

**BIO-OIL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS USING
FAST PYROLYSIS IN A FLUIDIZED-BED REACTOR**

BY

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CERTIFICATION

I, Moses Hensley Duku, hereby declare that this submission is my own work towards the PhD and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgment has been made in the text.

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ABSTRACT

This study focused on bio-oil production from lignocellulosic biomass using fast pyrolysis in a fluidized-bed reactor as a substitute or replacement energy source to reduce the dependence on imported and expensive fossil fuels for transportation and stationary engines applications. Seven major lignocellulosic biomass, mostly agricultural crop residues (i.e. corn cobs and its straw, rice straw and its husk, sugarcane bagasse and cocoa pod husk) and wood processing residue (*Triplochiton scleroxylon* sawdust) were characterized using proximate, ultimate, chemical and x-ray fluorescence analyses. Fast pyrolysis was carried out in a pilot-scale fluidized-bed reactor to investigate the effect of temperature on product distribution, i.e. bio-oil, char and non-condensable gas yields. This was followed by characterization of the bio-oils obtained for fuel properties using physical and ultimate analyses. Based on the results obtained, a scheme was proposed for bio-oil production. The proximate analysis gave moisture contents (MCs) of 9.15 and 10.29 %wt. respectively for the corn stalk and cocoa pod husk and high volatile matter contents of 79.48, 80.48 and 80.72 %wt. respectively for the sugarcane bagasse, corn cobs and wawa sawdust. The XRF analysis gave high silica contents of 16.30 and 22.38%wt. for the rice husk and its straw respectively. Ultimate analysis gave carbon contents of 42.65, 43.32 and 43.87 %wt. respectively for the corn stalk and its cobs as well as cocoa pod husk and oxygen contents of 59.00 and 66.57 %wt. respectively for the rice husk and its straw. Wawa sawdust, sugarcane bagasse and corn residues performed well in both the proximate and ultimate analyses, giving carbon contents of 44.0 %wt and volatile content of 75.0 – 80.74 %wt and fixed carbon content of 7.60 – 12.01 %wt., while wawa sawdust, sugarcane bagasse and cocoa pod husk gave the lowest ash contents during the XRF analysis. Sulphur levels were, however, below 1.0 %wt. for all the biomass samples, while nitrogen levels were 1.49 and 2.23 %wt. respectively for the corn stalk and cocoa pod husks. Chemical analysis gave cellulose contents of 43.82 and 44.40 %wt. respectively for the corn stalk and wawa sawdust, hemicellulose content of 46.59 %wt. for the corn cobs and high lignin content of 41.08 %wt. for the rice husk. The highest HHV of 18.61 MJkg⁻¹ was recorded for the wawa sawdust. During the biomass fast pyrolysis, bio-oil yields increased from 53.0 to 60.0 %wt. for the rice straw as the temperature increased from 400 to 500 °C and then reduced to 50.3 %wt. at 700 °C. The non-condensable gas yields increased from 8.2 to 32.5 %wt. while bio-char yields decreased from 38.6 to 17.2 %wt. as the temperature increased from 400 to 700 °C. Similar trends in product distribution were obtained for other biomass samples. Maximum bio-oil yields ranged from 53.0 to 66.0 %wt. respectively at 550 °C for the cocoa pod husk and corn stalk. The high yield of bio-oil at high temperatures was due to primary

reactions, such as decomposition of cellulose and hemicellulose which resulted in the bio-oil production. At temperatures above 500°C, chemical reactions involving mainly the decomposition of lignin and secondary reactions involving the breakdown of the bio-oils resulted in high yields of bio-char. Characterization of the bio-oils obtained gave a pH ranging from 2.1 to 3.2 respectively for the wawa sawdust and corn stalk bio-oils, compared to a pH of 5.6 for light petroleum diesel oil. The high pH of the bio-oils makes them highly acidic, and thus corrosive, which is a problem. Carbon contents were 41.70 and 65.68 %wt. respectively for bio-oils obtained from the rice husk and its straw, lower than those of fossil diesel fuels. The highest MC of 26.7 %wt. was recorded for the cocoa pod husk bio-oils compared to very low MCs in light petroleum and heavy fuel oils. The HHVs, which ranged from 16.80 to 23.30 MJkg⁻¹ respectively for the corn cobs and sugarcane bagasse bio-oils were lower than those of light petroleum oil (40.0 MJkg⁻¹) and heavy fuel oil (40.0 MJkg⁻¹). These results indicate that the bio-oils obtained had lower fuel properties than fossil fuels. The low sulphur and nitrogen levels indicate, however, that low SO₂ and NO₂ would be expected to be emitted during combustion. The bio-oils can, however, be upgraded by hydrodeoxygenation which, reduces the oxygen content and thus the acidity. Of all the biomass samples characterized, the corn stalk, corn cob, wawa sawdust and sugarcane bagasse samples performed the best for bio-oil production due to their high carbon, cellulose and volatile matter contents as well as HHVs and produced the highest bio-oil yields. The cocoa pod husk and rice husk, however, performed the least due probably to high silica, low carbon and cellulose contents. Slight differences in maximum bio-oil yields obtained and trends of the other product yields may be due to differences in proximate, ultimate and chemical compositions of the biomass samples. This work would have significant economic and environmental benefits since it would reduce the dependence on imported and expensive fossil fuels for transportation and stationary engine applications. The proposed scheme could result in cost-effective bio-oil production at both the national and international levels at a low production cost since lignocellulosic biomass is cheap and fast pyrolysis is also a cheap process.

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LIST OF ABBREVIATIONS AND ACRONYMS

ADF	Acid Detergent Fibre
ASTM	American Standard for Testing Materials
AFEX	Ammonia Fibre Explosion
BtL	Biomass-to-Liquid
CO ₂	Carbon dioxide
CO	Carbon monoxide
C:O	Carbon-to-oxygen molar ratio
CFB	Circulating Fluidized-Bed
CHP	Combined Heat and Power
C ₂ H ₆	Ethane
C ₂ H ₄	Ethene
C5	Five-carbon sugar
FAO	Food and Agriculture Organization of the United Nations
GHG	Greenhouse Gases
HHV	Higher Heating Value
H:C	Hydrogen-to-carbon molar ratio
HAA	Hydroxyacetaldehyde
IEA	International Energy Agency
MJ/kg	Mega joules/kilogram
CH ₄	Methane
MSW	Municipal Solid Waste
NREL	National Renewable Energy Laboratory
NDF	Neutral Detergent Fibre
NO ₂	Nitrogen dioxide
NCG	Non-condensable gas
OECD	Organization for Economic Co-operation and Development
C ₃ H ₈	Propane
SHF	Separate Hydrolysis and Fermentation
SSF	Simultaneous Saccharification and Fermentation
C6	Six-carbon sugar
SO ₂	Sulphur dioxide
UNEP	United Nations Environment Programme
UN	United Nations Organization
H ₂ O	Water

CHAPTER ONE

1.0 INTRODUCTION

This chapter provides an introduction to biofuels as replacement or sources of energy to fossil fuels for transportation and technologies utilized in industry for biofuel production. It highlights current global energy problems, which result from the utilization of fossil fuels. It also discusses lignocellulosic biomass and conversion technologies such as biochemical and thermochemical processes for its conversion to biofuels. The principles of biomass fast pyrolysis are discussed. Finally, the objectives of this thesis are stated, together with the novelties that have been carried out.

1.1. Biofuel as a substitute or replacement energy source to transportation fuel

1.1.1 Types of biofuels

Biofuels, liquid fuels produced from biomass (FAO, 2008), are drawing increasing attention globally as alternative sources to petroleum-derived transportation fuels to help address high energy costs and global warming concerns associated with fossil fuels. Currently, the use of biofuels is being promoted as a sustainable means of increasing energy independence, reducing greenhouse gas (GHG) emissions, contributing to farmer income, opening new business opportunities, reducing poverty and promotion of rural development (FAO, 2008; Howarth *et al.*, 2008).

Biofuels can be categorized into three major groups, namely first-generation, second-generation and third-generation types. The main distinction among them is the type of feedstock used in the production process, their current and future availability (OECD/IEA, 2008; UNEP, 2009) (Table 1.1). First generation biofuels are currently produced in large commercial quantities in many countries from agricultural crops such as sugarcane, maize,

soybean and jatropha through well-established technologies such as hydrolysis, fermentation and trans-esterification (UNEP, 2009). Bioethanol and biodiesel are the two most well-known examples of first-generation biofuels used in the transport sector and account for over 90% of global biofuel usage. Other first-generation biofuels include vegetable oil and biogas. These are globally produced for the replacement of conventional fossil gasoline or fossil diesel oil or as additives in the transport sector and feedstock in the chemical industry. Bioethanol is produced by fermenting sugar extracted from feedstocks such as sugarcane, sugar beets, sugar extracted from starch contained in maize, wheat, sweet sorghum, cassava and potatoes (FAO, 2008; UNEP, 2009; USDE, 2010).

Biodiesel such as fatty acid methyl ester is produced from fatty acids obtained from feedstocks such as rapeseed, soybean, sunflower, coconut, oil palm, *Jatropha curcas*, recycled cooking oil and pure plant oils through trans-esterification usually with methanol in the presence of catalysts such as sodium hydroxide, potassium hydroxide or acids (Schuchardta *et al.*, 1998). Glycerol results as a by-product. Acid catalysts give very high yields of biodiesel, but the reactions are slow and require temperatures above 100 °C and more than 3h to reach complete conversion. Current industrial processes, therefore, are usually carried out using base catalysts (Schuchardta *et al.*, 1998). Trans-esterification reduces long-branched molecules, which are less suitable as fuels to short straight-chained fatty acid methylesters of lower viscosity, which are readily combustible (Heywood, 1988; Connor and Hernandez, 2008).

Biogas, which is composed mainly of methane (CH₄), carbon dioxide (CO₂) and hydrogen (H₂), is generated from organic materials including cow dung, poultry droppings, pig manure,

kitchen waste, grass, faecal matter and algae under anaerobic conditions (Table 1.1 refers). Biogas technology has been commercialized since long (Arthur *et al.*, 2011).

Second-generation biofuels may be produced from lignocellulosic biomass such as agricultural crop residues, forestry and wood processing wastes, organic components of municipal solid waste (MSW) and energy crops such as *Mischantus giganteus*, using either thermochemical or biochemical processes (Vantomme, 2006; UNDESA, 2007; OECD/IEA, 2008; UNEP, 2009). However, they are currently not produced on a commercial scale because of the high cost of the processes. Cellulosic ethanol or ethyl alcohol ($\text{CH}_3\text{-CH}_2\text{OH}$) and cellulosic butanol ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{OH}$) are two well-known examples produced from lignocellulosic biomass through biochemical processes. They can be used as alternative sources to petroleum-gasoline for transportation (OECD/IEA, 2008). While the properties of cellulosic ethanol are similar to those of first-generation bioethanol, the relative abundance and wide range of lignocellulosic biomass used as feedstock, which is non-food, give them an advantage (Vantomme, 2006; UNDESA, 2007; UNEP, 2009).

Third-generation biofuels are, however, produced from feedstocks such as micro- and macro-algae, vegetable oils and biodiesel. Green algae, in particular, produce as much as 60% of their body weight as triglycerides when deprived of key nutrients such as nitrogen and potassium. Algae fuel, also called oil-algae and referred to as a third-generation biofuel, is produced using trans-esterification (OECD/IEA, 2008; UNEP, 2009).

Table 1.1: Types of biofuels – overview with basic technologies, feedstocks and examples of co-products

Biofuel	Basic technology	Feedstock	Co-product
Solid biofuels	Traditional use of dried biomass for energy.	Fuel wood and dried manure.	
First generation biofuels			
Plant oils	As transport fuel. For electricity and heat generation (CHP).	Rapeseed oil, sunflower, palm oil, jatropha, waste vegetable oils.	Oilcake as animal feed
Biodiesel	Trans-esterification of oils and fats to produce biodiesel as transportation fuels.	Rapeseed, sunflower, soya, oil palm, jatropha and castor.	Oilcake as animal feed; Glycerine
Bioethanol	Fermentation (sugar); hydrolysis and fermentation (starch); used as transportation fuels.	Corn, sugarcane and Cassava	Animal feed, DDGS (dried distillers grains with soluble)
Biogas (CH ₄ , CO ₂ , H ₂)	Fermentation of biomass (as purified biomethane).	Energy crops (e.g. maize, miscanthus; short rotation wood; bio-degradable waste	Residues used as fertilizer
Solid biofuels	1) Densification of biomass by carbonisation (charcoal); 2) Residue and waste for generation of electricity and heat (CHP).		
Second generation biofuels			
Bioethanol	Breakdown of lignocellulosic biomass in several steps including hydrolysis and fermentation.	Agricultural crop residues, wood, energy crops (e.g. miscanthus and sugarcane bagasse).	
Biodiesel, biohydrogen, biomethanol	Gasification of low-moisture content biomass (<20% moisture content) produces syngas	Lignocellulosic biomass	Fischer-Tropsch process
Third generation biofuels			
Biodiesel, aviation fuels, bioethanol	Bioreactors for ethanol; trans-esterification.	Micro- and macro-algae	Animal feed, bio-polymers and fertilizer.

