

**TORREFACTION AND CHARACTERIZATION OF MAHOGANY SAWDUST FOR
SOLID FUEL PRODUCTION**

BY

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ABSTRACT

As interest in biomass utilization into combustion fuels grows, the torrefaction, becomes ever more important. Torrefaction is aimed to maximize energy by removing undesirable components (water, hemicellulose and volatile matter) which cause poor ignition characteristic, excessive smoking and low combustion efficiency when used for energy generation in boilers and blast furnaces. In this research, the effect of torrefaction on the physiochemical and combustion characteristic of tropical biomass (Mahogany Sawdust) were investigated. The proximate and ultimate analyses of the tropical biomass were determined before torrefaction and at different torrefaction temperature (200, 250 and 300 °C). The Sawdust was subjected to thermal degradation test via Thermogravimetric Analysis (TGA). Fourier Transform Infrared Spectroscopy (FT-IR) analyses were also carried out to determine the presence of active functional group in the raw biomass and the resulting torrefied biomass. Electron Microscopy (SEM) analysis was finally carried out to determine the morphologies of the raw and torrefied biomass. The result of biomass weight loss as function of temperature variation revealed that at relatively low torrefaction temperature of 200 and 250 °C the weight loss were very pronounced, whereas at torrefaction temperature of 300°C, the weight loss of the tested biomass becomes relatively negligible. In the fixed bed furnace, the change in sawdust mass yield between 10 min was (21.37%) and 30 min (32.14%) at 200°C was about 10.77% and it increased between 200°C and 300°C. The oxygen-carbon ratio deduced from the ultimate analysis of the torrefied biomass displayed a low and concentrated distribution in the Van Krevelin plot than those of raw biomasses. The thermal stability of the biomass feedstock from TGA were found to be in the decreasing order of 300>250>200°C. TGA curves for raw sawdust and torrefied sawdust showed three main decomposition with the curves of torrefied sawdust shifting to higher temperatures. The energy yield of torrefied sawdust is higher than that of untorrefied sawdust. The optimal heating value of the torrefied SD was found to be 28.2 MJkg⁻¹ against 19.5MJkg⁻¹ of the raw SD depicting 44.62% increase of the heating value. The FTIR showed that torrefied sawdust at 300°C has more C=C than sawdust torrefied at 200°C and 250°C. The plot of conversion against temperature and ln g (α) against 1/T for SD using first order kinetic shows first order kinetic shows a linear relationship with regression coefficient (R²) of 0.7442. The torrefied briquettes strength was in order of: 300°C>250°C>200°C. The finding from this study revealed that the Sawdust from mahogany can be used as a solid renewable and environmentally friendly fuel as an alternative or potential replacement for coal.

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CHAPTER ONE

1.0

INTRODUCTION

1.1 Background to the study.

Energy has always played a significant role in life, survival and development of mankind and one of the major challenges of the 21st century is bridging the gap between energy supply and demand with pure dependable and cheap energy.

There are several sources of energy ranging from fossil to renewable source (Garba *et al.*, 2013). Most of this world energy needs are met through fossil fuel such as coal, oil and natural gas. Fossil fuels are non-renewable and demand for this energy is projected to increase which creates concern for sustainability. To find a balance between growing economy, environmental protection and improved quality of life in future, there is need for renewable energy source. Biomass demand as a better fuel is high but raw biomass has a relatively low density, energy and contains too much moisture which can rot during storage, and also is difficult to comminute into small particles. If agricultural wastes are properly recycled, it would rid the environment of solid waste and enhance the aesthetics.

Energy and fuel are the important links in civilization and human development. For effective economic growth and development of a country, the energy has to be adequate and affordable. Also, the economic development of a country can be examined through the method of consumption of the energy and richness of energy availability (Mahmoud *et al.*, 2012). The extensive use of fossil fuels for energy has become a major cause of global warming due to increasing emission of carbon dioxide into the atmosphere.

In Nigeria, the major source of energy in the rural community is fuel wood. According to (Davies, 2013) the demand and need for fuel wood was projected to rise to 213.4×10^3 metric

tonnes, while the supply will decrease to about 28.4×10^3 metric tonnes by the year 2030. The uncontrolled level of cutting of wood for fire wood and charcoal for combustion and for other domestic and industrial uses is now a serious problem in Nigeria. This has led to environmental degradation, deforestation, and misuse of soil forests and water resources. Bio-energy is one among the highly promising energy resources that is renewable which hold not just the key to the present fuel problems but also a future solution (Omemu *et al.*, 2008).

Biomass is organic matter derived from living, or recently living organisms. As an energy source, biomass can either be used directly through combustion to produce heat, or indirectly after converting it to various forms of bio fuel. Burning biomass appears not to be the only way in which its energy can be released; it can be transformed to other means of energy. Conversion of biomass to bio fuel for instance, can be achieved by different methods which include thermal, chemical and biochemical methods. In a statement made by Pondel (2015), biomass is generally characterized by its high moisture content and volatility and also by its low Higher Heating Value (HHV) and energy density levels compared to fossil fuels. From history, humans have used biomass-derived energy since the time when people began burning wood to make fire. Even today, biomass is the only source of fuel for domestic use in many developing countries. The potential for the use of biomass as energy source in Nigeria is very high because about 80% of Nigerians are rural and semi-urban dwellers and they solely depend on biomass for their energy needs (Onuegbu *et al.*, 2011).

Also, a high quantity of agricultural and forestry residues produced annually have not been properly utilized or have been vastly under-utilized. The practice that is common is to set ablaze these residues or abandon them to decompose. Coconut shell for instance, is an agricultural waste which has not been fully utilized. Previous studies by (Jekayinfa and Omisakin 2015) found that coconut shell has a calorific value between 18.1 and 20.8 MJ/Kg which is relatively high and it is coupled with relative low ash content of 3.5-6%. To

efficiently use this biomass material, different conversion methods have been employed to enhance its fuel characteristics. Also, it can be combined with other biomass materials. (Its benefits are that it is cheap, can be found in areas where wood is scarce, it is renewable and contain a reasonable amount of energy. Cow dung, for example, which when converted into biogas contains around 50% methane and 30% carbon dioxide by mass, which means fewer energy extractions when burnt directly. Cow dung is estimated to have an approximated energy density of 12 MJ/Kg if it is burned with an efficiency of 100 % Demirbas (2015).

A technology that meets all these challenges mentioned above and also improves the quality of biomass as fuel is torrefaction. Torrefaction and briquetting of biomass process improves the handling characteristics of the biomass, enhances its volumetric calorific value and reduces transportation cost, (Sandip, 2014). This technology among so many advantages is eco-friendly and mahogany is the most used wood in Nigeria making the sawdust from it generally available in a large quantity.

Torrefaction is a pre-treatment technology aimed at processing biomass fuels to facilitate or enable their use in thermochemical processes. It is a mild form of pyrolysis, where biomass is subjected to temperatures around 230-320 °C in a non-oxidizing atmosphere (Muhammad *et al.*, 2014). As studied by Sandip (2014), the main components of biomass are cellulose, hemicellulose and lignin which are collectively called lignocellulose. These lignocellulose bio-materials can be briquetted without binder. The torrefaction process enhances the effectiveness of biomass as solid fuel which leads to improvement of combustion properties such as increased calorific value, adiabatic flame temperatures and reduced volatility (Muhammad *et al.*, 2014). Torrefaction also leads to increased hydrophobicity, better grinding and decrease in biological degradation activity. The degree to which the biomass properties are altered depends on the supposed “severity” of torrefaction, which relates to the residence time and temperature used in the process (Yash *et al.*, 2014).

The chemical structure of the torrefied material is altered, which produces water, carbon monoxide, carbon dioxide, methanol, and acetic acid. Investigations cited in the open literature are often related to farming application or conversion to value added-product. For instance, Omemu *et al.* (2008) studied the effect of different pretreatment of maize cob on growth of the six different fungi. Ashish *et al.* (2005) evaluated the biochemical parameters in reduced time and temperature in order to optimize cellulose production by *Aspergillus terreus* on ground nut shell. Mahmoud *et al.* (2012) and Oyetola *et al.* (2006) reported the use of ground nut shell and rice husk in sand-crete block production.

The fundamental mechanism in all these processes is devolatilization. Devolatilization of biomass materials is the decomposition of the biomass into permanent gases, condensable vapours and solid residue. Biomass Devolatilization starts at a temperature of about 227°C, and fast rates are attained at about 300°C and the process is terminated at 300-320 °C (Shafizadeh, 2009). Once the devolatilization species enter the gas phase, the volatile species may interact depending on the biomass property and its composition, heating condition, surrounding gas atmosphere and residence time distribution. Renewable denotes energy from sources that are naturally replenishing but flow limited. They are virtually exhausted in duration but limited in amount of energy that is available per time. Majorly this form of energy source includes solar, wind, geo thermal, hydropower and biomass.

Pyrolysis represents the chemical decomposition of organic matters by heating in the absence of oxygen. The biomass decomposes into vapor, aerosol and char; the proportion of these three states depends on temperature and duration of pyrolysis. This process can be fast, slow or mild depending on the time, temperature and the properties of product desired. Thermal fast pyrolysis gives the highest yield of liquid and could be demonstrated as gasification and liquidification. To obtain some desired improved fuel quality of biomass, there is need for mild

pyrolysis to be applied in conversion and the major thermo chemical conversion process for it is known as Torrefaction.

1.2 Statement of the Research Problem

Energy is an essential tool for economic growth and development. However, the energy should be available and affordable. The present energy sources are nonrenewable, expensive, finite and not environmentally friendly. Therefore the need for a cheaper, renewable and environmentally friendly fuel source.

Also, Sawdust has been used over the years as a fuel especially in rural part of Nigeria where wood is scarce. Unfortunately, burning sawdust efficiently is more difficult than burning wood efficiently. It produces some pollutants and is a major health hazard in countries where it is burnt indoors with limited ventilation. There is therefore the need to improve the fuel characteristics of this sawdust for complete utilization of the energy contained in it. This research presents a technology that has the potential to ameliorate many or all of these deficiencies through a form of thermal processing known as “Torrefaction”.

1.3 Aim and Objectives

The aim of the study was to carry out torrefaction and characterization of mahogany saw dust for solid fuel production.

The objectives of this study were to:

- i. collect mahogany saw dust, removal of impurities and drying.
- ii. carry out the ultimate analysis and proximate analysis of the raw biomass.
- iii. carry out fix bed pyrolysis experiment on Saw dust to enhance the fuel properties of the biomass.

- iv. carry out the ultimate analysis and proximate analysis of the raw and torrefied biomass
- v. determine of the mass yield and energy yield and of the torrefied biomass.
- vi. characterize of the biomass and torrefied biomass using FTIR, TGA and SEM.
- vii. determine the kinetic parameter of the samples

1.4 Justification for the Study.

The importance of energy in economic growth and development cannot be over emphasized, however, for this energy to be effective, it has to be affordable and available. This research used biomass material (Mahogany wood saw dust) which are so abundant and also cheap. The biomass material being cheap and found locally in almost all saw mills within the country without any need for importation will help in enhancing the gross domestic product of the nation and also help in converting waste to wealth thereby combating the waste management problem which has been a major setback for the country. Also, the fuel produced which is environmentally friendly will serve as an alternative to the fossil fuel thereby solving the problems associated with fossil fuels.

1.5 Scope of the Study

The scope of this work is limited to collection of raw mahogany Saw Dust (SD), removal of impurities, carrying out proximate and ultimate analysis, torrefaction at different temperatures and residence time and characterisation of the solid fuel using TGA, FTIR, and SEM .

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1 Biomass

The world economy is slowly but steadily changing from non-renewable fossil fuels energy to renewable and sustainable energy. Energy from biomass can be regarded as carbon neutral owing to the carbon cycle. Unlike fossil fuels, biomass is a renewable source of energy that can be replenished; exploiting biomass for energy production does not result to net greenhouse release to the atmosphere. A good example is wood, which is obtained from trees. Wood absorbs sunlight and CO₂ from the atmosphere during photosynthesis to produce cellulose from sugar, thus, the cellulose which keeps in stored chemical energy, released this energy as heat when combusted and the CO₂ liberated as off-gas is the same to the amount absorbed during photosynthesis process. Hence, biomass can be greenhouse gas emission neutral. Increasing the use of biomass for energy purpose thus help to reduce the release of Greenhouse Gases (GHG) emission.

The word “biomass” initially meant the total mass of living matter within a stated environmental area. But recently it also explains plant product, vegetation or agricultural residues used as energy source. Tumuluru *et al.* (2010) also defined biomass material as a composite of carbohydrate polymers, with a small quantity of inorganic substance and low molecular weight extractable organic elements. Others defined biomass as a biological or organic material, which can be used as a source of renewable energy after executing certain processes. It can also be grouped as a carbon base material, comprises of organic molecule having hydrogen, oxygen, nitrogen and small amount of atoms containing alkali, alkaline earth and heavy metals. Energy content of biomass are collected from the sunlight and stored in form of chemical energy, stored energy from biomass can be converted into heat energy at any suitable time with certain transformation processes.

Biomass feedstock can be from agricultural crops, trees or crops grow for energy production, wood residues, wood wastes, agricultural residues, animal or human wastes and municipal wastes.

2.1.1 Biomass component

The plant cell wall is a strong, usually flexible but sometimes rigid layer which provides structural support from external, mechanical and physical forces. Biomass is made up of three main polymeric constituents; hemicelluloses, cellulose and lignin and generally they cover 20-40, 40-60 and 10-25 wt% for lignocelluloses biomass (Yang *et al.*, 2005 and McKendry, 2012). The main components of biomass are cellulose ($(C_6H_{10}O_5)_n$), hemicellulose ($(C_5O_4)_n$), and lignin (polymer with phenol units or cross linked phenyl propane polymer) which are all lignocellulose. Lignocellulose is an important resource for the production of fuels, in the past; it has been used in low value due to its lower energy density as compared to fossil fuel.

2.1.1.1 Cellulose:

Cellulose, the common organic compound on Earth, is the primary structural component of cell walls in biomass. Its amount varies from 90% (by weight) in cotton to 33% for most other plants. Cellulose is highly insoluble and, though a carbohydrate is not digestible by humans. It is a dominant component of wood, making up about 40 to 44% by dry weight (Kalia *et al.*, 2011). Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of units. Cellulose has no taste, is odourless, hydrophilic with the contact angle of 20-30. It is biodegradable, insoluble in water and most organic solvents and it is also chiral. Properties of cellulose depend on its long chain length or degree of polymerization, the number of glucose units that make up one polymer molecule.

Molecules having very small chain length as a result of breakdown of cellulose are known as cellodextrins. As compared to long-chain cellulose, cellodextrins are relatively soluble in water and organic solvents.

Plant derived cellulose is usually found in a mixture with hemicellulose, lignin, pectin and other substances, whereas bacterial cellulose is quite pure, has a much higher water content and higher tensile strength as a result of higher chain lengths (Klemm *et al.*, 2005). At high temperatures above 350 °C, cellulose undergoes thermolysis also called pyrolysis decomposing into solid char, vapors, aerosols and gases such as carbon dioxide. Bio-oil is formed at 500 °C at maximum yield of the condensation of vapours. At high temperatures of 350-600 °C (pyrolysis temperatures), semi crystalline cellulose polymers react in a few seconds, the transformation occurs through a solid-to-liquid-to-vapour transition with the liquid known as molten cellulose existing for only a fraction of seconds. The major combustible component of non -food energy crops is cellulose with lignin second. Cellulose is the raw material in the manufacture of nitrocellulose which is used in smokeless gunpowder. In the industries, cellulose is mainly gotten from wood pulp and cotton. In the separation of cellulose from lignin which is also a major component of plant matter, the Kraft process is used (Klemm *et al.*, 2015).

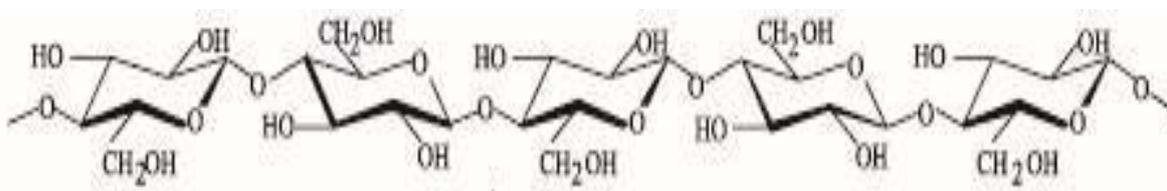


Figure 2. 1: Chemical Structure of Cellulose (Kalia *et al.*, 2011)

2.1.1.2 Hemicellulose

Hemicellulose is another constituent of the cell walls of a plant. While cellulose is of a crystalline, strong structure that is resistant to hydrolysis, hemicelluloses has a random, amorphous structure with little strength. Hemicellulose is a polysaccharide related to cellulose that comprises about 20 % of the biomass of most plants. Unlike cellulose, hemicellulose is derived from several sugars in addition to glucose especially xylose but also including mannose, galactose, rhamnose and arabinose. As compared to cellulose, hemicellulose consists of shorter chains between 500-3000 sugar units. It is also branched while cellulose is unbranched as shown by Gibson (2013). Hemicellulose is any of a group of complex carbohydrates that with other carbohydrates e.g. pectin surrounds the cellulose fibre of plant cells. Also, any of several polysaccharides that are more complex than a sugar and less complex than cellulose and found in plant cell walls is hemicellulose. Like cellulose, most hemicellulose functions as supporting material in the cell wall. Most hemicellulose has a degree of polymerization of only 200. The amount of hemicellulose of the dry weight of wood is usually between 20 to 30 %.

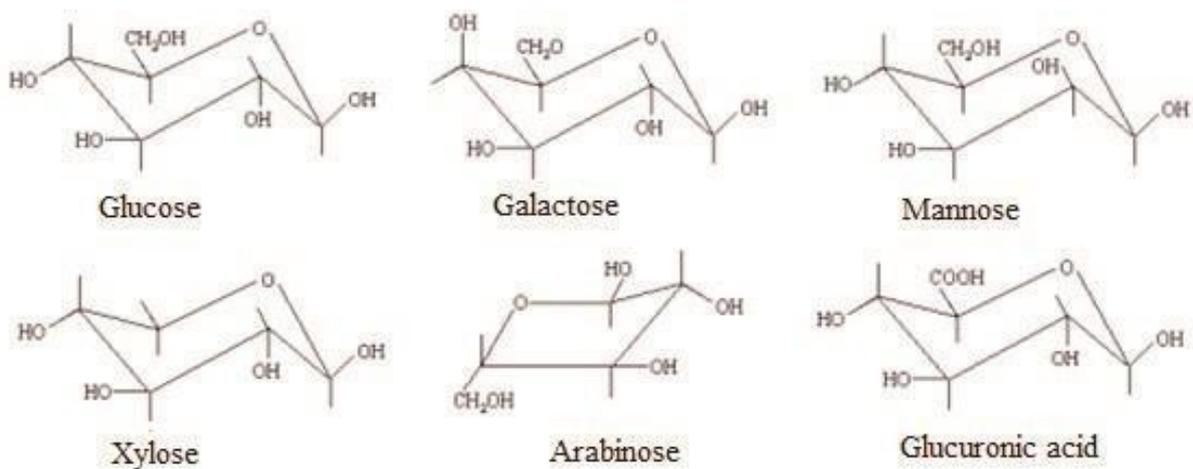


Figure 2.2: Chemical Structures of Main Components of Hemicelluloses (Gibson 2013)

2.1.1.3 Lignin:

Lignin is a complex highly branched polymer of phenyl propane and is an integral part of the secondary cell walls of plants. It is primarily a three dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2,5-dimethoxy phenol. It is one of the most abundant organic polymers on Earth (exceeded only by cellulose). It is the third important constituent of the cell walls of woody biomass (Van Soest *et al.*, 2011). Lignin is an organic substance binding the cells, fibres and vessels which constitute wood and the liquefied elements of plants as in straw. After cellulose, it is the most abundant renewable carbon source on earth. Lignin is a class of complex organic polymers that form important structural materials in the support tissues of vascular plants and some algae. Lignin has a unique attribute of being the only large scale biomass source of an aromatic functionality. Also, it is composed of up to three different phenyl propane monomers depending on the species. Lignin and cellulose work together to produce a structural function in plants analogous to that of epoxy resin and glass fibres in a fibre glass boat. The fibrous components, cellulose or glass fibres are the primary load-bearing elements while the matrix, lignin or epoxy resin provides stiffness and rigidity. Therefore trees (lignin content between 20 and 30 % of dry weight) grow much taller than grasses (lignin content below 20 %) before they bend under their own weight. Besides their structural function, lignin plays several other biological.

