PYROLYSIS OF SHEA BUTTER SHELL TO PRODUCE BIO-BASED PRODUCTS

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ABSTRACT

This research work focused on the production of bio-based products and response optimization of bio-oil yield operating parameters from shea butter shell. The Thermogravimetry Analysis (TGA) was used to determine the thermal stability of the shea butter shell and found to be stable at temperature 400 °C. Also, for the bio-char produced, it was found to be stable at temperature 700 °C. Design of Experiment (DOE) was applied to establish optimal pyrolysis conditions for the biomass (shea butter shell) using 2^3 factorial design module of Response Surface Methodology (RSM) available in Design Expert® Software version 7.0.0. Furthermore, the effect of temperature (300-600 °C), residence time (10-60 min), and heating rate (10-30 °C/min) at constant feedstock mass of 100g per run was studied. The results of operating variable effects shows that bio-oil yield depends on significant variables of the process. Temperature and heating rate were found to be significant to obtain optimum bio-oil yield experimentally. Optimum yield of the study was 51.50 %wt. against 71.00 %wt. of the predicted model. Physicochemical analysis shows that the bio-oil has pH 3.14 and Heating values of 26.03 MJ/kg. The Gas Chromatogram revealed phenolic and carboxyl compounds are dominant in the bio-oil with alcohol, ketones, aldehydes and aliphatic hydrocarbons were equally present. Characterization of the bio-based products using Fourier-Transform Infra-Red (FTIR) revealed that bio-oil contains predominantly the organic functional groups of alkanes, alcohol, acids, aldehydes, ketones, some phenolic compounds and water impurities from the studies. Bio-char was characterized to determine the external surface area and BET surface area, following values were obtained 196.022 m^2/g and 170.025 m^2/g. Moreover, the values obtained for the pore volume and pore size of the bio-char were 0.0055cm^3/g and 1.410 nm respectively. Bio-char from shea butter shell pyrolysis can be upgraded as potential adsorbent in waste water treatment as bio-adsorbent.

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LIST OF ABBREVIATIONS, GLOSSARIES AND SYMBOLS

ANOVA   Analysis of Variance

ATR   Attenuated Total Reflectance

BET   Bruneuer Emmett Teller

C   Carbon

CCD   Central Composite Design

CV   Coefficient of Variation

CSP   Concentrate Solar Power

DOE   Design of Experiment

FF   Fossil Fuel

FTIR   Fourier Transform Infra-Red

GC-MS   Gas Chromatography Mass Spectroscopy

GHG   Green House Gases

H   Hydrogen

HHV   High Heating Value

LPG   Liquefied Petroleum Gas

LHV   Low Heating Value

N   Nitrogen

O   Oxygen

PV   Photovoltaic

PEG   Polyethylene Glycol

RSM   Response Surface Methodology

S   Sulphur

SEM-EDX   Scanning Electronic Machine with Electron Disperse X-ray

SBS   Shea Butter Shell

TGA   Thermogravimetry Analysis

TR   Tubular Reactor

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

World patronage of a particular energy source depends on its availability, accessibility of technology, quantity of energy obtainable and fuel source. Fossil fuels is the primary source of energy supply worldwide. However, the use of fossil fuel energ is associated with emission of gases which have negative impact on the environment, finding an alternatives use of environmental friendly and economical viable renewable sources of energy and chemicals become necessary (Yaman, 2004; Smets *et al*., 2013).

Biomass is a renewable resource with great potential as an alternative to fossil fuels for supplying energy (Kumar *et al*., 2009; Garba *et al.,* 2018). The potential of biomass to supply much larger amounts of useful energy with reduced environmental impacts compared to fossil fuels has stimulated substantial research and development of systems for handling, processing, and converting biomass to heat, electricity, solid, liquid and gaseous fuels, and other chemicals and products. The use of biomass to substitute fossil resources results in low sulphur dioxide emissions and almost no net atmospheric carbon emissions. Hence, it serves to mitigate greenhouse gases (GHG) and global climate change impact (Kumar *et al*., 2009).

Biomass has the potential to offer alternative sources of energy and chemicals, with agricultural wastes being better alternative to residues from consumable food products. Agricultural waste could be converted into chemicals by thermochemical conversion processes such as combustion, gasification and pyrolysis (Bulushev and Ross, 2011).

Shea butter shells are a major source of agricultural waste in West Africa and were used as raw material. It is non consumable for both man and animal. Therefore, use of shea butter shell as

biomass for alternative source of energy will help in the environmental waste management (Noumi *et al.* 2013; Ouedraogo, 2017).

However, the pyrolysis process is regarded as a promising process for the biomass utilisation at suitable operating process parameters. The process offers an important opportunity for the utilisation of the biomass from agricultural and forestry residues. (Auta *et al.*, 2014).

Pyrolysis is a thermal conversion process in the absence of oxygen, at atmospheric pressure and temperature range of (300-600 °C). It has been practiced for thousands of years to produce charcoal by slowly heating at temperature ranging between 300 °C and 400 °C, which is known as slow pyrolysis (Tamer *et al*., 2018). High temperature and longer residence time favours the formation of gas than liquid fuels, this technology is known as gasification (Venderbosch, *et al.,* 2011; Garba *et al.,* 2018). Fast pyrolysis is the volatilisation of biomass at high temperature (400-700 °C) and heating rate (50-1000 °C/min) under inert atmosphere (Demirbas *et al.*, 2008).

Fast pyrolysis is an irreversible thermo-chemical process in which a biomass is thermally heated at high temperature in the absence of oxygen, whereby the biomass decomposed and can be separated into distinct fractions of bio-oil, char and gas. Fast pyrolysis processes produce 40-75 wt. % of liquid bio-oil, 15-25 wt. % of solid char, and 10-20 wt. % of non-condensable gases, depending on the feedstock used (Demirbas *et al.*, 2008).

Many studies had been carried out to determine the operating parameters that influence the distribution of pyrolysis products as well its composition. Temperature, heating rate, residence time, biomass initial moisture content, particle size, and type of biomass are parameters that can affect the yield of the pyrolysis products (Hu *et al*., 2018). Therefore, it is important to study the effects of these parameters in order to optimise the pyrolyzed products from biomass shea butter shell (SBS) (Chadwick *et al.*, 2014; Heidenreich and Foscolo, 2015).

1.2 Statement of Research Problem

 The challenge of finding an alternative source of energy to meet global demand of energy need to be considered. Exploring the potential of Shea Butter Shell (SBS) biomass to produce bio-oil. However, protection of environment against emission from fossil fuel based energy with use of eco-friendly bio-energy from biomass has been consider for this research study.

1.3 Aim and Objectives

The aim of this study was to evaluate the potential of Shea Butter Shell (SBS) as a source of bio-based products. This was achieved through the following objectives:

1. To characterise shea butter shell (SBS) for its proximate, ultimate and thermal properties; heating values and stability temperature.

2. To evaluate the effects of pyrolitic operating conditions (temperature, heating rate and residence time) on the yield of the bio-oil.

3. To evaluate the optimal devolatisation operating parameters (temperature, heating rate and residence time) on the yield of the bio-oil.

4. To determine the physicochemical properties of the bio-oil produces from shea butter shell (SBS).

1.5 Justification

It was projected that the global supply of energy reserves of fossil fuel may be exhausted by 2050 (McKendry 2002; Sexana *et al.,* 2009). Biomass from shea butter shell (SBS) have high utilisation potential among renewable energy resources. It is cheap and largely available in most

rural communities in Nigeria with no secondary usage after it has been removed from the kernel. Therefore, bio-oil from this biomass as a close substitute for the depleting fossil fuel, is very promising to halt the increase of carbondioxide, CO_2 concentration in the atmosphere.

1.6 Scope of the Research

The scope of this research is to develop a novel scientific framework and operating parameters for the efficient conversion and utilisation of shea butter shell biomass to obtained optimal bio-oil yield in a laboratory scaled pilot plant (pyrolyser).

CHAPTER TWO

2.0   LITRATURE REVIEW

2.1 Energy Sources, Demand and Consumption

Biomass has the potential to serve as sources of energy and chemicals, with agricultural wastes being rated as a better alternative than the use of biomass that can be consumed as food. Agricultural waste could be converted into chemicals by hydrolysis or thermochemical routes (Bulushev and Ross, 2011).

Various fuels use different technologies to produce various energy forms for example heat, light and electricity. Fuel affordability and availability determine user fidelity of energy conversion technologies. Hence, the regular use of wood and charcoal in most developing countries especially in Africa is influenced by these factors. Domestic energy demand in sub-Saharan Africa in 1994 was 63 % and 9 % dependence on wood and charcoal respectively. In 2019, more than two billion world population uses wood for cooking and heating particularly in household in the developing countries (Bulushev and Ross, 2011; FAO, 2019).

The world population growth increases waste production with a corresponding demand and consumption for foods, fuel and other forms of energy. The recovery of combustible materials from waste for energy production minimizes the dependence on wood reducing deforestation (Forbid, 2012).

The statistics of energy consumption percentage in Sub-Sahara Africa is as shown in Figure 2.1 (Forbid, 2012).
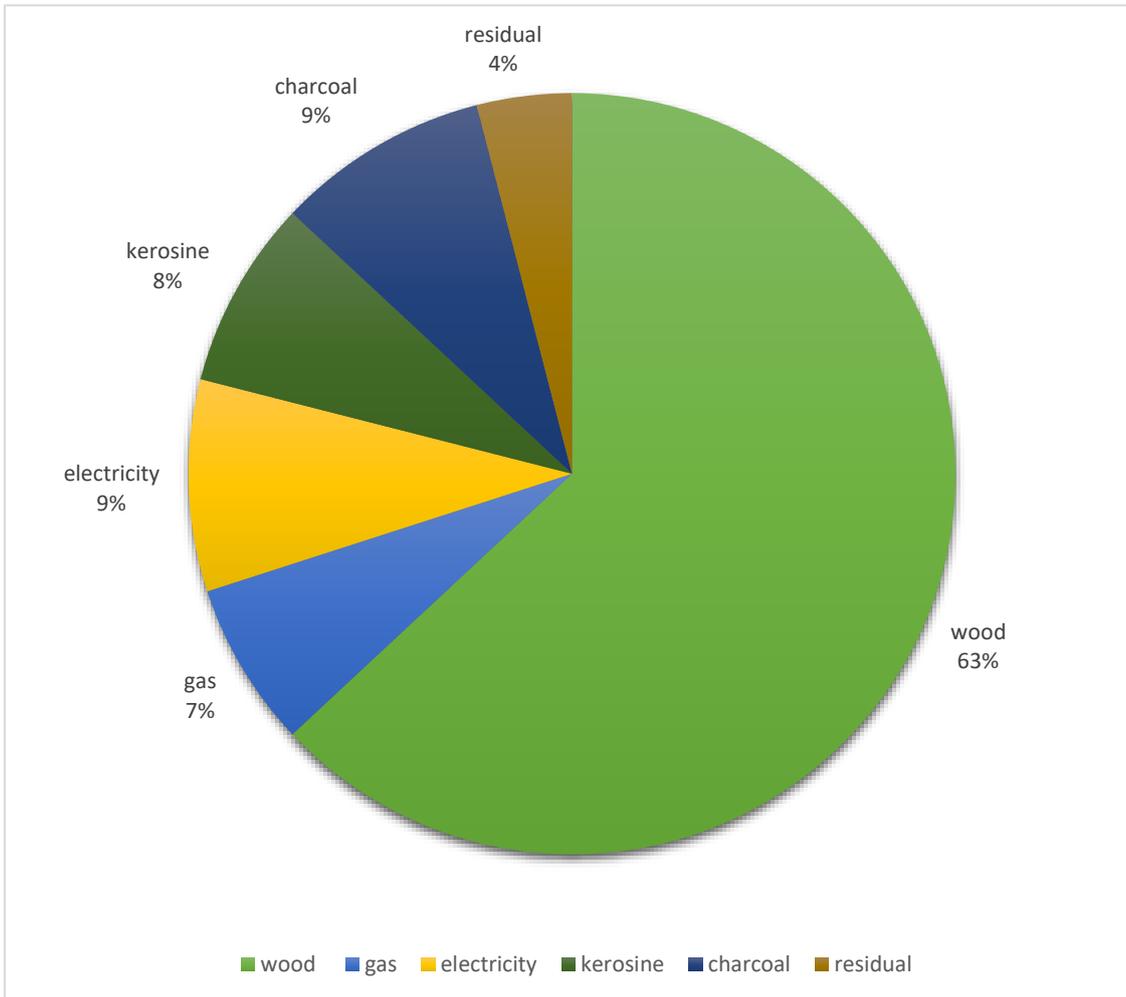
Figure 2.1: The chart with energy consumption percentage in Sub-sahara Africa in 1994

2.2 Renewable Energy Sources

There are many renewable sources of energy such as solar energy, geothermal energy, wind power, hydropower and biomass (Michaelides, 2012). Renewable resources have become gradually more important with several factors affecting the global population, the planet, the quality of life, etc. Some of these factors are: increasing demand of world energy, increase in oil prices, global warming due to emission of GHG, waste recycling that is becoming more costly

and problematic, population growth that will require more energy and consumer products (Zabaleta, 2012).