Source: UNEP (2009).

1.1.2. Types, structure and chemical composition of lignocellulosic biomass

Lignocellulosic biomass is the major structural component of woody and non-woody plants, and represents a major source of renewable organic matter. It includes wood processing waste, forest residues, agricultural crop residues, organic portion of municipal solid waste, (MSW) and special energy crops such as *Miscanthus giganteus* (Table 1.2). It is composed of, depending on its origin and type, cellulose (40–50%), hemicellulose (20–30%) and lignin (20–30%) (Malherbe and Cloette, 2002; Jarvis, 2005; Mohan *et al.*, 2006; Howarth *et al.*, 2008) (Table 1.3).

Cellulose and hemicellulose are tightly bound to lignin by covalent and hydrogen bonds (Mohan *et al.*, 2006). Cellulose is a linear crystalline polymer of hexose sugars, which consists of glucose units linked by β -(1,4)-D-glycosidic bonds (Figure 1.1). This is in contrast to starch, which is a polymer of glucose linked by α -(1,4)-D-glycosidic bonds (Duff and Murray, 1996). Chemically, glucose is a monosaccharide or a simple sugar while starch is a complex carbohydrate. Starch and glucose are also chemically different in terms of size, physical properties and uses.

The β -(1,4)-D-glycosidic bonds make it highly resistant to de-polymerization by either enzymatic or acidic hydrolysis. The hydrogen bonds between adjacent cellulose polymers, whilst forming crystalline structures that give plants structural strength, make them difficult to react since they prevent water penetration (Viikari *et al.*, 1991). The chain length or degree of polymerization (DP) of cellulose, which depends upon its source is 3,000–15,000. The DP affects the yields of fast pyrolysis products. During fast pyrolysis, cellulose undergoes de-polymerization and fragmentation to form bio-oil, non-condensable gas and char (Mohan *et al.*, 2006).

$$DP = \frac{\text{Molecular weight of cellulose}}{\text{Molecular weight of one glucose unit}} \dots\dots\dots \text{Equation 1}$$

Hemicellulose is a highly branched polymer composed of five-carbon sugar, that is, pentoses (C5), mostly xylose, and hexoses (C6), mostly mannose (Figure 1.2). In general, the percentage composition of pentose sugars in hemicellulose is 6–26 %wt of dry mass, while hexose is 40–70%. Hemicellulose is thermally less stable than cellulose due to lack of crystallinity. It is easier to extract and decompose into its constituent sugars than cellulose (Mohan *et al.*, 2006; Centi, 2009). Its molecular weight is also lower than that of cellulose. However, its exact composition depends on the type of lignocellulosic biomass (Jarvis, 2005; Centi, 2009; Sanchez, 2009).

Table 1.2: Types of lignocellulosic biomass and their current uses

Lignocellulosic biomass source	Residue type	Competing uses
Grain harvesting: Rice, corn, sorghum	Straw, cobs, stalks	Animal feed, burnt as fuel, compost, soil conditioner
Grain processing: Corn, rice	Husk	Animal feed
Fruit harvesting and processing	Husk, peels	Animal and fish feed
Sugarcane	Bagasse, molasses	Burnt as fuel
Oil seed plants: Nuts, cotton seeds	Shells, husk, presscake	Animal feed, fertilizer
Animal waste	Manure	Soil conditioners
Log harvesting	Wood residues, bark	Soil conditioners, burnt
Sawmill and plywood waste	Sawdust, chips, shavings	Chip and fiber board
Municipal Solid Waste	Organic content	Burnt

Source: Howarth *et al.* (2008)

The third major component of lignocellulosic biomass, lignin, is amorphous and composed of amorphous, high-molecular-weight, chemically-related compounds. It constitutes about 15–25% of the composition of lignocellulosic biomass (Figure 1.3) (Mohan *et al.*, 2006). The building blocks of lignin are a three-carbon chain attached to phenyl-propane. Lignin binds cellulose and hemicellulose in lignocellulosic biomass. It also prevents microbial and fungal

attack of these components (Mohan *et al.*, 2006). Many linkages such as carbon-carbon, ether bonds and covalent bonds exist within its individual units, which enhance the bond strength in lignin. The physical and chemical properties of lignin differ, depending on either its extraction or isolation technology (Mohan *et al.*, 2006). Lignin pyrolysis yields phenol through the cleavage of ether and carbon-carbon linkages. It also produces more char as a residue than the pyrolysis of cellulose. Lignin decomposition in wood has been proposed by Mohan *et al.* (2006) to begin at 280 °C and continues to 450–500 °C with a maximum yield at 350–450 °C.

Extractives, which constitute about 5–10 %wt of lignocellulosic biomass, include various compounds such as fats, waxes, alkaloids and phenols. They function as energy reserves and also defend attacks by microbes and insect (Laine, 2005; Mohan *et al.*, 2006). Lignocellulosic biomass contains also small amounts of minerals composed of various elements including nitrogen, phosphorus, potassium, silicon and calcium, which occur as oxides, silicates, carbonates, sulphates and chlorides. These compounds end up in the products of pyrolysis. The mineral content depends on the biomass type and composition and affects the yields of pyrolysis products by catalyzing secondary reactions, which result in bio-char formation (Raveendran *et al.*, 1995; Sanchez, 2009). Elements present in biomass are involved in ash fouling and slagging. Calcium and potassium combine with sulphur to form alkali sulphates and with silica to form alkali silicates. These compounds melt or soften at temperatures below 700 °C causing ash deposition problems. Chlorine is also a major factor in ash formation. It facilitates the mobility of major inorganic elements, in particular potassium (Jenkins *et al.*, 1996).

Table 1.3: Chemical composition of lignocellulosic biomass (% dry weight)

Lignocellulosic biomass	Cellulose	Hemicellulose	Lignin
Hardwood stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Corn cobs	45	35	15
Paper	85–99	0	0–15
Rice straw	32	24	18
Sugarcane bagasse	46	30	19
Switch grass	45	31	12
Grasses	25–40	25–50	10–30

Source: Howarth *et al.* (2008)

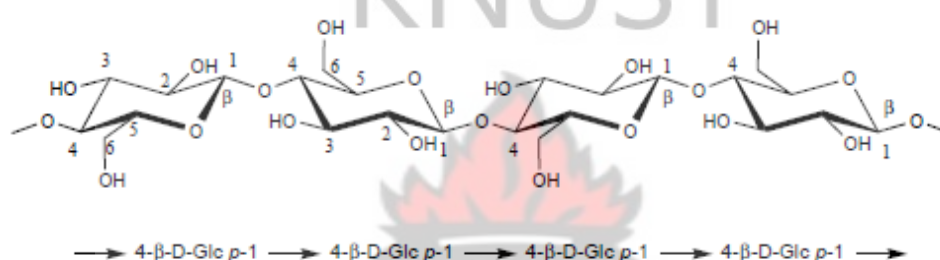
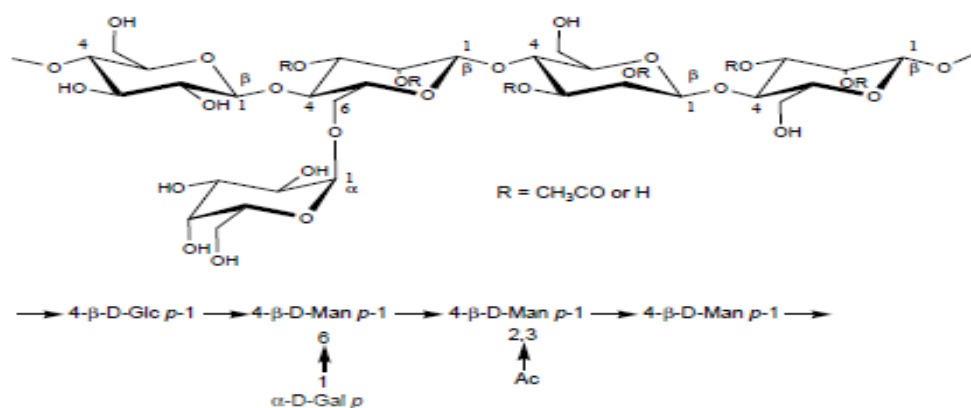


Figure 1.1: Structure of softwood cellulose - a linear polymer of 1,4- β -D-glucopyranose units with the chemical formula $(C_6H_{10}O_5)_n$. Source: Laine (2005)

Glucomannan



Xylan

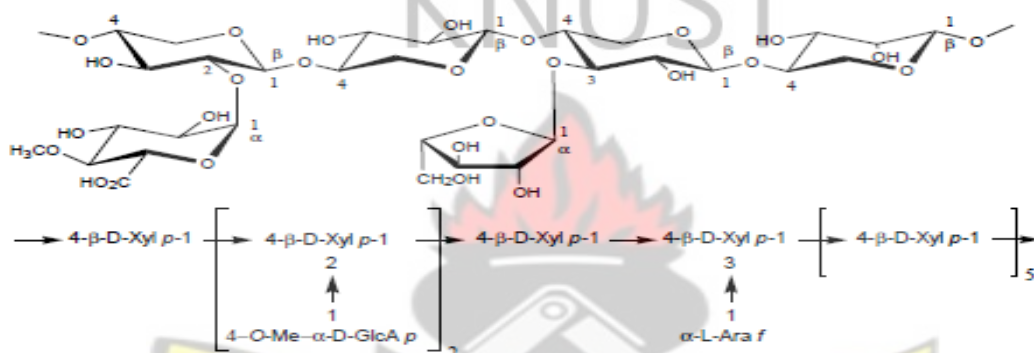


Figure 1.2: Structure of major softwood hemicellulose, a branched-chain polymer composed of different sugars and side groups, showing a 1,4-β-D-xylopyranose fragment with 4-O-methyl-D-glucopyranosyl uronic acid side chains. Source: Laine (2005).

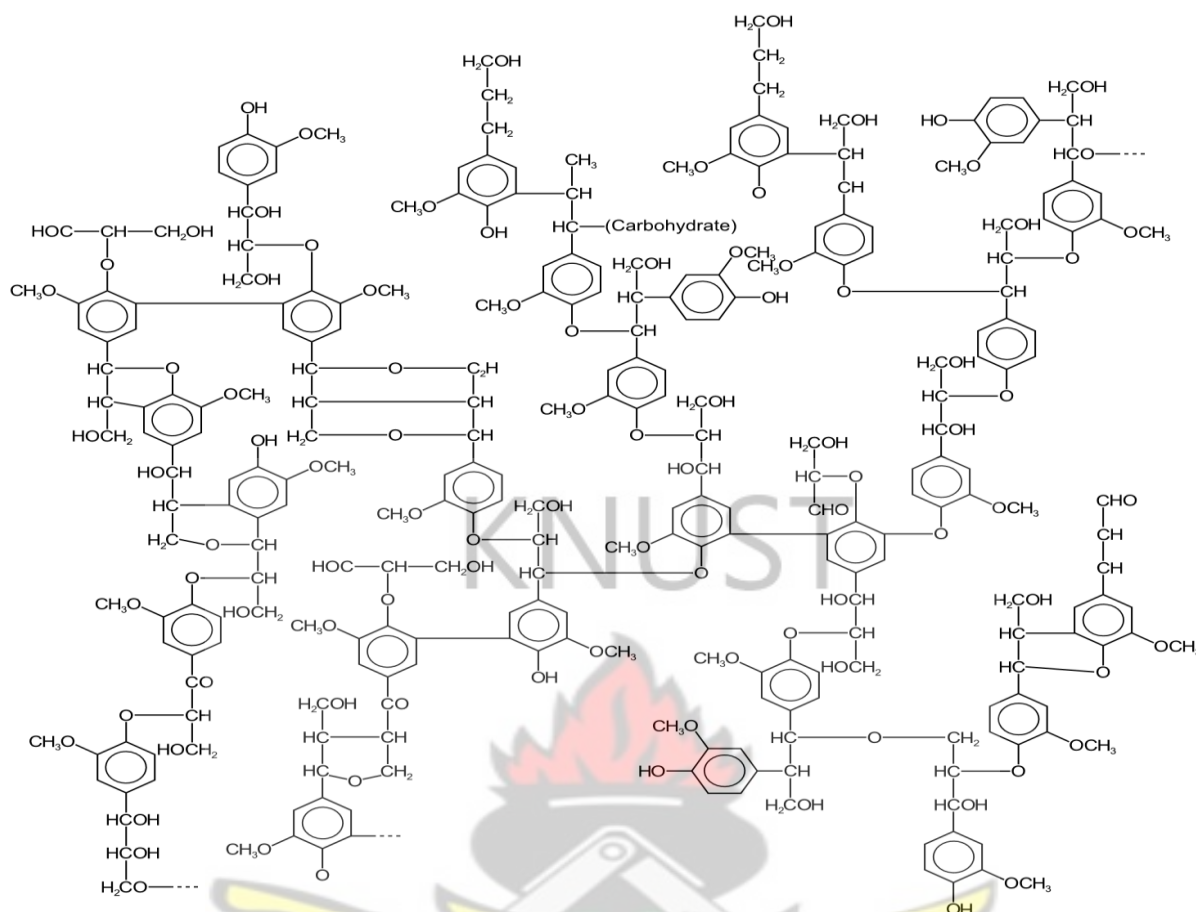


Figure 1.3: Structure of softwood lignin, a 3-dimensional phenolic polymer based on hydroxy- and methoxy-substituted phenylpropane units. Source: Laine (2005).