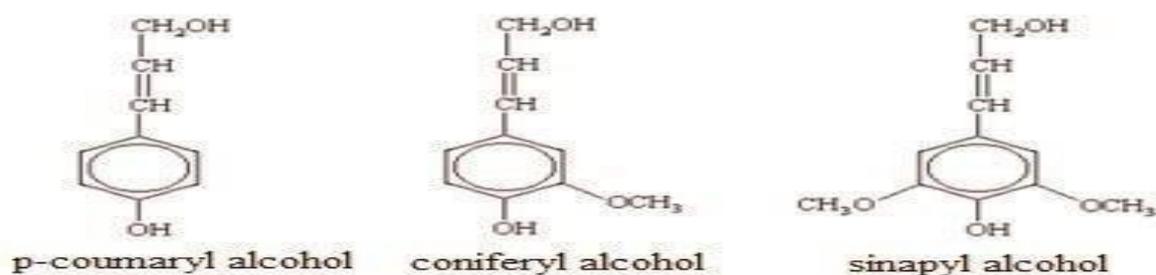


Figure 2. 3: Chemical Structures of Main components of Lignin (Van Soest *et al.*, 2011)

Table 2.1: Lignocellulosic Compositions of Some Agricultural Wastes

Agricultural waste	Cellulose	Hemicellulose	Lignin
Palm shell	29.0	47.7	53.4
Coconut shell	15.0	35.0	50.0
Almond shell	32.5	25.5	24.8
Cocoa pod	41.1	35.26	0.95
Delonix regia pod	13.9	24.13	23.36
Sugarcane bagasse	42.16	36.0	19.30
Apple pulp	16.0	16.0	21.0
Coconut husk	0.52	23.70	3.54
Plantain peel (ripe)	13.87	15.07	1.75
Plantain peel (unripe)	10.15	11.38	1.75
Kola nut pod	38.72	40.41	21.29
Soft wood	36.0	18.5	30.5

(Munir *et al.*, 2015)

2.1.2 Category of biomass material

From the definition of biomass, biomass for energy can include a variety of materials, biomass have being classified for easy description. The basis classes of biomass material are five which are listed in Table 2.2

Table 2.2: Category of Biomass Material

Biomass Type	Sources
Virgin wood	Forestry, wood processing plant.
Energy	High yield crop specification for energy application.
Agricultural residue	Residue from agriculture, harvesting or processing.
Food waste	Drink and food manufacturing, preparation, processing and post consumers waste.
Industrial waste and co-products	Manufacturing and industrial process

(Nakoo *et al.*, 2009)

2.1.3 Fuel Characteristics of biomass

Fuel descriptions of biomass depends on the origin of the biomass which are classified by their chemical and physical properties, sizes shapes, specific capacity, thermal conductivity, moisture content, bulk density, grindability and porosity described the physical properties of the biomass, the chemical properties are described by proximate and ultimate analyses and thermal decomposition. The ultimate analysis of biomass gives the elemental structures of biomass by weight percentage in the form of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), chloride (Cl), and ash elements such as sodium (Na), and potassium (K) compounds etc. However, the proximate analysis gives the percentage weight of fixed carbon (FC), moisture contents (MC), ash content (AC), and volatile matter (VM) in biomass, the method of analysing these analyses are based on the standards in ASTM, ISO etc. These chemical compositions change with oxygen concentration during torrefaction, temperature and residence time for all types of biomass fuels. Cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches also affect the combustion process of biomass. The concentration on

each time of compounds differs depending on species, nature of plant tissues, phase of development and growing environment (Jenkins *et al.*, 1998).

2.2 Method and Technique for Biomass Conversion

There are three methods for the conversion of biomass, they include;

1. Biochemical methods
2. Mechanical methods
3. Thermochemical methods

2.2.1 Biochemical method of conversion

This involves the addition of chemical and biological organisms such as bacteria, fungi, enzymes to act on the material so as to produce some toxic material to enhance its decomposition and decay, such methods of conversion includes

1. Anaerobic digestion with full scale production of combustible biogas by using phototrophic microorganism such as algae.
2. Fermentative process for production of bio-hydrogen.
3. Plant nutrient to support crop production.

2.2.1.1 Anaerobic digestion

This involves the breakdown of complex organic materials and the biogas is formed by following hydrolysis, acidogenesis, acetogenesis and methanogenesis. The solid compound gets liquefy in acidogenesis and converted in to acid, alcohol and volatile fatty acids. Bio-hydrogen production is carried out by following three steps such as photosynthetic production by algae in two stage photosynthesis and hydrogen production, photobiological production by photo-fermentative bacteria and by anaerobic fermentative bacteria.

Anaerobic digestion is a commercially proven technology and is widely used for recycling and treating wet organic waste and waste waters. It is a type of fermentation that converts organic

material into biogas, which mainly consists of methane (approximately 60%) and carbon dioxide (approximately 40%) and is comparable to landfill gas. Similar to gas produced via gasification above, gas from anaerobic digestion can, after appropriate treatment, be burned directly for cooking or heating. It can also be used in secondary conversion devices such as an internal combustion engine for producing electricity or shaft work. Virtually any biomass except lignin (a major component of wood) can be converted to biogas—including animal and human wastes, sewage sludge, crop residues, industrial processing by products, and landfill material (Gierlinger *et al.*, 2008) The conversion of animal wastes and manure to methane/biogas can yield significant health and environmental benefits. Methane is a Greenhouse Gas (GHG) that is 22 to 24 times more powerful than carbon dioxide (CO₂) in trapping heat in the atmosphere. By trapping and utilizing the methane, GHG impacts are avoided. Further, the pathogens existing in manure are eliminated by the heat generated in the bio digestion process and the resulting material provides a valuable, nutrient-rich fertilizer (Shaffizedeh, 2009).

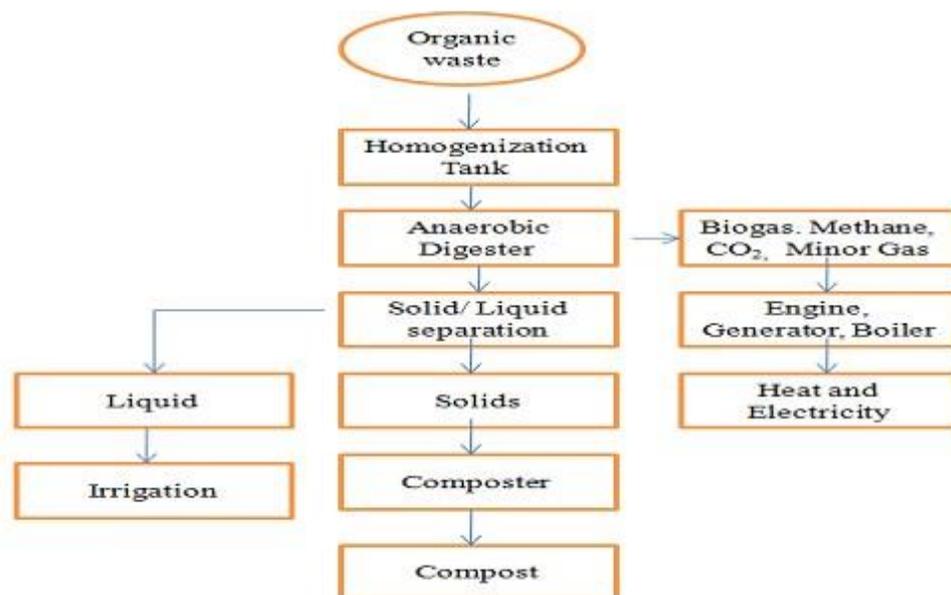


Figure 2.4: Flow Diagram of Anaerobic Digestion Process and End Points of products (Gierlinger *et al.*, 2008).

2.2.2. Mechanical method of conversion

Some of the material use in briquetting and pelletization defines the mechanical of the biomass which has to do with its density and compaction. Nature has created a diversity of biomass with varying specifications in order to create highly efficient biomass energy chains. Torrefaction of biomass in combination with densification (pelletisation and briquetting), it is a promising step to overcome logistic economics in large scale green energy solutions.

2.2.3 Thermochemical method of conversion

This method does not necessarily produce useful energy directly, but under controlled temperature and oxygen conditions are used to convert the original biomass feedstock into more convenient forms of energy carriers, such as producer gas, oil or methanol. The carrier gases are either more energy dense and therefore reduce transport costs or have more predictable and convenient combustion characteristics allowing them to be used in internal combustion engines and gas turbines. These methods of conversion are sub-divided into; carbonization, gasification, pyrolysis and torrefaction. Thermochemical conversion is a high temperature chemical reforming process that breaks apart the bonds of organic matter and converts these intermediates into char, syngas and highly oxygenated bio oil. It can also be described as a conversion technology which uses methods under controlled temperature and oxygen conditions to convert the original biomass feedstock into more convenient forms of energy carriers such as producer gas and methanol. The advantages of thermochemical conversion include; no fugitive gas emission, short processing time on the order of minutes and high temperature elimination of pathogens. The products of this conversion method have more

combustion characteristics allowing them to be used in internal combustion engines and gas turbines. This technique of conversion involves; torrefaction, gasification, carbonization, pyrolysis and direct liquefaction.

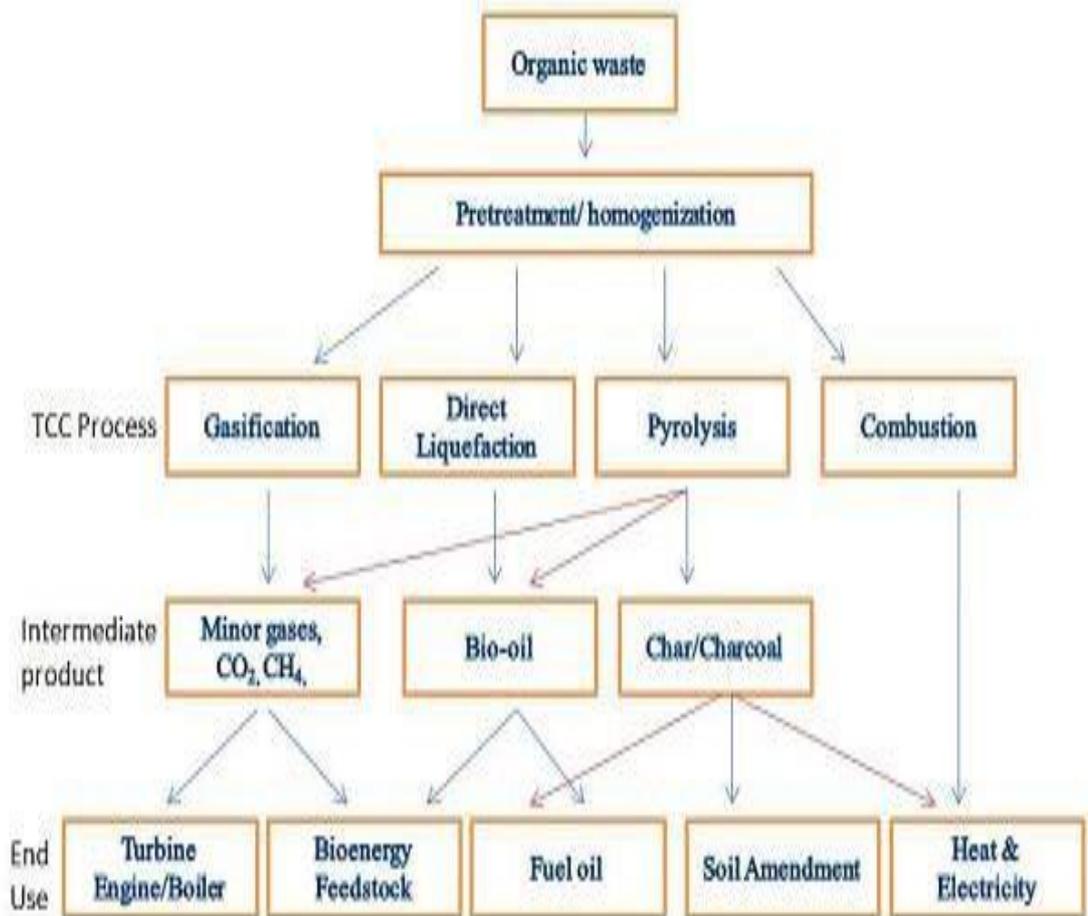


Figure 2.5: Main Thermochemical conversion processes, their intermediate products and suggested end use. (Shafizedh, 2009)

2.2.3.1 Direct combustion boiler and steam turbines

Combustion Biomass Power technologies convert renewable biomass fuels to heat and electricity using processes similar to those employed with fossil fuels. At present, the primary approach for generating electricity from biomass is combustion direct-firing. Combustion systems for electricity and heat production are similar to most fossil-fuel fired power plants. The biomass fuel is burned in a boiler to produce high-pressure steam. This steam is

introduced into a steam turbine, where it flows over a series of turbine blades, causing the turbine to rotate. The turbine is connected to an electric generator.

The steam flows over and turns the turbine. The electric generator rotates, producing electricity. This is a widely available, commercial technology. Combustion boilers are available in different designs, depending on application and biomass characteristic (McKendry, 2001).

The main options are to burn the biomass on a grate (fixed or moving), or to fluidize the biomass with air or some other medium to provide even and complete burning. Steam turbine designs also vary in terms of their application. To maximize power production, condensing turbines are used to cool steam.

Most biomass-fired steam turbine plants are located at industrial sites that have a steady supply of biomass available. These include factories that make sugar and/or ethanol from sugarcane at pulp and paper mills. At these sites, waste heat from the steam turbine can be recovered and used for meeting industrial heat needs—further enhancing the economic attractiveness of such plants. Referred to as combined heat and power (CHP) facilities (also called cogeneration facilities), these facilities are highly resource efficient and they provide increased levels of energy services per unit of biomass consumed compared to facilities that generate power only. Conventional thermoelectric stations convert only about one-third of the fuel energy into electricity. The rest is lost as heat. The adverse effect on the environment through wasteful use of power—particularly detrimental in light of rising fuel costs—means that the efficiency of thermoelectric stations must be increased. CHP provides more efficient production of electricity, where more than four fifth of the fuel's energy is converted into usable energy, resulting in both economic and environmental benefits. Cogeneration is the consecutive (simultaneous) production and exploitation of two energy sources, electrical (or mechanical) and thermal, from a system utilizing the same fuel. CHP could be applied to industry in West

Africa where there is simultaneous demand for electricity and heat. In UEMOA countries, there is also significant need for cooling (including refrigeration and air conditioning). Heat from a CHP plant can be used to produce cooling via absorption cycles. At present, most biomass-fired power plants rely on low-cost (or no-cost) biomass residues.

2.2.3.2 Co-firing concept

A modern practice which has allowed biomass feed stocks an early and cheap entry point into the energy market is the practice of co-firing a fossil-fuel (usually coal) with a biomass feedstock. Co-firing has a number of advantages, especially where electricity production is an output. Firstly, where the conversion facility is situated near an agro industrial or forestry product processing plant, large quantities of low cost biomass residues are available. These residues can represent a low cost fuel feedstock although there may be other opportunity costs. Secondly, it is now widely accepted that fossil-fuel power plants are usually highly polluting in terms of sulphur, CO₂ and other GHGs. Using the existing equipment, perhaps with some modifications, and co-firing with biomass may represent a cost-effective means for meeting more stringent emissions targets. Biomass fuel's low sulphur and nitrogen (relative to coal) content and nearly zero net CO₂ emission levels allows biomass to offset the higher sulphur and carbon contents of the fossil fuel (Mathew *et al.*, 2016). Thirdly, if an agro-industrial or forestry processing plant wishes to make more efficient use of the residues generated by co-producing electricity, but has a highly seasonal component to its operating schedule, co-firing with a fossil fuel may allow the economic generation of electricity all year round. Agro-industrial processors such as the sugarcane sugar industry can produce large amounts of electricity during the harvesting and processing season; however, during the off-season the plant will remain idle. This has two drawbacks, firstly, it is an inefficient use of equipment which has a limited life-time, and secondly, electrical distribution utilities will not pay the full premium for electrical supplies which can't be relied on for year round production. In other

words the distribution utility needs to guarantee year round supply and may therefore, have to invest in its own production capacity to cover the off-season gap in supply with associated costs in equipment and fuel. If however, the agro-processor can guarantee electrical supply year-round through the burning of alternative fuel supplies (i.e. coal and bagasse in Mauritius, then it will make efficient use of its equipment and will receive premium payments for its electricity by the distribution facility.

2.2.3.4 Concept of gasification

High temperatures and a controlled environment lead to virtually all the raw material being converted to gas. This takes place in two stages. In the first stage, the biomass is partially combusted to form producer gas and charcoal. In the second stage, the CO₂ and H₂O produced in the first stage are chemically reduced by the charcoal, forming CO and H₂. The composition of the gas is 18 to 20% H₂, an equal portion of CO, 2 to 3% CH₄, 8 to 10% CO₂, and the rest nitrogen (Makunda, 2018). These stages are spatially separated in the gasifier, with gasifier design very much dependant on the feedstock characteristics.

Gasification requires temperatures of about 800°C and is carried out in closed top or open top gasifiers. These gasifiers can be operated at atmospheric pressure or higher. The energy density of the gas is generally less than 5.6 MJ/m³, which is low in comparison to natural gas at 38 MJ/m³ providing only 60% the power rating of diesel when used in a modified diesel engine (Makunda, 2018).

Gasification technology has existed since the turn of the century when coal was extensively gasified in the UK and elsewhere for use in power generation and in houses for cooking and lighting. Gasifiers were used extensively for transport in Europe during World War II due to shortages of oil, with a closed top design predominating.

A major future role is envisaged for electricity production from biomass plantations and agricultural residues using large scale gasifiers with direct coupling to gas turbines. The potential gains in efficiency using such hybrid gasifier/gas turbine systems make them extremely attractive for electricity generation once commercial viability has been demonstrated. Such systems take advantage of low grade and cheap feed stocks (residues and wood produced using short rotation techniques) and the high efficiencies of modern gas turbines to produce electricity at comparable or less cost than fossil-fuel derived electricity. Net atmospheric CO₂ emissions are avoided if growth of the biomass is managed to match consumption. The use of BIG/STIG (Biomass Integrated Gasifier Steam Injected Gas turbine) initially and BIG/GTCC (Biomass integrated Gasifier Gas Turbine Combined Cycle) as the technology matures, is predicted to allow energy conversion efficiencies of 40 to 55%. Modern coal electrical plants have efficiencies of about 35% or less. Combined Heat and Power systems could eventually provide energy at efficiencies of between 50 to 80%. The use of low-grade feed stocks combined with high conversion efficiencies makes these systems economically competitive with cheap coal-based plants and energetically competitive with natural gas-based plants (Johansson *et al.*, 2003).

Studies are continuing in the use of such technologies for the cost effective treatment of MSW e.g. in the Netherlands a study by Faaij *et al.*, (1992) considers that "gasification can become a strong competitor to anaerobic digestion, composting and incineration for biomass waste treatment." This is based on the use of BIG/STIG technology with the system gasification using Atmospheric Circulating Fluidized Bed (ACFB) technology.

