining and Geology*, 47 (21), 97 – 99.
- Ogunkeyede, A.O. (2016). Conventional and microwave pyrolysis remedation of crude oil contaminated soil. PhD thesis. University of Nottingham, 5(3), 8 - 84.
- Oluwatoni. (2017). Integrating Renewable Energy Into Nigerias Energy mix: Implications for Nigerias Energy Security, 3(3):12-13.
- Onal, E., Uzun ,B, B., and Putin, A. E. (2014). Bio-oil production via co-pyrolysis of Almond Shell as Biomass and high polyethylene. *Energy Conversion and Management* 78, 704-10.
- Osueke., and Ezugwu. (2011). Study of Nigeria Energy Resources and its Consumption. *International Journal of Scientific and Engineering Research*, 2(12), 17-18.
- Oyedepo, S. O. (2012). Renewable and Sustainable Energy Review journal, 5 (4), 2584 – 2585.
- Pradhan. (2012). Liquid fuel from oil seeds by pyrolysis. Department of Chemical Engineering. National Institute of Technology Rourkela, 5(3), 43.
- Rapu, S. C., Adenuga, O., Kanya, W.J., Abeng, M. O., Golit, P.D., Hilili, M. J., Uba, I.A., and Ochi. E.R. (2015). Analysis of energy market condition in Nigeria. Central Bank of Nigeria. Occupational paper, 2(55), 32 -35.

- Reyhaniash, E. (2013). Upgrading pyrolysis oil to produce liquid transportation fuels. Electronic thesis and dissertation repository. The University of Western Ontario, 2(3), 3- 4.
- Rice, U. (2013). The information of fossil fuels, 4(1), 2 – 6.
- Richard, U. (2012). Sand and fines in multiphase oil and gas production. Norwegian University of science and technology, 5(2), 1 -3.
- Brownsort., K.P. (2009). Co-pyrolysis of Karanja and Niger Seeds with waste polysterene to produce liquid fuels, 153, 492 – 498.
- Saifuddin, N., Bello, S., Fatihah, S., & Vigna, K.R. (2016). Improving electricity supply in Nigeria potential for renewable energy from biomass. *International Journal of applied engineering research*. 11(14), 8322 – 8323.
- Sambo, A. S. (2005). Renewable energy for rural development. The Nigerian perspective. *ISESCO science and Technology vision* 1, (12 – 22), 12 – 13.
- Sonibare, O. O., Ehinola, O.A., and Egashira .R. (2005). Thermal and geochemical characterization of lokpanta oil shales, Nigeria. *Energy conversion and management*, 46 (5), 2335 – 2336.
- Sorbo, I. G. (2016). Polar components in crude oils and their correlation to physiochemical propeerties master thesis in chemistry, 5(1), 1 -2.
- Sorensen, T. E. (2016). Catalytic Conversion of Kerogen in Enhanced oil Production from Shales. Norwegian University of Science and Technology, 3(2), 3-8.
- Stashenko, E., and Martinez .J.R. (2014). Gas chromatography mass spectrometry: [Research center for biomolecules, CIBMOL, CENIVAM, Universidad industrial de santander, Bucaramanga colombia](#), 4(3), 2 -3.
- Kumar., and Singh. (2011). Basic Petroleum Geochemistry for Source Rock Evalution. As the search for oil and gas prospects grows increasingly complex 3(4), 32- 34.
- Tian, H., Zhang, J., and Wang, J. (2018). Characteristics of oil shale pyrolysis in two stage fluidized bed China. *Journal of Chemical Engineering*, 24(6), 407-408.
- Tiwari., and Deo .(2012). Compositional and Kinetic analysis of oil shale pyrolysis TGA-MS, 94, 333-334.
- Tiwari, P., Bauman, J., and Deo, M. (2011). Mathematical modelling of oil shale pyrolysis. Institute for clean and secure energy. The University of Utah and Petroleum Research Center College of Engineering, 3(1), 4-5.

- Tsepav, M.T., and Mallam, A. (2017).Spectral depth analysis of some segments of the Bida Basin.Nigeria using aeromagnetic data.*Journal of applied science environmental management*,21(7),1331 – 1332.
- Wang, J. (2013).Effect of heating rate on products yields and characteristics of non-condensable gases and shale oil obtained by the retorting Dachengzi oil shale, 5(2), 49-50.
- Wijayapala, R., Karunanayake, A. G., Proctor, D., Yu, F., Pittman, C.U., and Misna, T. E. (2015).Hydrodexoxygenation (HDO) of Bio- oil Model Compounds with Synthetic Gas using a Water-Gas Shift Catalyst with a Mo/Co/K Catalyst.W –Y.Chem et al.(eds).Handbook of Climate Change Mitigation and Adaptation, 10,14 -6431- 0-79-1.
- World Energy Resources. (2016).Global Oil Demand by region from 2014-2018,2(3), 4-5.
- Yeboah, I. (2015).Characterization and thermal/Catalytic upgrading of kerogen in a Green River Oil Shale.Norwegian University of Science and Technology,2(1),16 -30.
- Zhao, L., Qiu, X., Han, D. H., Geng, J., Yang, Z., and Cao, H. (2016).Rock-Physics Modelling for the elastic properties of organic shale at different maturity stages.*Geophysics Journal*, 81(5),D527-D532.