1.1.3 Conversion of lignocellulosic biomass into biofuels

Various processes have been proposed for the production of second generation biofuels from lignocellulosic biomass (Lee *et al.*, 2005; Bridgwater, 2007; Garcia-Perez *et al.*, 2007; Howarth *et al.*, 2008; Lima *et al.*, 2009; Sanchez, 2009; Sierra *et al.*, 2009). Two major pathways are available for lignocellulosic biomass conversion into biofuels. These are: (i) biochemical process and (ii) thermo-chemical process (Figure 1.4).

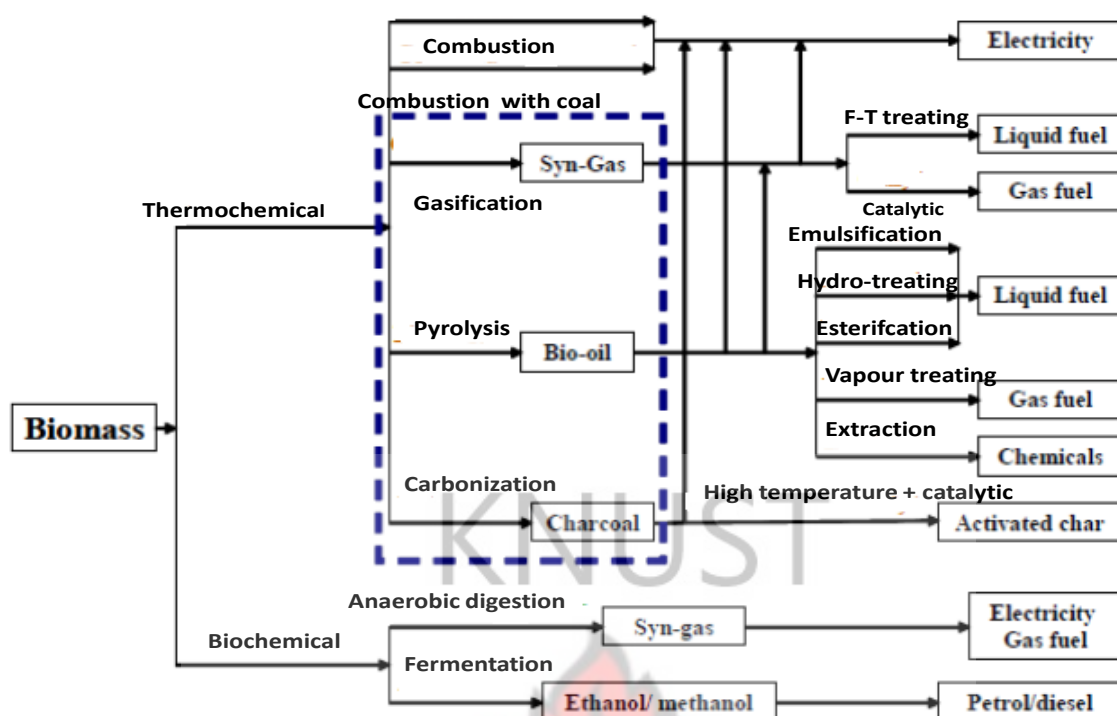


Figure 1.4: The established thermochemical and biochemical conversion technologies of biomass to energy. Source: Shen and Gu (2009) and Sanchez (2009).

1.1.3.1 Biochemical conversion of lignocellulosic biomass into biofuels

Biochemical conversion of lignocellulosic biomass into biofuels consists of processes which include: (1) pre-treatment; (2) hydrolysis of the polymers to produce sugars such as hexose and pentose that can be readily fermented; (3) fermentation of the sugars to biofuels (4) separation and (5) purification (Lee *et al.*, 2005; Liu *et al.*, 2008; Sanchez, 2009; Joshi *et al.*, 2011).

Pre-treatment changes the structure of the lignocellulosic biomass such as its surface area and thereby makes cellulose and hemicellulose more accessible to hydrolysis (Wyman *et al.*, 2007; Centi, 2009; Shi *et al.*, 2009). Pre-treatment methods can be categorized into three major groups, namely (i) mechanical processes, i.e. physical such as grinding or milling, (ii) chemical means (iii) and biological means (Centi, 2009). Dilute sulphuric acid (H_2SO_4) pre-treatment gives high yields, and is the preferred option because of its extensive development

(Wyman *et al.*, 2007; Joshi *et al.*, 2011). According to Centi (2009), pre-treatment was the most expensive step in the conversion of lignocellulosic biomass into biofuel. It accounted for 22% of the global ethanol production cost in 2009. Fungal pre-treatment has also been proposed for bioethanol production using lignocellulosic biomass (Sanchez, 2009; Salvachúa *et al.*, 2011). Generally, it is a slow process, which is carried out under mild conditions (Sanchez, 2009).

Hydrolysis is carried out using acids, enzymatic processes and biological processes. Dilute acid hydrolysis, for example, which is a fast process, is carried out at 120 °C. However, it yields high amounts of waste products, which are required to be disposed of (Centi, 2009; Sanchez, 2009). Cellulose hydrolysis yields sugars, which are mainly hexoses. Hemicellulose hydrolysis, however, yields a mixture of hexoses such as glucose and pentoses such as xylose and arabinose

A major challenge with the fermentation of sugars derived from cellulose and hemicellulose is to ferment all the hexoses and pentoses at high rates and yields. The fermentation of pentose, however, gives lower rates (0.29 g /g/h) and yields (10–40 wt.%) than those of hexose (> 0.3 0 g /g/h ; 30–50 wt%) (Jarvis, 2005; Dien *et al.*, 2006; Centi, 2009).

1.1.3.2 Thermochemical conversion of lignocellulosic biomass

Thermochemical processes for the conversion of lignocellulosic biomass into biofuels include combustion, torrefaction, pyrolysis and gasification (Zanzi *et al.*, 2002; Trifirò, 2007). They are rapidly becoming an alternative source for renewable energy production globally. However, the sustainability of the processes requires the availability of sufficient biomass as feedstock to satisfy the demand of emerging bio-energy industries.

Combustion, which is the easiest and oldest means of producing heat energy from biomass, converts solid biomass in the presence of air to heat in boilers, burners or turbines. Depending on the type of combustion equipment, some types of biomass require pre-treatment, which is associated with high operating and financial costs (McKendry, 2002).

Torrefaction, a process which is carried out at low temperatures (200–300 °C) in the absence of oxygen and long residence time, is used to upgrade biomass. It completely dries the biomass and makes it easy to grind. The process partially removes hemicellulose, dehydrates cellulose and increases the calorific value of the biomass (Garcia-Perez, 2010). Biomass, which has been torrefied is similar to char and can be used as feedstock in various thermochemical applications for heat and power generation, and also for liquid fuel production.

Gasification, a partial oxidation of biomass, is carried out under pressure at high temperatures, which range between 650–900 °C. The primary products are syngas, bio-oil and char as the main products. Syngas, which consists mainly of carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂) and traces of ethane, ethene, water, char particles, ash and tar, can be fed into turbine power plants for energy production (FWPA, 2007; Trifirò, 2007).

Pyrolysis, the decomposition of biomass by heating either in the absence or in a limited supply of oxygen, is carried out at 400–800 °C with bio-oil, non-condensable gases and char as the main products. Based on the heating rate, it can be grouped into three main categories, namely: slow pyrolysis (<283 °C/min), intermediate pyrolysis (373 °C/min) and fast pyrolysis (>1273 °C/min) (Bridgwater, 2007; Papadikis *et al.*, 2009; Zhang *et al.*, 2009; Duku *et al.*,

2011). These categories produce different product yields, each of which has a potential economic use (Yoder, 2009; Mullen *et al.*, 2010).

Slow pyrolysis of biomass, which is carried out under a slow heating rate, results in higher yields of char and lower yields of bio-oil than fast pyrolysis due to enhanced dehydration and condensation reactions. Therefore, it has often been employed in industry for charcoal production (Ganesh and Banerjee, 2001; Papadikis *et al.*, 2009; Yoder *et al.*, 2009). Fast pyrolysis, however, is carried out between 400 and 550 °C with bio-oil, char and non-condensable gas as the main products. It gives high yields of bio-oil. Its major steps include (i) biomass drying, (ii) reduction of the biomass to small particle-sized (0.5–1 mm), (iii) fast pyrolysis, (iv) bio-char separation and (vi) liquid recovery or collection after condensation of the vapours (Bridgwater, 2007). Its key characteristics are very fast heating rate (376 °C/s) at a controlled temperature and a short vapour residence time (<2s) (Aho *et al.*, 2008; Papadikis *et al.*, 2009). Rapid heating and cooling rate of the vapours reduce the extent of secondary reactions, which result in high yields of bio-oil (Antal and Grønli, 2003; Asadullah *et al.*, 2008; Zhang *et al.*, 2009; Mullen *et al.*, 2010).

During fast pyrolysis, the main components of lignocellulosic biomass contribute differently to product yields. Cellulose fast pyrolysis yields bio-oil, which contains many oxygenated organic compounds such as levoglucosan, alcohols and esters (Antal and Gronli, 2003). Fast pyrolysis of hemicellulose also yields similar products (Zhu *et al.*, 2006). Fast pyrolysis of lignin, however, gives higher yields of char but lower bio-oil yields than either that of cellulose or hemicellulose (Antal and Gronli, 2003). The extractives volatilise to yield mainly liquid and gas (Antal and Grønli, 2003; Garcia-Perez *et al.*, 2007). Minerals, particularly

alkaline metals, catalyze secondary decomposition reactions of cellulose and hemicellulose, which result in high char yields but low bio-oil yields (Bain, 2009).

Many types of pyrolyzers such as fluidized-bed, transported, circulating fluidized-bed, fixed bed, ablative and vacuum have been developed and applied in biomass fast pyrolysis (Asadullah *et al.*, 2007; García-Pérez *et al.*, 2007; Zhang *et al.*, 2009). Fluidized-bed is proposed for this study because it is a well developed technology. Moreover, it can provide a high heating rate of more than $1000\text{ }^{\circ}\text{C s}^{-1}$. It uses small-sized biomass particles with diameters below 2 mm to ensure rapid heat transfer (Yoder *et al.*, 2009).

Bio-oils are generally dark-brown organic liquids, acidic, unstable and immiscible with diesel oil. They have a high viscosity and an unpleasant odour. They are also chemically complex due to the presence of many oxygenated organic compounds. Compared with petroleum diesel oil, they have higher oxygen and water content. These characteristics limit their direct application as fuels for transportation (Trifirò, 2007; Zhang *et al.*, 2009). They can, however, be upgraded through processes such as hydrogenation and catalytic cracking into bio-gasoline and bio-ethanol, and used as alternative sources to fossil fuels for transportation (Yoder *et al.*, 2009). Upgrading reduces their oxygen, water and alkali content (Demirbas, 2001; Bridgwater, 2007; Chiaramonti *et al.*, 2007; Mullen *et al.*, 2010).

Bio-oil production using fast pyrolysis could, therefore, help reduce the dependence on fossil fuels and further contribute to climate change mitigation. Fast pyrolysis has a great potential for large-scale production of bio-oil due to the large availability of a wide range of lignocellulosic biomass, and its high mass conversion and energy efficiency. Char, a co-product, can be used as renewable source of energy or to enhance soil fertility since it has a

high water and nutrient holding-capacity. It can also be used for carbon sequestration to mitigate climate change due to its high carbon stability (Yoder *et al.*, 2009; Duku *et al.*, 2011).