2.2.3.5 Pyrolysis concept

Pyrolysis is a thermochemical process that has emerged as one of the most useful technology for converting waste to wealth. The term pyrolysis is used to refer to the process by which a

substance is subjected to heat at elevated temperatures usually between (400-800° C) in an environment that is oxygen free in order to cause degradation of such substance into valuable products (Hassan *et al.*, 2016). When a solid material is cracked using pyrolysis, three main products are generated which are, pyrolysis liquid, pyrolysis gas and pyrolysis solid or char

The biomass feedstock is subjected to high temperatures at low oxygen levels, thus inhibiting complete combustion, and may be carried out under pressure. Biomass is degraded to single carbon molecules (CH₄ and CO) and H₂ producing a gaseous mixture called "producer gas." Carbon dioxide may be produced as well, but under the pyrolytic conditions of the reactor it is reduced back to CO and H₂O; this water further aids the reaction. Liquid phase products result from temperatures which are too low to crack all the long chain carbon molecules so resulting in the production of tars, oils, methanol, acetone, etc. Once all the volatiles have been driven off, the residual biomass is in the form of char which is virtually pure carbon (Moyoral *et al.*, 2001).

Pyrolysis has received attention recently for the production of liquid fuels from cellulosic feedstock by "fast" and "flash" pyrolysis in which the biomass has a short residence time in the reactor. A more detailed understanding of the physical and chemical properties governing the pyrolytic reactions has allowed the optimisation of reactor conditions necessary for these types of pyrolysis. Further work is now concentrating on the use of high pressure reactor conditions to produce hydrogen and on low pressure catalytic techniques (requiring zeolites) for alcohol production from the pyrolytic oil (Salman *et al.*, 2014). During the heating of the biomass, gas, liquid and char are formed in proportions that depend on the mode of pyrolysis and the type of pyrolysis system used. Hemicellulose decomposes between 250 and 400 °C and gives up to 20 wt.% of char upon heating to 720 °C, cellulose requires slightly higher temperatures, 310-430 °C, and gives about 8 wt.% of char; and lignin decomposes at 300-530 °C, yielding about 55

wt.% of char (Dmitri and Julia, 2011). Heat transfer is a critical area in pyrolysis as the process is endothermic and sufficient heat transfer surface has to be provided to meet process heat needs. The products of pyrolysis include bio-char, bio-oil and gases including methane, hydrogen, carbon monoxide and carbon dioxide. Depending on the thermal environment and the final temperature, pyrolysis will yield mainly bio-char at low temperatures, less than 450 °C when the heating rate is quite slow and mainly gases at high temperatures greater than 800 °C with rapid heating rates. At an intermediate temperature and under relatively high heating rate, the main product of pyrolysis is bio-oil. In comparison with torrefaction, pyrolysis majorly maximise liquid and gaseous yield of biomass and not solid yield.

2.3 Concept of Torrefaction

Various literature have being able to defined torrefaction in many ways. Acharya *et al.* (2012) defined torrefaction as a thermal pre-treatment process in which isothermal pyrolysis of biomass takes place at a temperature range of 200°C to 300°C for a good residence time, with minimum oxygen concentration. However almost all definitions reveal similarities in terms of processes, the operating temperature range differs from research to research depending on the types and categories of biomass that was study.

Bergman *et al.* (2005), Rousset *et al.* (2011) and Mani (2009) stated that torrefaction temperature ranges from 200°C to 300°C. Prins *et al.* (2006a) and Pimchuia *et al.* (2010) gave temperature range between 230°C-300°; meanwhile Arias *et al.*, (2008) stated temperature range between 220°C-300°C. Most of the research has shown that biomass reveals different performance to thermal treatment owing to their varieties, origin and properties (Bridgeman *et al.* 2008) hence; the commencement of biomass decompositions hangs on the type of biomass.

It produces three major products such as dark color solid product s, yellowish color acidic aqueous products, and non-condensable gaseous products. Torrefaction is usually performed at a low heating rate, which gives a higher yield of solid product. Unlike pyrolysis, the major

motivation of torrefaction is the maximization of the solid yield. Decomposition, devolatilization and depolymerization are the three major reactions that occur during the torrefaction process. This process releases condensable hydrocarbon, hydrogen, oxygen, and some carbon content from the biomass in the form of water, carbon monoxide, and carbon dioxide (Pimchuai *et al.*, 2010). During the torrefaction process, drying is considered to be a more destructive as it breaks inter- and intramolecular hydrogen, C-O, and C-H bonds (Tumuluru *et al.*, 2010). This leads to emissions of hydrophilic and oxygenated compounds, forming a blackened hydrophobic energy dense product.

The main motive of torrefaction is to upgrade the fuel quality of biomass to make it more suitable for the thermochemical conversion. A torrefied biomass can be used in briquetting, pelletization, gasification, and co-firing thermal power plants (Bridgeman *et al.*, 2010). The torrefaction of biomass destructs the tenacity and fibrous structure of the biomass, and also increases its energy density.

Numerous studies concluded that the torrefied biomass can avoid many limitations associated with the raw biomass because it produces moisture free hydrophobic solid products (Acharjee *et al.*, 2011), decreases O/C ratio (Prins *et al.*, 2006), reduces grinding energy (Repellin *et al.*, 2010), enhance energy density (Yan *et al.*, 2007), increases bulk density and simplifies storage and transportation (Bergman,2005), improves particle size distribution(Mani, 2009), intensifies combustion with less smoke , shifts combustion zone to the high temperature zone in a gasifier (Courhert *et al.*, 2009) and increases the resistance to the biological decay (Chen *et al.*, 2012). Many of these improvements make the torrefied biomass more suitable than the raw biomass for co-firing in the conventional coal power plants, with minor modifications .The removal of volatiles (light gases) during the torrefaction leads to a decreased in O/C ratio, and increased the energy density of the biomass. The losses of carbonyl and the carboxyl groups from cellulose, the carboxyl group from hemicellulose, and the aromatic ring and the methoxyl

groups from lignin are the major sources of mass loss during this thermal treatment of biomass (Yang *et al.*, 2007). These components have less energy content than the biomass itself.

Thus, their loss increases the energy density of biomass after torrefaction. The increase in the energy density in the torrefied product may also be due to the higher fraction of lignin (heating value of 25 MJ/kg), and a reduced fraction of hemicellulose and cellulose with heating value 18.6 MJ/kg (Gupta and Demirbas, 2010). The hydroxyl group, which can establish ions and attract water molecules, is responsible for the hydrophilic behavior of biomass. The hydrophilic nature of biomass decreases as the torrefaction reduces the hydroxyl groups through decomposition reactions. The removal of hydroxyl groups also decreases the capability of forming hydrogen bonds that in turn reduces the moisture-absorbing capacity of biomass.

This effect leads to the transformation of polar molecules into non-polar unsaturated molecules and produces a hydrophobic product. The tenacious and fibrous nature of raw biomass established due to a complex structure of interlinked polymeric components increase the grinding cost of biomass. The heat applied during the torrefaction process modifies the complex structures of the interlinked polymeric components. It thus breaks down the hemicelluloses matrix, and depolymerizes the cellulose structure, resulting in a decrease in the fiber length (Bergman and Kiel, 2005). The decomposition of the hemicellulose matrix produces mainly light volatile gases such as CO₂, CO, CH₄ and traces of H₂ (Prins *et al.*, 2006). The decomposition and the depolymerization of the macro-polymeric components to the micro-monomers, which decreases fiber length as well as increases porosity, increase the grindability of biomass. The improvement in the grindability reduces slenderness in the ground particles, producing a uniform particle size distribution suitable for co-firing power.

2.3.1 Types of torrefaction

The process can be under dry condition (dry torrefaction) or wet condition (wet torrefaction).

Wet torrefaction:

This process involves the thermal treatment of solid feed stock utilizing a hydrothermal media or hot compressed water at sub critical pressure. The process is popular for high moisture feedstock like sewage slug, animal manures and fresh biomass because it does not need pre-drying process. The feed stock is submerged in water. It uses water as a medium. Wet torrefaction has been favored owing to the low cost and environment friendly aspect.

Dry torrefaction (DT):

This the thermal treatment of biomass in an inert environment at atmospheric pressure and with low heating rate less or about 50°C/min. The holding time at the maximum temperature can vary but generally are less than an hour. The product of dry torrefaction is majorly bio-char which contain about 90% of the energy in the remains, 70% of the mass, a condensable mixture mostly water, organic components and lipids. The product of dry torrefaction does not exhibit biological activities like rotting.

2.4 Biomass Torrefaction for Energy Application

Thermal pre-treatment or torrefaction is a process that improves the solid fuel properties of biomass. It is a mild temperature pyrolysis that removes moisture content and a proportion of the volatile content, leaving a dry hydrophobic solid product with increased grindability. The changes that occur enhance the fuel properties, making it more favourable for a number of purposes including densification, gasification, dedicated combustion and co-firing. Three time phases are recognised in torrefaction. The reaction time of torrefaction is said to be the sum of heating time from 200⁰C to desired temperature plus reaction time/holding time at desired torrefaction temperature ($t_{tor,h} + t_{tor}$) and the duration of the torrefaction stage usually 30mins.

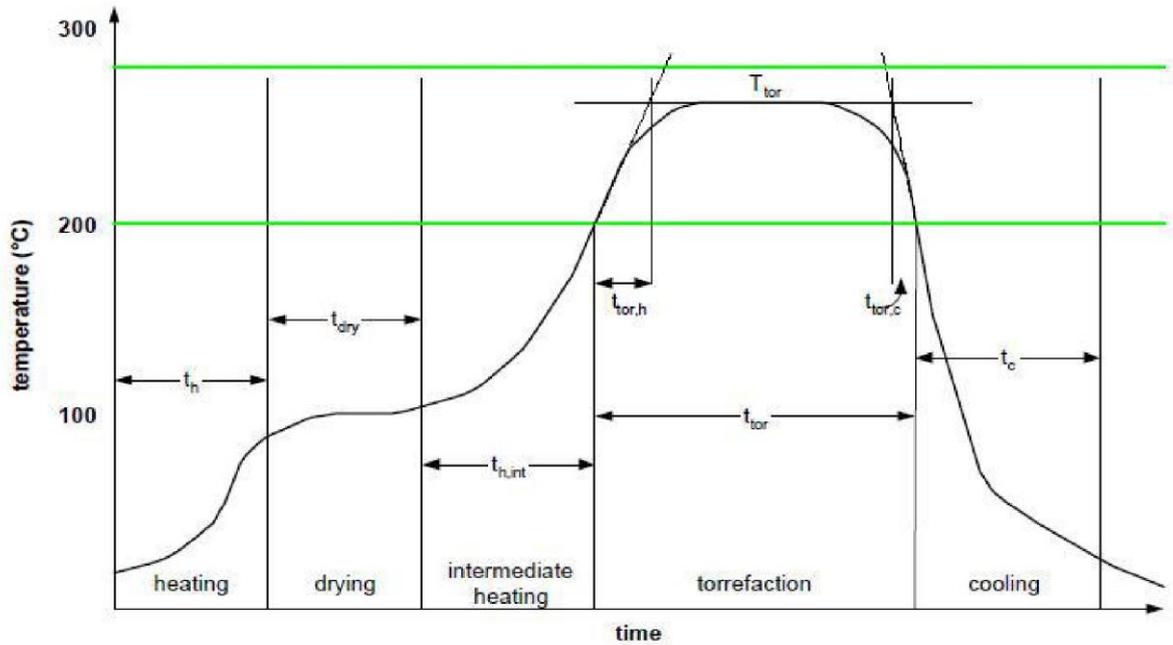


Figure 2.6: Heating Stages of Drying Biomass during a Typical Torrefaction Batch Process (Akinwale, 2011)

Where

T_{tor} = Torrefaction temperature

t_h = heating time to drying

t_{dry} = drying time

$t_{h,int}$ = intermediate heating time to torrefaction

t_{tor} = reaction time/holding time at desired torrefaction temperature

$t_{tor,h}$ = heating time from 200°C to desired temperature

T_{tor} $t_{tor,c}$ = cooling time from T_{tor} to 200°C t_c = cooling time to ambient temperature.

After torrefaction, the last stage is the cooling of the biomass from 200°C to ambient temperature (Akinwale, 2011).

2.5 Physical and Chemical Changes that Takes Place in Biomass Fuels upon Torrefaction.

2.5.1 Colour

One of the physical changes that occur upon torrefaction is in colour of the wood, the colour change to an intense brown product depending on the condition of torrefaction, whether it is in increase in temperature or longer residence time (Brigdeman *et al.*, 2010).

2.5.2 Particle Size and Shape

Another visible change is in the particle size and shape (Arias *et al.*, 2008). Using an optical microscope looked into the changes with a deeper insight of structural modification of the wood that was torrefied. And observed that particle size decreases with increase condition (temperature and residence time).

2.5.3 Mass Loss

Mass loss occurs due to loss in moisture content through evaporation during the drying process and also through the release of reaction water vapour and the production of volatile from the degradation of hemicelluloses and minor decomposition of cellulose during the treatment process.

2.5.4 Moisture Content

The moisture content of biomass is the quantity of water in the material, expressed as a percentage of the material's weight (Raju *et al.*, 2014). This weight can be referred to on wet basis and on dry ash free basis. If the moisture content is determined on a 'wet' basis, the

water's weight is expressed as a percentage of the sum of the weight of the water, ash, and dry-and-ash-free matter. Similarly, when calculating the moisture content on a 'dry' basis, the water's weight is expressed as a percentage of the weight of the ash and dry-and-ash-free matter. Finally, the moisture content can be expressed as a percentage of the "dry and-ash-free" matter content. In that last case, the water's weight is related to the weight of the dry biomass. Because the moisture content affects the value of biomass as a fuel, the basis on which the moisture content is measured must always be mentioned. This is particularly important because biomass materials exhibit a wide range of moisture content (on a wet basis), ranging from less than 10 percent for cereal grain straw up to 50 to 70 percent for forest residues. Moisture content is one of the main parameters that determine the briquette quality. A lower moisture content of briquettes implies a higher calorific value (Deepak and Jnanesh, 2015). Small moisture content is good for the storability and combustibility of the briquettes. Before the first stage of combustion can occur, any water in the system must be driven off, requiring energy and thus, reducing the overall system efficiency and potentially reducing combustion temperature below the optimum. Furthermore, reduction in the combustion temperature may lead to incomplete combustion of the fuel giving rise to the emission of tars and creosote. High efficiency combustion systems are designed to operate within a range of parameters to ensure that performance meets emissions and efficiency specification and a range of acceptable moisture content for the fuel is usually specified. If fuel outside this specification range is used, the system may shut down automatically. Many biomass gasifiers are designed to operate on very low moisture feedstock of about 10-20 %. In terms of transportation, it is more efficient to transport biomass material with low moisture content. High moisture content biomass has a much lower energy density by mass, owing to the weight of water, but also by volume owing to the energy required to evaporate the water. This means that transport is less efficient as a significant proportion of the load will be water. Storage of high moisture content biomass

material is also less efficient. The moisture content is determined according to the method described in the Forestry Hand Book (Wenger, 1984). 10 g of sample is taken immediately upon sampling and then air dried. This air-dried sample is taken immediately in an aluminium moisture box and kept in an oven heated at $105^{\circ} \pm 3$ °C until constant weight is obtained. The difference of the oven dry weight of the sample and the fresh weight of the sample is used to determine the percentage of moisture content as follows:

$$\text{Moisture content \%} = \frac{\text{Fresh weight} - \text{oven dry weight}}{\text{Fresh weight}} \times 100 \quad (2.1)$$

2.5.5 Ash content

After combustion, the residue that remains is the ash content (Chai *et al.*, 2015). Biomass residues usually have much lower ash content but their ashes have a higher percentage of alkaline minerals especially potash. These constituents have the tendency to devolatilize and condense on tubes, especially those of super heaters. These constituents also lower the sintering temperature of ash, leading to ash deposition on the boiler's exposed surfaces. Ash content is the inorganic matter after the complete combustion of biomass. Generally, it contains mainly calcium, magnesium and phosphorus elements that affect the ash fusion (Raju *et al.*, 2014). Ash behaviour agro-waste during thermochemical conversion is one of the most important matters to be studied". The minerals present with the feedstock, when subjected to high temperature and certain conditions, can agglomerate and deposit inside the thermal device leading to slag formation, fouling and bed agglomeration. Inorganic constituents, such as organically bound cations, inorganic salts and minerals make up the ash present in or on the surface of biomass. Ashes are usually formed of CaO, K₂O, Na₂O, MgO, SiO₂, Fe₂O₃, P₂O₅, SO₃ and Cl. The ash content of agricultural waste affects its slagging behaviour together with the operating temperature and mineral composition of ash. Several researchers reported that,

the higher the fuel's ash content, the lower its calorific value. For determination of ash content, ASTM Test No. D-271-48 is followed.

Table 2.3: Ash Content of Different Biomass Type

Biomass	Ash content	Biomass	Ash content
Corn cob	1.2	Tamarind husk	4.2
Jute stick	1.2	Coffee husk	4.3
Saw dust (mixed)	1.3	Cotton shell	4.6
Spine needle	1.5	Tannin waste	4.8
Soya bean stalk	1.5	Almond shell	4.8
Bagasse	1.8	Areca mit shell	5.1
Coffee spent	1.8	Castor stick	5.4
Coconut shell	1.9	Groundnut shell	5.4
Sunflower spent	1.99	Coir pith	6.0
Jovar strain	3.1	Bagasse pith	8.0
Olive pits	3.2	Bean straw	10.2
Alhar stalk	3.4	Barley straw	10.3
Latina camera	3.5	Tobacco dust	19.1
Sababul leaves	3.6	Rice husk	22.4

(Yao *et al.*, 2017).

At first, an empty 25 ml silica crucible as well as the sample is heated in a moisture oven. Sample is weighed accurately to 2 g. The sample in the crucible is kept in muffle furnace with the lid cover. Muffle furnace temperature is set at 550 °C ± 50 °C and kept for 6 hours. After 6 hours of burning crucible is removed from the furnace and placed in desiccators and weighed accurately. Percentage of ash content was calculated as follows:

$$\text{Ash content \%} = \frac{\text{Weight of ash}}{\text{Weight of sample}} \quad (2.2)$$

The ash content of different biomass materials is an indication of slagging behaviour of the biomass. Generally, as the ash contents gets higher, the slagging behaviour increases simultaneously. The temperature of operation, the mineral compositions ash and their percentage combined determine the slagging behaviour. If conditions are favourable, then the degree of slagging will be greater.

2.5.6 Volatile matter

A good biomass generally contains a high volatile matter content of around 70 % to 86 % and low char content. A torrefied biomass whose volatile matter content falls within this range is also an indication of easy ignition of the torrefied and proportionate increase in flame length (Keil *et al.*, 2008). High volatile matter content indicates that during combustion, most of the torrefied biomass will volatilise and burn as gas in the cook stove. Volatile matter of samples is determined by ASTM Test No. D- 271- 48. A clean platinum crucible of 10 ml. capacity is taken and heated in a furnace at 950 °C for 2 minutes and cooled in desiccators for 15 minutes. Crucible weighed to nearest 0.1 mg. Sample filled crucible is weighed and heated in a furnace at 950 °C for 2 minutes. After volatile matter escaped, the crucible is removed from furnace and cooled in air 2 to 5 minutes and then in desiccators for 15 minutes. The percentage of weight loss of the samples is reported as volatile matter as follows:

$$VM = \frac{Wt. loss of dry sample}{Net wt. of dry sample} \times 100 \quad (2.3)$$

$$VM = \frac{Gross wt. of wet sample}{100 - percent moisture} \times 100 \text{ (wet samples)} \quad (2.4)$$

2.5.7 Determination of fixed carbon content

Carbon content refers to the percentage of carbon in a particular sample. The fixed carbon of a fuel is the percentage of carbon available for char combustion. It is not equal to the total amount of carbon in the fuel (the ultimate carbon) since a significant amount is released as a hydrocarbon in the volatiles. Fixed carbon (FC) is determined by ASTM

Test No. D-271-48

$$FC \text{ (on dry basis)} = 100 - (\% \text{ of volatile matter} + \% \text{ of ash}) \quad (2.5)$$

$$FC \text{ (on wet basis)} = 100 - (\% \text{ of volatile matter} + \% \text{ of ash} + \% \text{ of moisture}) \quad (2.6)$$

2.5.8 Calorific value

The Calorific Value (CV) can be defined as the energy content or heat value released when a unit value of it is burnt in air (McKendry, 2002). According to Acharjee *et al.* (2011), calorific value or heat value of a fuel is the most important fuel property.