The world energy demand chart from year 1987 to prospect of year 2035 is as shown in Figure 2.2 (WEO, 2013).
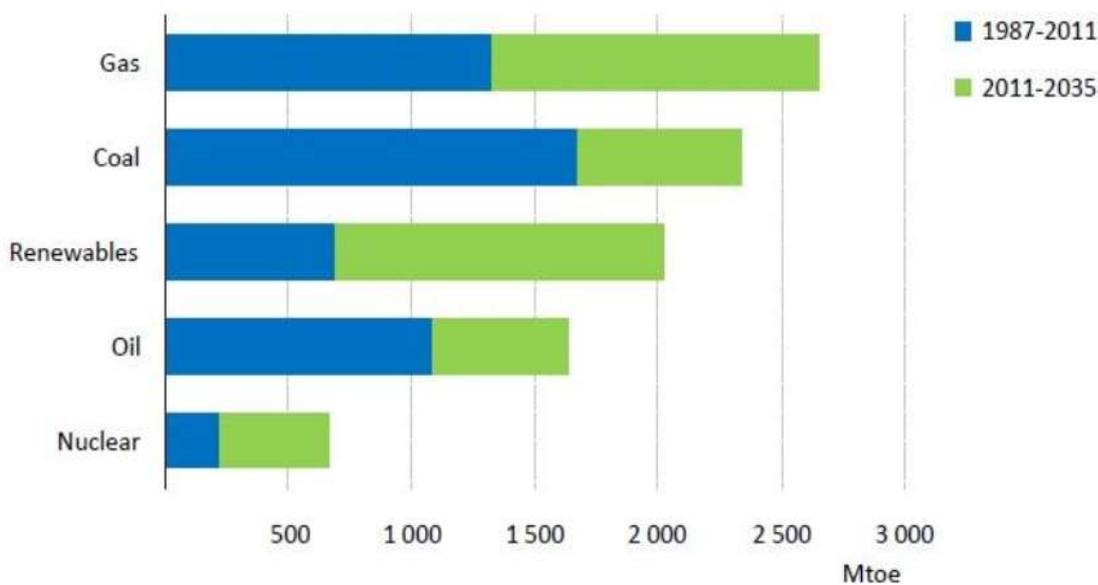
Figure 2.2: The world energy demand chart

2.2.1 Direct solar energy

The word "direct" solar energy refers to the energy base for those renewable energy source technologies that draw on the Sun's energy directly. Some renewable technologies, such as wind and ocean thermal, use solar energy after it has been absorbed on the earth and converted to the other forms. Solar energy technology is obtained from solar irradiance to generate electricity using Photovoltaic (PV) (Asumadu and Owusu, 2016) and Concentrating Solar Power (CSP), to produce thermal energy, to meet direct lighting needs and, potentially, to produce fuels that might be used for transport and other purposes (Edenhofer *et al.,* 2011).

2.2.2 Geothermal energy

Geothermal energy is obtained naturally from the earth's interior as heat energy source. The origin of the heat is linked with the internal structure of the planet and the physical processes occurring there. Although heat is present in the earth's crust in huge quantities, not to mention the deepest parts, it is unevenly distributed, rarely concentrated, and often at depths too great to be exploited mechanically (Haman, 2015).

2.2.3 Wind energy

The emergence of wind as an important source of the World's energy has taken a commanding lead among renewable sources. Wind exists everywhere in the world, in some places with considerable energy density (Manwell *et al.,* 2010). Wind energy harnesses kinetic energy from moving air. The primary application of the importance to climate change mitigation is to produce electricity from large turbines located onshore (land) or offshore (in sea or fresh water) (Asumadu *et al.,* 2016).

2.2.4 Hydropower

Hydropower is an essential energy source harnessed from water moving from higher to lower elevation levels, primarily to turn turbines and generate electricity. Hydropower projects include Dam project with reservoirs, run-of-river and in-stream projects and cover a range in project scale (Asumadu *et al.,* 2015). Hydropower technologies are technically mature and its projects exploit a resource that vary temporarily. The operation of hydropower reservoirs often reflects their multiple uses, for example flood and drought control, irrigation, drinking water and navigation (Edenhofer *et al.,* 2011).

2.2.5 Bio-energy

Bio-energy is a renewable energy source derived from biological sources. Bio-energy is an important source of energy, which can be used for transport using biodiesel, electricity generation, cooking and heating. Electricity from bio-energy attracts a large range of different sources, including forest byproducts such as wood residues; agricultural residues such as sugar cane waste; and animal husbandry residue such as cow dung (Twidell and Weir, 2015).

One advantage of biomass energy-based electricity is that fuel is often a by-product, residue or waste product from the above sources. Significantly, it does not create a competition between land for food and land for fuel (Urban and Mitchell, 2011).

2.3 Biomass Composition

Biomass have more chemical compounds than coal. Biomass contains three distinctly different building blocks, that is, cellulose, hemicellulose and lignin. The cellulose and hemicellulose are quite different from coal structures while the lignin has more resemblance with coal, containing aromatic moieties (Solomon *et al.,* 1993; Bassilakis *et al.,* 2001). Cellulose consists largely of anhydrous glucose held together in a giant straight-chain molecule bound by $β$-(1,4)-glycosidic linkages (Demirbas, 1999).

Unlike cellulose, hemicellulose consists of different monosaccharides. The polymer chains of hemicellulose have short branches and are amorphous, leading to the partial water solubility. Lignins are polymers of aromatic compounds, which provide structural strength and sealing of the water-conducting system that links roots with leaves, and protect plants from degradation. Lignin occurs throughout the plant cell wall, yet is largely concentrated in the primary cell wall and middle lamella (Adler *et al.,* 2013).

Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure, consisting primarily of three units: guaiacyl (G), sinapyl (S), and p-hydroxyphenyl (H)

units linked by aryl ether or C-C bonds (Zeng *et al.,* 2014). Grass lignin which is different from those of softwood or hardwood. Furthermore, hydroxycinnamic acids, mainly p-coumaric and ferulic acids can be present in grasses (Sun *et al.,* 2010).

Additionally, both wood and herbaceous in biomasses contain high amounts of extractives which affect the biomass mechanical strength. In grasses, waxes (up to 30 % dB) are located in the plant's cuticula, whereas softwood may incorporate resin acids, fatty acidsn sterols, and alcohols and rest compounds (2-15 %wt.) (Ross *et al.,* 2012). Wood and grasses contain the lipid and protein fractions in a lower concentration than the carbohydrate components. The protein fraction in herbaceous biomasses (up to 12.3 %wt.) is higher than in wood (up to 2.1 %wt.) as reported (Klass, 1998).

Besides the organic components in biomass, the inorganic matter is dispersed throughout the cells. Coal incorporates a high level of transition metals, while biomass contains more alkali and alkali-earth metals, usually in the form of salts. Herbaceous biomasses contain significantly higher amounts of potassium (K) and chlorine (Cl) than wood and coal. The high presence of potassium chloride (KCl) in herbaceous biomass could cause high-temperature corrosion that limits the superheater temperature and decrease thereby the power plant efficiency. Biomass contains less sulfur than coal, leading to lower sulfur emissions (Dasappa, 2011).

2.3.1 Cellulose

Cellulose is a complex carbohydrate which consists of unbranched chains of linked glucose unit. Cellulose is found to be a major component of the plant cell walls. It is a glucose-

based polysaccharide and the repeating unit of the cellulose polymer consists of two glucose anhydride units, called as cellobiose unit (Mc Kendry, 2002).

Cellulose has the general formula $(C_6H_{10}O_5)_n$ and there are covalent bond, hydrogen bond and Van Der Waals forces of attraction within the polymer. Besides, cellulose is a strong substance because the straight-chain molecule hydrogen bonds, forming a pseudocrystalline structure which gives rigidity to the structure. Cellulose is odourless, insoluble in water and most organic solvents. It can be broken down chemically into its cellubiose units by treating it with concentrated acids at high temperature (Mohan *et al*., 2006).

Cellulose forms long chains that are bonded to each other by a long network of hydrogen bonds. Groups of cellulose chains twist in space to make up ribbon-like micro-fibril sheets, which are the basic construction units for a variety of complex fibers. These micro-fibrils form composite tubular structures that run along a longitudinal tree axis. The crystalline cellulose structure resists thermal decomposition better than hemicelluloses (Mohan *et al*., 2006).

2.3.2 Hemicellulose

Hemicelluloses are a heterogeneous class of polymers representing, in general, 15-40 % of plant biomass and which may contain d-xylose, d-mannose, d-glucose, dgalactose, l-arabinose, d-glucuronic acid, 4-0methyl-d-glucuronic acid (MeGlcA), d-galacturonic acid, and to a lesser extent, l-rhamnose, l-fucose, and various 0methylated sugars (Mohan *et al*., 2006).

The chemical structures of the main components of hemicelluloses has been reported (Doherty *et al.,* 2011). Their molecular weights are usually lower than that of cellulose and they have a weak undifferentiated structure compared to crystalline cellulose. The most abundant hemicelluloses are xylans and glucomannans. Xylans are the main hemicellulose components of secondary cell walls constituting about 20-30 % of the biomass of hardwoods and herbaceous plants. Xylans are usually available in huge amounts as by-products from forest, agriculture, agro-industries, wood

and pulp and paper industries. Mannan-type hemicelluloses like glucomannans and galactoglucomannans are the major hemicellulosic components of the secondary wall of softwoods whereas in hardwoods they occur in minor amounts (Doherty *et al.*, 2011).

2.3.3 Lignin

As a major cell wall component, lignin provides rigidity, internal transport of water and nutrients and protection against attack by microorganisms. Lignin is an amorphous polymer consisting of phenylpropane units, and their precurcors are three aromatic alcohols (monolignols) namely p-coumaryl, coniferyl and sinapyl alcohols. The respective aromatic constituents of these alcohols in the polymer are called p-hydroxypheny1, guaiacy1 and syringy1 moieties. Wood lignins mainly contain guaiacyl and syringy1 units, whereas the lignins of herbaceous plants contain all three units in significant amounts with different ratios (Mohan *et al*., 2006; Doherty *et al.*, 2011).

2.3 Structural Representation of Biomass Compositions

Lignocellulosic material is the non-starch, fibrous part of plant materials. The most abundant low-tech source of biomass is trees. Wood fuel can be derived from conventional forestry practice such as thinning and trimming as part of sustainable management of wood land to ensure the production of high-quality timber for construction and wood products (Jansen, 2013).

The main advantages of its utilization focus on the natural structures and structural elements that are being preserved, on the raw materials that are inexpensive, on the large product varieties that are possible and on the fact that there is no competition with food production (Zabaleta, 2012).

The chemical structure of cellulose, hemicellulose and lignin in biomass are as shown on Figure 2.3 (Doherty *et al*., 2011).
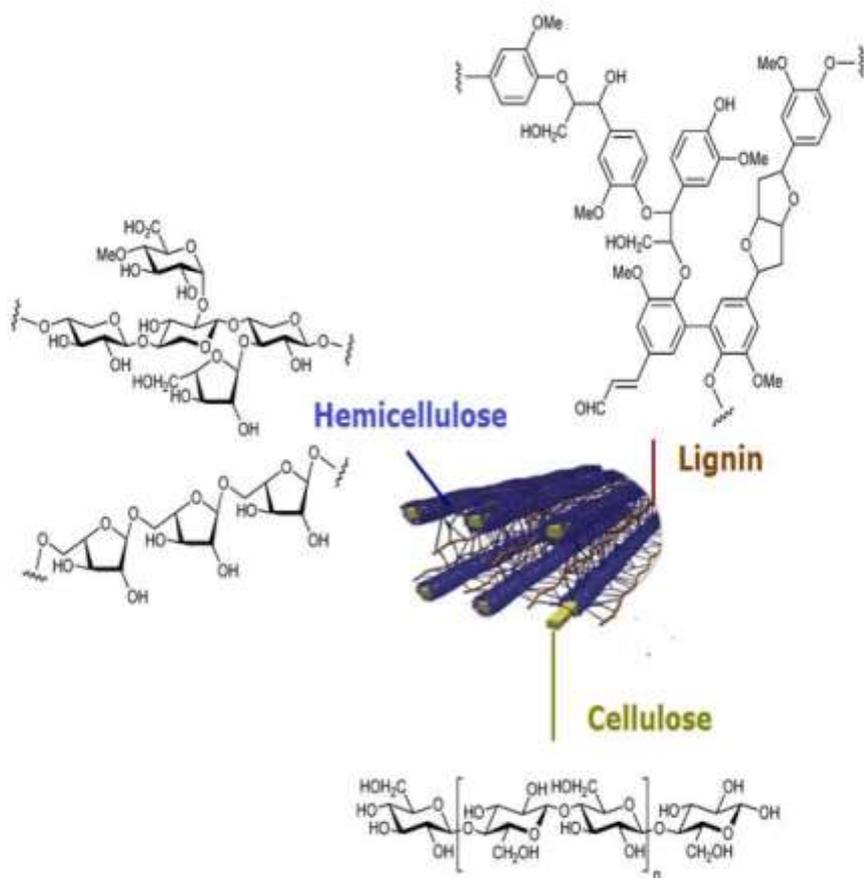
Figure 2.3: Model representation of cellulose, hemicelluloses and lignin in lignocellulosic biomass

2.4 Shea Shell Biomass

Shea butter tree (*Vitellaria paradoxa*) is a parkland woody tree, which is not commonly cultivated. It grows wild extensively in the dry savannah belt of West Africa, stretching from Senegal, Ghana, and Nigeria in the west to Sudan in the east (Bernice, 2011). Shea butter tree is one of many indigenous fruit trees which although not grown domestically but plays an important role in sustaining the livelihoods of people living in the villages areas. Shea butter trees attains maturity during March to April, and the fruit become matured in June to July (Alander, 2004).