1.2 Scope of the global fuel problem

The use of fossil fuels, particularly for transportation, has been associated with many problems. Fossil fuels are finite, expensive and not globally distributed. Moreover, their use is associated with GHG emission such as CO₂, CH₄, SO₂ and NO₂. Since 1990, considerable focus has been placed on the development of technologies for the conversion of lignocellulosic biomass into biofuels as alternative liquid transportation fuels to gasoline and diesel oil (Shi *et al.*, 2009). Among the major reasons cited for the development of biofuel technologies are high crude fuel prices, reduction of dependence on fossil fuels, growing concerns about GHG emissions, which contribute to climate change, potential contribution to sustainable development and rural revenue generation (Worldwatch, 2006; Crutzen *et al.*, 2007; FAO, 2008; Bertuccio, 2008).

Globally, about 60% of fossil fuels produced is utilized for transportation. Approximately 98% of transportation fuels used is produced from crude oil. However, the availability, economic sustainability and GHG emissions associated with their utilization pose major problems with transportation fuels (Bertuccio, 2008). Transportation including GHG emissions from the production of transportation fuels, constitutes about 25% of global energy-related GHG emissions, and this is gradually increasing (Worldwatch, 2006). Globally, crude fossil fuel prices have been increasing sharply, and reached a record high of about US\$147 per barrel in 2008 (Shi *et al.*, 2009).

In Ghana, the price of transportation fuels such as gasoline rose to a high level of GH¢5.6 per 4.5 litre in 2008, which created serious imbalances in the national economy. The intervention of the government caused a considerably huge debt to crude oil importing and refining companies including the Tema Oil Refinery (Casely-Hayford, 2011).

Generally, biofuels are considered to have the potential to play a major role in providing locally available renewable energy with GHG emission reduction benefits. Worldwatch (2006) reported that biofuels could provide 37% of transportation fuels in the USA within the next 25 years, and up to 75% if the automobile fuel economy is doubled. Similarly, they could replace 20–30% of fossil fuels used in European Union countries during the same period.

Current global production of first-generation biofuels is based on the utilization of agricultural crops (Reynolds, 2000; Duku, 2007; Dupont, 2007; RFA, 2007; Ahiataku-Togobo and Ofosu-Ahenkorah, 2009). These preferences for agricultural food crop feedstock are based on the availability of relatively inexpensive feedstock. The long-term availability and sustainability of agricultural crops, however, raise several concerns with regard to global food and animal feed security, particularly with increased demand for biofuels for transportation (Shi *et al.*, 2009). The use of agricultural crops for biofuel production is considered to compete directly with global food crop production and supply (OECD/IEA, 2008). Oilseed production for biodiesel, for example, is presumed to have the tendency to cut into food supplies. Production of energy crops could cause expansion of the agricultural frontier, deforestation, mono-cropping and water pollution.

Biodiesel could be seen not only as one way to displace petroleum-based fuels but also as a way to help farmers by providing an additional market for oilseed crops, particularly those grown primarily for animal feed. Farmers can grow oilseed crops in rotation with food crops such as wheat and maize. Rural communities may benefit from having biodiesel processing facilities that provide job opportunities and other sources of income to surrounding communities. Small-scale biodiesel production that makes use of local crops and supplies local energy needs could be a viable solution to energy needs in rural areas. Since biofuels tend to increase income to farmers, benefitting them economically. Labourers on those farms would also benefit. However, higher food prices could cause increased food insecurity for the urban poor.

In 2007, about 5% of global production of cereals was used for the production of biofuels. In the USA, for example, about 24% of corn harvested in that year was used for bioethanol production (FAO, 2008). Corn prices also rose significantly from US\$87 to US\$217 per tonne between 2006 and 2007, driven mainly by increases in global food demand, use of corn as feedstock for bioethanol production and high fuel prices (UNCTAD, 2007; FAO, 2008; Tyner, 2008).

Second-generation biofuel technologies such as fast pyrolysis based on low-cost lignocellulosic biomass for bio-oil production are, therefore, required to be developed. Bio-oils could be used as an alternative source to fossil fuels in stationary engines since they generate less NO₂ and SO₂. They can also be refined and used as an alternative source to reduce the dependence on fossil fuels for transportation and also contribute to GHG emission reduction.

1.3 Problem statement

Current high prices of fossil fuels for transportation, and dependence on imported fossil fuels impact significantly both on the national and global economy. Crude fossil fuel prices have been increasing sharply to US\$147 per barrel in 2008. The price of transportation fuels such as gasoline rose to a high level of GH¢5.6 per 4.5 litre in 2008 in Ghana, which created serious economic imbalances. In most sub-Saharan African countries including Ethiopia, Tanzania, Uganda and Zimbabwe, economic development has been challenged by continuous increases in crude oil prices and the transport sectors in these countries are totally dependent on imported fossil fuels and fuel bills, which constitute over 50% of their budget.

Consumption of diesel oil, for example, in Ethiopia in 2004–2005 was approximately 742,000 tonnes amounting to US\$900 millions. This situation compelled the country to focus on renewable energy, especially biofuels with the aim to reduce high fossil oil import bills. Similarly, in Tanzania and Uganda, although energy resources include fossil oil, energy supply and use is dominated by biomass resources. Zimbabwe, which has no fossil oil resources imports all petroleum products, which accounts for approximately US\$120 million per annum and about 18 percent of the country's foreign exchange earnings. This situation, coupled with the emission of greenhouse gases has compelled several governments to consider alternative sources of fuels for transportation and stationary engines.

Biofuel presents itself as a suitable option and has received considerable attention in recent years. However, the production of first-generation biofuels competes with global food crop production. Fast pyrolysis is a viable option since it uses a non-food renewable resource, which is low cost and globally available unlike fossil fuels, which are finite and located in just a few regions in the world. Bio-oil production as replacement or supplement would

reduce the dependence on fossil fuels for transportation and consequently contribute to the national economy through foreign earning savings, job creation and rural development. Moreover, the use of bio-oils would result in reduced GHG emissions compared to conventional fossil fuels.

1.4. Justification

One of the options available to reduce the competition among food, animal feed and fuel associated with the production of first-generation technology biofuels, such as ethanol and biodiesel, which use agricultural crops as feedstock, is to widen the range of feedstock through second generation technologies, which use lignocellulosic biomass. Evidently, sustainable availability of feedstock for biofuel production, its costs and potential competition with food and feed are major problems to the biofuel manufacturer, feedstock producer and governments.

Lignocellulosic biomass is an abundant renewable resource and is globally available. A broad range has been considered as potential biofuel feedstock, which includes agricultural crop residues such as corn stover, cobs and stalk, rice straw and husk, sugarcane bagasse, herbaceous energy crops such as switchgrass and *Miscanthus* spp., wood processing residues and the organic content of municipal solid waste (MSW) (FWPA, 2007; Shi *et al.*, 2009).

Current forestry, wood processing and agricultural practices generate considerably large amounts of residues and wastes, which either remain in mills or are normally left on farms during harvesting (UNEP, 2009). They offer no significant value but rather pose serious environmental disposal problems. However, they could be considered as potentially sustainable and suitable feedstock for biofuel production because of their abundance, high

cellulose and hemicellulose content and high calorific values ($12.6\text{--}18.6 \text{ MJ.kg}^{-1}$), the need to identify uses for these problematic wastes, their high heating values and low cost nature (Liu *et al.*, 2008). This has necessitated the development of technologies for bio-oil production and its utilization as an alternative source to major fossil fuels for transportation fuels and stationary engines.

Bio-oil production will have several benefits for the country and globally especially countries, which utilize considerable quantities of agricultural crops for ethanol production and also have projections to increase their levels of production. In Ghana, bio-oil production and use will reduce the dependence on gasoline and diesel oil importation, create jobs and contribute to rural development.

This study focused on bio-oil production from lignocellulosic biomass using fast pyrolysis in a fluidized-bed reactor to serve as an alternative source to fossil or petroleum-derived fuels for transportation. The results provide relevant and critical information for the development of the biofuel industry at the national level. Of much importance is the development of a scheme for bio-oil production, which is based on the results and conclusions of the characterization of the selected lignocellulosic biomass based on cellulose, carbon and hydrogen contents as well as heating values, the effect of reaction temperature on pyrolytic product distribution and fuel characteristics of the bio-oils produced as well as their availability in the country as determined by a biomass resource mapping in five regions (Hagan and Duku, 2012).

The scheme could be tested and further scaled-up for industrial applications initially at the national level. This will contribute to reduction of dependence on imported fossil fuels for

transportation, savings in the national economy and poverty reduction. However, since bio-oil has some undesirable characteristics such as high water and oxygen content as well as high acidity, there is a need to upgrade it before it could be used for transportation.

To the biofuel manufacturer, these lignocellulosic biomasses would provide a relatively low cost, readily available and sustainable feedstock for bio-oil production. To the feedstock producer, they would provide an additional source of income, and thus help in poverty reduction. To the government, bio-oil production will provide a means for rural development through the establishment of industries in rural areas.

Since lignocellulosic biomass is a non-food resource, its use will not compete with either national or global food security. Rather, it will reduce food, feed and fuel competition. Most of these wastes and residues would, otherwise, either end up in landfills, burnt or left at mills and on farms during harvesting if not utilized for bio-oil production.

1.5 Objective of the study

Main objective

To use fast pyrolysis to produce bio-oil from lignocellulosic biomass as a substitute or replacement for diesel oil or gasoline to reduce dependence on expensive and imported fossil fuels for transportation and stationary applications. To use bio-oil to reduce the emission of greenhouse gas (GHG).

Specific objectives

1. To characterize selected major lignocellulosic biomass such as agricultural crop residues and wood processing residues using proximate, ultimate and compositional analyses and

determination of heating values. Proximate analysis characterizes the moisture content, ash content, fixed carbon content and volatile matter content. Ultimate analysis determines the elemental constituents, namely carbon, hydrogen, oxygen, nitrogen, sulphur and chlorine contents. Compositional analysis, however, determines cellulose, hemicellulose and lignin contents.

2. To investigate the effect of temperature on the distribution of products of fast pyrolysis (bio-oil/tar, non-condensable gas and char yields) of the biomass samples.
3. To characterize the bio-oils for energy purposes using different analytical techniques including physical and elemental analyses, and determination of calorific values.
4. To develop a scheme for bio-oil production from the selected lignocellulosic biomass types using fast pyrolysis in a fluidized-bed reactor.

1.6 Project novelty

This thesis expands on previous research, which has been carried out in the field of fast pyrolysis using lignocellulosic biomass as feedstock in countries such as UK, China and USA by researchers including Demirbas (2001), Garcia-Perez *et al.* (2002), Czernik and Bridgwater (2004) and Crutzen *et al.* (2007). Such studies have provided information on the characteristics of some lignocellulosic biomasses available in those countries, which make them favourable as feedstock for bio-oil production as well as the dependence on temperature on the yields of products of fast pyrolysis.

This work, however, provides information on the pyrolytic characteristics of selected biomasses in Ghana, which have not as yet been studied and further develops a scheme for bio-oil production using fast pyrolysis in a fluidized-bed reactor. The large availability of this resource determined through biomass mapping enhances the potential industrial application

of the scheme (Hagan and Duku, 2012) (Appendix 4 refers). Lignocellulosic biomass is currently not considered as a major feedstock in the country's biofuel policies. Agricultural crop residues, which are largely left on farms, have not as yet been characterized for biofuel production. Moreover, bio-oil has not been considered as a major alternative energy source to fossil fuels for transportation and stationary applications. This is due to current limited knowledge of their availability and suitability for thermochemical applications such as bio-oil production using fast pyrolysis as well as the suitability of bio-oil as an alternative energy source to fossil fuels. The results of this thesis indicate that the selected biomasses analyzed are suitable biomass sources for bio-oil production using fast pyrolysis.

1.7 Thesis structure

The thesis consists of the following chapters:

Chapter 1(Introduction) provides introductory comments on current global energy situation and an insight into transportation fuels and available technologies utilized in industry for the generation of energy. It discusses biofuels as an alternative energy source to transportation fuels. The effect of temperature on product distribution during fast pyrolysis is also highlighted. The objective of this thesis is given together with the novelty, which has been carried out.