Calorific value is determined by using a 5EAC/ML Automatic Microprocessor

Calorimeter. The torrefied material is nicely ground and pellets of 10 mm diameter are prepared from grounded material. The pellets are placed inside a crucible so that tungsten wire touches the pellet. The calorific value is analysed by the Automatic Microprocessor Calorimeter or auto bomb calorimeter. The system has facilities such as water cycling system,

automatic water feeding, temperature adjusting with a PT 500 temperature sensor, zero drift bridge temperature circuit to ensure that temperature resolutions reach 0.0001 , auto-diagnose, remote data transfer and auto weight entry.

2.6 Difference Found in Deciduous, Coniferous Woods and Herbaceous Crops

Different biomass behaves differently upon thermal treatment. Prins *et al.* (2006) studied the difference in the torrefaction of two deciduous woods (willow and beech), coniferous wood (larch) and herbaceous crop (straw) at three increasing temperatures and decreasing residence times (230°C,50 mins; 270°C, 15 mins). The result showed that temperature plays a vital role in torrefaction process, where the solid yield decreased with increased temperature. Larch produced the highest yield follow by willow, beech and straw. At 270°C and a residence time of 15 min, the solid yield of torrefied larch was about 92%, while that of torrefied willow was about 83%. The difference can be explained in relation to the hemicelluloses structures of both deciduous and coniferous woods.

Table 2.4: Summary of Torrefied Pallets Properties Verses Coal

Parameter	Wood	Wood pallets	Torrefied Pallets	Coal
Moisture content (% wt)	30-40	7-10	1-5	10-15
Calorific value (MJ/kg)	9-12	15-16	20-24	23-28
Volatile (%db)	70-75	70-75	55-65	15-30
Fixed carbon (db)	20-25	20-25	28-35	50-55
Bulk density (kg/m ³)	200-250	550-750	750-850	800-850
Dust explosibility	Average	Limited	Limited	Limited
Hydroscopic properties	Hydrophilic	Hydrophilic	Hydrophobic	hydrophobic
Biological degradation	Yes	Yes	No	No
Milling requirement	Special	Special	Classic	Classic
Handling properties	Special	Easy	Easy	
Transport cost	High	Low	Low	

(Klemm *et al.*, 2005)

Additionally a number of researches has found out that pelletisation improve the biomass bulk and volumetric density. A combination of torrefaction and pelletisation technique yield a torrefied pallets resulting in easier handling and storage than raw biomass pellets due to their hydrophobicity and resistance to biodegradation (Uslu *et al.*, 2008; kiel *et al.*, 2008). The comparism in fuel characteristics and handling behaviour of raw wood, wood pallet, torrefied wood pallets, coal and charcoal is presented in table 2.4.

Table 2.5: Ultimate Analysis of Feedstock and Thermal Pre-Treated Fuels

Sample	C	H	N	S	O	HHV (KJ/Kg) dry	
						Calculated	Measured.
Willow<10mm	48.6	6.4	0.58	nd	44.4	19000	_____
Willow>20mm	49.3	6.3	0.58	nd	48.8	19300	_____
Willow A.	56.3	6.2	0.83	nd	36.5	24000	21800
Willow B	54.3	6.0	0.76	nd	38.5	21400	21000
Willow C	51.9	6.3	0.36	nd	41.4	20500	_____
Willow D	60.3	5.8	0.52	nd	33.4	23900	23600

(Friedl et al., 2005)

2.6.2 Structure, properties and composition of sawdust

The physical structures, major chemical compositions, and chemical structures of wood are extremely important for studying thermal, chemical behaviours of wood. Wood is composed of micro fibrils, bundles of cellulose molecules (C6 polymers) surrounded by hemicelluloses (predominantly C5 polymers but including C6 species). In between the micro-fibrils, lignin consisting of phenyl-propane molecules is deposited. The cellulose molecules consist of long chains of glucose molecules (normally 8000-10000 glucose molecules), with a general formula of $(C_6H_{10}O_5)_n$ (Sjostrom, 2013). Cotton is almost pure α -cellulose. Cellulose is insoluble in water. The hemicelluloses also consist of glucose molecules and other simple saccharides (normally up to 200 glucose/saccharide molecules), with a general formula of $(C_5H_8O_4)_n$. Unlike cellulose, hemicelluloses are soluble in dilute alkali and consist of branched structures.

The most abundant hemicelluloses are Xylan, Lignin is highly branched, substituted, mononuclear aromatic polymers in the cell walls of certain biomass, especially woody species. Lignin can be broken by treatment with strong sulphuric acid, in which lignin is insoluble. Normally, a tree consists of 3-8% bark, 3-8% needles (leaves), 7-15% branches, and 65-80% trunk . Softwoods are referred to gymnosperm trees (evergreens), which account for about 80% of the timber production source in the world. Hardwoods refer to the wood from angiosperm (deciduous) trees. Table 2.2 shows the differences of major chemical compositions of soft woods and hardwoods. It is seen that in general softwoods have much higher lignin content than hardwoods. Conifers such as pine, spruce and fir belong to softwoods. Typically, the pine consists of 40% cellulose, 28% hemi-celluloses, 28% lignin, and 4% extractives, and the outer bark of pine has more lignin, up to 48%.

Table 2.6: Chemical Compositions of Dry Hardwoods and Softwoods

Softwoods (%)	Hardwoods (%)	
	Softwoods (%)	Hardwoods (%)
Cellulose	40-44	43-47
Hemicelluloses	25-29	25-35
Lignin	25-31	17-23
Extractives	1-5	2-8

(Ebozigbe *et al.*, 2013)

2.6.2 Thermal treatment of wood

During thermal treatment, the decomposition of wood can start at a temperature higher than 300°C (Chen *et al.*, 2003). The hemicelluloses, the cellulose and the lignin behave differently

as shown in fig 2.1. Hemicellulose, the most reactive compound breaks down at temperature range of 225-325°C, cellulose at 305-375°C and lignin gradually over the temperature range of 250-500°C (Shafizadeh, 2009)

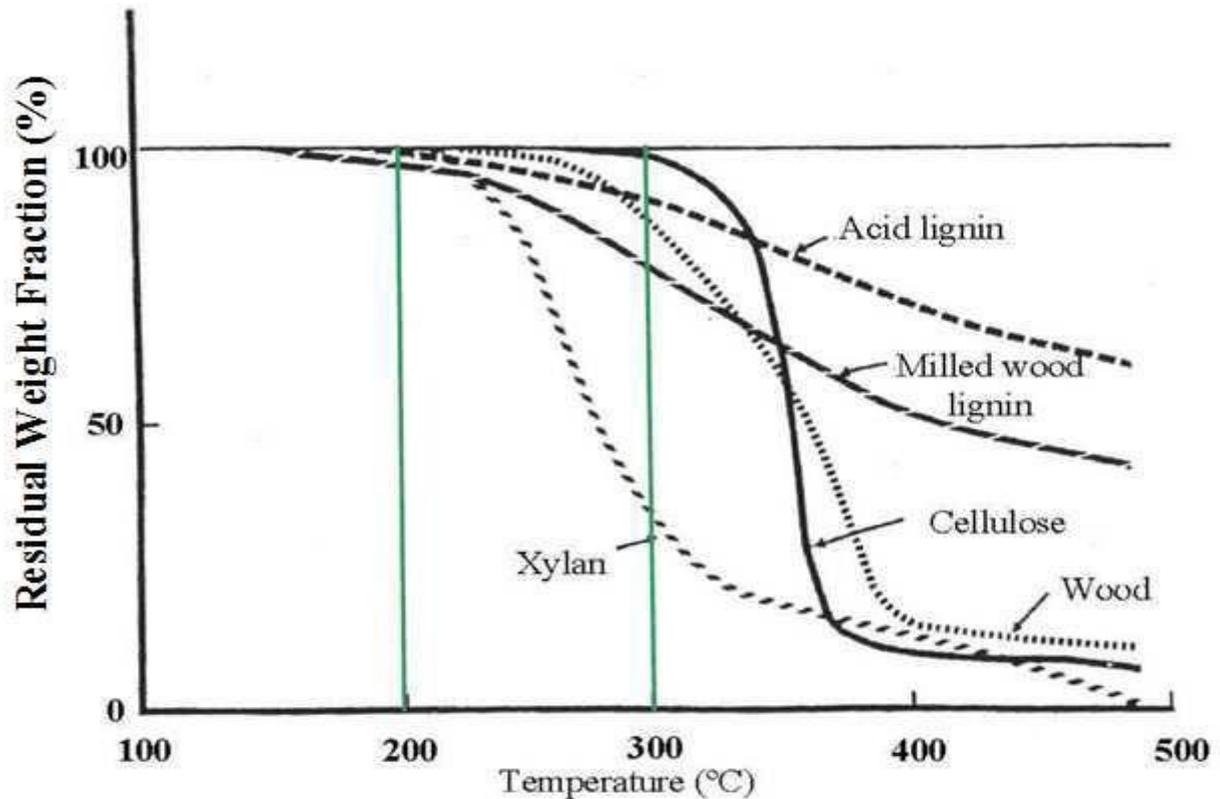


Figure 2.7 Thermal decomposition of wood Modified from Shafizadeh (2009) with permission from Elsevier.

All of these decomposition stages can be grouped into five main reaction regimes at different temperatures:

Regime A: Conventional drying,

Regime B: Glass transition (also called softening) and infusion of lignin,

Regime C: De polymerization followed by condensation of the shortened polymers,

Regime D: De volatilization and carbonization of polymers,

Regime E: Extensive carbonization of all polymers and structures.

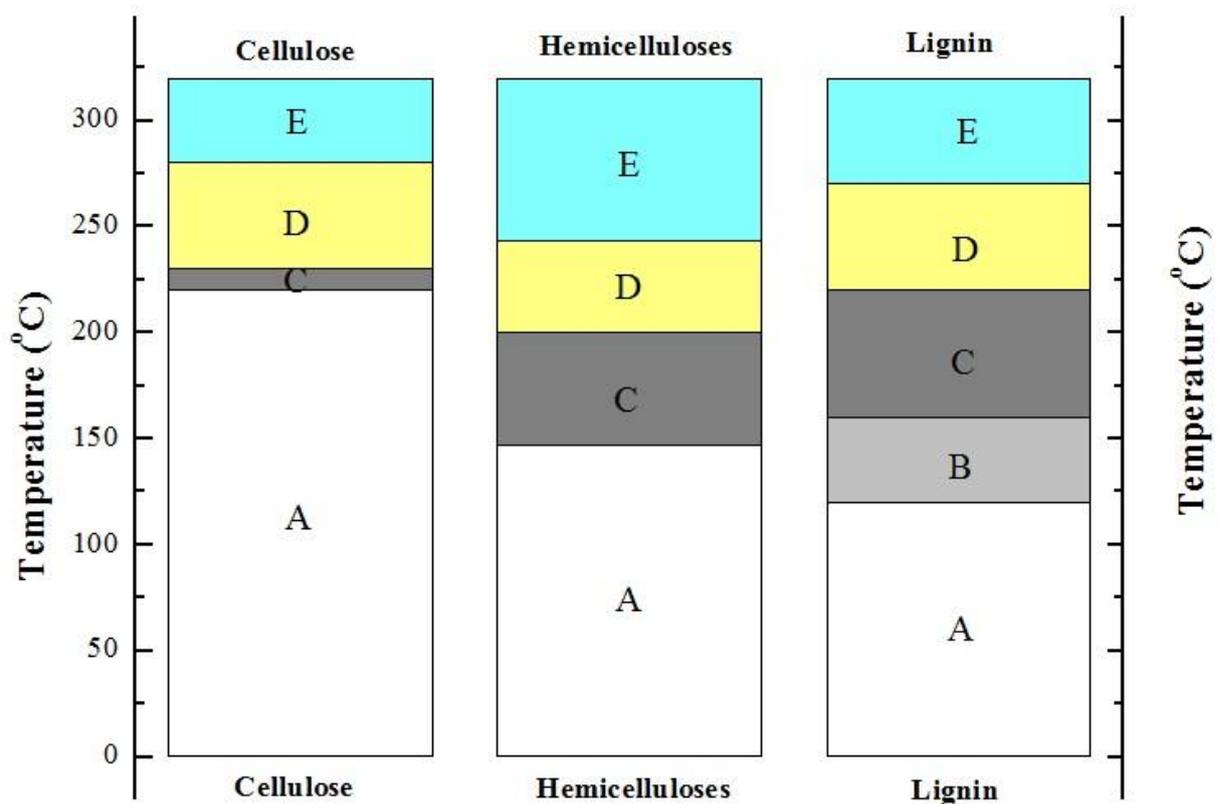


Figure 2.9 Main physico-chemical phenomena of the main components of wood

(A: Drying, B: Glass Transition/Softening, C: De-polymerization and Re-condensation, D: Limited Devolatilization and Carbonization, E: Extensive Devolatilization and Carbonization).

Based on the operation temperature, the thermal treatment of wood can be divided into four processes: conventional drying, heat treatment, torrefaction, and pyrolysis. The conventional drying process occurs at the temperature below 100-130°C for evaporating most moisture. Heat treatment also called low temperature torrefaction, takes place in kilns with superheated steam at the temperature range of 185-220°C for increasing the durability, mechanical dimensional stability and water repellent characteristics.

Torrefaction, also called mild pyrolysis, is a thermal treatment without oxygen in the temperature range of 200-300°C, and usually, the reactions occur at low particle heating rates ($<50 \text{ K min}^{-1}$) with longer residence time, and the final product called torrefied wood (Prins, 2005). Its aimed at maximizing mass and energy yield of the final solid product, which has low H:C and O:C ratios.

Pyrolysis is a process without air or oxygen for thermal conversion of wood at temperatures in the range of 400-800°C. For this range of temperature, most of the hemi celluloses, cellulose and part of the lignin will disintegrate to form smaller and lighter molecules, which are mostly gases. As these gases cool, some of the vapours condense to form a liquid, which is called bio-oil (or tar). The remaining wood residue, mainly from parts of the lignin, is a solid called charcoal. The pyrolysis product distribution depends on the heating rate, residence time and maximum reaction temperature. The main aim is to increase the production of the liquid and to reduce the yield of the charcoal.

2.7. Origin of Briquettes

Although, compaction of loose combustible materials for fuel making purposes is a technique which has been in existence thousands of years ago, industrial method of briquetting seems to be dated back to eighteenth century. The use of organic briquettes (biomass briquettes) started more recently compared to coal briquette. It seems to have been common during world war and during the 1930s depression.

Historically, biomass briquetting technology has been developed in two ways. Europe and the United States have adopted and perfected the piston press while Japan has independently invented and developed the screw pressed technology. Although both technologies have their advantages and disadvantages, it is universally accepted that the screw pressed briquettes are far superior to the piston pressed solid briquettes in terms of their storability and combustibility (Raju *et al.*, 2014).

Worldwide, both technologies are being used for briquetting of locally available residues. The importance of biomass briquettes as substitute for fuel wood, coal and lignite is well recognized, nonetheless, the numerous failures of briquetting machines in almost all developing countries have inhibited their extensive exploitation.

Briquetting technology is yet to get a strong foothold in many developing countries because of technical constraints involved and the lack of knowledge to adapt the technology to suit local conditions. Biomass densification, which is also known as briquetting of saw-dust and other agro-residues, has been practiced for many years in Japan in 1945. As of April 1969, there were 638 plants in Japan engaged in manufacturing sawdust briquettes.

2.7.1 Nature of briquettes

A briquette is a block of flammable matter such as esclade, which can be used to start a fire. A briquette is a block of compressed coal, biomass or charcoal dust that is used as fuel to start and maintain fire. Some briquettes are compressed and dried brow coal (lignite) extruded into hard blocks. This is a common technique for low rank coals. They are typically dried to 12 -18 % moisture, and are primarily used in household and industries.



Plate I: Briquette Sample

Biomass briquette are made from agricultural waste and a replacement for fossil fuels such as oil and coal, and can be used to heat boilers in manufacturing plants, and also have application in developing countries. Biomass briquettes are a renewable source of energy and help reduce carbon content in the atmosphere. Biomass briquettes also provide more calorific value and save around 30-40 per cent of boiler fuel cost.

2.7.2 Briquetting technologies

Briquetting or densification is the process of compacting agro-residues to a product of higher density. Two main high pressure technologies or binderless technologies which consist of the following;

- a. Screw Press
- b. Piston Press
- c. Mechanical Press

2.7.2.1 Screw press

The major parts of the machine are a driving motor, screw die, die heaters and a power transmission system. When the motor is started and raw materials (e.g. rice husk and corn cobs, sawdust etc.) are fed to the screw (housed in a circular tube), the biomass becomes compressed and are extruded through the die (heated by an external electrical coil heater). Lengthways on the inner surface, the cylindrical die has five grooves, which prevent the densified material from rotating with the screw. The design of the screw results in the formation of a central circular hole or concentric hole in the briquette, which acts as an escape route for steam produced during Briquetting. The screw extrusion press briquetting is a popular choice suitable for small scale application in developing countries.

The process can produce denser and stronger briquettes than those produced by piston press. This is as a result of the concentric hole which gives better combustion characteristics due to a large specific area. The screw press briquettes are also homogenous and do not disintegrate easily. Having a uniform and high combustion rate, these can substitute for coal in most applications and in boilers. These briquettes can also be carbonized. A screw extrusion press has a capacity of about 90 kg/hr and is driven by a 20 horse power electrical motor. Major

maintenance problems are mainly concerned with the wear of the screw (Okeh 2015). The merits of Screw Extrusion press includes:

- i. the outer is continuous and the briquette is uniform in size.
- ii. the outer surface of the briquette is partially carbonized facilitating easy ignition and combustion. This also protects the briquette from ambient moisture.
- iii. a concentric hole in the briquette helps in combustion because of sufficient
- iv. circulation of air.
- v. the machine runs very smoothly without any shock load.
- vi. the machine is light compared to the piston press because of the absence of reciprocating parts and fly wheel.
- vii. the machine parts and oil used in the machine are free from dust or raw material contamination.

2.7.2 .2 Piston press

In the piston/ram press this biomass is pressed in a die by a reciprocating ram at a very high pressure. The briquettes produced by a piston press are completely solid. The piston press contact parts e.g., the ram and die do not wear easily as compared to the screw press. This machine has a 700 kg/hr capacity and power of 25 kW. The ram moves approximately 270 times per minutes in the process of producing a briquette of 60 mm in external diameter. The Merits of Piston Press includes:

- i. there is less relative motion between the ram and the biomass hence, the wear of the ram is considerably reduced.
- ii. it is the most cost-effective technology.
- iii. some operational experiences have now been gained using different types of biomass.
- iv. the moisture content of the ram material should be less than 12 % for the best result.

2.7.2.3. Hydraulic piston press

Hydraulic Piston Press: Another type of briquetting machine is the hydraulic piston press. This is different from the mechanical piston press in that the energy to the piston is transmitted from an electric motor via a high pressure hydraulic oil system. This machine is compact and light. Because of the slower press cylinder compared to that of the mechanical machine, it results in lower outputs. The briquettes produced have a bulk density lower than 1000 kg/m³ due to the fact that pressure is limited to 40-135 kg/h. This machine can tolerate higher moisture content than the usually accepted 15 % moisture content for mechanical piston presses (Salman *et al.*, 2014).

2.7.3 Advantages of briquettes

Briquettes produce from briquetting of biomass are fairly good substitute for coal, lignite, fire wood and offer numerous advantages. These advantages includes

- i. densities fuels are easy to handle, transport and store
- ii. they are uniform in size and quality.
- iii. the process helps to solve the residual disposal problem.
- iv. the process assists the reduction of fuel wood and deforestation.
- v. it provides additional income to farmers and creates jobs.
- vi. briquettes are cheaper than coal, oil or lignite and cannot be replaced .
- vii. there is no sulphur in briquettes.
- viii. there is no fly ash when burning briquettes.
- ix. Briquettes have a consistent quality, have high burning efficiency, and are ideally sized for complete combustion.