The fruit are harvested during June to September once they fall to the ground from the trees or sometimes forced to fall and harvest (Alander, 2004). Shea fruit consist of a green epicarp (the

outer part), a fleshy mesocarp (pulp), and a relatively hard endocarp (shell) containing embryo (shea kernel). The shell is always removed from the nut and disposed around rural without any use which eventually lead to land pollution (Olaniyan *et al.,* 2007).

2.5 Concept of Pyrolysis of Biomass

Pyrolysis is a thermal conversion process in the absence of oxygen, at atmospheric pressure and temperature range of 300-600 °C. It have been practiced for thousands of years to produce charcoal by slowly heating at temperature ranging between 300 and 400 °C, which is known as slow pyrolysis. High temperature and longer residence time favours the formation of gas than liquid fuels. This technology is known as gasification. Fast pyrolysis was conducted at moderate temperature of 500 °C and short vapour residence time of 15 minutes (Venderbosch, *et al.,* 2011; Bridgwater, 2012).

The process can be adjusted to favour the formation of charcoal, pyrolysis oil or gas. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Converting the solid biomass into liquid fuels, solid chars and non-condensable gases via pyrolysis have been experiencing rapid developments during the last decades (Bridgwater, 2004; Acikgoz and Kockar, 2007).

2.6 Reaction Conditions and Mechanisms of Pyrolysis

Pyrolysis is a thermochemical process and conversion in which the biomass feedstock is heated in an oxygen free atmosphere at around 500 °C to produce gas, liquid and solid products. The liquid product of the process which is also called bio-oil, usually the target product because of its eligibility to be used in applications as a substitute to those of petroleum oil such as heat and power generation. It can also be used as a feedstock for chemicals and transportation fuels production. The gas product is a mixture of mainly carbonmonoxide (CO), hydrogen (H_2),

carbondioxide (CO_2), and some low molecular weight hydrocarbons such as methane. Regarding the product distribution and quality, it has been strongly believed that the pyrolysis of biomass constituents is a superposition of three primary mechanisms and secondary mechanisms (Van de Velden *et al.,* 2010; Collard and Blin, 2014). The primary mechanisms which are:

2.6.1 Char formation

This reaction pathway is favoured at low reaction temperatures, below 500 °C, and low heating rates (Collard and Blin, 2014). It is characterised by rearrangement reactions leading to the formation of a thermally stable solid product called bio-char which has a polycyclic aromatic structure. Water and incondensable gases are formed as a result of these rearrangement reactions (Van de Velden *et al.,* 2010; Collard and Blin, 2014).

2.6.2 Depolymerisation

This pathway involves the breakage of the bonds between the monomer units leading to the formation of shorter chains. Depolymerisation continues until the produced molecules become volatile at the operating conditions (Collard and Blin, 2014). Cellulose depolymerisation leads to the formation of levoglucosan as the primary product with concentration up to nearly 60 % (Demirbaş, 2000; Patwardhan *et al*., 2011).

2.6.3 Fragmentation

This involves the breakage of covalent bonds including those within the monomer units leading to the formation of low MW molecules and incondensable gases (Collard and Blin, 2014). This pathway is favoured at high temperatures of 600 °C and more (Van de Velden *et al*., 2010).

2.7 Pyrolysis Types, and Thermal Conversion Process

The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this

process; thermal decomposition of organic components in biomass starts at 350-550 °C and goes up to 700-800 °C in the absence of air/oxygen (Fisher *et al*., 2002).

However, type of pyrolysis process depends on the operating condition parameter, pyrolysis can be classified into four main categories: ablatives, conventional slow, fast and flash pyrolysis. These differ in process temperature, heating rate, solid residence time and biomass particle size. However, relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters (Fisher *et al*., 2002).

2.7.1 Ablative pyrolysis

The concept of this technology is different from the others in that instead of using a heat carrier, the biomass particles are contacted with a hot metal surface (Oasmaa *et al.,* 2015). The char layer formed on the particle's surface during the reaction is continuously removed as a result of an ablative force applied on the particle through either high gas velocity flowing tangentially to the reactor walls (gas ablation) or mechanically using a rotary disc/blade (Ringer *et al.,* 2006; Bridgwater, 2012).

2.7.2 Fast pyrolysis

Pyrolysis is a thermochemical process in which materials are converted into solid (bio-char), liquid (bio-oil), and gaseous products (non-condensable) under an inert environment (Bridgwater, 2012; Eom *et al.,* 2012). Fast pyrolysis can produce up to 80 % bio-oil, 12 % bio-char, and 13 % non-condensable gas at temperature around 500 °C, with high heating rates, a short vapour residence time of about 1 s, and rapid cooling of volatiles (Bridgwater, 2012).

2.7.3 Slow pyrolysis

Biomass is pyrolysed at slow heating rates (5-7 K min^{-1}). This leads to less liquid and gaseous product and more of char production. Significant amount of work has been done on this process.

It was reported that in Japan and Latvia that slow pyrolysis was conducted using sugarcane bagasse for char production and obtained 23-28% yield of charcoal (Zendersons *et al*., 1999).

2.7.4 Combustion

The biomass is directly burnt in the presence of air to convert chemical energy stored in biomass into heat, mechanical power, or electricity. It is possible to burn any type of biomass but in practice, combustion is feasible only for biomass with moisture content of $< 50\%$. Combustion process has got many disadvantages. Biomass rarely arises naturally in an acceptable form of burning. In most of the cases it requires some pretreatment like drying, chopping and grinding. Which in turn is associated with financial costs and energy expenditure (Bridgwater, 2000; McKendry, 2012).

2.7.5 Gasification

In this process, biomass is converted into a combustible gas mixture by the partial oxidation of biomass at high temperature, in the range 800-900 °C. The biomass is heated in insufficient supply of air. The reactions are as follows. (Bridgwater, 2000)

$$C + O_2 \rightarrow CO_2, \tag{2.1}$$

$$C + \frac{1}{2}O_2 \rightarrow CO, \tag{2.2}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2, \tag{2.3}$$

$$CO_2 + C \rightarrow 2CO. \tag{2.4}$$
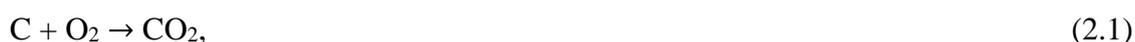
Methane and hydrogen are also formed simultaneously by thermal splitting of organic material.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \tag{2.5}$$

2.7.6 Torrefaction

Torrefaction on the other hand, is a mild pyrolysis process usually carried out in an inert environment at a temperature between 200 and 300 °C for a certain period of time. Pre-treated sample from this approach is easier to handle, thereby making it less energy intensive. This technique is generally employed to improve the characteristics of a solid fuel relative to the original biomass for combustion and gasification applications (Chen *et al.,* 2015).

2.8 Bio-oil

Bio-oil is found to be the main product of fast pyrolysis. It is a substance with many components in its mixture of different size molecules obtained from the thermal depolymerization and fragmentation of cellulose, hemicelulose and lignin (Czernik *et al*., 1997; Zhang *et al.*, 2007). Review have shown that properties of bio-oil have been studied in several publications. Also there are several chemical groups in bio-oil, including ketones, aldehydes, alcohols, acids, esters, sugars, phenolics, furan and other multifunctional compounds (Diebold, 2002).

2.9 Bio-char

Bio-char is also obtained from fast pyrolysis of biomass but rather the main component of slow pyrolysis that occur at temperature less the 400 °C. Bio-char is a porous carbonaceous solid material with a high degree of aromatisation and strong anti-decomposition ability which resulted from the decomposition of biomass from plant or animal waste under limited oxygen conditions (Pandey *et al*., 2015).

It has received much attention during the last few years for its potential applications in various agronomic and industrial sectors. Bio-chars have a tremendous range of physical and chemical properties (Gul *et al.,* 2015), which greatly affect their wide applications. Recent research suggests that the biomass and the method by which the bio-char is produced has a significant impact on bio-char characteristics, including concentrations of elemental constituents, density, porosity, and pH, which collectively impact the ability of the bio-char for various applications. In agriculture, it is used to upgrade the soil quality (Aller *et al.,* 2017; Werner *et al.,* 2018).

2.10 Pyrolysis Oil Properties

Bio-oil has many very peculiar properties, which need to be considered carefully and Bridgwater (2011) reviewed extensively this matter. Bio-oil is a mixture of hundreds of oxygenated compounds; the major chemical groups are water (15–30 %wt), monomeric carbonyls, sugars, organic acids, phenols, and oligomeric moieties from carbohydrates and lignin degradation is resulting in a wide range of molecular weights up to 8-10000 Da (Bridgwater, 2004; Vispute, 2011; Yang *et al.*, 2018).

Water in pyrolysis oil comes from original moisture and as reaction product (Meier, 2013), the latter including both dehydration and degradation reactions (Demirbas, 2004). A negative effect of high moisture content in the feed is that, for the same particle size, the release of water vapour by devolatilisation slows down the heating up of the particle, resulting in a longer time to attain the desired process temperature, a slower heating rate and more energy consumed in the process, since enthalpy of vaporization of water is around 2.3 $kJ \cdot g^{-1}$, compared to a Low Heating Value (LHV) around 14-18 $kJ \cdot g^{-1}$ for lignocellulosic feedstock. Pyrolysis liquids are highly polar, containing about 35-40 %wt oxygen, while mineral oils contain oxygen at ppm level. Moreover, they are not miscible with fossil fuels (Oasmaa and Peacocke, 2010), but bio-oil/diesel emulsions have been successfully produced in laboratory equipment with the aid of surfactants and tested in laboratory scale combustion equipment (Chiaramonti *et al.,* 2003; Qi *et al.,* 2008).

Pyrolysis oil can be mixed with polar solvents such as methanol, acetone and isopropanol. It is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketones, sugars, carboxylic

acids, and phenolics. Ageing of pyrolysis oil causes unusual time-dependent behaviour. Properties such as viscosity increases, volatility decreases, phase separation and deposition of gums change with time (Mohan *et al.,* 2006).

2.11 Application of Biomass Energy

The application of biomass as a source of energy has advantages such as the ability to convert, with varying level of effort into three states of matter: solid, liquid and gas, and with many modes of conversion into useful energy (Martinot, 2013). They are more sustainable in nature than fossil fuel energy sources, as they can be restored immediately after utilization. Biomass either in solid, liquid or gas form can be used for electricity generation, heating and fuel (Evans *et al.* 2010; Moriarty and Honnery, 2011).

Biomass energy resources are universally available in the world and allow energy needs to be met at all times as there is seldom a supply problem; a wide network of retailers covers the supply chain, particularly in developing countries. In comparison unreliable fossil fuel sources, particularly Liquefied Petroleum Gas (LPG) supply, are undermined in terms of regular use (Owen *et al.,* 2013). Researchers have argued that use of biomass could serve as a means to achieving negative GHG emissions. Shunmugam (2009) stated that a biomass energy system is carbon neutral: biomass combustion emits CO_2 during conversion processes. However, plants subsequently absorb an equivalent amount of CO_2 as they grow (carbon capture and storage) which eventually reduces the global warming effect (Hilbers *et al.,* 2015).

Mann and Spath (1997) claimed that only 95 % of the emitted carbon dioxide is absorbed by the plants when grown renewably. Similarly, (Manish *et al.* 2006) reported that biomass power generation can reduce greenhouse gases (GHG) emission by approximately 95 % when compared with coal-based power generation. More so, it is cost competitive with fossil fuel (FF) energy

systems particularly in developing countries and for rural application (Dasappa, 2011, Mahapatra and Dasappa 2012, Garba and Kishk 2015; Garba *et al.*, 2016).

2.12 Effect of Temperature on Pyrolysis

Temperature is one of the important parameters for the pyrolysis process. Decomposition and devolatilisation of biomass components undergo in different temperature ranges. At low temperature below 300 °C, decomposition of hemicellulose and non-condensable gases produces heavy tars. At high temperatures (>550 °C), decomposition of biomass to its various fragments produces numerous types of compounds. Compounds such as acetic acid, 1evoglucosan, hydroxyacetaldehyde and 5-hydromerthylfurfural are originated from cellulose, whereas phenolics compounds are originated from 1ignin (Ronsse *et al.,* 2012). Various studies are reported in literature which discussed the role of temperature in pyrolysis process (Luo *et al*., 2004; Zhang *et al*., 2005).

2.13 Effects of Residence Time on Pyrolysis

Residence time is an important parameter for the production of liquid fuels. The optimum residence time to achieve maximum liquid yield in pyrolysis is of few seconds to few minutes. Generally, low temperature and low residence time are preferred. In pyrolysis, as time increases, secondary reaction takes place, which decreases the yield of liquid product (Quan *et al*., 2009).