Chapter 2 (Literature Review) provides a comprehensive review of technologies for lignocellulosic conversion into biofuels with a focus on thermochemical and biochemical conversion processes. Emphasis is placed on the principles of fast pyrolysis for the production of bio-oils and types of fast pyrolysis reactors. Chapter 3 gives an account of materials and methods, which were employed to achieve the four objectives of this work. Chapter 4 presents the results of the various analyses. It consists of four sub-chapters,

namely: (i) biomass characterization, (ii) fast pyrolysis in a fluidized-bed reactor (iii) characterization of the bio-oils for energy and (iv) the development of a scheme for bio-oil production using the selected lignocellulosic biomasses, which basically forms the novelty in this work.

Chapter 5 consists of four sub-chapters and discusses the results of biomass characterization, fast pyrolysis product distribution with temperature and characterization of the bio-oils obtained. The last sub-chapter discusses the scheme developed for bio-oil production using the selected lignocellulosic biomasses based on the results of objectives 1, 2 and 3. Chapter 6 summarizes the conclusions that were drawn throughout the preceding chapters of the thesis and the novelty made as a result of this work. Finally, recommendations are made for the future work in the field of biomass fast pyrolysis.



CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter provides an extensive review on technologies currently available for the conversion of lignocellulosic biomass into biofuels and environmental benefits of biofuel use in transportation and stationary engine applications. It consists of two sub-chapters, namely technologies for lignocellulosic biomass conversion into biofuels and environmental benefits of biofuel use. The sub-chapter on thermochemical processes looks at various technologies for the generation of energy, biomass fast pyrolysis including the types of pyrolyzers currently available and the utilization of the main products of fast pyrolysis. The sub-chapter on biochemical conversion processes covers pre-treatment of lignocellulosic biomass, hydrolysis and fermentation of the sugars produced.

2.1 Conversion of lignocellulosic biomass to biofuels

Biodiesel and bioethanol are currently the major biofuels used for transportation, stationary engines and feedstock for chemical production (OECD/IEA, 2008). Bioethanol is employed either as an octane enhancer, petrol additive or a chemical feedstock, while biodiesel is used as an alternative to conventional fossil diesel oil (FAO, 2008). Major reasons for the development of biodiesel and bioethanol technologies are high fuel prices, perceived risks of fossil fuel dependence, growing concerns about greenhouse gas emissions from the use of fossil fuels, potential contribution to sustainable development and rural revenue generation (OECD/IEA, 2008; FAO, 2008). Moreover, crude fossil fuel deposits are located in just a few regions.

Biofuel production is, however, based on a wide range of biomass, which are globally distributed. It could be undertaken at the source of the feedstock, and thus create significant

employment to improve the livelihoods of the inhabitants. The low sulphur and nitrogen content in biofuels would reduce GHG emissions when used as transportation fuels or in stationary engines (FAO, 2008).

Commercial scale production of bioethanol is based on starch and sugars derived from corn, wheat or sugar cane in several countries including the USA, Brazil and France, and cassava in the Philippines. Ethanol produced from these feedstocks has been found to be more expensive than fossil fuels, which has resulted in high transportation fuel prices (Howarth *et al.*, 2008). However, bio-ethanol can be produced also from lignocellulosic biomass using second generation biofuels technologies (OECD/IEA, 2008).

In recent years, considerable investments have been made to develop and commercialize second-generation biofuel technologies. It is projected that if high prices of fossil fuels persist, cellulosic biofuels production is expected to become a major source of commercial activity (FAO, 2008). According to Hahn-Hagerdal *et al.* (2007), future large-scale use of bioethanol would be based on production from lignocellulosic biomass.

Another potential biofuel that could be produced from lignocellulosic biomass is bio-oil, which is also called pyrolysis oil using fast pyrolysis. Bio-oil has a number of advantages over fossil fuels since it is renewable, non-toxic and in case of any spillage, it does not spread on water. The use of lignocellulosic biomass as an alternative feedstock for biofuel production lies in its widespread availability and abundance.

Technologies available for the conversion of lignocellulosic biomass into biofuels can be categorized into two main groups, that is, biochemical and thermochemical conversion

technologies (Figure 1.4). Generally, the moisture content (MC) of biomass affects the conversion technology that can be employed. Conversion processes for biomass with low MC include gasification, pyrolysis, torrefaction, carbonization and combustion (Figure 2.2) and occur very fast, which yield complex products. Processes for the conversion of biomass with high MC include fermentation and anaerobic digestion. They are slow and result in either a single or specific products (Figure 2.1) (Garcia-Perez, 2010).

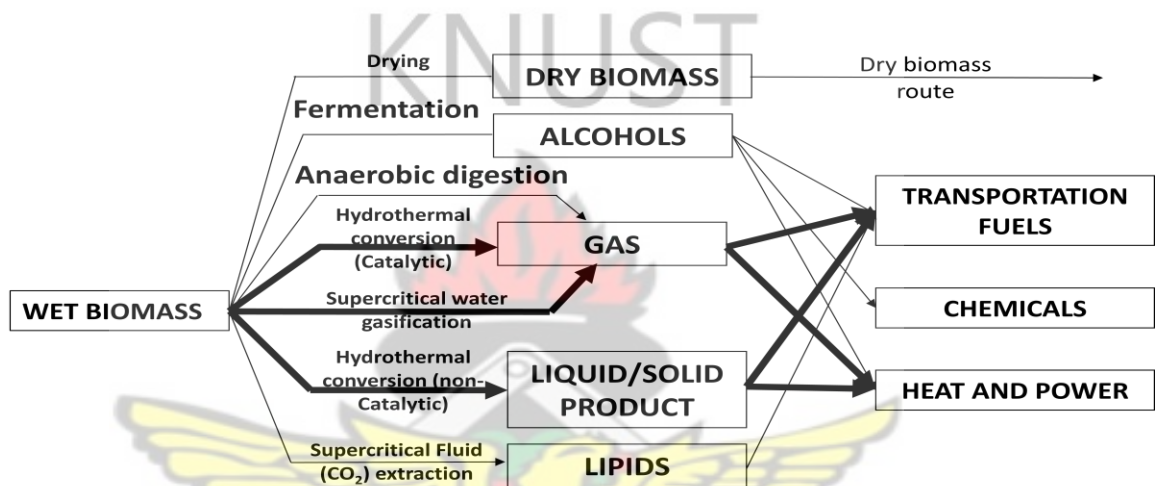


Figure 2.1: Conversion and utilization options for wet biomass. Source: Garcia-Perez (2010).

2.1.1 Thermochemical conversion

Thermochemical conversion refers to the thermal decomposition of the organic components in biomass to yield biofuel. The major processes are pyrolysis, gasification, torrefaction and combustion (McKendry, 2002; Bain, 2004; Tsukahara and Suwayama, 2005; Garcia-Perez, 2010) (Figures 2.2-2.4). These processes are discussed below.

2.1.1.1 Combustion

Combustion, the thermal decomposition of biomass at 1,500 °C into volatile gases such as CO₂, CO, CH₄, C₂H₆ and C₃H₈, and char by means of an oxidizer such as oxygen, releases a significant amount of energy as heat. CH₄, C₂H₆ and C₃H₈ are formed through the decomposition of compounds such as acetic acid in biomass. Combustion technology has been used commercially for a long time but with GHG emission problems and a low efficiency at a small scale. During this process, three major reactions, namely oxidation (reactions 1 and 2) and reduction (reaction 3) occur (Figure 2.5) (Bain, 2004; Garcia-Perez, 2010). These reactions convert chemical energy in biomass into heat, mechanical power or electricity using process equipment such as stoves, furnaces, boilers, steam turbines and turbo-generators.

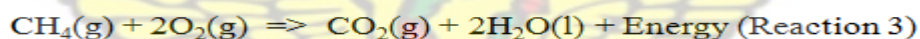
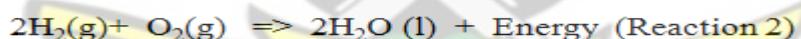
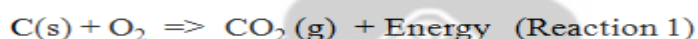


Figure 2.5: Major chemicals reactions that occur during the combustion of biomass

Four distinct stages can be distinguished in the combustion of biomass, namely (i) drying, (ii) de-volatilization, (iii) flaming and (iv) combustion of char. Drying reduces the moisture content of the biomass through evaporation of the water. De-volatilization, which comprises both pyrolysis and reduction occurs at 400–500 °C, and removes all the volatile matter from the biomass. The flaming stage, shown by yellow flames involves combustion of volatile gases by reduction. Char burning is characterised by either blue or glowing flames (Bain, 2004; Garcia-Perez, 2010).

2.1.1.2 Torrefaction and liquefaction

Torrefaction, a process for upgrading lignocellulosic biomass, is carried out at 200–300 °C in the absence of oxygen under low temperature and long residence time. It completely dries the biomass and makes it easy to grind. It also partially removes hemicellulose, hydrates cellulose and increases the calorific value of the biomass (Garcia-Perez, 2010). Torrefied solid fuel is similar to bio-char and can be used as a feedstock in various thermochemical processes for heat and power generation as well as for liquid hydrocarbon production. It has a lower moisture content, higher heating value and increased energy density than normal biomass. It is also more brittle than normal biomass. Since, it is hydrophobic, it does not absorb any moisture in storage and is, therefore, more stable and resistant to fungal attack.

The liquefaction process produces a liquid from biomass at a low temperature (250–330 °C) and a high pressure (5–20 MPa) in the presence of a catalyst usually sodium carbonate and a solvent such as water and an organic solvent. The liquid fuel obtained has a low oxygen content, which makes it compatible with some conventional fuels. It is also stable on storage and requires less upgrading to produce liquid hydrocarbon fuel than bio-oil. However, the process is expensive (Demirbas, 2001).

2.1.1.3 Gasification

Gasification, a process that uses heat, pressure and steam to convert carbonaceous materials into syngas and char, is usually conducted at high temperatures (above 700 °C) with a controlled amount of oxygen (Kumar *et al.*, 2009; Sohi *et al.*, 2009; Garcia-Perez, 2010). Syngas may be used for electricity generation using either gas or steam turbines, and for the manufacture of chemicals and fertilisers. It can also be cleaned and used as a liquid fuel (Sohi *et al.*, 2009). Its ability to mix more readily with chemical catalysts than solid fuels greatly

enhances the possibility for its conversion to transportation fuels using processes such as the Fischer-Tropsch process (McDowellBomani *et al.*, 2009). Gasification has been used on a commercial scale for over 50 years, mainly in refining, fertiliser and chemical industries, and also for electricity generation. Currently, there are over 140 gasification plants in operation globally, which produce chemicals such as methanol, ammonium compounds and urea (Sohi *et al.*, 2009).

2.1.1.4 Pyrolysis

2.1.1.4.1 Types and process of pyrolysis

Pyrolysis, the thermal decomposition of biomass by heating either in the absence of oxygen or in a limited supply of oxygen, is carried out at 400–800 °C. The main products are usually referred to as condensable (tars) and non-condensable volatiles and char. The condensable volatiles are often classified as liquids (bio-oils), while the non-condensable volatiles are gases, mainly CO, CO₂, H₂, ethane and ethene (Aho *et al.*, 2008; Papadikis *et al.*, 2009). The composition of pyrolytic products depends upon the type and composition of the lignocellulosic biomass, operating conditions, particularly reactor temperature and the rate of heat flow. Pyrolysis can be tailored for the high production of one of the pyrolytic products, namely bio-oil, char and non-condensable gas.

Based on the heating rate, pyrolysis can be grouped into three main categories, namely slow pyrolysis (<10 °C/min), intermediate pyrolysis (between 10 °C and 100 °C/min) and fast pyrolysis (>100 °C/min) (Demirbas, 2001). These categories produce different proportions of products (Table 2.1 refers). Slow pyrolysis, also known as conventional or carbonization, occurs under a slow heating rate, and is associated with a high yield of bio-char. Therefore, it has often been employed for charcoal production (Ganesh and Banerjee, 2001; Papadikis *et*

al., 2009). In this process, biomass feedstock is slowly heated to 450–500 °C in an inert atmosphere such as nitrogen gas with vapour residence time of 5–30 min. The residence time is controlled by slowly feeding the nitrogen gas through the reactor. Long residence time causes the vapours to continue reacting, and further allows secondary reactions of vapours to occur, which reduce the liquid yield (Bridgwater, 2007).

Slow pyrolysis produces approximately 35 %wt. of char, 30 %wt. of liquid and 35 %wt. of gas (Table 2.1). Vacuum pyrolysis is a more recent technology than slow pyrolysis. It is carried out under vacuum at 10–20 kPa instead of using nitrogen gas. This reduces the extent of secondary reactions, which results in high bio-oil yields and low gas yields (Bridgwater, 2003). The low pressure makes the biomass evaporate more easily and removes the biomass particles from the reaction zone. Bio-oil obtained from vacuum pyrolysis is composed of lower insoluble compounds and viscosity than that from conventional pyrolysis.