2.7.4 Disadvantages of biomass briquetting

- i. High investment cost and energy consumption input to the process
- ii. Undesirable combustion characteristics often observed e.g., poor ignitability, smoking, etc.
- iii. Tendency of briquettes to loosen when exposed to water or even high humidity weather.

2.7.5 Factors affecting densification briquetting

The factors that greatly influence the densification process and determine briquette quality are: temperature and pressure. It was found that the compression strength of densities biomass depended on the temperature at which densification was carried out. Maximum strength was achieved at a temperature around 220 °C. It was also found that at a given applied pressure, higher density of the product was obtained at higher temperature.

2.7.6 Parameters of quality assessment of briquettes

Durability, shear strength and impact resistance of briquettes are the basic parameters to assess the quality of briquettes in terms of handling and transportability of fuel briquettes.

2.7.6.1 Durability

Durability of briquettes gives the mechanical handling of the solid fuel. This is measured by standard procedure ASAE S269.4. To measure durability, 100 g of sample is taken and sample is tumbled at 50 rpm for 10 minutes in a dust tight enclosure of size 300 mm × 300 mm. Metal cloth of aperture size 4mm is used to retain crumbled briquettes after tumbling.

$$\text{Briquettes durability index in \% given by} = \frac{\text{weight of briquette sample left after tumbling,g}}{\text{Original weight of briquette sample,g}} \times 100 \quad (2.7)$$

The test set up is fabricated according to specification of ASAE S269.4. The set up consists of a box 300 mm× 300 mm × 125 mm mounted on a frame. The box can be rotated by wooden handle or a motor at 50 rpm for 10 minutes which simulates the probable conditions of briquettes under transport by truck or conveyer belt into furnace.

Figure below shows a durability measuring test set up made according to specification.

2.7.6.2 Shear Strength Test

To measure shear strength, a simple test is done. Briquette is sheared between two planes and shear force developed is the shear strength of briquette (Saikia and Baruah, 2013).



Plate II: Durability test set up



Plate III: Shear strength test set up

Shear strength test set up

To measure shear strength, shearing test set up has been fabricated. The instrument consists of three wooden plates. The middle plate with a central cylindrical hole of 45 mm diameter and 30 mm thickness slides over the bottom plate. In the top plate, a cylindrical hole of same diameter as that of moving plate with 20 mm thickness is being provided in such a way that it coincides with the one that is provided in the movable plate when this plate is fully inserted between top and non-moving bottom plate. The movable plate is connected to dead weights.

$$\text{Shear strength (kPa)} = \frac{2F}{\pi D^2} \quad (2.8)$$

Where F = Force causing shear in briquette, (KN)

D = Diameter of briquette, (m)

2.7.6.3 Impact resistance test

This test stimulates the forces encountered during emptying of densified products from trucks onto ground, or from chutes into bins. Drop test can be used to determine the safe height of briquette production during mass production. ASTM D440-86 method is used to determine impact resistance index. In the drop test, briquettes are dropped twice from a height 1.83m onto a concrete floor. An impact index (IRI) is calculated.

$$IRI = \frac{100 \times N}{n}$$

(2.9)

Where,

N = Number of drops, n = Total number of pieces.

The upper limit of IRI is 200 which would result if the briquettes are not broken even after dropping twice.

2.7.6.4 Combustion rate

Combustion rate or burning rate is the mass loss per unit time. The briquettes are dried at 105 °C so that it does not effect on combustion or burning. Dried briquette is placed on a steel wire mesh grid resting on three supports allowing free flow of air (Chen *et al.*, 2012) Now the whole system is placed on mass balance. Briquette is ignited from top s and mass loss data is taken at an interval of 30 seconds.

2.7.6.5 Biomass density

Density is defined as the physical property of briquettes. It can also be defined as the structural packing of the molecules of the substance in a given volume. The size and density affects the burning characteristics of biomass fuel by heating and drying rate during combustion. It also

dictates how the material is likely to behave during subsequent thermo-chemical or biological processing as a fuel or feed stock. Average mass is measured by Micro-balance and volume of dry biomass samples is determined by water displacement method. Since the briquettes produced are cylindrical of equal diameter, the various heights of the briquettes can be gotten using a veneer callipers. The volume can then be calculated using the formula $\pi r^2 h$. Then density can then be computed as the ratio of mass to the volume of briquette. The equation is given below;

$$\text{Density (g/cm}^3\text{)} = \frac{\text{mass (g)}}{\text{volume (cm}^3\text{)}} \quad (2.9)$$

2.8 Binders

Briquette binder plays a key role in the process of briquette production. The quality and performance of briquette also depend on the quality of briquette binder. Different types of briquette need different briquette binder. Binder used in briquetting process can be divided into inorganic binder, organic binder and compound binder. The inorganic binders have many excellent advantages, such as abundant resource, low cost, excellent thermos-ability and good hydrophobicity. However, a major problem arising from the usage of inorganic binder is related to the ash increased in significant amount. The organic binders have many excellent advantages, such as good bonding, good combustion performance and low ash. But organic binder is easy to decompose and burn when it was heated, so the mechanical strength and thermal stability of organic binder briquette are poor, and its price is high. The composite binders are composed of two binders at least; the different binder plays the different role. The compound binder can make full use of the advantages of all kinds of binder, such as it can reduce the supplying amount of inorganic binder, reduce the cost of organic binder, improve the quality of briquettes, and get better performance of briquettes. This review will cover briquette binder literature. Due to many factors taking into consideration for briquettes process,

up to the present, no uniform mechanism has been developed to solve briquette production. The clarification of briquetting mechanism of briquette binder is not only can provide a theoretical basis for binder development, but also can provide instructive theory for briquette industrial production. There are five main theories of non-binder briquetting mechanisms: bituminous hypothesis, humic acid hypothesis, capillary hypothesis, colloid hypothesis and adhesion molecules hypothesis respectively. But those hypotheses cannot fully explain the briquetting issues about lignite. There are three main theories binder briquetting mechanisms from the view of interaction of binders and the pulverized coal.

2.8.1 Examples of binders used in briquettes

- | | |
|----------------|-------------------|
| (i) Glycerine, | (iv) Paraffin |
| (ii) Molasses | (v) Starch |
| (iii) Lignin | (vi) Bio plastics |

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Preamble

The section is concerned with the experimental procedure on collection of sawdust, preparation of the raw sample, carrying out proximate and ultimate analysis on the raw sawdust, torrefaction of the saw dust at different temperatures and time, characterization of the torrefied sample using SEM, TGA, FTIR and determination of kinetic parameters of the torrefied sawdust of the samples.

3.2 Material and Equipment

Table 3.1: List of Materials

Materials	Source
Biomass feedstock (Mahogany saw dust)	Dede Sawmill, Abuja
Nitrogen gas	Central lab. N.C.R.I ,Badeggi (Niger state)

Table 3.2: List of Equipment: List of Equipment/Apparatus

S/N	EQUIPMENT	SOURCES	USES
1.	Furnace	Step-B Lab FUT Minna	Proximate Analysis
2.	Hot box Electric Oven	WAFT department	Drying of sample
3.	Horizontal Furnace	Step-B Lab FUT Minna	Torrefaction
4.	Weighing balance	Chem. Eng. Dept. lab.	Mass measurement
5.	Thermogravmetric Analyzer TGA	Step-B Lab FUT Minna	Proximate Analysis
6.	Milling Machine	Mech. Eng. Dept. FutMinna	Size Reduction
7.	Sieve	Chem. Eng. Dept. lab.	Size Analysis
8.	Gas cylinder	Step-B Lab FUT Minna	Introduction of N ₂ gas
9.	FTIR Spectometry	NARICT Zaria	FTIR Analysis
10.	Scanning Electron Microscope	NARICT Zaria	SEM Analysis
11	Mortal and Pistle	Chem. Eng. Dept. lab.	Size reduction

3.3 Sample Collection and Torrefaction Experiment

Saw dust was collected from Dede Sawmill in Abuja. To ensure it was specifically mahogany dust, mahogany wood was milled separately from other woods. After the impurities were removed; the sawdust wastes were oven dried for about 6 hrs at temperature of 105°C. Then the dried residues were pulverized to 0.5mm millimetre-size in the feed grinder. After grinding, they were passed through a 0.5mm sieve (laboratory test sieve model). Paying much attention to mesh size, the sieve fabric was joined into the receiving pan. The biomass was placed in the sieve stack. The procedure was repeated until sufficient quantity was recovered from the biomass materials.

The standard Scout Pro weighing balance was used to weigh 100g of sawdust after pre-treatment. The biomass was then dried in an oven until constant weight was achieved in order

to ensure laboratory environment that is relatively humid controlled. Temperature of 105°C was strictly adhered to.

A pyrolyzer used was constructed with high temperature glass with diameter of 60mm and 101mm long, this was inserted into a horizontal clamp furnace available in step B centre Federal University of Technology Minna. Nitrogen was used to create inert environment and supplied through gas cylinder beside the furnace. The flow was controlled manually by valve and flow meter. The outlet tube served as exit of the gas. 3g of sample with particle size of <150 micrometer were placed inside the crucible and inserted into the pyrolyzer. The system was closed and degassed with nitrogen for five minutes before the reaction at a flow rate of 0.5 L/min. The horizontal furnace was switched on, heated at the rate of 10°C/min and maintained at the set torrefaction temperature of 200°C at time of 10, 30 and 60 min. After the reactor had cooled down, the sample was removed through the exit. The final temperatures and residences time used were noted; the residence time is taken as the time at which the treatment dwells at the maximum reaction temperature. The experiment was repeated at 250 °C and 300 °C for 10, 30 and 60 min respectively. The torrefied product was weighed and the mass yield, (MY) was calculated as percentage of the original mass sample, as follows

$$MY = \frac{M_{treated}}{M_{raw}} \times 100 \quad (3.1)$$

Where MY represents the Percentage Mass Yield of the torrefied sample; $M_{treated}$ is the mass of the torrefied product and M_{raw} is the mass of the untreated biomass (bridgeman et al., 2010).

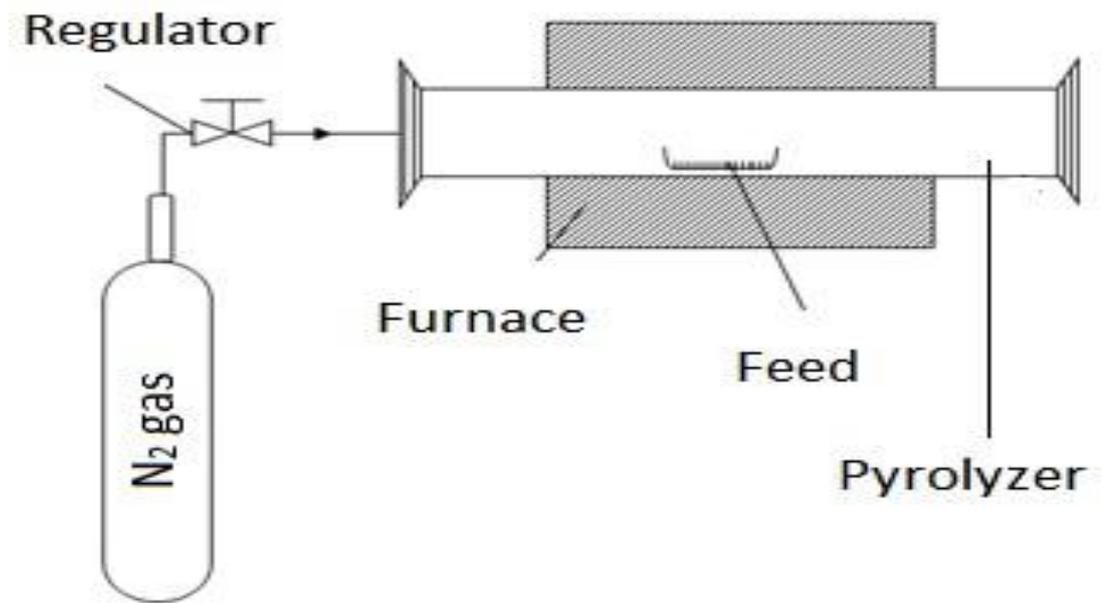


Figure 3.1 Experimental Set Up for Torrefaction Process

3.3.2 Proximate and ultimate analysis

Proximate analysis was extracted from the TGA except for fixed carbon (FC) which was determined by computing the difference between 100 and the sum of the moisture, volatile matter and Ash contents of the samples. Ultimate analysis carried out on the samples include nitrogen content, carbon and hydrogen content, sulphur content, oxygen content and calorific value determination respectively.

3.3.2.1 Moisture content

The moisture content of biomass was measured by oven dry method. Initially the sample with the known weight was kept in oven at 105 °C for one hour . The moisture content of sample was calculated using the following formula:

$$\text{M.C (\% wb)} = \frac{w_2 - w_3}{w_2 - w_1} \times 100 \quad (3.1)$$

Where,

W_1 = Weight of crucible, g

W_2 = Weight of crucible + sample, g

W_3 = Weight of crucible + sample after drying, g

3.3.2.2 Ash content

The residual sample in the crucible was heated without lid in a muffle furnace at 700 ± 50 °C for one half hour. The crucible was then taken out and cooled in desiccator and then weighed. Heating, cooling and weighing were repeated till a constant weight was obtained. The residue was recorded as ash on percentage basis.

$$\text{A.C. (\%)} = \frac{W_5 - W_1}{W_2 - W_1} \times 100 \quad (3.2)$$

Where,

W_1 = Weight of empty crucible, g

W_2 = Weight of crucible + sample gotten from equation (3.2)

W_5 = Weight of crucible + ash left in crucible, g

3.3.2.3 Volatile matter

The dried sample left in the crucible was covered with a lid and placed in muffle furnace, maintained at 750 °C for 2 hours (Mythili and Venkatachalam, 2013). The crucible was cooled first in air, then inside desiccators and weighed again. Loss in weight was reported as volatile matter on percentage basis. Calculated by the following formula,

$$\text{V.C (\%)} = \frac{W_3 - W_4}{W_2 - W_1} \times 100 \quad (3.3)$$

Where,

W_1 = Weight of empty crucible, g

W_2 = Weight of crucible + sample taken, g

W_3 = Weight of crucible + sample from equation (1), g

W_4 = Weight of crucible + sample after heating in muffle furnace, g

3.3.2.4. Fixed carbon determination

For the fixed carbon content, the same procedure used by Mythili and Venkatachalam (2013) was adopted. The values of then moisture content (M.C.), volatile matter (V.M.) and ash content (A.C.) were added together and the total was subtracted from 100. This can be better illustrated by the formula below,

$$FCC = 100 - (A.C + V.C + M.C) \quad (3.4)$$

Where,

A.C = Ash content

V.C = Volatile matter

M.C = Moisture content

3.3.3.1 Nitrogen content determination

One gram of sample was weighed into a digestion tube using weighing balance into the digestion tube containing sample, 0.5g of catalyst (mercuric oxide + potassium sulphate) was added as well as 2ml of concentrated H_2SO_4 . The digestion tube was installed into a kjeldatherm digestion block for three hours at $350^\circ C$. The sample was allowed to cool before making up to 100ml with distilled water using a volumetric flask. 10ml of the digested sample

in addition to 10ml of 40% Sodium hydroxide was ingested into the reaction chamber of Markham distillation unit while 2% boric acid was measured into 250ml beaker into which three drops of indicator (bromo cresol green + methyl red) were added. This 250ml beaker was the receiving flask placed under the tip of the condenser as the sample was allowed to distil until 50ml of the distillate was obtained.

Sample was then removed and titrated against 0.01N Hydrochloric acid (Garba *et al.*, 2004)



Plate IV Digestion Box

3.3.3.2 Carbon and Hydrogen Contents Determination

Carbon and hydrogen contents of biomass were determined simultaneously. 1g of sample was weighed and placed with the aid of 60-mesh/250 μm sieve in a closed system containing stream of dry oxygen to combust. Known weights of cupric oxide and sodium hydroxide were used as absorbents to absorb water and carbon dioxide respectively. The amounts of water and carbon dioxide were determined from the difference between the initial and final weight of respective absorbents.

3.3.3.3 Sulphur content determination

One gram of sample was weighed out into crucible of known weight and thoroughly mixed with 3 g of Eschka mixture (magnesium oxide + anhydrous sodium hydroxide).

The porcelain containing sample was covered and placed in a muffle furnace heated to a temperature of (800 ± 25) °C until oxidation is complete. The sulphur compound evolved during combustion reacts with Eschka mixture under oxidising condition to form sodium sulphate and magnesium sulphate in the residue. The sulphate in the residue was extracted and determined gravimetrically using 10ml BaCl_2 as titrant. Solution obtained after titration was decanted to retrieve precipitate of BaCl_2 formed. Precipitate obtained was weighed.

3.3.3.4 Oxygen content determination

The oxygen content was determined by computing the difference between 100 and the sum of the Nitrogen, Sulphur, Carbon and Hydrogen of the samples.

3.3.3.5 Calorific value determination

Moreover, HHV being an important fuel property is helpful in calculations of thermal systems. Chen et al., 2012, presented co-relation to evaluate HHV of different biomasses based on elemental composition, this co-relation is unified because it offers an average absolute error of 1.45% and bias error as 0.00% and thereby establishes its versatility and has been used by many researchers (Munir *et al.*, 2009).

$$\text{HHV} = 0.3491\text{C} + 1.1783\text{H} + 0.105\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{A} \quad (3.5)$$

3.3.3.6 Mass and energy yield

Mass yields of studied fuels were determined based on the formula as equated by Bergman *et al.* (2005):

$$Y_m = \frac{M_{\text{difference}}}{m_{\text{untorrefied}}} \times 100 \quad (3.6)$$

$M_{\text{difference}} = M_b - M_a$: M_b = Mass before torrefaction: M_a = Mass after torrefaction Energy yields of studied fuels were determined based on the formula as equated by Bergman *et al.* (2005):

$$Y_E = Y_m \times \frac{HHV_{\text{torrefied}}}{HHV_{\text{untorrefied}}} \quad (3.7)$$

Where Y_E = Energy yield, Y_m = mass yield, $HHV_{\text{untorrefied}}$ = untorrefied biomass and $HHV_{\text{torrefied}}$ = torrefied biomass

3.4 Scanning Electron Microscopy (SEM).

The morphological characterization of the samples were undertaken to determine the effect of torrefaction on the micro and macro-structural transformation of sawdust samples. These were examined using a SEM model JEOL (JSM-6390LV) (JEOL, Tokyo Japan) operating at 30keV. Samples were gold coated and placed on a specimen holder called a stub by a carbon double-sided tape and mounted in a sample chamber of the instrument for viewing. To reduce errors and confirm results, each analysis was repeated in triplicate under the same conditions. Included in each of one of the micrographic images of the torrefied and untorrefied sawdust are specific examination conditions of the analysis.

3.5 Thermogravimetric Analysis

A TG/DTG non-isothermal test was carried out on PerkinElmer thermogravimetric analyser (TGA-4000) for the three samples. The TGA equipment was purged with oxygen gas to simulate conventional combustion with flow rate of 20ml/min and heating rate of 10°C/min, the analysis were performed using a temperature scan 30°C to 900°C. The weight of empty crucible was zero and latter load with sample to be analysed. All the tests and experiments were repeated at least twice and deemed reproducible when the results were within $\pm 5\%$.