It is observed that for complete conversion, the residence time may be larger, but to attain maximum liquid yield, it should be low. Several studies are reported in literature to know the effect of residence time on bio-oil yield. Short residence time under reduced pressure has improved the yields of the liquid products. Effect of residence time is observed by using fir sawdust at a time range of 15–40 min. (Guo *et al*., 2016).

2. 14 Effects of Heating Rate on Pyrolysis

The rate of heating is an important factor for decomposition of biomass into products. In fast pyrolysis, a quick decomposition of biomass to its components requires high heating rates. Maximum liquid product is also formed at high heating rates and short residence times in this process. So, the time of contact of secondary reaction is less by which less amount of undesired products are formed. The amount of heating rates up to 1000 °Cmin^{-1} has been suggested. Various studies are reported by different researchers to know the effect of heating rates (Pütün *et al.*, 2007; Süensöz and Angõn, 2008). Fast pyrolysis of coconut biomass suggests that increasing the heating rate increased the yield of aliphatic and carbonyl compounds (Siengchum *et al.*, 2013).

2.15 Previous Research on Pyrolysis and Findings

Many research work that have been carried out by different researchers and finding in the last five years are as shown in Table 2.1a and 2.1b respectively.

Table 2.1a: Previous research and findings

Author	Topic	Findings
Prankash and Sheeba, 2014	Determination of kinetics parameters of biomass sample using thermogravimetry analysis	Degradation of bagasse hemi-cellulose is between 207.73 ºC and 391.94 ºC. Lignin degradation is between 391.94 ºC and 797.20 ºC.

Wang et al., 2015	Physico-chemical and sorptive properties derived from woody and herbaceous biomass.	Compared to low pyrolysis temperature, feedstock pyrolysed at higher temperature show lower bio-char yield production, higher carbon content, lower nitrogen, and hydrogen and oxygen contents.
Lazzari et al., 2016	Production and chromatographic characterization of bio-oil from pyrolysis of mango seed waste.	The highest bio-oil yield obtained in a fixed bed reactor was 38.8 % at temperature 600 $^\circ$C and 28.1 % at 450 $^\circ$C.
Kabir and Hameed, 2017	Recent progress on catalytic pyrolysis of lignocellulosic biomass to highgrade bio-oil and bio-chemicals.	Optimal variant conditions coupled with efficient heating sources like a microwave and active catalysts further improve the bio-oil yield and quality. Therefore, attention should be shifted to explore the synergistic tendencies between the different base and acid catalysts towards enhancing the fuel properties of the bio-oil.
Xiong et al., 2018	Effects of heating rate on the evolution of bio-oil during pyrolysis.	The results shows that polymerisation, cracking and volatilisaion of bio-oil components, recombination of radical fragments occur simultaneously during the fast pyrolysis at heating rate 200 $^\circ$C/s, intermediate heating rate 20 $^\circ$C/s and slow pyrolysis 0.33 $^\circ$C/s.

Table 2.1b: Previous research and findings

Author	Topic	Findings
Garba et al., 2018	Catalytic upgrading of bio-oil from bagasse: Thermogravimetric analysis and fixed bed pyrolysis.	The results revealed that bagasse contains high volatile matter, low ash, also the cellulose and lignin contents was high which

		make it a good biomass for production of quality bio-oil. The optimum temperature for production of bio-oil from non-catalytic and catalytic pyrolysis was 500°C, respectively. Detail analyses of the chemical composition reveals the presence of phenols and oleic acids as the components in the bio-oil.
Folasegun *et al.,* 2019	Upgrading Bio-Oil Produced from Corn Cobs and *Cedrela odorata* via Catalytic Olefination and Esterification with 3,7-Dimethyloct-1-ene and Butanol.	The FT-IR analysis of the crude and catalyzed biochars shows the sulfonation and hydroxyl peak, indicating the suitability of the catalyzed biochars for the catalysis process. The GC-MS analysis results show that the crude bio-oil was dominated by oxygenated compounds, while the catalytic olefination and esterification bio-oil are dominated with desirable compounds such as esters and phenolics, thereby showing a lower percentage of undesirable acidic compounds.

CHAPTER THREE

3.0   MATERIALS AND METHODOLOGY

3.1 Overview of Material and Methodology

This chapter outlines the materials, methods and techniques used in this research. It outlines all the analytical techniques and instruments used in material characterization and modifications, production and products evaluation. It also specifies the statistical method and software used for the experimental data analysis and optimization of process parameters.

3.2 Materials

Shea butter shell was used as biomass sample. The shea butter shell was obtained from the local shea butter production factory site Kuso-Tachin village via Bida Local Government of Niger State, Nigeria. The sample was pretreated by washing using water to remove the impurities.

The image of shea butter shell, bio-char and bio-oil obtained from fast pyrolysis of shea butter shell is as shown on Plate I.

PLATE I: (A) Shea butter shell (B) Bio-char (C) Bio-oil from fast pyrolysis

3.3 Proximate and Ultimate Analysis

The residual moisture was determined based on ASTM 1762/1964. It first determined the moisture pre-drying of shea butter shell. After pre-drying, it determined the residual moisture content of ground shea butter shell waste with an approximate particle size of 60 mesh. After removing moisture from the biomass, the following procedures were carried out. The standard

ash, volatile matter and fixed carbon were determined based on ASTM E 1755 and ASTM D 1762, respectively. CHNS Analysis Elemental Analyser Vario El Cube was used to determine the contents of Carbon, Hydrogen, Nitrogen and Oxygen content in the feedstock based on ASTM D 5291. The sulphur content was determined by LECO S-144 DR based on ASTM D 4239 (Xiong *et al.,* 2018).

3.3.1 Calorific value

The 6400 Automatic Isoperibol Calorimeter Paar was used to determine the High Heating Valueand Low Heating Value based on ASTM D 5865 (Xiong *et al.,* 2018)..

3.4 Design of Experiment Using Response Surface Methodology (RSM)

Design of Experiment (DOE) using Response Surface Methodology (RSM) is a statistical and mathematical technique which was the used for the design of experiments that provide reliable measurements of the desired response of the three operating parameters that is the temperature, heating rate and residence time.

A mathematical model used with the best fit is usually developed using data from the experimental design and the optimal value of the variables that produces maximum or minimum response are determined. In this study, the RSM was used following the Central Composite Design (CCD) method with the aid of Design Expert® Software (Version 7.0.0).

The CCD consists factorial points, axial points and centre points. After the experiment, results are fitted to second-degree polynomial model as shown in the equation is $(2^n + 2n + 6)$. The adequacy of the final model is tested using both graphical and numerical analysis and the experimental data are analysed statistically using analysis of variance (ANOVA) (Musa *et al.,* 2016).

3.5 Pyrolysis Reactor and Process

A Tubular Reactor (TR), placed in a pyrolyser (Philips Harris) was used for fixed-bed pyrolysis calibrated with a heating rate range from 5-30 °C/min and a temperature up to 1400 °C. Therefore it was easy to set the equipment to the desired temperature and heating rate for every run of the experiment.

The furnace consisted of a stainless steel tube with an alumina tube fitted with electrical heating elements and gas supply. The pure shea butter shell (SBS) sample weigh 100 g was loaded into the alumina boat placed in the furnace middle. The tubular reactor was purged with N_2 as the inert gas carrier. Once the preset temperature was reached at the desired residence time, the sample was kept for about 10 min or 4 h in the furnace to ensure complete conversion. In the current studies, the bio-oil and char were collected through fast pyrolysis in accordance with the method and procedures described by (Trubetskaya, 2016).

3.6 Thermogravimetric Analysis – TGA

Thermogravimetric analysis was carried out in thermogravimetric simultaneous thermal analyser (TGA) (STA 6000, Perkin Elmer Sdn Bhd, Selangor, Malaysia) in nitrogen atmosphere at 20 mL/min. About 10 mg (particle size of 0.2 mm) of samples were used. Samples were heated from ambient to 100 °C at 10 °C /min and held for 30 min to allow evaporation of physically absorbed moisture. Thereafter, each sample was heated to 900 °C under the same condition (Garba *et al.*, 2018).

The sample to be analysed was filled in the pan and its initial weight was recorded. Then, the equipment was made to run. The progress of the run was observed through the monitor connected to the equipment. Once the run was done, the furnace was cooled with the help of purge gas. Then TGA was switched off and purge gas was cut off. Before each trial temperature calibration

of the device was performed by measuring the melting point of aluminum metal piece in accordance with the method and procedures described by (Bassilakis *et al.,* 2001).

3.7 Determination of Physic-chemical Properties of Bio-oil

The ash content of the bio-oil was determined following the procedure outlined in ASTM D 482-80 for bio-based products. The solids content of the bio-oil was determined as ethanol insoluble material by Millipore (No. 4, Whatman) Filtration method. The pH of the bio-oil was observed using a digital pH meter (Accumet model 8250, Fisher Scientific, Fair Lawn, NJ). The minerals in the bio-oils were analyzed using the Inductive Coupled Plasma-Atomic Emission Spectrometer (ARL 3560, Waltham, MA). The heating value was measured as calorimetric value that is higher heating value (HHV) by a Parr 1341 Oxygen Bomb Calorimeter (Parr Instrument Co., Moline, IL). The elemental ratio (C/H/N/O/S) of the samples was analyzed using an elemental analyzer (Leco 600, St. Joseph, MI). Water in the bio-oils was determined using a Karl Fischer titrator (Schott, Mainz, Germany; ASTM D 1744). The dynamic viscosity of oils was determined with a rotational viscometer (Brookfield DV-E, Middleboro, MA; ASTM D 445). The Brookfield rotational viscometer is equipped with a cover for preventing the evaporation of volatiles. The kinematic viscosity of the bio-oils was calculated by the dynamic viscosity divided by the density. Measurements for samples were taken at 20 °C (Moreire *et al*., 2016).

3.8 GC-MS Analysis of Bio-oil

The bio-oil identification and composition determination were performed on a Gas Chromatography, GC Agilent series 6890 with an Agilent mass selective detector of series 5973. A capillary polar wax column, polyethylene glycol (PEG)-coated (length of 30 m, internal diameter of 0.25 mm, and film thickness of 0.25 μm). Chromatographic conditions were as follows: İnjection volume of 0.2 μL, oven at 40 °C (1 min) 6 °C min^{-1} up to 300 °C per (10 min) split mode with a ratio of 100:1 and injection temperature of 290°C. Time taken was 50.01

minutes, He (helium) as carrier gas with a flow rate of 2.9 mL min^{-1}. The computer matching of mass spectra was performed using the NIST98 and WILEY7.0 library and the retention times of known species injected in the chromatographic column were used for identification of the peaks (Garba *et al.*, 2018).

3.9 Bio-Oil Analysis Using FTIR

The bio-oil sample obtained during pyrolysis was analyzed using Fourier infrared and Raman spectrometer (FT-IR) purchased from Bruker Company, type EQUINOX 55. The column was operated in a constant flow mode using helium as the carrier gas (1 µL/min, purity > 99.99 %) and initially maintained at 40 °C for 3 min before it was increased to 250 °C at a heating rate of 5 °C/min, and thereafter held for 10 min. The integrated area obtained was multiplied by a correction factor "mass of trapped solution/mass of feedstock" to express the area on the basis of "per gram of feedstock". FTIR Spectroscopy, The FTIR spectra of bio-oil were recorded in the region 4000–800 cm^{-1} in a spectrometer Nicolet 6700 FTIR infrared using in Attenuated Total Reflectance (ATR) with a Zinc Selenide (ZnSe) crystal (Moreire *et al*., 2016).

3.10 Bio-char Analysis Using SEM-EDX

Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Analysis (EDX) The SEM micrographs and EDX analysis were performed on a Jeol microscope (JSM-6010LA). EDX analyses were performed at different locations of the surface and the percentage of the elements corresponds to the average of these measurements (Moreire *et al*., 2016).

3.11 Brunauer–Emmett–Teller (BET) Analysis of Bio-char

Total surface area, pore size and pore volume were measured with NOVA 1200 analyzer using Brunauer–Emmett–Teller (BET) method using N_2 adsorption isotherms Briefly, 1 g of sample was added to 20 mL DI water. The suspension was shaken with a mechanic shaker at 40 rpm for 1 h, and equilibrated for 5 min before it been injected in the anlyser (Sun *et al.,* 2014).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Overview of the Results and Discussions

This chapter gives the detailed discussion of proximate and ultimate analysis of bio-based products. It enumerate the effects of pyrolysis temperature, heating rate and residence time collectively on product distributions. Subsequently, it discusses optimization of pyrolysis process variables for optimum bio-oil yield using Response Surface Methodology (RSM) based on a central composite design (CCD) version 7.0.0 and evaluates characteristics of pyrolysis products.

4.2 Characterisation of Shea Butter Shell (SBS)

The results obtained for the proximate and ultimate analysis of shea butter shell and the bio-char compared to the previous studies in the literature are as shown on Table 4.1.