Fast pyrolysis is, however, currently of particular interest as high yields of bio-oils can be produced that are easy to store and transport from small plants to a large processing facility. It occurs between 450 °C and 500 °C and in a few seconds. The main products are bio-oil, non-condensable gas and char (Aho *et al.*, 2008; Papadikis *et al.*, 2009). It is an advanced process with carefully controlled parameters to give high yields of bio-oils. Key characteristics include: (i) a very high heating rate and heat transfer rate, (ii) finely ground biomass feed (with particle size <1-5 mm), (iii) short vapour residence time of typically less than 2s, (iv) rapid cooling of the vapours to give bio-oil and (v) minimum exposure to char and alkali metals since they act as catalysts in cracking the bio-oil.

Since heat and mass transfer as well as chemical reaction kinetics play a major role in fast pyrolysis, it is critical, therefore, to bring the reacting biomass particles to the optimum process temperature as quickly as possible in order to release the volatile vapours. High heating rates are achieved by using biomass with small particles, particularly in fluidized-bed reactors. The alternative is to transfer heat very quickly to the particle surface that contacts the heat source. The volatiles are then cooled quickly to minimise the occurrence of secondary reactions. Bio-oil is obtained in high yields of up to 75 %wt. on a dry-feed basis (Czernik, 2010). During fast pyrolysis, fine particles of char collect in the liquid product and act as a catalyst in cracking the volatiles. Since these reduce the liquid product yields, it is important to rapidly remove them from the reactor. This is achieved by means of either cyclones or hot vapor filtration (Bain, 2004; Czernik, 2010; Czernik *et al.*, 2011).

Table 2.1. Typical product yields from some thermochemical conversion technologies

Process	Liquid (bio-oil)	Solid (bio-char)	Gas (Syngas)
Fast pyrolysis: Moderate temperature (~500 °C); short vapour residence time (<2s)	75 % (25% water)	12%	13%
Intermediate pyrolysis: Low-moderate temperature (450–500 °C), moderate vapour residence time (>2s).	50% (50% water)	25%	25%
Slow pyrolysis: Low-moderate temperature (450–500 °C). long residence time.	30% (70% water)	35%	35%
Gasification: High temperature (>800 °C), long vapour residence time	5% tar (55% water)	10%	85%

Source: OECD/IEA (2008)

A simplified flow chart for fast pyrolysis is represented by Figure 2.6. The process steps include (i) drying the feed to typically less than 10% moisture content in order to minimize

the water content in the bio-oil, (ii) comminution, i.e. grinding the biomass to a small particle size of approximately 2 mm in the case of fluidized bed reactors to ensure a rapid reaction rate, (iii) pyrolysis, (iv) separation of the solid (char), (v) quenching and (vi) collection of the liquid product (bio-oil). The non-condensable gas can be used within the process to provide the heat, while char can be used for soil amendment and climate change mitigation (Bain, 2004).

While any form of biomass can be considered as a feedstock for fast pyrolysis, wood has been the major feedstock used because of high yields of bio-oils. Currently, over 100 different kinds of biomasses have been tested, which include forestry wastes such as barks, wood processing wastes, agricultural crop residues such as straw, husk, shells and sugarcane bagasse, energy crops such as *Mischantus* spp. and sorghum (Mohan *et al.*, 2006).

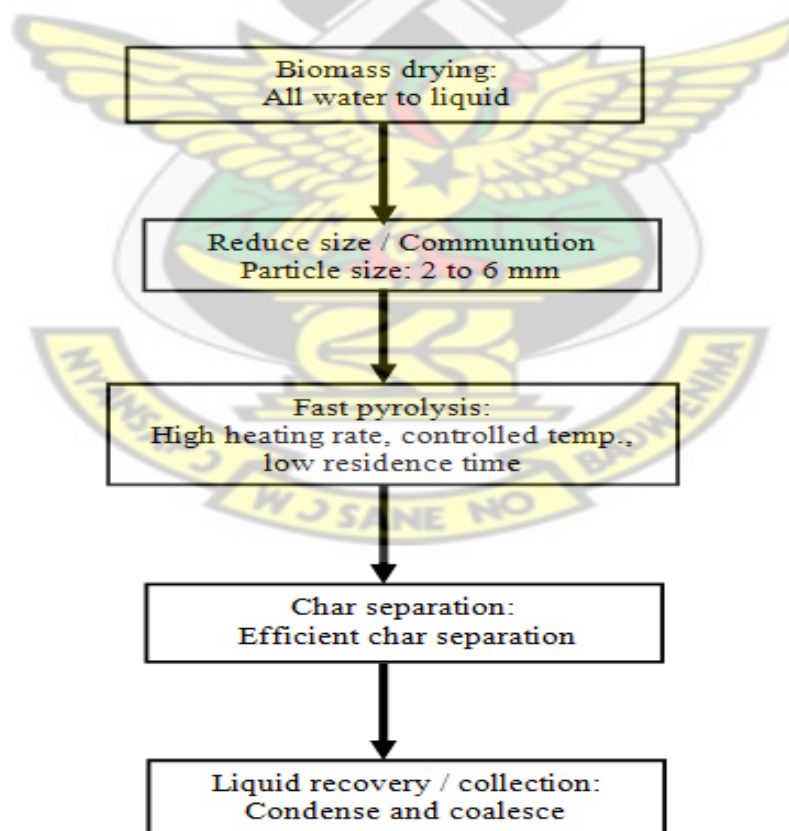


Figure 2.6: Flow chart of biomass fast pyrolysis (Bridgwater, 2007).

Fast heating rates of the biomass allow the solid particles to pass the charring zone at low temperatures more quickly, which reduce the production of char, but improve bio-oil yield. Low heating rates, however, promote slow pyrolysis, which produces mainly bio-char. Liquid yields in fast pyrolysis are optimized at 450-500 °C. At low temperatures, char yield is high, while above 500 °C, the production of non-condensable gas is enhanced. Bio-oil yields could be improved by using biomass with a particle size lower than 2 mm (Bridgwater, 2003). Kumar *et al.* (2009) reported that biomass with a large particle size decreases bio-oil yields but increased char and non-condensable gas yields. Therefore, in order to obtain high yields of biofuels, it is necessary to reduce the biomass to small particle sizes.

The vapour residence time, which is the average time a vapour gas molecule spends in the reactor, is a function of reactor volume and sweep gas flow rate. Antal *et al.* (2003) reported that an increase in residence time caused a rapid decrease in bio-oil yield due to secondary reactions of the primary products, which promote cracking and polymerization. Char particles, which are entrained in the vapour during fast pyrolysis act as a cracking catalyst for secondary reactions. Therefore, they should be separated from the system as rapidly as possible using cyclones. Filtration of the liquid product could be carried out by the application of a ceramic cloth or candle filters (Czernik, 2010).

Efficient liquid collection poses a challenge in fast pyrolysis due to the complex nature of bio-oils (Bridgwater, 2003). Simple heat exchange causes preferential deposition of lignin-derived components, which could result in liquid fractionation and blockages. While quenching of the liquid product in an immiscible hydrocarbon solvent is widely carried out, electrostatic precipitation is the preferred method at small-scale and pilot plants. The rate of cooling affects the efficiency of liquid collection. Slow cooling rate yields a large amount of

compounds derived from lignin, which increases the viscosity of the bio-oil. Rapid quenching of the process is, therefore, required to prevent secondary reactions from occurring (Czernik, 2010).

2.1.1.4.2 Types of fast pyrolysis reactors

Considerable attention has recently been focused on the development of fast pyrolysis. A key technical barrier is efficient heat transfer to the reactor. This has resulted in the development of various reactor designs, which include fluidized bed, fixed bed, ablative, rotating cone and circulating fluidized bed (Table 2.2) (Bridgwater, 2007). Two of the most commonly applied designs are fluidized-bed and entrained flow reactors (Czernik, 2010).

Table 2.2: Different configurations of reactors developed for fast pyrolysis

Type of pyrolyzer	Capacity and Location
Fluidized bed	400 kg/h at Dynamotive; 20 kg/h at RTI; Many research units: Aston University; Hamburg University, Leeds University, NREL
Circulating fluid bed	1000 kg/h at Red Arrow (Ensyn); 350 kg/h at Fortum, Finland
Rotating cone	200 kg/h at BTG (the Netherlands); Twente University
Vacuum	3500 kg at Pyrovac; Laval University/Pyrovac
Auger	200 kg/h at Renewable Oil International (ROI), Mississippi State, USA
Ablative	>100 kg/h Aston University, UK
Entrained bed	200 kg/h at Egemin, Belgium
Transported bed	Up to 1000 kg/h at Ensyn Inc Canada

Source: Bain (2004) and Mohan *et al.* (2006)

Bubbling fluidised beds, also referred to as fluidized-bed (FB) reactors, use solids such as sand as a heat carrier. They require biomass with a small particle size, which is 2–3 mm in order to achieve a rapid heating rate (Figure 2.7). The residence time of solid and vapours is controlled by the fluidising gas flow rate. Bio-oil yields of 60–70 %wt. and 40–60 %wt. have been obtained from hardwoods such as aspen and poplar and agricultural crop residues

respectively at a vapour residence time of 0.5 seconds. The removal of char is by means of either ejection or entrainment in cyclones (Czernik, 2010). The major advantage of fluidized bed reactors is that they are easy to scale up. Moreover, the technology is well understood, and has been employed for several years. Good temperature controls could be maintained, while high bio-oil yields, which range from 70–75 %wt. could be obtained (Figure 2.7).

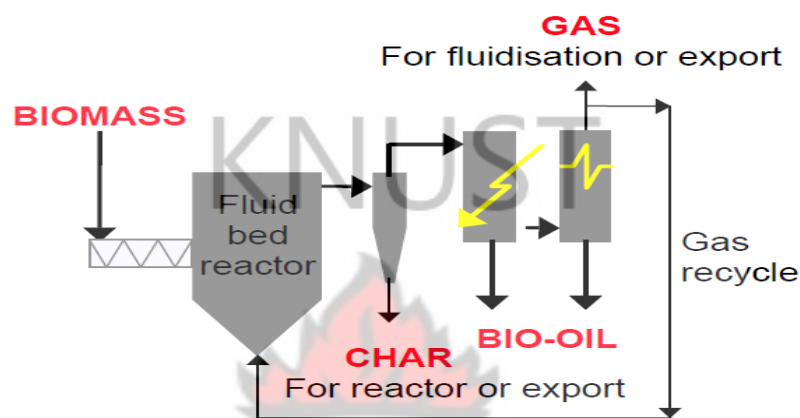


Figure 2.7: Fluidized-bed pyrolysis. Source: Czernik (2010).

Circulating fluid-bed (CFB), vacuum moving-bed, rotating cone and ablative pyrolyzers have also been employed for bio-oil production, with yields of 35–50 %wt. (Table 2.2) (Czernik, 2010). CFB reactors are similar to fluidized-bed types, but use biomass with a large particle-size (Figure 2.8). Heat supply is usually from the re-circulation of the heated sand. High char yields are obtained as a result of long contact of the char with the vapour. The advantages of CFB reactors are that the technology is well-understood, and are suitable for large-scale production of bio-oil. Moreover, they are able to maintain a good temperature control. However, they have a complex design, which makes them expensive.

A bubbling fluidized-bed reactor was used in this work because the temperature for the pyrolytic process could be controlled in order to achieve high bio-oil yields while the residence time of solid and vapours could also be controlled by the fluidising gas flow rate.

Moreover, the technology is well understood, easy to scale up and has been used for many years. The use of biomass with small particle size (~ 1.0 mm) enabled a rapid heating rate to be achieved.

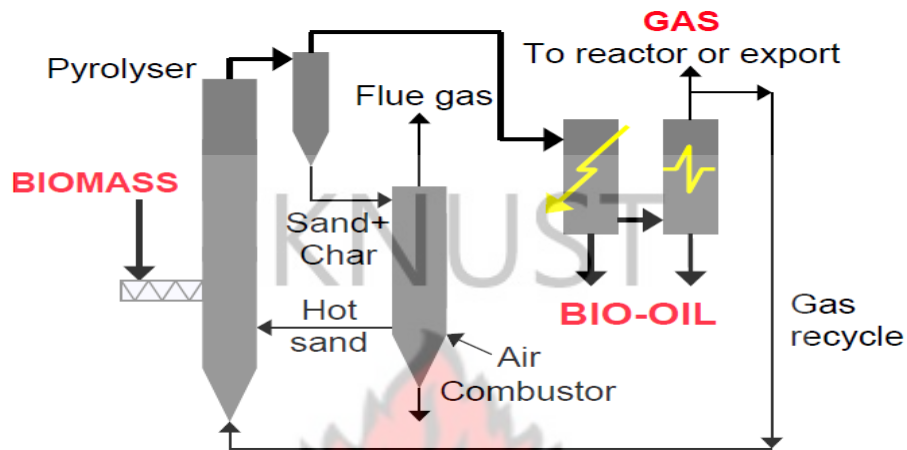


Figure 2.8: Circulating fluid-bed pyrolysis. Source: Czernik, 2010.