3.6 ATR-FTIR

ATR-FTIR spectroscopy is a facile method which provides direct information from the outer (3mm) sample surface layers with no requirement for prior sample preparation. The spectra recorded provide basic and in principle quantitative information on the sample cell wall polymers and their chemical modifications. Samples with size fraction between 250 and 600 μm were used for the FTIR test. Before the test, samples were dried in the oven at 40 $^{\circ}\text{C}$ for 24 h. ATR-FTIR spectra (4500 - 500 cm^{-1}) were recorded using a Fourier transform infrared spectrometer (Nicolet 6700 FTIR, Thermo Electron Corporation, USA). The system was equipped with a thermostat controlled ATR unit ($T = 30^{\circ}\text{C}$) where the sample was pressed against the diamond surface using a springloaded anvil. All spectra were obtained with 128 scans for the background (air) and 100 scans for the sample with a resolution of 4 cm^{-1} . Spectra were recorded from 10 different subsamples for each sample condition, and these spectra were normalized at around 690 cm^{-1} where the spectra are free of distinct IR bands. The average spectrum of the 10 normalized spectra was presented for each sample condition.

3.7 Determination of Kinetic Parameters

Several non-isothermal TGA kinetic analyses have been employed in the determination of kinetic parameters for thermal decomposition of biomass samples. These methods include Coat-Redern, Criado linearization and DTG curve fittings. However, this research shall be limited to Coat-Redern method for the determination of suitable model for TGA data. Coat-Redern linearization technique:

In the non-isothermal experiments, the sample mass loss was recorded as a function of the temperature. The rate of conversion, dx/dt , can be written as:

$$\frac{dx}{dt} = k(T)f(x) \quad (3.81)$$

Where $\frac{dx}{dt}$ is the degradation rate, x is the conversion degree for individual pyrolysis phase, which represents the decomposed amount of the sample at time t which is the reaction time (s), T is the absolute temperature (K), $k(T)$ is the temperature-dependent rate constant, and $f(\alpha)$ is the temperature-independent function of conversion and can be generally expressed as $f(\alpha) = (1 - \alpha)^n$ (chen *et al.*, 2015). Arrhenius equation, k as a function of T can be written as:

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3.82)$$

where A is pre-exponential or frequency factor (s^{-1}), E is the activation energy ($kJ \text{ mol}^{-1}$), and R is the universal gas constant. The conversion function $f(x)$ is expressed as:

$$f(x) = (1 - x)^n \quad (3.83)$$

Where n is the reaction order.

The conversion "x" in this research is expressed as:

$$x = \frac{m_0 - m_t}{m_0 - m_f} \quad (3.84)$$

Where m_0 is the initial mass of the sample, m_t the mass of sample at time t and m_f is the final indecomposable mass of the sample in the reaction.

The combination of Equations (3.81)–(3.84) gives:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - x)^n \quad (3.85)$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = dT/dt$ ($^{\circ}C \text{ min}^{-1}$); E is the activation energy; R is the universal gas constant ($8.3145 \text{ kJ mol}^{-1} \text{ K}^{-1}$); T is the absolute temperature (K), the re-arrangement of Equation (5) gives:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3.86)$$

Equations (3.85) and (3.86) are the fundamental expressions of the analytical methods used to calculate kinetic parameters on the basis of TGA data. For $n \neq 1$,

$$\frac{(1-n)^{1-n}-1}{(n-1)T^2} = \ln \left[\frac{AR}{\beta Ea} \left(1 - \frac{2RT}{Ea} \right) \frac{Ea}{RT} \right] \quad (3.87)$$

When $n = 1$, Equation (3.5) becomes:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta Ea} \left(1 - \frac{2RT}{Ea} \right) \right] - \frac{Ea}{RT} \quad (3.88)$$

Equation (3.9) is the developed model for TGA data.

Where $\frac{Ea}{RT}$ is the slope and $\ln \left[\frac{AR}{\beta Ea} \left(1 - \frac{2RT}{Ea} \right) \right]$ is the intercept.

From the slope and the intercept of these plots, activation energy (Ea) and frequency factor (A) are calculated from the Equations (3.8) and (3.9) respectively.

$$Ea = \text{slope} \times R \times T$$

$$Ea = \frac{Ea}{RT} \times R \times T$$

$$(3.89) \text{ And } A = \frac{\exp(\text{intercept}) \times \beta \times Ea}{R \times \left(1 - 2 \frac{RT}{Ea} \right)}$$

This implies that:

$$A = \frac{\exp \left(\ln \left[\frac{AR}{\beta Ea} \left(1 - \frac{2RT}{Ea} \right) \right] \right) \times \beta \times Ea}{R \times \left(1 - 2 \frac{RT}{Ea} \right)} \quad (3.90)$$

3.8 Briquetting

Briquetting of the samples was done using the hydraulic press briquetting machine. The briquettes produced were from torrefied mahogany sawdust and untorrefied mahogany sawdust. The samples were weighed using a weighing balance. The mixing of samples as done

in a deep bowl using hand by adding 20 g of torrefied sawdust at 300^oC, 20 g of torrefied sawdust at 200^oC and 10g of starch to produce a 50 g briquette. Same mixing was done for 40g of untorrefied sawdust and 10 g of starch to produce a 50 g briquette. The samples were then placed inside the moulds of the hydraulic press briquetting machine and covered with the lid which was then screwed. The jack of the machine was lifted up and down and as that was done; water was seen to be dropping from under the moulds. This was done until the jack became stiff and difficult to lift, then the lid was opened and the well-formed cylindrical briquettes were removed.



Plate V Briquetting Set Up.

3.8.1 Preparation of binder

The binder used for this study was starch gotten from cassava flour. The amount of starch that was used was 100 g for the production of ten briquettes using 10 g of the binder for each. To

get the starch ready for use, water was boiled and then continuously added slowly to the starch and stirred vigorously to make sure no lumps were formed and until it attain a sticky nature.



Plate VI Sample of the prepared Starch as Binder.

3.8.2 Briquette quality test

The following tests were carried out on the briquettes to determine the quality of the briquettes produced from the torrefied and untoorrefied biomass samples.

3.8.3 Shatter resistance test: This test was done to determine the hardness of the briquettes. The length and weight of the briquettes were measured and recorded after which the briquettes were dropped from a height of one meter on a concrete floor for ten minutes. After the disintegration of the briquettes, the weight and shape of the briquettes were recorded. The percentage loss was recorded. The shatter resistances of the briquettes were calculated using the equation (3.12)

$$\text{Percentage weight loss} = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.12)$$

$$\% \text{ Shatter Resistance} = 100 - \% \text{ weight loss} \quad (3.13)$$

Where,

W_1 = Weight of briquette before shattering, g

W_2 = Weight of briquette after shattering, g

3.8.4 Resistance to water penetration

This is the measure of percentage water absorbed by a briquette when immersed in water. The briquettes were immersed in 25 mm of water at room temperature for 30 seconds. The percentage water gained was calculated by the equations 3.14 .Water gained by briquette

$$= \frac{W_1 - W_2}{W_1} \times 100 \quad (3.14)$$

$$\% \text{ Resistance to water penetration} = 100 - \text{Water gain} \quad (3.15)$$

Where,

W_1 = Initial weight of briquette

W_2 = Final weight of briquette

3.8.5 Durability

This is a test carried out on a briquette to check the ability of the briquette to withstand mechanical handling. To achieve that, the briquette samples were dropped repeatedly from a height of 1.5m onto a metal base. The fraction of the briquette that remained unshattered was used as an index of briquette durability. This was expressed as a percentage of initial mass of the material remaining on the metal plate. The equation is given as:

$$\text{Durability (\%)} = \frac{W_r}{W_i} \times 100 \quad (3.16)$$

Where,

W_r = Weight of the briquette remaining, W_i = Initial weight of the briquette.

CHAPTER FOUR

4.0

RESULT AND DISCUSSION

4.1 Mass Yield of Torrefied Saw Dust

Table 4. 1: Total mass balance for torrefaction experiment of sawdust

Raw biomass moisture content (%)	Process parameters		Torrefied biomass yield (%)	Yield of condensation (%)	Yield of permanent Gas (%)
	Temp(°C)	Time(min)			
3.2	200	20	97.1	0.02	0.4
3.2	250	10	86.6	1.79	1.2
3.2	300	30	84.4	4.07	1.4
22.1	200	10	98.1	13.30	2.7
22.1	250	10	98.1	0.39	0.5
22.1	300	30	98.4	0.40	0.6
32.1	200	20	86.2	4.32	1.3
32.1	250	20	85.3	4.37	1.3
32.1	300	20	83.4	4.39	1.5
42.1	200	20	83.5	4.26	1.4
42.1	250	20	83.4	4.09	1.4
42.1	300	20	58.0	11.52	2.0

There was an overall trend toward a decrease in yield of solids, and increase in yield of permanent gases and condensable products as both temperature and reaction time increased. Loss of solids was much more pronounced between 250 and 300 °C, than between 200 and 250 °C, regardless of moisture content of samples. This was likely due to higher reactivity or more extensive devolatilization and carbonization of hemicellulose fraction above 250 °C.

Along with degradation of hemicellulose, initial reactions of cellulose decomposition might occur in this temperature regime, as proposed by other researchers

The same trend was observed for the yield of condensable and permanent gases. However, at 300 °C, regardless of moisture content of raw feedstock, yield of condensable was much higher than yield of permanent gases, which might be evidence of more intensive decomposition of not only hemicellulose, but also other polymer fractions (lignin). This would support the production of heavier compounds responsible for tar formation observed in condensed phase. There was an evident influence of moisture content on dry matter loss at 250 °C and especially at 200 °C, where mass loss of samples with 45% moisture content was 3 times higher than that of samples with 3 and 22% raw biomass moisture content.

4.2 Fuel Characterization 4.2. 1 Proximate and ultimate analysis

Calorific value of biomass is vital in determining the quality of solid fuel when combustion is concerned. It has been well established that when fuel is burned, C plays an exothermic role whereas O plays an endothermic role. As seen in Table 4.2, the higher the torrefaction temperature, the higher C and the lower O. This leads to the increase of calorific of torrefied sawdust, as shown in Table 4.2. This also suggests that the calorific of Torrefied sawdust was increased by factor of 1.3 at the torrefaction temperature of 300°C.

Table 4. 2: Ultimate analysis and HHV of the raw and Torrefied Sawdust.

Samples	C	H	O	N	S	HHV (MJ kg ⁻¹)
Raw	47.35	2.3	37.2	1.0	0.4	19.5
300TSD	48.6	3.61	39.86	0.92	0.13	21.75
250TSD	47.99	3.50	38.40	0.95	0.20	20.00
200TSD	47.60	3.20	38.00	0.98	0.30	19.90

Table4. 3: Proximate analysis of the raw and Torrefed Sawdust.

	SD	TSD at 200 ^o C	250 ^o C	300 ^o C
Moisture content	9.78	7.95	6.00	4.95
Volatile matter	72.49	50.67	33.5	20.67
Fixed Carbon	17.2	40.63	59.0	72.65
Ash Content	0.53	0.75	1.50	1.73
Heating value (dry basis) (MJ kg ⁻¹)	19.5	20.2	24.5	28.2

The ultimate analysis of the fuel as shown in Table 4.2 revealed some alterations in the chemical composition that biomass undergoes when it is exposed to torrefaction at different temperatures: the hydrogen, oxygen and sulphur content were observed to decrease; whilst the carbon content was increased. The exception is nitrogen content which remained almost constant. Calculation of the calorific value shows how these changes impact on the energy content. Table 4.2 illustrates the higher the torrefied temperature the greater the calorific value. During the torrefaction reaction the released compounds contain lower proportions of carbon than oxygen and hydrogen, thus raising the carbon content in the solid residue. Higher heating

values were calculated from Equation (3.5) using elementary analysis results of all the fuels given in Table 4.2 and 4.3.

4.2.2 The mass and energy yield

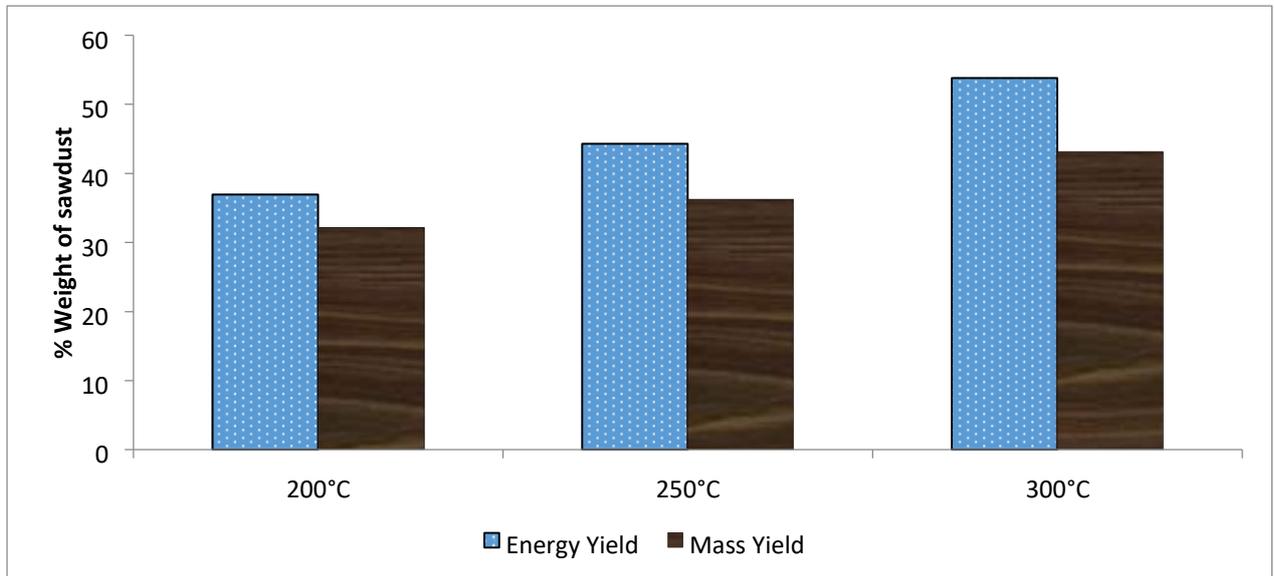


Figure 4.1 Torrefied SD at 60 minutes for (a) 200 °C (b) 250°C and (c) 300 °C

The results of the energy and mass yield calculations are shown in Figure4. 1. Comparing the untorrefied and torrefied Sawdust revealed that the energy yield of torrefied sawdust was greater than the mass yield of SD. The effect of heat became less pronounced for higher temperature torrefaction at 300°C

4.2.3 Characteristic feature of TGA curves for untorrefied and torrefied Sawdust

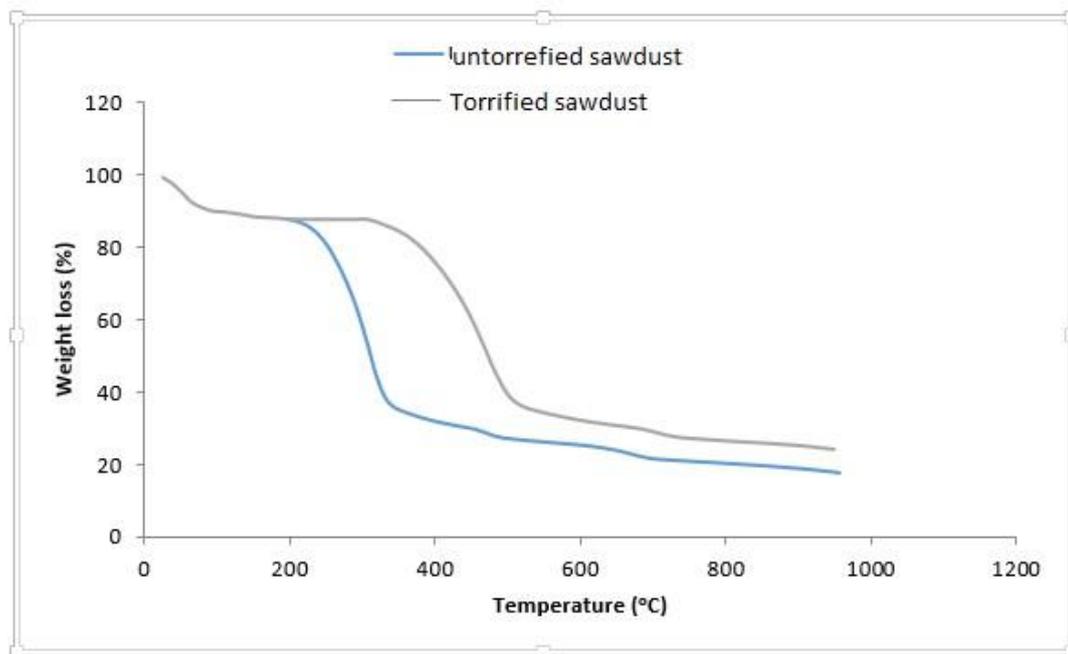


Figure 4.2 TG curve for the raw and torrefied SD

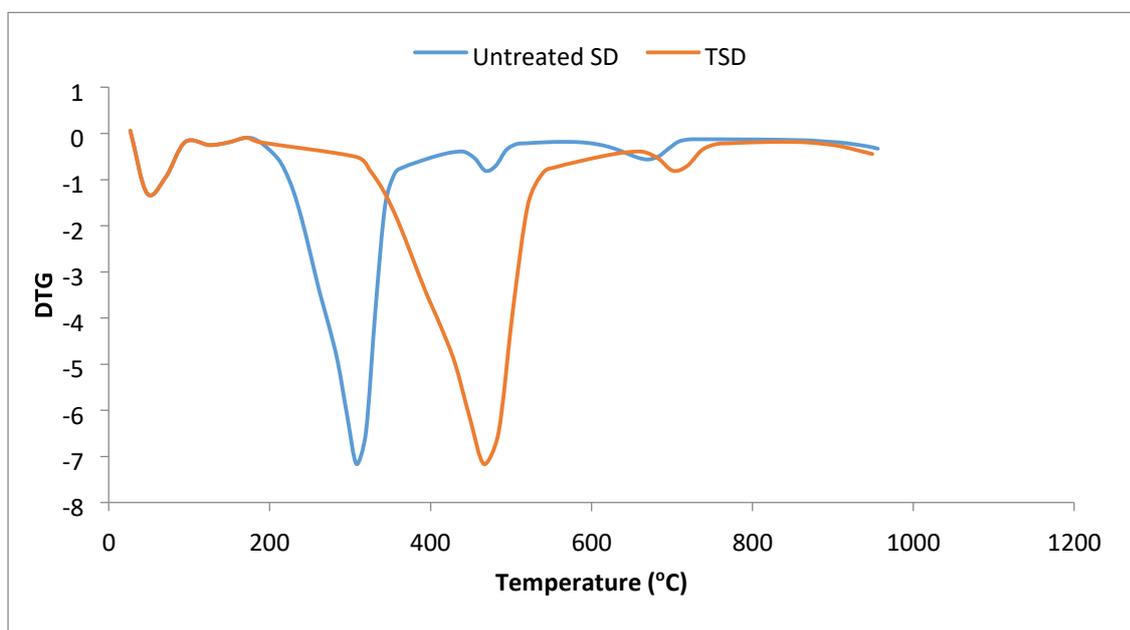


Figure 4. 3 DTG curve for the raw and torrefied SD

Figure 4.3 shows mass loss (TG) curves for untorrefied and TSD at $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. In general, the pyrolysis process can be divided into three stages: moisture

evaporation, main devolatilization and continuous slight devolatilization. In the first stage, about 3.81% moisture was loss at 181.51°C for raw SD while about 2.208% moisture was loss at 157.35°C for torrefied SD. This result has shown that torrefied SD at 300°C and 60 minutes resulted in a decrease in moisture by about 42%. In the second stage where the major decomposition occurs and a large amount of volatile is evolved. Raw SD decompose in the range of 181.51–250°C with about 66% volatile matter released, while torrefied SD degrades at the higher temperature range of 250-320°C with lower amount (about 63%) of volatile matter released. Torrefied SD has higher volatile matter and ash content compared to raw SD.

The value suggests that, the deduction in the percentage mass of the torrefied samples with temperature was due to moisture loss during the drying stage. It could also be attributed to the further removal of water vapour and the release of volatiles, which results from the breaking down of the samples composition (mainly the hemi-cellulose, and to a lesser degree; lignin) throughout the torrefaction process. This result presented in this study is quite similar to that presented by Sadaka and Sunita, 2009 and Bridgeman *et al.* 2007 in their studies “effects of temperature on rice husk torrefaction”.