Table 4.1: Proximate and utimate analysis of shea butter shell

	Proximate Analysis (wt. %)				Utimate Analysis (wt. %)				
	Moisture Content	Ash Content	Volatile Matter	Fixed Carbon	C	H	S	N	O
Shell	10.34	0.80	80.80	16.14	47.10	10.19	0.30	0.59	43.40
De Conto *et al.* 2016	10.63	8.26	72.54	19.20	39.63	6.31	0.20	1.70	52.16
Bio-char at 450 °C	0.23	1.72	14.00	19.00	84.66	7.00	0.20	0.30	4.86

The results of the heating values and heat capacity of the shea butter shell is obtained as follows:

Low Heating Value (LHV) = 139.0 kJ/kg

High Heating Value (HHV) = 20400 kJ/kg

Heat Capacity = 11800 HJ/kg.

4.2.1 Discussion of proximate and ultimate results

The characteristics of shea butter shell biomass used in this study and bio-char form at temperature of 450 °C are summarized in Table 4.1. The proximate analysis result obtained showed significant difference relative to similar properties of biomass reported in the recent literature. Higher volatile matter and lower fixed carbon and ash contents were recorded and compared well to the values reported (De Conto *et al*., 2016).

In order to determine the differences in the quality of biomass waste and the bio-char produced by the pyrolysis, analysis was performed. As with raw sample material, the composition was determined by the value of the water content (moisture in air dried sample), ash (ash content), easy fly material (volatile matter), solid carbon (fixed carbon), and calorific value. The moisture content of the dried shell and bio-char was determine to be 10.34 % and 0.23 %, respectively.

This shows that the water content have been evaporated due to high heating effect of the process. Result of the shell sample was in close agreement with those reported by (Yin, 2011) to be 10.07 % for wood waste and bio-solid mixture. The ash content was observed for both sample to be 1.72 % and 0.80 %, respectively.

According to Jaya *et al.* (2012), ash content influence the deposition rate of the biomass and incase of wood fuel has low ash compare to herbaceous straw grasses and bark content in the fuel. Therefore, the low ash content and high volatile matter of the biomass was recorded 80.80 % for the dried shea butter shell which enhanced the bio-oil yield of the pyrolysis. After thermal process, the volatile matter reduced to 14.00 % which made it suitable for further adsorbent processing. The carbon, hydrogen, sulphur, nitrogen and oxygen were recorded in the Table 4.1, high carbon content shows that the biomass contains high level of cellulose, hemicellulose, lignin which later decomposed thermally to yield bio-oil. The shea butter shell has higher heating value 20400 kJ/kg compared to what was reported in the studies of Braga *et al*. (2015) that was 15600 kJ/kg.

4.3 Effect of Process Parameters on Pyrolysis Products Distribution

Effects of the independent variables considered for this studies: temperature 350-600 °C, heating rate (10-30 °C) and residence time (10-60 min) on intermediate pyrolysis of shea butter shell in a vertical fixed bed reactor were evaluated through different levels as summarized in Table 4.2. The range of temperature and nitrogen flow were chosen to allow complete thermal decomposition of organic components of shea butter shell particularly, the lignin which has high thermal stability and to ensure that the residence time in the reactor at constant inert flow rate, a requirement for the fast pyrolysis process.

The results of surface response design matrix of experimented and predicted bio-oil yield percentage from pyrolysis of shea butter shell are as shown in Table 4.3.

Table 4.2: Surface response design matrix for the production of bio-oil

Run	A: Temperature (ºC)	B: Residence Time (min)	C: Heating Rate (ºC/min)	Experimented: Bio-oil Yield (%)	Predicted: Bio-oil Yield (%)
1	350	10	10	5.00	6.95
2	600	10	10	25.30	21.56
3	350	60	10	4.50	6.95
4	600	60	10	22.55	21.56
5	350	10	30	24.00	24.91
6	600	10	30	51.20	71.00
7	350	60	30	25.55	24.91
8	600	60	30	51.50	53.45
9	265	35	20	4.50	5.75
10	685	35	20	47.20	47.25
11	475	7	20	23.00	23.25
12	475	77	20	23.00	23.25
13	475	35	3	4.50	3.54
14	475	35	36	49.00	50.01
15	475	35	20	22.55	23.25
16	475	35	20	22.50	23.25
17	475	35	20	22.50	23.25
18	475	35	20	23.00	23.25
19	475	35	20	22.55	23.25
20	475	35	20	22.55	23.25

4.3.1 Response surface design discussions

From analysis of variance (ANOVA), of bio-oil yield, the Model F-value of 40.42 (Table 4.3) implies the model is significant. Lack of Fit F-value of 0.76 indicates that it is not significant relative to the pure error, which is desirable. In the case of bio-oil, the significant model terms are A, and C, with the corresponding F-value of 13.20, and 16.46. It can also be observed that the most significant model term on the bio-oil yield with B with less value shows that is less significant. The following order $AB>B^2>BC>AC>A^2>B^2$ with the quadratic terms interaction does not have a significant effect on the bio-oil yield.

The coefficient of determination, R^2 for the bio-oil is 0.7992 (Table 4.4). Another regression parameter considered is the adjusted R^2, which improves the coefficient of determination (R^2) in relation to the sample size and the model terms, the corresponding values are 0.6184. The R-squared and adjusted R-squared values for the individual model are high enough and close, which indicate that the selected quadratic response surface model for the pyrolysis products is sufficiently describe the experimental data within the selected operating conditions. Predicted R-squared value of the bio-oil is 0.7992 which is in good agreement with the respective adjusted R-squared values. Adequate precision (Adeq Precision) is a measure of signal to noise ratio and a ratio greater than 4 is desirable.

This high value of Predicted Residual Error Sum of Squares (PRESS) 7.434 indicate adequate signal and the models can be used to navigate the design space. Coefficient of variation (CV), which is a measure of the reliability of the experiment, for the design it expresses the overall experimental error as a percentage of the overall mean. The CV value recorded for all the pyrolysis products are less than 5 %, hence, this experiment can be said to be reliable since the lower the CV value, the higher is the significant of the experiment.

The Analysis of variance for effects of operating parameter on bio-oil production is as shown in Table 4.3.

Table 4.3: ANOVA for response surface quadratic model estimated regression coefficient and their effects for bio-oil production

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	P-value Prob>F
Model	8383.15	9	931.46	40.42	0.0148
A-Temperature	2781.68	1	2781.68	13.20	0.0046
B-Residence Time	861.26	1	861.26	4.09	0.0707
C-Heating Rate	3466.77	1	3466.77	16.46	0.0023
AB	55.12	1	55.12	0.26	0.6201
AC	190.12	1	190.12	0.90	0.3645
BC	144.50		144.50	0.69	0.4269
A^2	467.90	1	467.90	2.22	0.1670
B^2	91.23	1	91.23	0.43	0.5253
C^2	467.90	1	467.90	2.22	0.1670
Residual	2106.60	10	210.66		
Lack of Fit	906.60	5	181.32	0.76	0.6171
Pure Error	1200.00	5	240.00		
Cor Total	10489.75	19			

The R-squared estimates of the response methodology model of the experiment is as shown in Table 4.4.

Table: 4.4: R-squared estimates

Standard Deviation	14.51	R-Squared	0.7992
Mean	32.75	Adj R-Squared	0.6184
C.V. %	4.32	Pred R-Squared	0.1797
PRESS	8604.36	Adeq Precision	7.434

The linear plot reletionship between predicted model yield and experimental bio-oil yield in

weight percent is as shown in Figure 4.1.
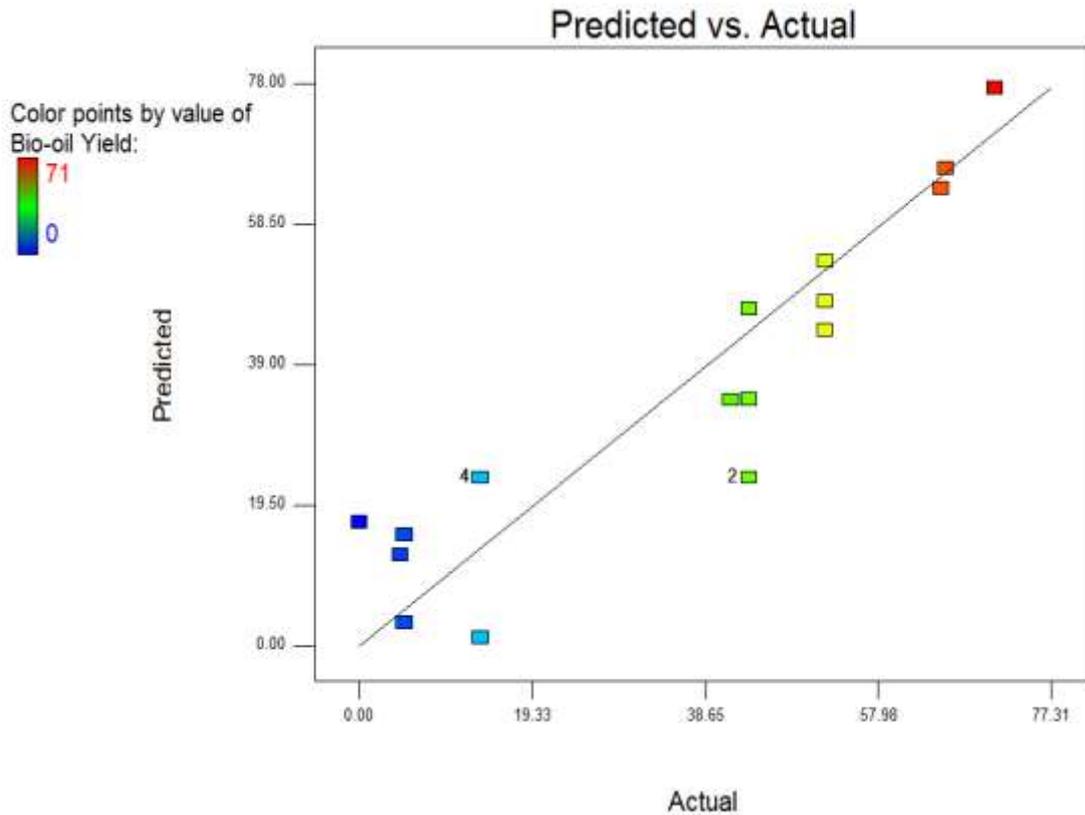
Figure 4.1: Plot of predicted and actual bio-oil yield

4.3.2 Design equation

Final Equation in Terms of coded Factors:

Bio-oil Yield$= +23.25 + 14.27A + 7.94B + 15.93C + 2.63AB - 4.87AC + 4.25BC\ 5.70A^2 +$

$2.52B^2 + 5.70C^2$ (4.1)

Final Equation in Terms of Significant Factors*:*

Bio-oil Yield$= +24.85211 - 0.18366A +\ 0.57156C$ (4.2)

Where; A = Temperature

   B = Residence Time

   C = Heating Rate.

4.3.3 Discussion of the linear plot of the bio-oil yield

The linear relationship between the predicted and experimented yield is as shown in Figure 4.1. Points in the relationship between the actual bio-oil yield and the model predicted values plots are distributed approximately on a straight line along the diagonal for the pyrolysis product models. This trend depicts that the error terms are normally distributed and independent of each other.

4.3.4 Effect of process variables on bio-oil yield

The use of 3D plots as a method of analyzing the effects of the pyrolysis process variables on the yields, is to show the interaction between the process parameters chosen for this experimental design. Although, it is not possible to present the effects of all the three parameters studied on the same 3D, as such, the response surface plots are presented by varying two factors and keeping one factor constant. The interaction between the temperature and residence time at a constant heating rate (20 °C /min) on the bio-oil yield (Figure 4.2) shows that increase in the residence time from 10 min to 60 min and temperature from 350 °C to 600 °C have slight increased the bio-oil yield. The oil yield became maximum at 600 °C for both residence time but at a different times.

Lower residence time (10 min) produced 51.20 wt% oil compared to 25.30 wt% oil yield at the same 600 °C. The decreased oil yield at the same residence time could be as a result of more uncondensed volatiles leaving as part of non-condensable gas. Declines in the oil yields were observed at temperature can be relate to degradation of more lignin, and secondary reactions of pyrolysis vapour and more decomposition of bio-char at the elevated temperature (Soetardji *et al.,* 2014).