2.1.1.4.3 Properties of bio-oils

Bio-oils are dark-brown mobile, combustible and water miscible liquids but immiscible with hydrocarbons. They are acidic and have a pH of approximately 2.5. They have a pungent odour and density of about 1.2 kg/l, and age with their viscosities increasing. They have a high water content (15–30 %wt.), which results from the original moisture in the biomass and dehydration reactions (Czernik and Bridgwater, 2004). The high water content lowers both the heating value and flame temperature, delays ignition, decreases combustion rate and reduces the viscosity of bio-oil compared to diesel fuels.

Bio-oils are composed of several oxygenated organic compounds such as acetone, acetaldehyde, organic acids mostly acetic and formic acid. They are corrosive and less stable than conventional petroleum fuels due to the high content of volatiles and oxygenated compounds. Their complex nature gives them some unusual characteristics such as the

tendency to undergo various reactions such as polymerization, esterification, phase separation and increase in viscosity during storage (Czernik and Brigdwater, 2004; Ingram *et al.*, 2008).

The main differences between bio-oils and conventional hydrocarbon fuels such as lower HHV (16–22 MJ/kg) is due mainly to the high oxygen content, which is approximately 35–40 %wt (Garcia-Perez *et al.*, 2002; Czernik and Brigdwater, 2004; Mohan *et al.*, 2006; Mullen *et al.*, 2010) (Table 2.3). Their low viscosity, which ranges from 35–1000 cP at 40 °C enhances their flow characteristics since it improves the ability to pump and atomize them during combustion. Increases in the viscosity of bio-oils during storage and at high temperature could be reduced by the addition of 10–20 %wt. of either alcohol such as methanol and ethanol or polar solvents such as acetone (Diebold, 2002; Czernik and Brigdwater, 2004). Ash content in bio-oils, which exceeds 0.1 %wt. could cause corrosion in turbines and boilers during combustion (Diebold, 2002; Garcia-Perez *et al.*, 2002; Qi *et al.*, 2007).

Table 2.3: Comparison of physical and chemical properties of bio-oil with heavy fuel oil

Chemical and physical properties	Bio-oil	Heavy fuel oil
Moisture content, %wt.	15–30	0.1
pH	2.5	-
Density (kg/m ³)	1200	940
<i>Elemental composition, % wt.</i>		
C	54–58	85
H	5.5–7.0	11
N	0–0.2	0.3
O (By difference)	35–40	0.1
Ash (wt.%)	0–0.2	0.1
HHV, MJ/kg	16–19	40
Viscosity (at 50 °C), cP	40–100	180

Source: Czernik and Brigdwater (2004) and Mohan *et al.* (2006).

2.1.1.4.4 Applications of bio-oils

Crude bio-oils could be used in boilers and turbines for heat and electricity generation, and as feedstock for the production of chemicals such as resins, fertilisers and fine chemicals such as levoglucosan. Alternatively, they can be up-graded using either physical or chemical methods and used as transportation fuels (Figure 2.9). Physical methods include filtration, emulsification with hydrocarbons and solvent addition, whereas chemical methods include reaction with alcohols and catalytic de-oxygenation (Mohan *et al.*, 2006; Czernik, 2010) (Appendix 2). Bio-oils are currently not used as transportation fuels due to their high cost, which ranges from 10–100 % more than fossil fuel. Furthermore, their availability is limited to supplies for testing only. Several other factors, which include lack of quality standards also inhibit the wide usage of bio-oils (Czernik, 2010).

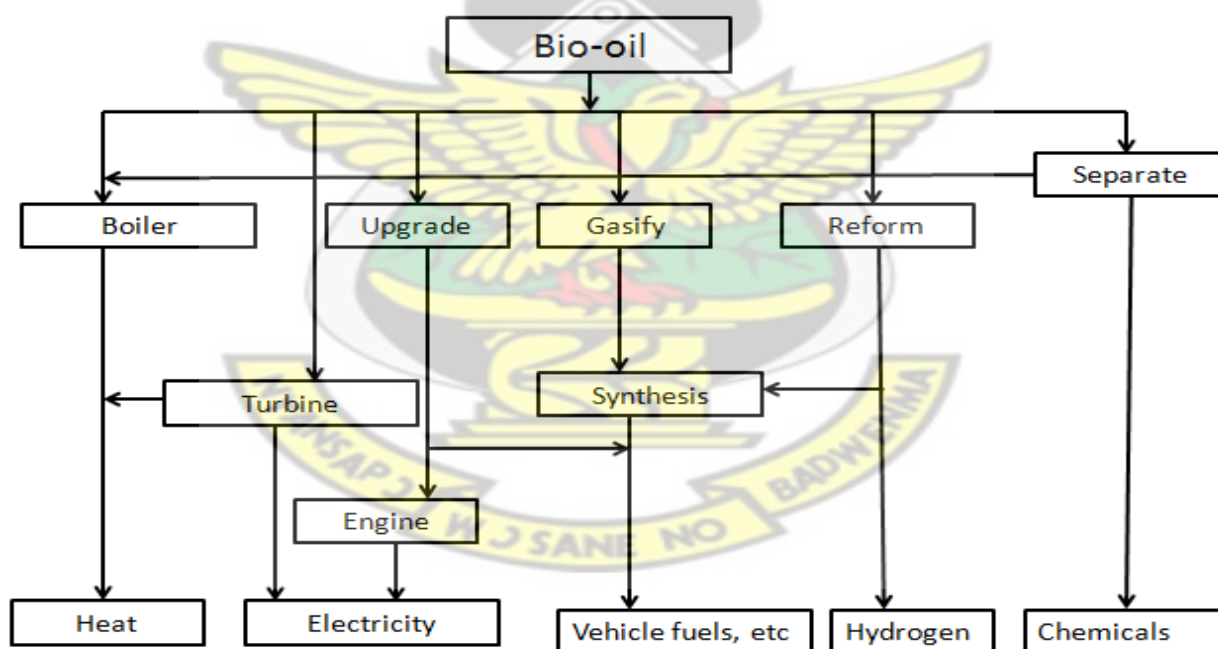


Figure 2.9: Potential applications of bio-oil produced using biomass fast pyrolysis.
Source: Bain (2004).

2.1.1.4.5 Co-products

Char, a co-product of fast pyrolysis, has the potential to make major contribution towards mitigating climate change and to enhance agricultural productivity. It is a fine-grained, highly

porous charcoal. Its characteristics include high organic matter, high nutrient and water-holding capacity and soil microbial activity. Mullen *et al.* (2010) reported HHVs for char produced from corn cobs as 21.0 MJ kg⁻¹ and nitrogen levels to be 0.5–1.5 %wt, while sulphur levels were 0.02–0.15 %wt., indicating that it could be used as a renewable energy source with low NO₂ and SO₂ emissions (Laird, 2008).

The harvesting of agricultural crops from farms can have negative environmental and soil quality impacts including decreases in soil carbon content and depletion of plant nutrients and water as well as increases in soil erosion (Mullen *et al.*, 2010). However, the application of char in soil enhances its fertility. Char application yields growth increases of 10 %, while some studies have found growth by up to 100 % or more. It could also contribute to climate change mitigation through carbon sequestration due to its stable structure (Glaser *et al.*, 2002; Mullen *et al.*, 2010).

2.1.1.4.6 Mechanism for fast pyrolysis of lignocellulosic biomass

Fast pyrolysis of lignocellulosic biomass results in the degradation of the chemical bonds of its major components, that is, cellulose, hemicellulose, lignin and extractives, resulting in the formation of complex products. Thermal degradation of cellulose and hemicellulose occurs at relatively low temperatures, which range from 200 to 400 °C (Figure 2.10) (Shen and Gu, 2009). The pathways and subsequent product distribution are influenced by many factors including biomass composition and characteristics, temperature, heating rate, pressure and reactor configuration.

Fast pyrolysis of cellulose consists of a series of primary and secondary reactions. Many models have been postulated to explain the reaction kinetics of cellulose primary degradation

(Koufopoulos *et al.*, 1991; Varhegyi *et al.*, 1994; Srivastava *et al.* 1996; Lee *et al.*, 2005; Yang *et al.*, 2007; Fahmi *et al.*, 2007; Hosoya *et al.*, 2008; Prakash and Karunanithi, 2008). During pyrolysis, cellulose initially undergoes a series of primary thermal reactions at 180–320 °C, resulting in the formation of various intermediate compounds such as active cellulose. This is followed by de-polymerization and fragmentation, which result in the formation of volatile compounds and char (Figures 2.10–2.13) (Varhegyi *et al.* 1994; Shen and Gu, 2009; Garcia-Perez *et al.*, 2010). De-polymerization of cellulose occurs above 300 °C through a breakdown of glycosidic linkages to yield compounds such as levoglucosan and furan. Fragmentation, however, yields compounds such as hydroxyacetaldehyde (HAA), acetol, alcohols and esters.

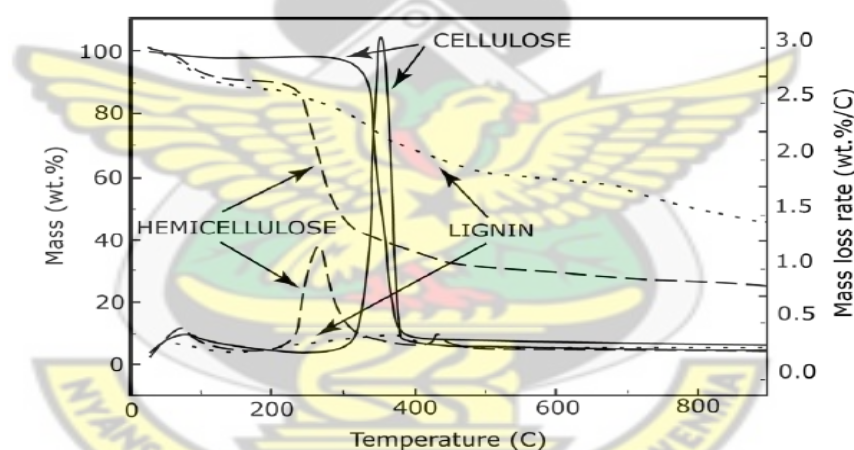


Figure 2.10: Thermogravimetric analysis of the pyrolysis of lignocellulosic biomass components. Source: Sohi *et al.* (2009).

Factors that influence the primary pyrolysis of cellulose include: (i) its crystallinity, (ii) the degree of polymerization, (iii) the presence of additives and (iv) interactions between cellulose and lignin. Above 300 °C, cellulose becomes more reactive and yields mainly bio-oil (Garcia-Perez, 2010) (Figure 2.12). Significant interactions also occur between cellulose

and lignin at 800 °C. However, comparatively weak interactions exist between cellulose and hemicellulose (Garcia-Perez, 2010) (Figure 2.12).

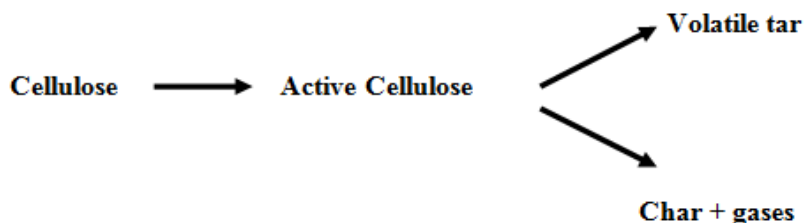


Figure 2.11 : Briodo-Shafizadeh reaction model for the pyrolysis of cellulose. Source: Garcia-Perez (2010).