4.3 Fourier Transform Infrared Spectroscopy Analysis

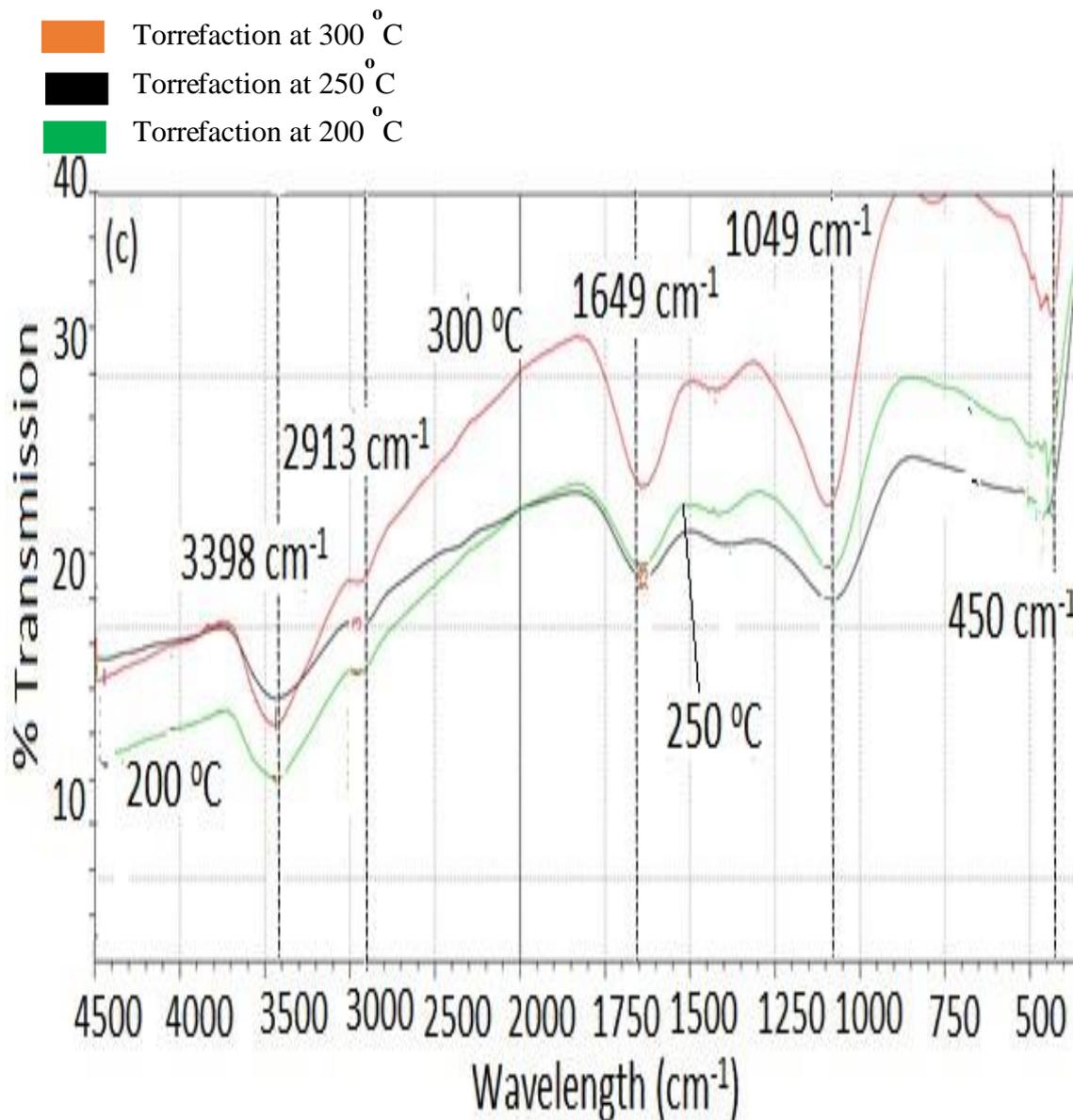


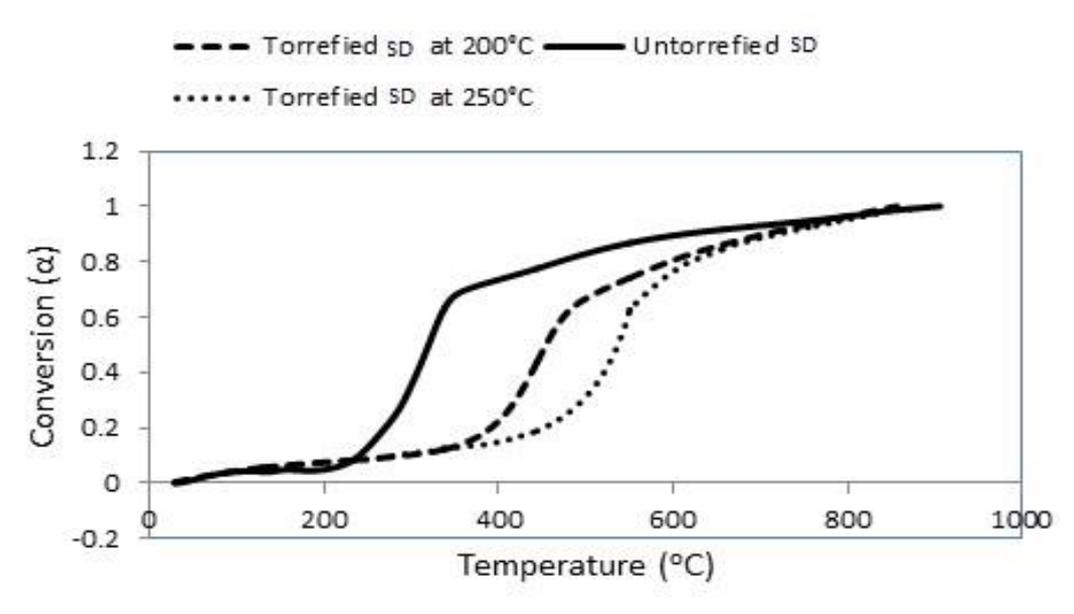
Figure 4.4: FT-IR Spectra of torrefied Sawdust at 200°C, 250 °C and 300 °C.

Infrared spectra taken from SD samples torrefied at different temperatures are shown in Figure 4.4 with the bands of interest being identified by their wavenumbers. The band at 450 cm⁻¹ is characteristic for cellulose and is an OH torsional vibration band. The fact that a significant decrease of this band is seen only for the highest temperatures between 250 °C and 300 °C shows that the cellulose component is largely stable until these temperatures were reached. The band at 1049.67 cm⁻¹ is attributed to the antisymmetric stretching of C-O-C glycosidic linkages in both cellulose and hemicelluloses (Pandy, 2009). Its

decrease was attributed to depolymerization and was most significant at the higher temperatures, and for 300 °C the band is practically absent. Gierlinger *et al.* 2018 attributed the band at 1649 cm⁻¹ to the anti-symmetric stretching of C-O-C of acetyl groups. There are no acetyl groups existing in the hemicelluloses of sawdust. However, for both reference xylans a band is found at 1245 cm⁻¹ and is of approximately the same strength as the (xylan) 900 cm⁻¹ band. The assignment of the 1240 cm⁻¹ band to lignin can also not be ruled out. The peak observed at 1850 cm⁻¹ is diagnostic of lignin (laing *et al.* 2008) and is placed in a spectral region devoid of polysaccharide peaks. No clear change of this peak is observed for most of the temperature range. However, at 300 °C it does appear to have diminished. The band at 1850 cm⁻¹ is attributed to the carbonyl stretching band of carboxylic acid groups in hemicelluloses. It starts to decrease from 250 °C, signifying a reduction in the amount of the carboxylic acid groups of hemicelluloses. This reduction is paralleled by the appearance of a new degradation product band at 1700 cm⁻¹. When torrefaction temperature reaches 300 °C, the 1850 cm⁻¹ band is completely eliminated, which suggests the complete removal of hemicelluloses. The narrow CH₂- stretching bands (superimposed a broader band) at approximately 2913 and 3398 cm⁻¹ are ascribed to the aliphatic fractions of wax. These bands for the C-H stretching can clearly be seen in spectra of extracted wax using hexane by work of Van Stelte, *et al.* (2011). These bands appear not to change significantly due to the heat treatment of torrefaction although a small decrease of these bands is suggested for the highest temperatures. It is possible that the higher molecular weight waxes may still be present in the samples torrefied at 300 °C, although further work needs to be done to confirm this. By analyzing the FTIR spectra of the torrefied SD samples, it can be concluded that there is no major structural change of the SD samples torrefied below 200 °C. Increasing the temperature from 200 to 250 °C introduces distinct changes in the spectrum. A higher temperature effect is most notable for the 250 to 300 °C transition and consists of the degradation of lignin and

cellulose. The change of transmittance intensities indicates a variation in the lignocelluloses concentration. Figure 4.4 show that torrefied TSD at 300°C had C=C bond more prevalent than torrefied SD at 200°C and 250°C, with –OH, O-H, functional groups more prevalent. Changes were largely due to the degradation of hemicellulose in the biomass. Functional groups of interest were those in the regions where most of the transformation could be seen, namely, in the O–H, C=O, C=C, C–H and C–O–C groups. Similar changes have been observed by Rousset *et al.* (2011) who torrefied bamboo at 220-280°C and saw the shifts of two major bands due to stretching vibrations in the C=O and C–O–C groups. However, a significant shift in wave numbers could also be observed in the C=C group vibrations. In brief, the study showed that the most severely treated biomass had its functional group vibrations shifted towards the lower wavenumbers and noticeable changes in the intensity can be observed.

4.4 Conversions



(a) Figure 4.5a Variation of conversion (α) with temperature during pyrolysis of untorrefied and torrefied SD at 200 and 250 °C.

(b)

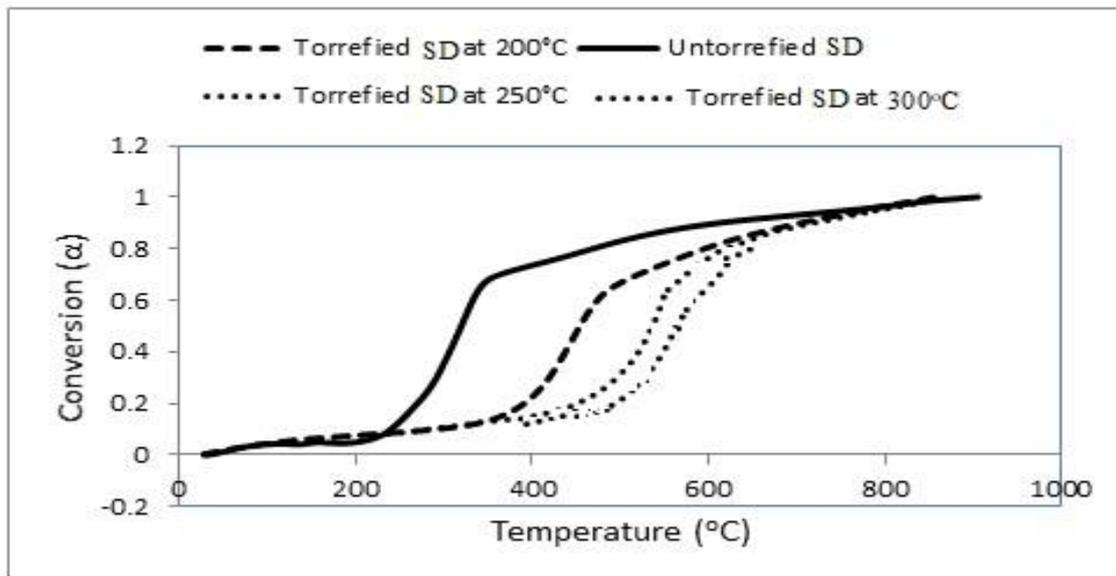
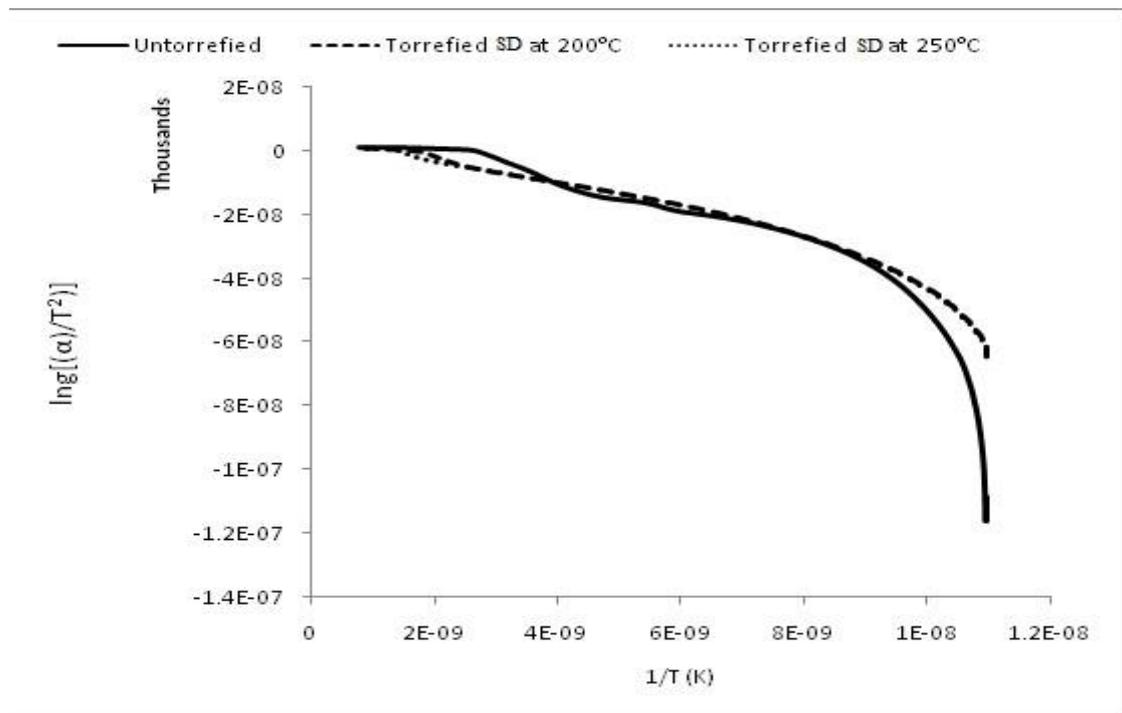


Figure 4.5(b) Variation of conversion (α) with temperature during pyrolysis of untorrefied and torrefied SD at 200, 250 and 300 °C

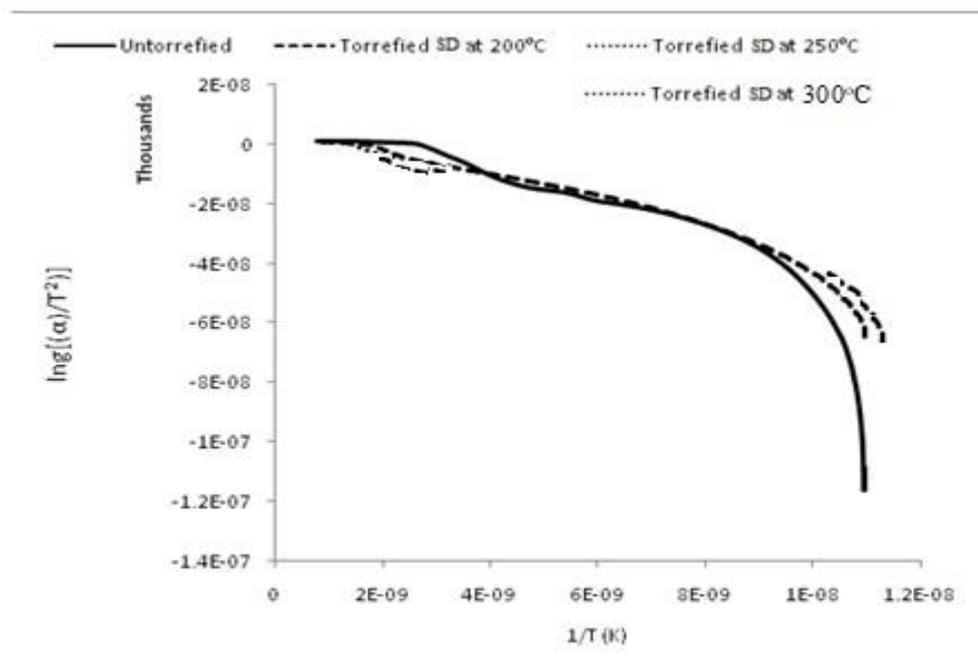
Figure. 4.5a represent α versus T curves for untorrefied and torrefied SD at 200 and 250 °C. Figure 4.5 show the conversion and weight loss against temperature for untorrefied and torrefied SD at 200 and 250°C. The conversion fraction was calculated as the ratio of the mass loss at a given temperature to the total mass loss at the end of the process. The devolatilization range were between 181-300°C corresponding to conversion range of 0.045486-0.717088.

A quick thermal conversion is observed in the range of 220 to 320°C and the untorrefied SD shows the highest conversion as reported in the literature. After this quick increase, conversion continues on the SD smoothly and slowly until the end of the experiment. Torrefaction at higher temperature (at 250°C) finishes the conversion faster. The conversion behavior is almost similar except for a difference in temperatures which is the basis of torrefaction approach for kinetics analysis.

4.6 Kinetics



(a)



(b)

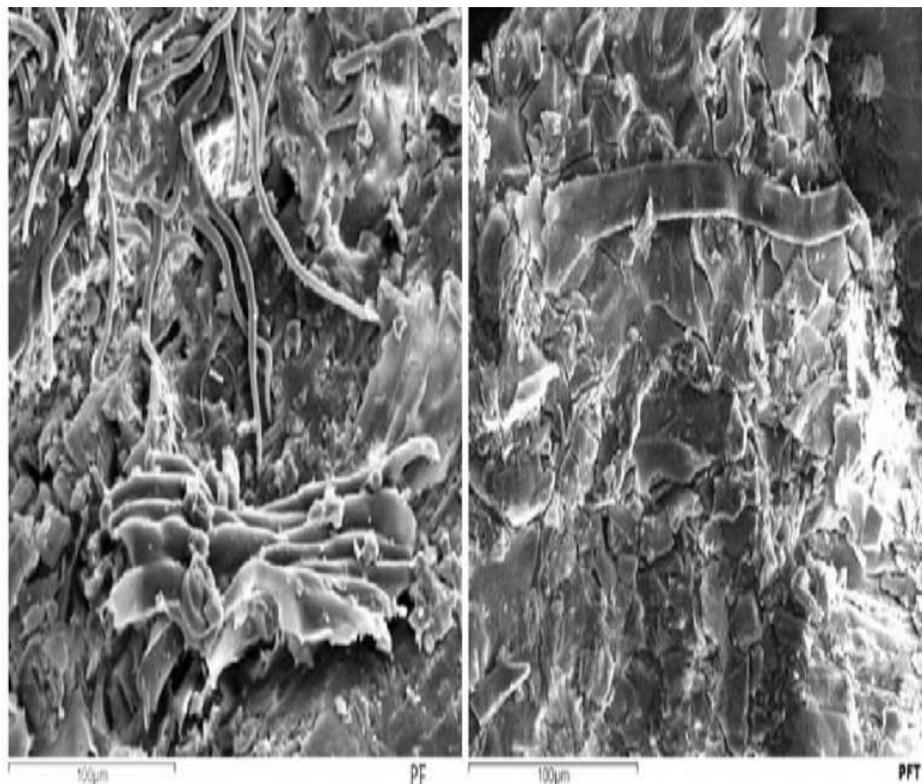
(b) Figure 4.6 Plot of $\ln(g(\alpha)/T^2)$ against $1/T$ for Sawdust torrefied at the three different temperatures.