The response surface contour for interaction between temperature and residence time at constant heating rate on bio-oil yield is as shown in Figure 4.2.
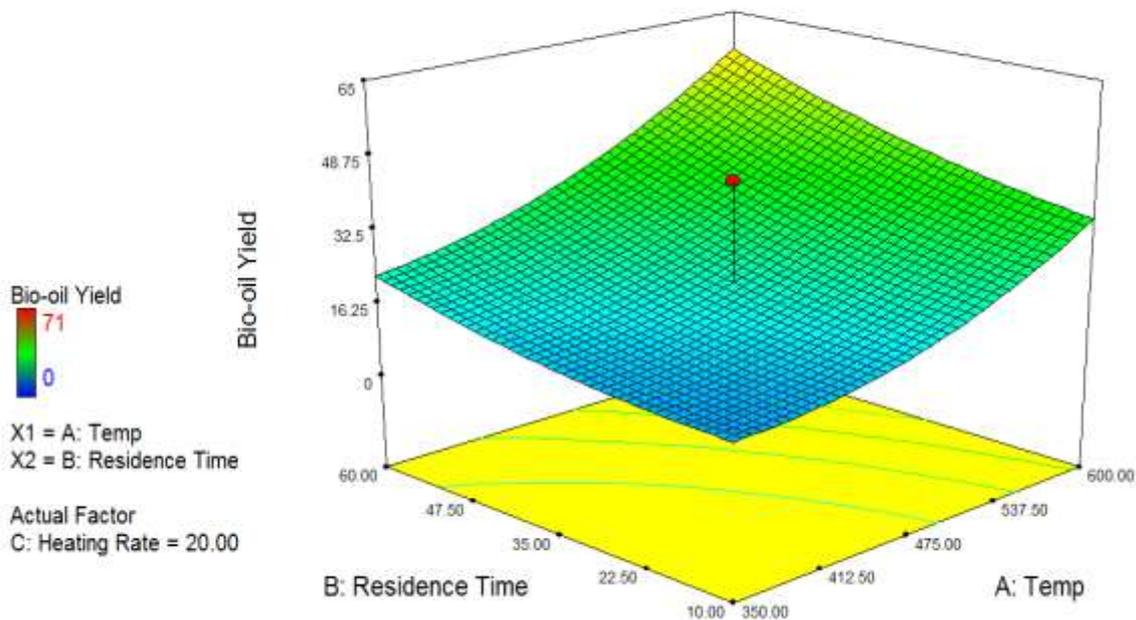
Figure 4.2: **The response surface contour for interaction between temperature and residence time on bio-oil yield**

The effect of heating rate and temperature on the bio-oil yield at a constant residence time (35 min) is presented in Figure 4.3. Increasing temperature from 350 to 600 °C and heating rate between 10 and 60 °C /min increased the oil yield from 5.00 to 22.50 wt% and 23.00 to 51.20 wt%. The yield of more bio-oil at 30 °C/min relative to 10 °C/min under the same pyrolysis temperature is attributed to fast heat depolymerization of the biomass to primary volatiles at the higher heating rate (Yorgun and Yildz, 2015).

The response surface contour for interaction between temperature and heating rate at constant residence time on bio-oil yield is as shown in Figure 4.3.
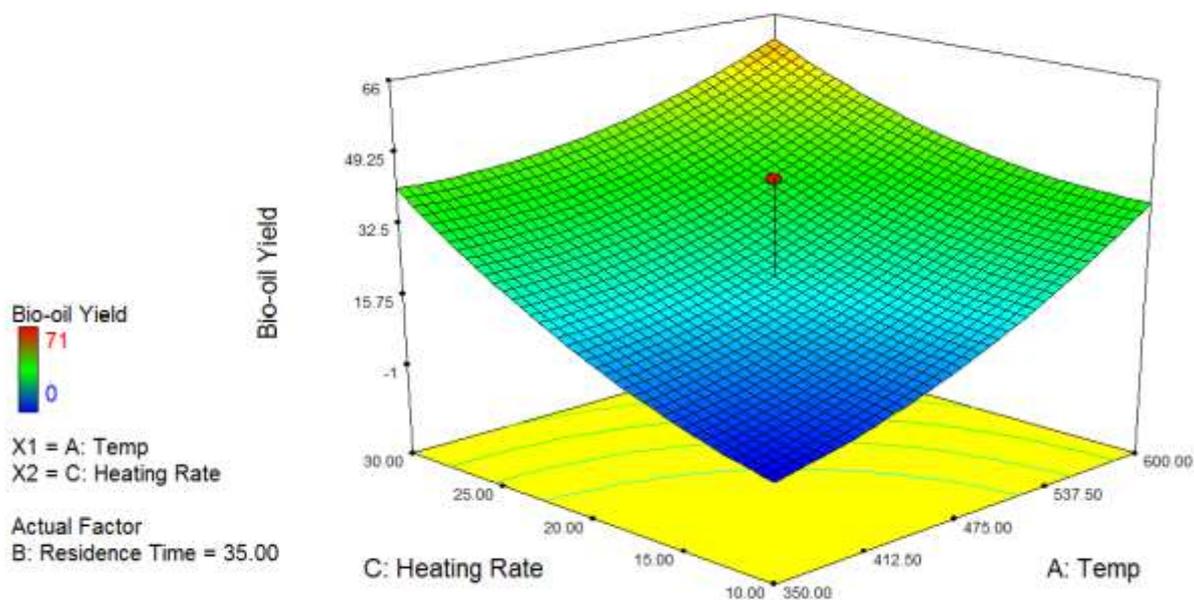
Figure 4.3: The response surface contour for interaction between temperature and heating rate on bio-oil yield

Combined effects of heating rate and residence time at a constant pyrolysis temperature of 450 °C on the bio-oil yield is shown in Figure 4.4. As the retention time increased from 5 min to 20 min, bio-oil yield at 10 °C /min heating rate remained higher compared to the oil collected at 30 °C /min but no significant residence time was observed in both cases. Bio-oil yield at 10 °C /min was between 22.55 and 25.55 wt% relative to 51.20-51.55 wt% oil recorded at 30 °C /min. residence time used throughout the experiment show the show the it is not significant to the bio-oil yield. Rather the high heating rate and temperature of the pyrolysis gives the maximum yield of the bio-oil.

The response surface contour for interaction between residence time and heating rate at constant temperature on bio-oil yield is as shown in Figure 4.
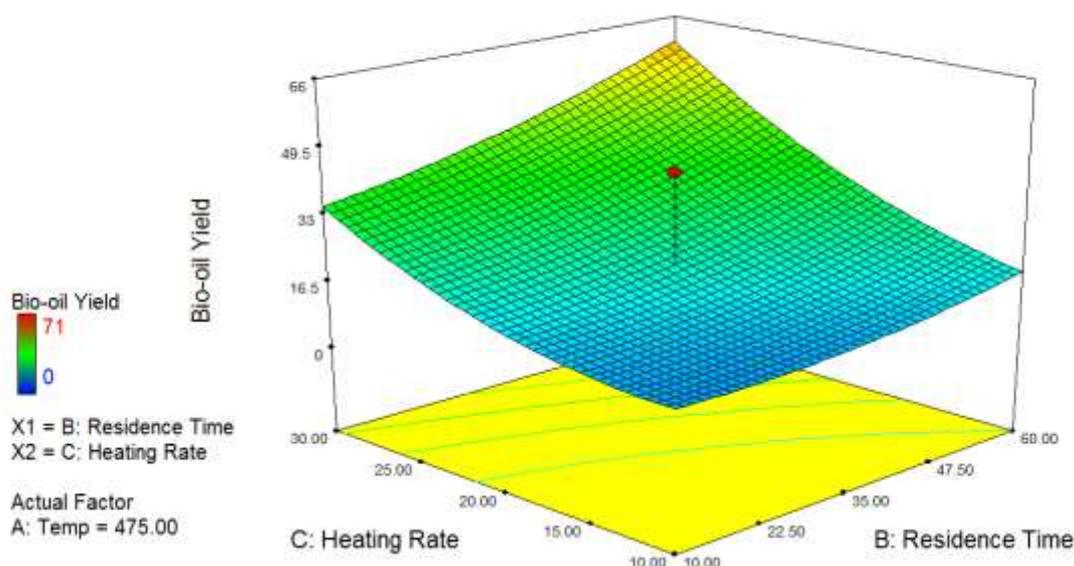
Figure 4.4: **The response surface contour for interaction between residence time and heating rate on bio-oil yield**

4.4 Thermogravimetry Analysis (TGA) Discussion

The TG curve of shea butter shell and bio-char produced in the pyrolysis in Figure 4.5. In the both plots, two distinct endotherms are observed. As illustrated in Figures 4.5, thermal decomposition of samples is divided into three Zones. The area covered by the first endotherm is taken as Zone 1. The region within the ambit of the second endotherm is considered as Zone 2. Zone 3 corresponds to the region after the second endotherm. Zone 1 is due to the evolution of moisture, whereas Zone 2 due to the degradation of cellulose and hemicellulose components. Zone 3 literally corresponds to the decomposition of lignin and inorganics present in the samples (Prakash and Sheeba, 2013; Yang *et al.,* 2004).

The thermal decomposition of lignin in the shea butter bio-char is considered intricate because of its complex structure. During the decomposition of shea butter shell, hemicellulose and cellulose degrades first followed by lignin. As hemicellulose and cellulose often degrades at a very close temperature range, they undergo degradation at the same time and their degradation zones did not

overlap with each other. Hence, for the hemicellulose and cellulose degradation two distinct endotherms cannot be obtained in the TG curve. Previous research work on TGA on pyrolysis of biomass has reported hemicellulose degradation below 350 °C, cellulose decomposition between 250 and 500 °C and lignin deterioration above 400 °C (Bo *et al.,* 2009).

The second reaction zone or primary pyrolysis zone (198.53–394.62 °C) is due to hemicellulose and cellulose degradation while third reaction zone or secondary pyrolysis zone (391.94–797.20 °C) corresponds to lignin decomposition. Therefore the shell was observed stable at about 500 °C around the zone 2 with in approximately 30 % weight. And the stability of the bio-char found around zone 3 within region of plot mark (a) at about 700 °C with approximately 100 % weight.

The thermograms of the thermogravimetry analysis, TGA of shea butter shell and bio-char are as shown in Figure 4.5.
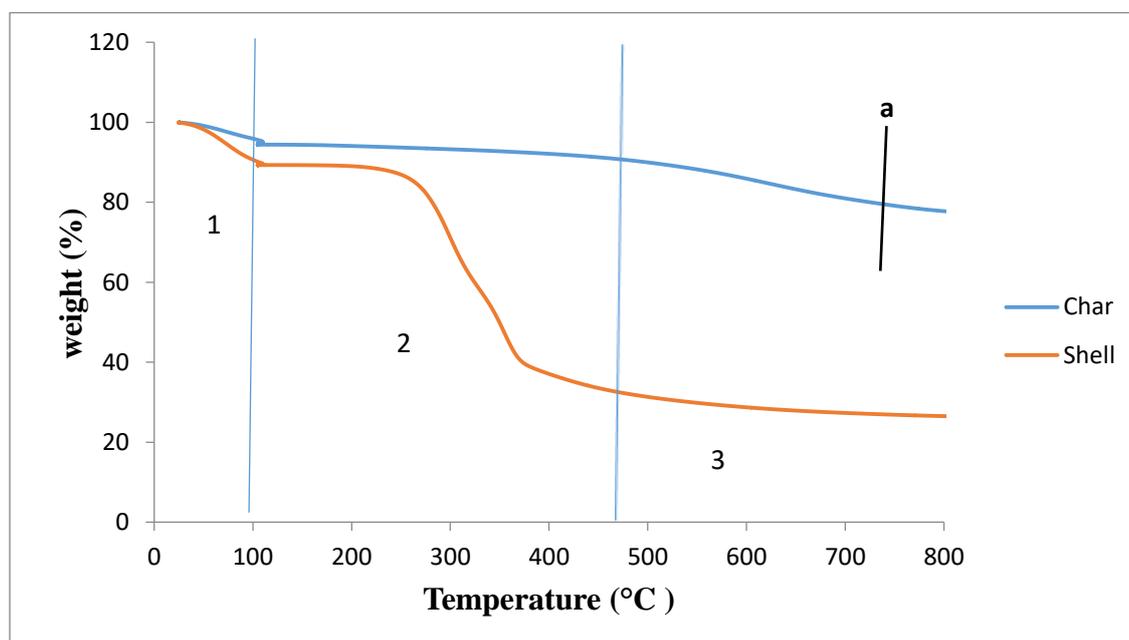

Figure 4.5: TGA Thermograms of shea butter shell and bio-char

4.5 Physico-chemical Properties of Bio-Oil

The important chemicals and physical properties of bio-oil obtained from fast pyrolysis of shea butter shell are as shown in Table 4.5

Table 4.5: Bio-oil properties

Properties (units)	Bio-oil of shea butter shell	Convectional Bio-oil
pH	3.14	2.0-3.8
Density at 20 ºC (g/mL)	1.12	1.1-1.4
Specific gravity	0.83	0.71-0.91
Viscosity at 20 ºC (mPa.s)	174	-
Heating Value (MJ/kg)	26.03	42.0-44.0
Water content (wt%)	15.46	10-40
Ash content (wt%)	0.09	0.03-0.3
Solid content (wt%)	0.36	<1
Carbon (wt%)	50.72	55.3-63.5
Hydrogen (wt%)	6.25	5.2-7.0
Nitrogen (wt%)	0.02	0.07-0.39
Sulphur (wt%)	0.00	0.00-0.05

4.5.1 Discussion of physic-chemical properties of bio-oil from SBS

The pH value of bio-oil from the fast pyrolysis of shea butter shell is 3.14. Most convectional bio-oils have a pH in the range of 2.0–3.8 because of the presence of organic acids, mostly acetic and formic acid. As the pH value of bio-oil becomes less, the oil becomes more acidic. Because of the higher acidity, the bio-oil becomes corrosive and hence corrosion resistance material should be used in the bio-oil production and storage system. The pH value in the bio-oil depends on many factors including the type of biomass used for the bio-oil production (Greenhalf *et al.,* 2013).