APPENDIX

Appendix A: Analysis of Rock Eval Pyrolysis

TOC- Total Organic Carbon wt %

S1- Volatile hydrocarbon (HC) content, mg HC / g rock

S2- Remaining HC generative potential, mg HC / g rock preparation

S3- Carbon dioxide, mg CO₂ / g rock

Meas of %R- Measured vitrinite reflectance

HI-Hydrogen Index = $S2 \times 100 / TOC$, mg HC / g TOC

OI- Oxygen Index = $S_3 \times 100 / \text{TOC, mg CO}_2 / \text{g TOC}$

PI- Production index = $S_1 / (S_1 + S_2)$

Tmax- Maximum Temperature at S2 peak

Genetic Potential = $(S_1 + S_2)$

TR- Transformation Ratio = $T_{\text{max}} \times S_1 / (S_1 + S_2)$

Appendix B: List of Compounds Identified GCMS Analysis of liquid products

Compound	Formula	R.T
Pyridine, 2, 6-dimethyl	C ₇ H ₉ N (3.51%)	5.406
Pyridine, 2-ethyl	C ₇ H ₉ N (1.62%)	6.044
Butyrolacetone	C ₄ H ₆ O ₂ (7.18%)	6.257
Pyridine, 2, 5-dimethyl	C ₇ H ₉ N (4.18%)	7.070

Pyridine, 2-ethyl-6-methyl	C ₈ H ₁₁ N (2.77%)	8.227
Phenol	C ₆ H ₅ OH (25.96%)	9.559
Phenol, 2- methyl	C ₇ H ₈ O (4.68%)	12.318
Phenol, 2- methoxy	C ₇ H ₈ O ₂ (11.24%)	12.819
Phenol 2, 6- dimethoxy	C ₈ H ₁₀ O ₃ (38.86%)	22.239

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	5.406	46	51	78	rVB3	403770	2186897	9.02%	3.506%
2	6.044	144	153	166	rBV3	196836	1008917	4.16%	1.618%
3	6.257	168	187	205	rVV	730069	4477569	18.48%	7.179%
4	7.070	311	317	348	rBV4	293051	2609132	10.77%	4.183%
5	8.227	496	502	536	rVB4	273056	1730144	7.14%	2.774%
6	9.559	689	715	719	rBV3	2564619	16190869	66.81%	25.960%
7	12.318	1129	1156	1159	rBV5	420019	2921483	12.05%	4.684%
8	12.819	1224	1236	1285	rVB4	660410	7008868	28.92%	11.238%
9	22.239	2727	2742	2800	rBV3	1548212	24235595	100.00%	38.858%

Sum of corrected areas: 62369474

Unknown Spectrum: Apex minus start of peak
 Integration Events: RTE Integrator - lscint.e

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	5.406	3.51	C:\Database\NIST11.L			
			Pyridine, 2,6-dimethyl-	5196	000108-48-5	95
			Pyridine, 2,6-dimethyl-	5195	000108-48-5	94
			Pyridine, 2,6-dimethyl-	5183	000108-48-5	86
2	6.044	1.62	C:\Database\NIST11.L			
			Pyridine, 2-ethyl-	5164	000100-71-0	87
			Pyridine, 2-ethyl-	5171	000100-71-0	86
			Pyridine, 2-ethyl-	5172	000100-71-0	70
3	6.257	7.18	C:\Database\NIST11.L			
			Butanoic acid, 4-hydroxy-	4696	000591-81-1	83
			Butyrolactone	1649	000096-48-0	83
			Butyrolactone	1651	000096-48-0	78
4	7.070	4.18	C:\Database\NIST11.L			
			Pyridine, 2,5-dimethyl-	5198	000589-93-5	94
			Pyridine, 2,5-dimethyl-	5184	000589-93-5	94
			Pyridine, 2,5-dimethyl-	5197	000589-93-5	91
5	8.227	2.77	C:\Database\NIST11.L			
			Pyridine, 2-ethyl-6-methyl-	9627	001122-69-6	87
			Pyridine, 2-ethyl-6-methyl-	9632	001122-69-6	64
			Acetamide, N-(4-formylphenyl)-	33176	000122-85-0	53
6	9.559	25.96	C:\Database\NIST11.L			
			Phenol	2592	000108-95-2	91
			Phenol	2591	000108-95-2	90
			Phenol	2593	000108-95-2	86
7	12.318	4.68	C:\Database\NIST11.L			
			Phenol, 2-methyl-	5374	000095-48-7	87
			Phenol, 2-methyl-	5380	000095-48-7	87
			Phenol, 2-methyl-	5379	000095-48-7	87
8	12.819	11.24	C:\Database\NIST11.L			
			Phenol, 2-methoxy-	10417	000090-05-1	91
			Phenol, 2-methoxy-	10420	000090-05-1	91
			Phenol, 2-methoxy-	10418	000090-05-1	91
9	22.239	38.86	C:\Database\NIST11.L			
			Phenol, 2,6-dimethoxy-	27407	000091-10-1	96
			Phenol, 2,6-dimethoxy-	27403	000091-10-1	94
			Phenol, 2,6-dimethoxy-	27406	000091-10-1	90