Figure 4.6a shows a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ for RH first order kinetic with a linear relationship and coefficient of regression (R^2) of 0.7618 and activation energy of 0.1528. The

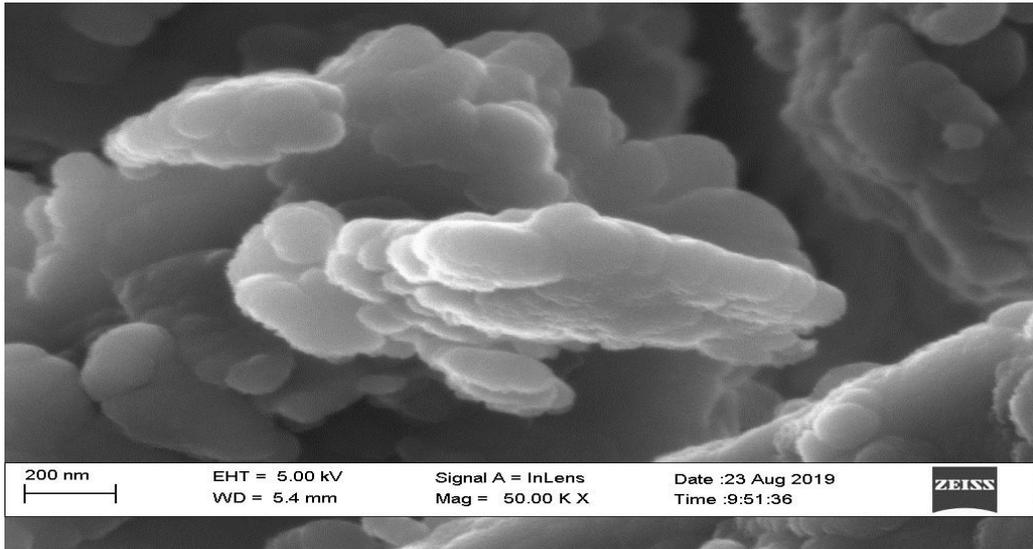
same activation energy of 0.1528 was obtained for SD, but with a slight variation in regression analysis ($R^2=0.7442$). The closer the value of coefficient of regression to unity, the better the model fit. However, the linear relationship in conversion plot (fig 4.5) confirms that heat transfer is the rate controlling the mechanism in the devolatilization of the sample.

4.6: Scanning Electron Microscopy (SEM) Results

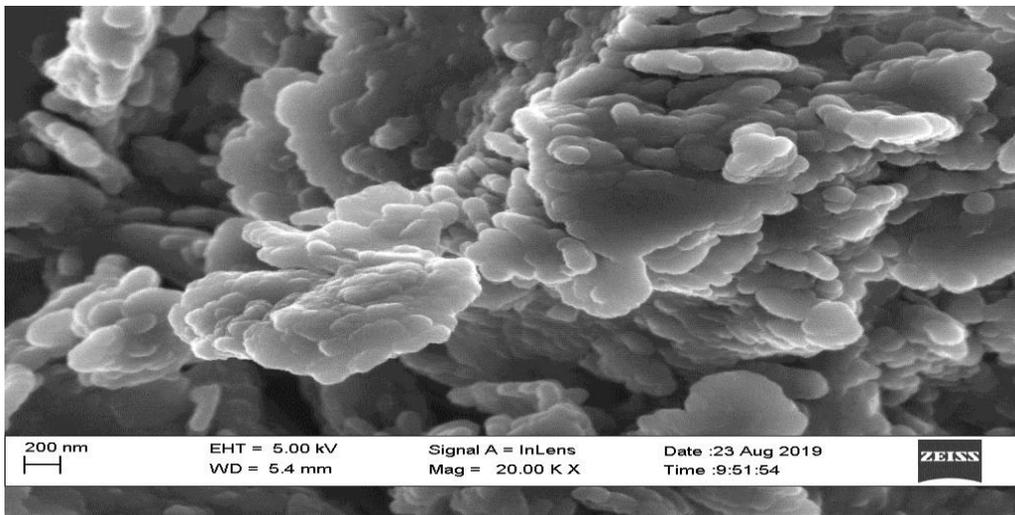
The structural morphology of the raw and torrefied Sawdust was examined using SEM.



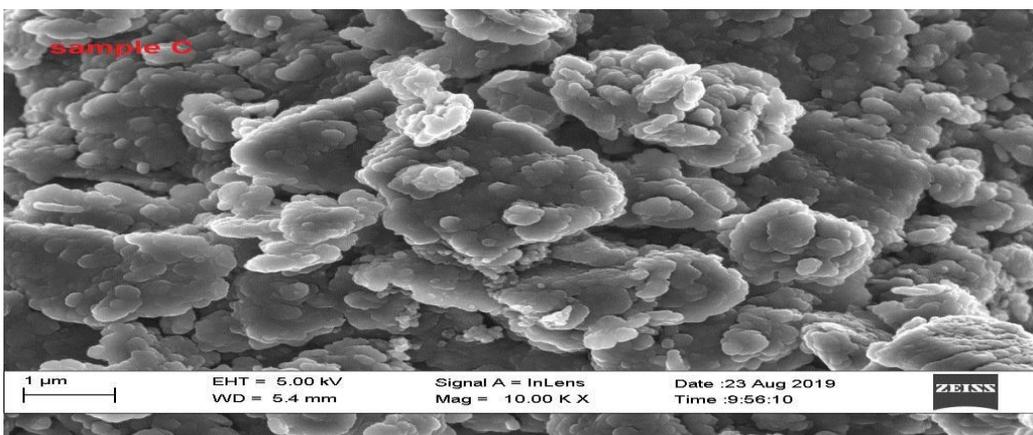
(a)



(b)



(c)



(d)

Figure (a) shows the SEM image of untorrefied sawdust, while figures (b), (c) and (d) show the SEM images of torrefied Sawdust at 200°C, 250°C and 300°C respectively.

The low and medium magnification images show more inter-particle gaps and voids with increasing torrefaction temperature, indicating poor adhesion between adjacent particles and/or spring back effects. Images taken at higher magnification provided a deeper insight into the bonding and failure mechanisms of the Sawdust. The failure surface of sawdust indicates a cohesive failure with high energy absorption. Fiber ends and particles are sticking out of the surface and few voids are found. This suggests that lignin and hemicelluloses have exceeded their glass transition temperatures at the pelletization conditions (e.g., moisture content, temperature and pressure), allowing them sufficient mobility to flow into cracks and crevices and establish solid bridges between adjacent particles. The particles from torrefied dust have flatter failure surfaces than those of the untorrefied, indicating a minimized polymeric flow. The amount of hydrogen bonding sites decreases gradually with the torrefaction temperature (200 > 250 > 300°C) and the torrefied biomass contains less moisture, thus both hydrogen bonding between polymer chains of adjacent particles and a polymeric flow of the lignin and hemicelluloses (forming solid bridges) can be assumed less likely to occur (Saddawi *et al.*, 2011).

According to Robertson (1991) who has studied the binding mechanisms in biomass granules and agglomerates it is likely that Van der Waals forces and fibre interlocking remain as the major forces keeping sawdust together.

4.7 Briquette result

Table 4.4: Result of briquette test

Quality test	Torrefied briquette	Raw briquette
	Sample A	Sample B
Density (g/cm^3)	0.700	0.481
% shatter resistance	99.54	65.41
% resistance to water penetration	98.75	85.05
Durability (%)	86.5	73.5
Ignition time (s)	1.2	1.4
Burn-out time (min)	35.80	31.0

4.7 Briquette quality test.

This shows the physical quality of the torrefied briquettes in comparison with the untorrefied briquettes

4.7.1 Resistance to water penetration

The result for this test was recorded in Table 4.4. The resistance to water resistance penetration high in the torrefied briquette with a value of 98.75 % as compared to the untorrefied briquette with a resistance to water penetration value of 85.05 %. The reason for high resistance to water penetration value in the torrefied briquetted was attributed to its less porosity and high density. This indicates that the torrefied briquette is good for storability.

4.7.2 Shatter resistance

From **Table 4.4**, the maximum shatter resistance was observed in the torrefied briquette with a value of 99.54 % while the untorrefied briquette had a shatter resistance of 65.41 %. The high

value of shatter resistance value of the torrefied briquette is an indication that the briquette has a high shock and impact resistance. Due to these mechanical properties, the briquette was considered to be more suitable for handling and transportation.

4.7.3 Durability

From the result of the durability test obtained, the torrefied briquette had a durability of 86.5 % and the untorrefied briquette had a durability of 73.5 %. From these values, it is clear that the torrefied briquette had more durability than the untorrefied briquette. Therefore, this is an indication that the torrefied briquette will be better in terms of storage and transport.

4.7.4 Bulk density

Higher bulk density signifies maximum utilization of heat generated during combustion. From the results gotten in Table 4-1, the bulk density of the torrefied briquette which was 0.700 g/cm³ was observed to be more than that of the untorrefied briquette with a density of 0.481 g/cm³. Therefore, the torrefied briquette is better for transportation and storage.

4.7.5 Ignition time

From the result gotten for ignition time, the torrefied briquette had an ignition time of 1.2 seconds while that of untorrefied was 1.4 seconds. Studies show that a lower ignition time is preferred over a higher ignition time. Therefore the torrefied briquette in terms of easy ignition is better than the untorrefied briquette.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the torrefaction of mahogany saw dust has been studied with a batch reactor for temperatures between 200–300 °C and residence times of 10–60 minutes. Various properties of torrefied biomass, which are of paramount importance for co-fired power plants and fuel handling systems, have been investigated and the results have been presented. Biomass became darker with increasing torrefaction temperature, and the biomass has lost its shiny surface and smoothness, especially for dust torrefied at temperatures above 250⁰C. For all the three temperatures, higher torrefaction temperatures result in less moisture absorption and better grindability. The mass/energy yield of saw dust was found to decrease steadily with the increase of torrefaction temperature and residence time, whereas the type of experimental setup employed was found to have little or no effect on the mass yield of the torrefaction process. Furthermore, observation of the mass and energy yield chart also revealed that the torrefaction temperature is the most vital process parameter in influencing the mass/energy yield for the whole range of torrefaction study. On the other hand, the residence time becomes important only for torrefaction temperatures >250 °C.

Based on the ultimate analyses, the torrefaction process intensifies the carbon and reduces the oxygen content of the torrefied sample as the process conditions get more severe (high temperature and longer residence time). Of the three torrefaction temperatures studied, torrefaction at 300 °C has shown higher energy densification together with higher energy yield as compared to torrefaction at 250 °C and resident time of 30 min. These differences could be attributed to the difference in the initial particle size used for analysis and the composition of the biomass. Torrefaction temperature determines the characteristics of the torrefied fuel compared to other parameters like residence time and geometry of the reactor. There was a

significant increase in the higher heat value (HHV) from 19.5 to 28.5 MJkg⁻¹ accounting for 44.6% increase in heat value. The fixed carbon increased from 17.2 to 72.65 which showed 76.3% increase. The sawdust spectrum is found to be characteristic of a generic oxygenated hydrocarbon as it dominated by cellulosic biomass. The major bands have the largely disappeared in the biochar produced at 300^oC. The torrefied sawdust FTIR at different temperatures taken together indicates that mahogany sawdust is dominated by functional groups present in oxygenated hydrocarbons, reflecting the carbohydrate structure of cellulose and hemicellulose. The torrefied briquettes produced showed clearly a good fuel properties when compared with the untorrefied biomass justifying the fact that torrefaction technology is a welcome development toward enhancing the use of biomass waste for fuel. There was an improvement in combustion and mechanical properties of the briquette of torrefied sawdust when compared with untorrefied sawdust.

The briquette produced can serve as an alternative to fossil fuel since it is cheap, convenient to use and is environmentally friendly.

5.2 Recommendations

In a bid to further improve on the quality and quantity solid fuel obtain during torrefaction, the following recommendations are suggested for future scope of the research

1. Modification of reaction set up such as the use of fluidized bed reactor to achieve continuous operation
2. Comparative analysis of solid product from the torrefaction, co-pyrolysis and catalytic co-pyrolysis of mahogany saw dust
3. Life cycle assessment (LCA) is also recommendable to ascertain the viability of the fuel.
4. Other woody sawdust should also be used and briquettes should be produced with the torrefied sawdust

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APPENDIX 1
TORREFACTION ANALYSIS RESULTS

Technology	Resident time	Heat rate	Temperature(°C)	Major product
Slow torrefaction	10 minutes	Very low	200	Charcoal
Conventional torrefaction	30 minutes	High	250	Charcoal liquid
Fast torrefaction	60 minutes	High	300	Charcoal liquid

EFFECT OF RESIDENT TIME

S/N	Temperature(°C)	Time(minutes)	Bio char	Bio fuel
1	200	10	48g	-
2	250	30	40g	6ml
3	300	60	37g	9ml

EFFECT OF TEMPERATURE

S/N	Temperature(^o C)	Time (Minutes)	(Bio Char	Biofuel
1	200	10	37	9ml
2	250	30	34	18ml
3	300	60	30	22ml



PLATE VI. Mahogany tree in Nigeria.

Appendix 3

1. Shatter Test

$$\% \text{ Weight loss} = \frac{W_1 - W_2}{W_1} \times 100$$

$$\% \text{ Shatter resistance} = 100 - \% \text{ Weight loss}$$

Where,

W_1 = Weight of briquette before shattering, g

W_2 = Weight of briquette after shattering, g

a. Shatter test for torrefied briquette

$$\% \text{ Weight loss} = \frac{W_1 - W_2}{W_1} \times 100$$

$$\% \text{ Shatter resistance} = 100 - \% \text{ Weight loss}$$

Where,

$$W_1 = 37.6 \text{ g}$$

$$W_2 = 37.51 \text{ g}$$

$$\% \text{ Weight loss} = \frac{37.6 - 37.51}{37.5} \times 100 = 0.46\%$$

$$\% \text{ Shatter resistance} = 100 - 0.46 = 99.54 \%$$

b. Shatter test for untorrefied briquette

$$\% \text{ Weight loss} = \frac{W_1 - W_2}{W_1} \times 100$$

$$\% \text{ Shatter resistance} = 100 - \% \text{ Weight loss}$$

Where,

$$W_1 = 38.5 \text{ g}$$

$$W_2 = 25.3 \text{ g}$$

$$\% \text{ Weight loss} = \frac{38.5 - 25.3}{38.5} \times 100 = 34.28 \%$$

$$\% \text{ Shatter resistance} = 100 - 34.59 = 65.41 \%$$

2. Durability

$$\text{Durability (\%)} = \frac{W_r}{W_i} \times 100$$

$$\% \text{ Durability} = 100 - \text{Durability}$$

Where,

W_r = Weight of briquette remaining, g

W_i = Initial weight of briquette, g

- a. Durability test for torrefied briquette

$$\text{Durability (\%)} = \frac{W_r - W_i}{W_r} \times 100$$

% Durability = 100 - Durability

Where,

$$W_r = 37.6 \text{ g}$$

$$W_i = 32.53 \text{ g}$$

$$\text{Durability} = \frac{37.6 - 32.53}{37.6} \times 100 = 13.5 \%$$

% Durability = 100 - 13.5 = 86.5

- b. Durability for untorrefied briquette

$$\text{Durability (\%)} = \frac{W_r - W_i}{W_r} \times 100$$

% Durability = 100 - Durability

Where,

$$W_r = 27.5 \text{ g}$$

$$W_i = 20.215 \text{ g}$$

$$\text{Durability} = \frac{27.5 - 20.215}{27.5} \times 100 = 26.50 \%$$

% Durability = 100 - 26.5 = 73.50

3. Water resistance

$$\text{Water resistance} = \frac{W_1 - W_2}{W_1} \times 100$$

% Water resistance = 100 - Water resistance

Where,

W_1 = Initial weight of briquette, g

W_2 = Final weight of briquette, g

- a. Water resistance for torrefied briquette

$$\text{Water resistance} = \frac{W_1 - W_2}{W_1} \times 100$$

% Water resistance = 100 - Water resistance

Where,

$$W_1 = 33.2 \text{ g}$$

$$W_2 = 32.78 \text{ g}$$

$$\text{Water resistance} = \frac{33.2-32.78}{33.2} \times 100 = 1.25$$

$$\% \text{ Water resistance} = 100 - 1.25 = 98.75 \%$$

b. Water resistance for untorrefied briquette

$$\text{Water resistance} = \frac{W_1 - W_2}{W_1} \times 100$$

$$\% \text{ Water resistance} = 100 - \text{Water resistance}$$

Where,

$$W_1 = 33.5 \text{ g}$$

$$W_2 = 29.4 \text{ g}$$

$$\text{Water resistance} = \frac{33.5-28.49}{33.5} \times 100 = 14.95$$

$$\% \text{ Water resistance} = 100 - 14.95 = 85.05 \%$$

4. Density

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Volume of a cylinder = $\pi r^2 h$ Where, r = Radius of cylinder h = Height of cylinder

a. Density for torrefied briquette

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Volume of a cylinder = $\pi r^2 h$ Where, r = 2 cm h = 4.15 cm

$$\text{Mass} = 36.6 \text{ g}$$

$$V = \frac{22}{7} \times 2^2 \times 4.15 = 52.285 \text{ cm}^3$$

$$\text{Density} = \frac{36.6}{52.285} = 0.70318 \text{ g/cm}^3$$

b. Density for untorrefied briquette

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Volume of a cylinder = $\pi r^2 h$ Where, r = 2 cm h = 4.4 cm mass = 27.0 g

$$V = \frac{22}{7} \times 2^2 \times 4.1 = 56.13 \text{ cm}^3$$

$$\text{Density} = \frac{27.0}{56.13} = 0.481 \text{ g/cm}^3$$

Kinetic data of torrefied sawdust at different temperatures

Heating rate (non-isothermal)									
10 °C min ⁻¹ , 200 °C				20 °C min ⁻¹ , 250 °C			30 °C min ⁻¹ , 300 °C		
Serial No	E_a , kJ/mol	A , min ⁻¹	R^2	E_a , kJ/mol	A , min ⁻¹	R^2	E_a , kJ/mol	A , min ⁻¹	R^2
1	7.13	$9.80 \cdot 10^9$	0.86	6.71	$1.73 \cdot 10^{10}$	0.83	5.98	$2.81 \cdot 10^{10}$	0.79
2	6.13	$7.50 \cdot 10^9$	0.80	5.63	$1.26 \cdot 10^{10}$	0.73	4.70	$1.88 \cdot 10^{10}$	0.64
3	4.13	$3.97 \cdot 10^9$	0.54	3.46	$5.99 \cdot 10^9$	0.41	2.14	$6.22 \cdot 10^9$	0.19
4	5.83	$5.38 \cdot 10^9$	0.82	3.21	$1.44 \cdot 10^9$	0.21	4.65	$1.44 \cdot 10^{10}$	0.76
5	1.33	$3.46 \cdot 10^8$	0.64	5.42	$6.86 \cdot 10^8$	0.81	3.96	$2.74 \cdot 10^9$	0.47
6	1.53	$6.64 \cdot 10^8$	0.64	0.89	$9.34 \cdot 10^9$	0.06	0.51	$6.47 \cdot 10^8$	0.02
7	14.00	$1.54 \cdot 10^9$	0.83	16.00	$2.51 \cdot 10^9$	0.65	21.00	$3.45 \cdot 10^9$	0.74
8	20.05	$2.91 \cdot 10^9$	0.83	43.29	$1.34 \cdot 10^{16}$	0.85	27.21	$5.42 \cdot 10^9$	0.86
9	7.07	$6.67 \cdot 10^9$	0.68	8.16	$1.26 \cdot 10^9$	0.70	10.86	$2.27 \cdot 10^9$	0.79
10	16.00	$1.14 \cdot 10^9$	0.92	17.00	$1.94 \cdot 10^8$	0.86	19.93	$2.63 \cdot 10^8$	0.91
11	7.40	$1.10 \cdot 10^{10}$	0.82	5.18	$4.03 \cdot 10^9$	0.41	7.77	$8.52 \cdot 10^9$	0.59
12	8.50	$1.43 \cdot 10^{10}$	0.95	6.07	$5.35 \cdot 10^9$	0.51	8.69	$1.06 \cdot 10^{10}$	0.66