The density of the bio-oil was determined at temperature of 20 $^{\circ}$C and it was found to be 1.12 g/mL and the specific gravity was 0.83. Both density and specific gravity was in the range compared to values of the conventional bio-oil. These affects the energy value of the fuel. The two fuels having same heating value may have different energy quantity due to the variation of density. As the density increases, the energy content also increases. The normal range of density of pyrolysis oil is found as 1.10-1.40 g/mL found from the most common biomasses and this variation comes mainly due to the type of biomasses. It has been observed that density of bio-oil always decreases with increases in temperature which is found by measuring the density at various temperatures (Culcouglu *et al.,* 2005; Perez *et al., 2002*).

Bio-oils have a lower gross heating value than petroleum fuels and will therefore require an increased fuel flow to compensate the combustion in a firebox. The heating value of the crude bio-oil sample is 26.03 MJ/kg. It is similar as the gross heating values of bio-oil produced by other process but lower than that of conventional bio fuel (42 MJ/kg). Heating value or the calorific value of any oil indicates the energy content present in it, which is an important parameter for the selection of the oil for a particular application (Bertero *et al.,* 2014).

The viscosity of the pyrolytic oil varies in a wide range as it is produced from various biomasses, at different operating conditions using different parameters. It varies with temperature, but for this research the viscosity of the bio-oil was obtained at 20 $^{\circ}$C (174 mPa.s). The water content contained in the bio-oil was 15.46 wt%. The water content in the pyrolysis oil depends on moisture content present in the feedstock and also on the dehydration reaction that takes place during the fast pyrolysis process (Bertero *et al.,* 2014).

Ash content (0.09 wt%) and solid content (0.36 wt%) of bio-oil were within the range when compared to what was reported for convectional bio-oil. Depending on their size, solid particles can wear the fuel system, block the filter, and clog the fuel nozzle. Thereby the solids content is

important with respect to the particulate emissions during the combustion process (Culcouglu *et al.,* 2005).

Carbon (50.72 wt%), Hydrogen (6.25 wt%), and Nitrogen (0.2 wt%) of the bio-oil were observed to be within the expected range when compared to conventional values of bio-oil. Surphur was completely zero in the bio-oil that attributes to uniqueness of bio-based fuel, and make it suitable an alternative source of energy due it no or less impact on the environment (Boucher *et al.,* 2000).

4.6 GC-MS Analysis Result

The chromogram peaks of chemical composition of the bio-oil using Gas Chromography coupled with mass spectroscopy are as shown in Figure 4.6.

Time (min)
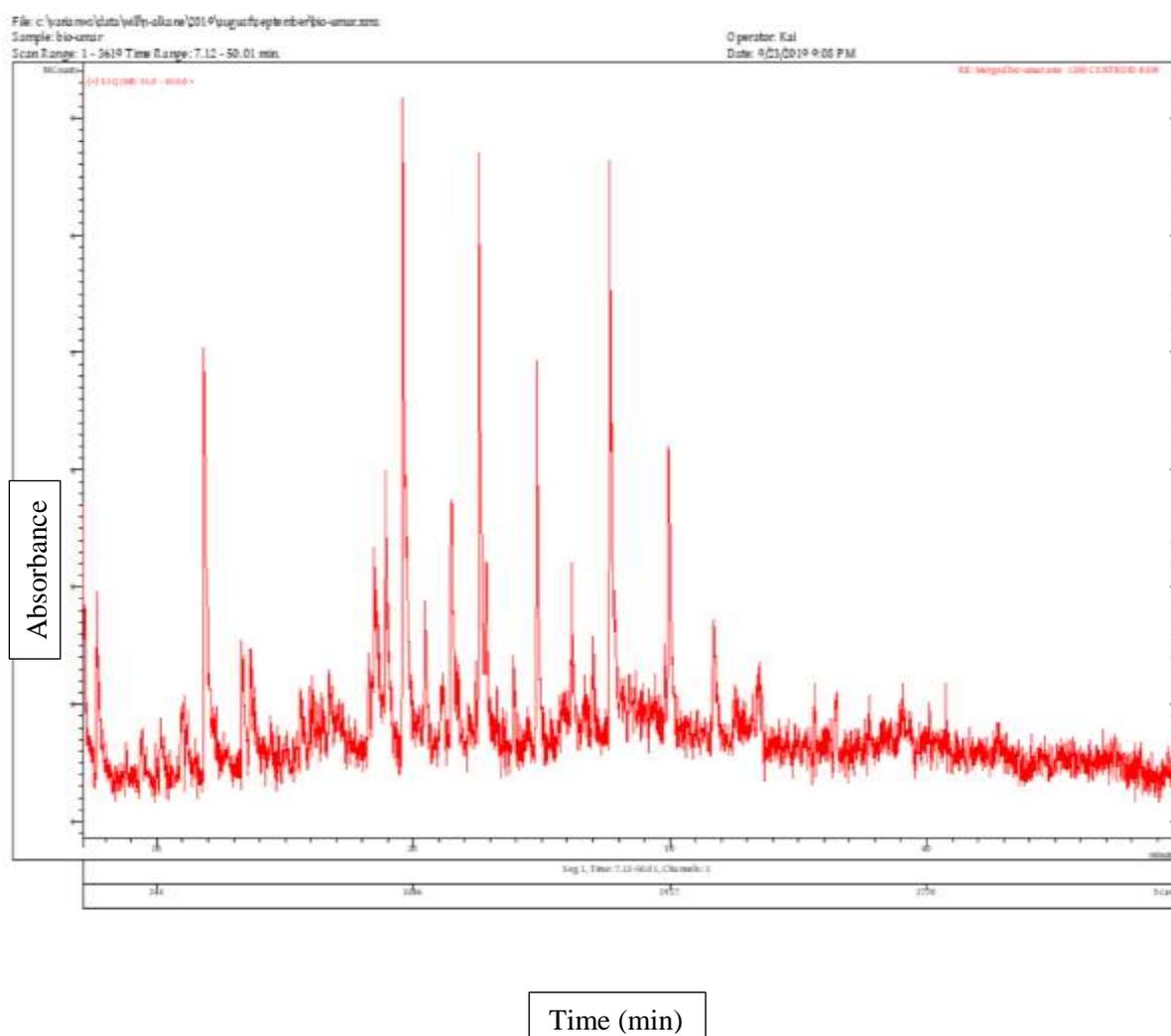
S/no.	Compound	Molecular Weight	Formular
1.	1-hydroxyl-2-propane	74	$C_3H_6O_2$

Figure 4.6: GC-MS Chromatogram peaks of bio-oil from shea butter shell.

The results of organic compounds present in bio-oil produced from pyrolysis of shea butter shell on using GC-MS to analyze are as shown in Table 4.6.

Table 4.6: Bio-oil compounds, molecular weight and formular

	2.	Furfural	96	$C_5H_6O_2$
4.6.1	3.	2-hydro-2-cyclo-pent-1-one	112	$C_6H_8O_2$
	4.	Phenol	94	C_6H_6O
	5.	2-methoxyl phenol	124	$C_7H_8O_2$
	6.	4-methyl phenol	108	C_7H_8O
	7.	2-methoxyl-4-methyl phenol	138	$C_8H_{10}O_2$
	8.	4-ethyl-2-methoxyl phenol	152	$C_9H_{12}O_2$
	9.	3,4-dimethoxl-phenol	154	$C_8H_{10}O_3$

Discussion of GC-MS results

Figure 4.9 Shows % area of chromogram peaks of alkane, alcohols, ethers, ketones, phenols, and aliphatic, aromatic and cyclic compounds in bio-oil obtained from pyrolysis of shea butter shell and their detail is also given in Table 4.8. It was observed the more the 50% of the organic content of the bio-oil are classes of phenolic compounds which means the bio-oil occupied with high molecular weight hydrocarbon. Most of the compounds identified through in the bio-oil originated due to the thermal cracking of cellulose, hemicellulose and lignin in the biomass. Numerous amounts of compounds were identified in the bio-oils (Mahinpey *et al.,* 2009).

4.7 Fourier-Transform Infra-Red (FTIR) Discussion

FTIR spectra of chemical species in the bio-oil samples are shown in Figure 4.8. The common broad peak around 3447.77 cm^{-1} and above implies that the samples contain chemical compounds with hydroxyl group (O−H) such as water impurities, polymeric (O−H) alcohols and phenol (Bordoloi *et al.*, 2015).

The peak at a frequency around 2923.86 cm^{-1} is due C−H stretching vibration indicating the presence of saturated hydrocarbon in the organic compounds such as alkanes. The stretch within the peak at a frequency around 2100 cm^{-1} common to both phases is ascribed to the C−C functional group (Guo *et al*., 2015; Ahmad *et al*. 2014). Vibration observed between 1654.10 cm^{-1} and 1718.28 cm^{-1} are attributed to presence of C=O groups such as the aldehydes, ketones or carboxylic acids. The vibration around 1508.08 cm^{-1} is ascribed to the presence of NO$_2$ which implies nitrogenous compound. The peak around 1458.43 cm^{-1} signifies C−H indicating the presence of cyclic alkanes and aromatic hydrocarbons. (Yorgun and Yildz, 2015).

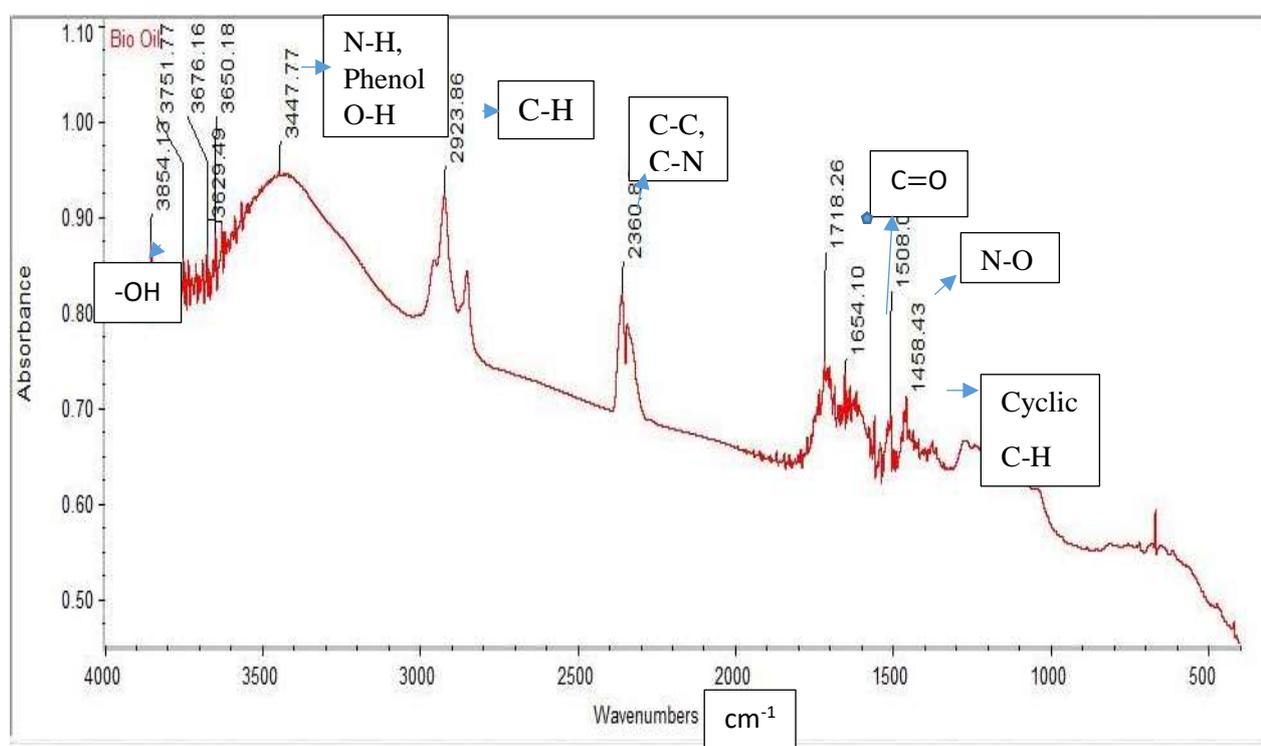The FTIR peaks of the bio-oil and the functional groups presents are as shown in Figure 4.7.

Figure 4.7: FTIR Spectrum of bio-oil obtained

The results of peaks and functional groups contains in the bio-oil of shea butter shell with expected compound found was revealed in Table 4.7

Table 4.7: FTIR peaks numbers and the functional groups

Peaks (cm^{-1})	Functional Groups	Compounds
3854.13	O−H	Water Impuritued, Polymeric Alcohols
3447.77-3751.77	Phenol, Bonded N−H O−H	Phenol Compounds, Proteins, Amines, Amides
2923.86	C−H	Saturated Hydrocarbons
2100-2360.86	C−C, C−N	Methane, Nitro-methanes
1654.10-1718.28	C=O	Ketones, Aldehydes, Carboxylics
1508.08	N−O	Nitrogeneous Compounds
1458.43	Cyclic C−H	Cycloalkanes

4.8 SEM and Electron Dispersive X-ray (EDX) Discussion

Scanning electron micrograph and elemental mapping of the bio-char (Figure 4.6) showed that the materials morphology. The sample shape revealed was not definite which attribute to its poor pore diameter. From elemental mapping from the EDX results of the bio-char (Figure 4.7) shows that the solid particle of the pyrolysis contains; carbon (C), nitrogen (N), oxygen (O), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P) and chlorine (Cl) constitute the major mineral elements in the bio-char. The micro elements in the bio-char are silicon (Si) and molybdenum (Mo) which exist in low percent weight compared to the micro elements.

The SEM image of the bio-char revealing the morphology at different magnifications are as shown in Figure 4.8.
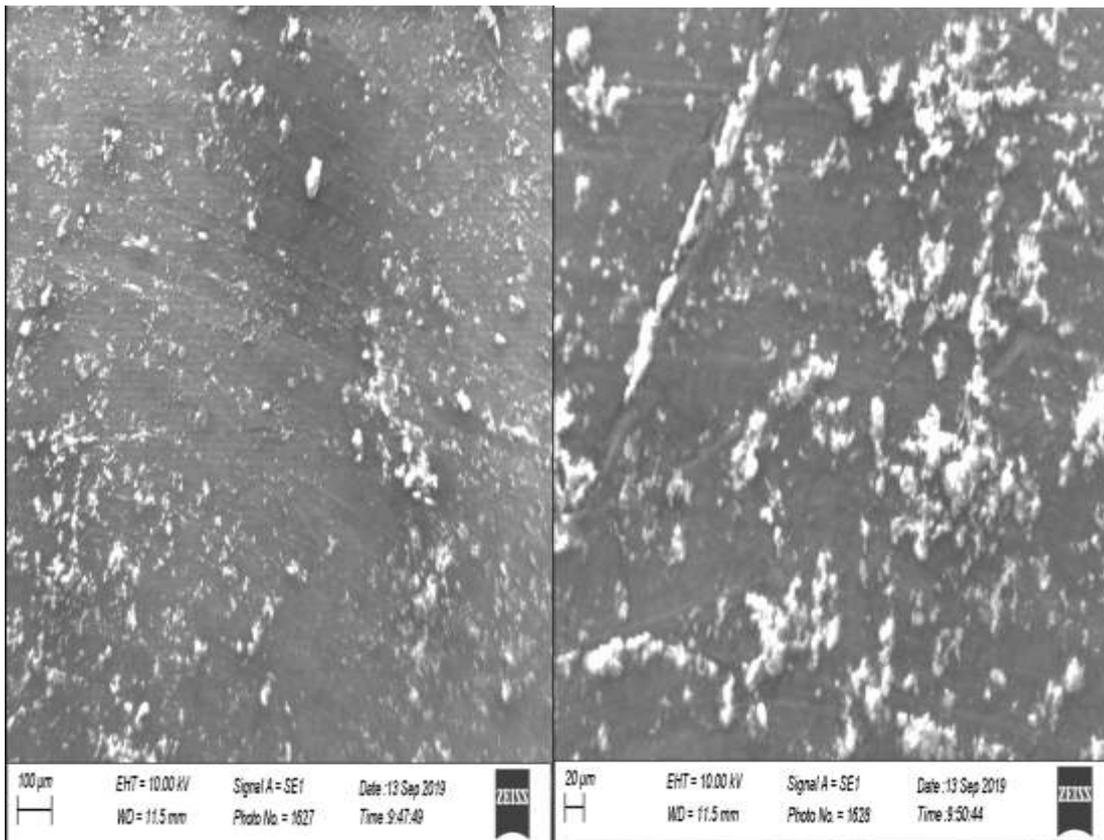
Figure 4.8: Scanning electron micrograph of shea butter shell bio-char showing the morphology.

The EDS spot and spectra revealing the elemental composition of the bio-char from shea butter shell are as shown in Figure 4.9.
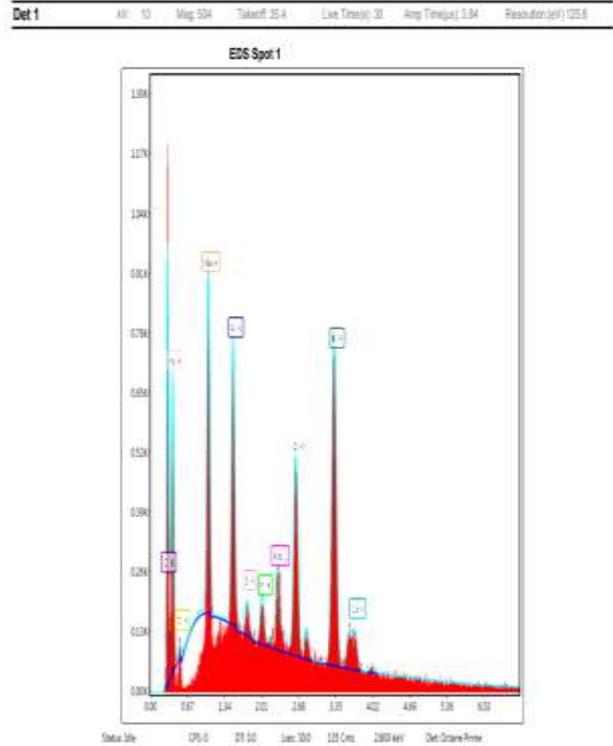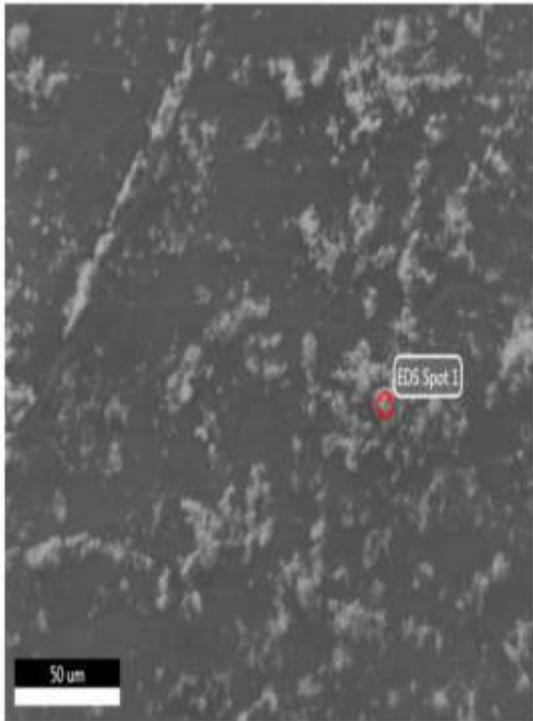
Figure 4.9: Electron Dispersive X-ray (EDX) image of the identifying the EDS spot for the spectra showing the elemental compositions of the bio-char

The elements present in the bio-char obtained at temperature of 450 °C with their respective compositions are as shown in Table 4.8.

Table 4.8: The chemical compositions of the bio-char at 450 °C

Elements	Composition of Bio-char at 450 °C (wt. %)
Carbon	13.53
Nitrogen	38.41
Oxygen	0.62
Sodium	6.44
Aluminum	4.59
Silicon	0.64
Phosphorus	1.23
Molybdenum	4.70
Chlorine	7.47
Potassium	19.37
Calcium	3.06

4.9 Brunauer Emmett Teller (BET) Surface Discussion

This result was further confirmed using BET to identify the physisorption that is the physical sorption properties such as surface area, pore volume and pore size of the bio-char as showed in Table 4.6. The specific BET surface area recorded for the bio-char produced from shea butter shell at 450 °C was 196.022 m^2/g and external surface area 170.025 m^2/g and the corresponding pore volume of 5.50×10^{-3} cm^{-3}/g as well as the pore size 1.410 nm was observed. The results of the surface areas was reduced when compared to the result char of B-550 obtained by Chowdhury *et al*. (2016) as shown in the Table 4.6. Also the pore volume and size is small. These is as a result of temperature at which the char was obtained.

The BET surface, pore volume and pore size of the bio-char revealing its sorption potential are as shown in Table 4.9.

Table 4.9: BET surface results

Sample	BET surface (m²/g)	External Surface (m²/g)	Pore Volume (cm³/g) x 10⁻³	Pore size (nm)
Bio-char obtained at 450°C	196.022	170.025	5.50	1.410
Bio-char B-550 (Chowdhury *et al.* 2016)	221.0	209.60	8.587	12.78

CHAPTER FIVE

5.0   CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, the key findings of this research work are summarized as follows:

1. Optimal bio-oil yield 51.50 wt% bio-oil was obtained at corresponding operating parameters of temperature (600 °C), heating rate (30 °C/min) and residence time (60 min).

2. Thermal stability of shea butter shell was range 350-450 °C and bio-char from the pyrolysis was at temperature above 700 °C.

3. Bio-oil from SBS pyrolysis was dark-brown in colour with pungent smell. It has pH of 3.14, which is in the acidic region. It also contains low moisture contents, ash contents and solid matters with moderate heating value of 26.03 MJ/kg.

4. GC-MS and FTIR revealed that the bio-oil obtained from shea butter shell is dominant with phenolic and carboxyl compounds equally present. Also groups of ketone, aldehydes, alcohols, and aliphatic hydrocarbons are present.

5. The bio-char from shea butter has surface area of 190.022 m^2/g, eternal surface area of 170.025 m^2/g with pore volume 0.0055 cm^3/g and pore size 1.410 nm.

5.2 Recommendations

The following recommendations can be considered as a way forward for further research.

1. Production of bio-oil from Shea butter shell should be carried out in a continuous pyrolysis system and optimization of process variables.

2. Bio-char from shea butter shell pyrolysis should be upgraded as potential adsorbent in waste water treatment as bio-adsorbent.

3. Upgrading study should be carried out in a continuous catalytic and refining system of the bio-oil from shea butter shell.

4. Bio-oil should be tested in internal combustion engines and compare its performance with diesel from fossil fuels.

5. Extraction of valuable chemicals from aqueous phase bio-oil derived from Shea butter shell after upgrading and refining processes to increase its volatization.

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APPENDIX A

Plot from BET Surface Analysis
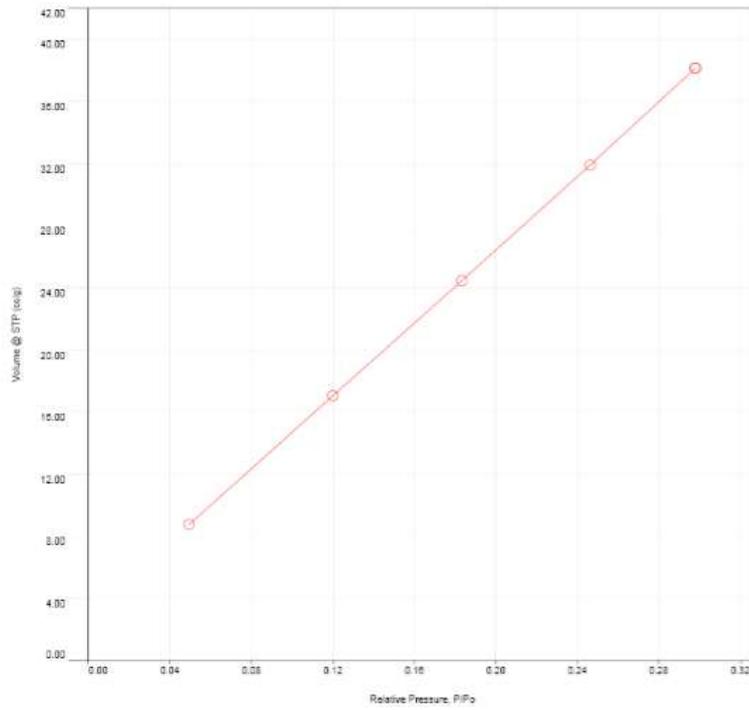
Plot of Volume against Relative Pressure.
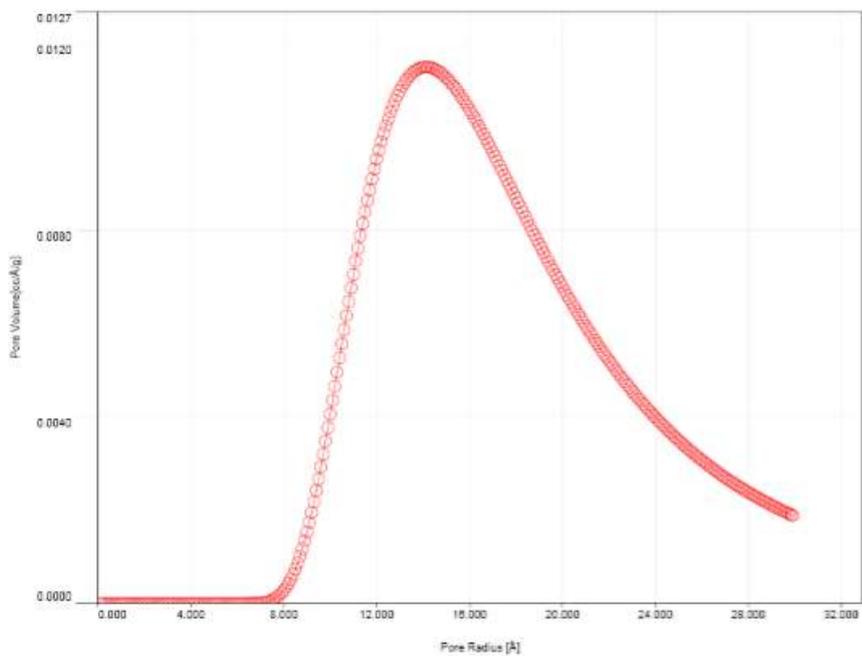
Plot of pore volume against pore radius.