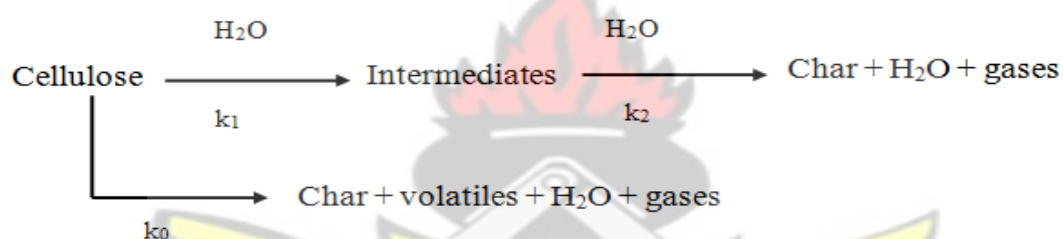


Figure 2.12. Kinetics of biomass pyrolysis proposed by Koufopoulos *et al.* (1991)

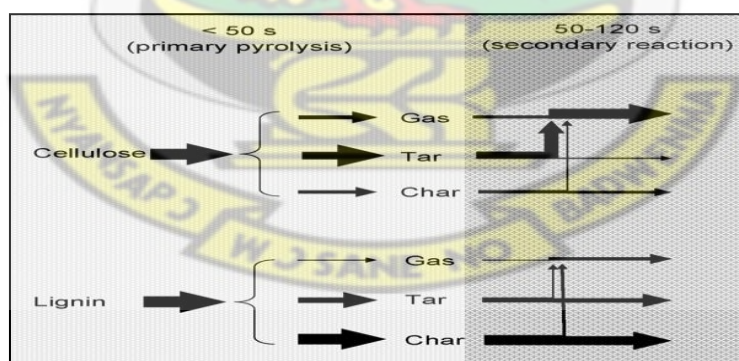


Figure 2.13: Pyrolysis of biomass. Source: Hosoya *et al.* (2008).

Hemicellulose is thermally less stable than cellulose due to lack of crystallinity, but its reaction mechanism during pyrolysis is similar to that of cellulose. Fast pyrolysis of glucomannan in hemicellulose results in products similar to those of cellulose, while products

obtained from the pyrolysis of xylan differ from those of cellulose (Zhu and Lu, 2010). Shen and Gu (2009) proposed detailed possible routes for the formation of major products from xylan chains as well as O-acetylxylan and 4-O-methylglucuronic acid units. The decomposition of both cellulose and hemicellulose is promoted by small amounts of ash or alkaline cations, which act as a catalyst, resulting in high yields of hydroxyacetaldehyde (HAA). Since HAA is also formed from the secondary cracking of the anhydrosugar products, it is the most abundant organic compound in bio-oils.

Primary pyrolysis of lignin begins around 200 °C with softening of the biomass and results in higher yields of char, but lower liquid yields than that of cellulose and hemicellulose. The major product is char, most of which is retained during the secondary reaction. The liquid products from the pyrolysis of lignin are classified into three major groups, namely, (i) large-molecular weight compounds, (ii) small molecular weight phenolic compounds and (iii) compounds such as methanol and acetic acid (Shen and Gu, 2009; Garcia-Perez *et al.*, 2010). According to Garcia-Perez (2007), lignin inhibits the de-polymerization of levoglucosan formed from cellulose. It, however, promotes the formation of low-molecular weight compounds such as methanol from cellulose. Cellulose also reduces char formation from lignin during the secondary reaction but enhances the yields of products such as guaiacol and 4-methyl-guaiacol.

2.1.2. Biochemical conversion of lignocellulosic biomass into cellulosic ethanol

The basic processes involved in biochemical conversion of lignocellulosic biomass into cellulosic ethanol are (i) pre-treatment (mechanical, chemical and biological) or delignification, (ii) hydrolysis/saccharification or de-polymerization of cellulose and hemicellulose into sugars (e.g. hexose or pentose sugars), (iii) fermentation of mixed hexose

and pentose sugars to produce ethanol, (iv) separation and (v) distillation (Aden *et al.*, 2002; Ballesteros *et al.*, 2004; Sanchez, 2009) (Figure 2.14 refers).

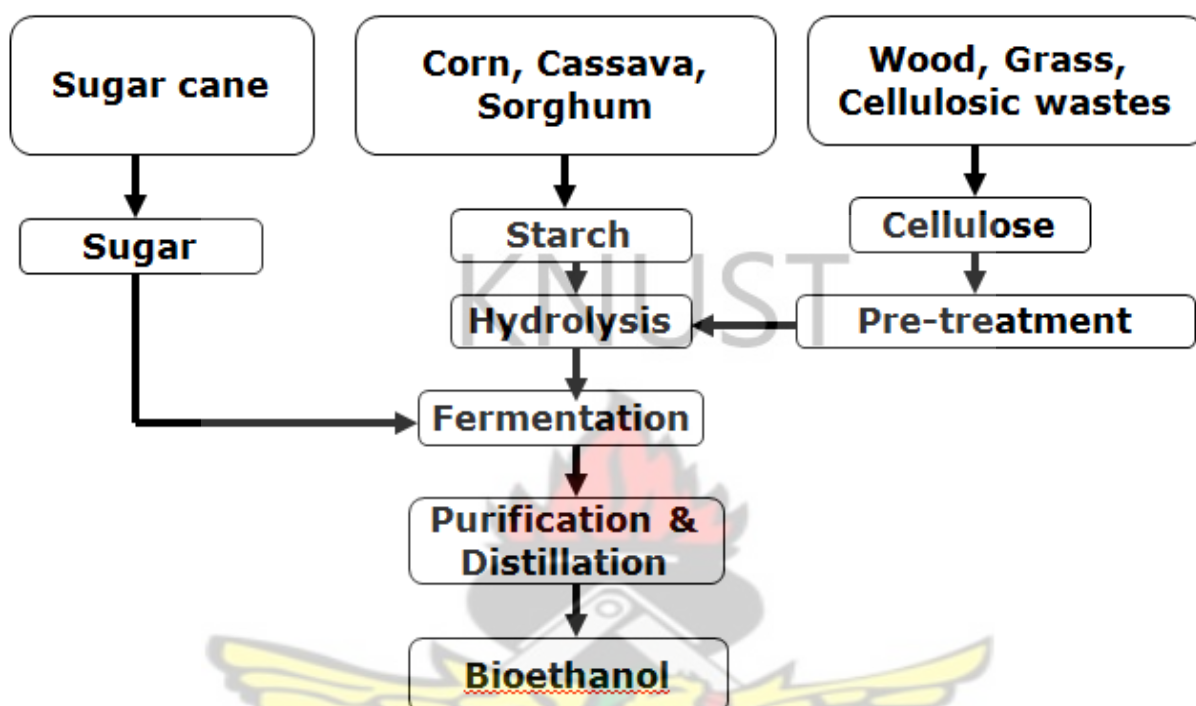


Figure 2.14: Bioethanol production processes. Source: Duku (2007).

2.1.2.1. Pre-treatment of lignocellulosic biomass

The complex chemical composition of lignocellulosic biomass makes it difficult to undergo biochemical conversion. Of the three components, lignin is the most recalcitrant to degradation. To overcome the recalcitrance shown by lignocellulosic biomass, pre-treatment of the feedstock is required. Pre-treatment changes the physical and chemical structure of the lignocellulosic biomass. It also improves the rate of hydrolysis of biomass by increasing its surface area. This makes cellulose and hemicellulose more accessible to hydrolysis for conversion into biofuels (Wyman *et al.*, 2007; Centi, 2009; Shi *et al.*, 2009).

Pre-treatment is one of the most expensive steps in the conversion of lignocellulosic biomass to cellulosic ethanol. It constituted about 27% and 22% of the total production cost of ethanol in 2005 and 2009 respectively. Pre-treatment improves enzyme access and effectiveness by: (i) altering the structure of lignin, (ii) removing acetyl groups from hemicellulose, (iii) reducing the degree of polymerization in cellulose and (iv) expanding the structure of cellulose so as to increase pore volume and internal surface area (Centi, 2009). During pre-treatment, lignin dissolves while cellulose and hemicellulose remain as solid.

Various chemical, physical and biological pre-treatment techniques have been employed for the conversion of lignocellulosic biomass into biofuels (Reynolds, 2000). Centi (2009) categorized biomass pre-treatment techniques into (i) chemical treatment, which includes dilute acid, alkali, ammonia fibre explosion (AFEX) and organo-solvents, (ii) hydrothermal treatment, which includes steam explosion, acid steam and new techniques such as wet oxidation, ultrasounds and ionic liquids. Kumar *et al.* (2009) reported that most pre-treatment methods result in high sugar yields above 90% of theoretical yield for wood, grasses and corn stover.

Centi (2009) and Sierra *et al.* (2009) considered an efficient pre-treatment process to exhibit certain characteristics. It should (i) preserve the cellulose and hemicellulose fractions, (ii) limit the formation of degradation products and (iii) require minimal energy usage. It should also be effective on several types of lignocellulosic biomass, and reduce both capital and operating costs of biofuel production. Centi (2009) also considered factors that influence the digestibility of lignocellulosic biomass to include (i) lignin content, (ii) hemicellulose content, (iii) acetyl content, (ii) crystallinity of cellulose, (iii) the degree of polymerization of

cellulose, (iv) the surface area and (v) pore volume. Hemicellulose and lignin are covalently bonded and can be disintegrated using either acid hydrolysis or enzymatic processes.

Wyman *et al.* (2007) evaluated different pre-treatment techniques including dilute acid hydrolysis, water, steam explosion, AFEX, controlled pH, hot water and lime using corn stover as the feedstock. Their results showed that all the different pre-treatment methods were effective in making cellulose accessible to enzymes. However, AFEX showed slightly higher yields than the other techniques. Dilute acid pre-treatment using 1% H_2SO_4 at 4–90 °C is an effective method of increasing the efficiency of lignocellulosic biomass digestion.

Other acids such as nitric (HNO_3), hydrochloric (HCl) and phosphoric (H_3PO_4) have also been employed. Temperature and acid concentrations employed for pretreatment affect enzymatic saccharification. Dilute acid pre-treatment is conducted at high temperatures and produces fermentable sugars and by-products such as furfural, hydroxymethyl furfural (HMF) and levulinic acid. Levulinic acid is a potential inhibitor during the pre-treatment process and therefore can lower ethanol yields and productivity (Centi, 2009).

Alkaline processes used for pre-treatment dissolve lignin and hemicellulose, which leave cellulose as a solid. Pre-treatment using wet oxidation, however, is conducted at a high temperature of 175 °C and a high pressure of 30 bars. It results in partial oxidation of lignin and the destruction of cellulose-lignin linkage (Centi, 2009). In the organic solvent (organosol) process, solvents such as acetone, ethanol, methanol and acetic acid are used to dissolve the lignin. It is conducted between 169 and 200 °C for 15–60 min. The major disadvantage of the organosol process is its complexity and expensive nature due to the high cost of the organic solvents and high pressure requirements (Centi, 2009).

Biological pre-treatment of lignocellulosic biomass includes the use of fungi such as the *Basidiomycetes*, which naturally degrade lignin through the secretion of enzymes including oxidases due to the presence of efficient enzymatic systems. The enzymes facilitate access to cellulose and hemicellulose during hydrolysis. Although similar enzymes are employed for the hydrolysis of cellulose and hemicellulose, a larger amount is required for the latter because of its heterogeneous nature (Sanchez, 2009).

Fungal pre-treatment of lignocellulosic biomass is slow and depends on the species employed. *P. chrysosporium*, for example, degrades cellulose, hemicellulose and lignin simultaneously, whereas *Ceriporiopsis subvermispora* degrades lignin initially before attacking either cellulose or hemicellulose. It is inexpensive and is carried out under mild conditions with little or no sugar degradation products. Its disadvantages, however, are that it requires a large amount of feedstock for biofuel production (Garcia-Pérez *et al.*, 2002; Sanchez, 2009; Martínez *et al.*, 2011).

2.1.2.2 Hydrolysis/Saccharification

Currently available methods for the hydrolysis of lignocellulosic biomass include (i) dilute acid hydrolysis, (ii) concentrated acid hydrolysis, (iii) enzymatic hydrolysis and (iv) hot compressed water. The hydrolysis of cellulose and hemicellulose produces sugars, which include hexoses such as glucose and pentoses such as xylose and arabinose. Compared with cellulose and hemicellulose, lignin cannot be easily hydrolyzed due to its complex structure (Sun and Cheng, 2001; Garcia-Perez *et al.*, 2002).

Acid hydrolysis of lignocellulosic biomass can be categorized into two major groups, i.e. dilute and concentrated hydrolyses. Dilute acid is used to hydrolyze hemicellulose and

cellulose hydrolyses, and results in lower yields of sugars than concentrated H_2SO_4 hydrolysis. It is conducted at high temperatures, and has lower yields than concentrated acid hydrolysis. Concentrated H_2SO_4 hydrolysis is, therefore, commonly used since it is less expensive and has high yields. It has, however, environmental implications since the acid has to be recovered after use (Centi, 2009). Edirisah-Aidoo (1975) reported that hydrolysis using HCl gave a better yield of sugar than with H_2SO_4 under the same conditions. Sugar yields were also found to depend on the cellulose content of the sawdust. An analysis of the sugars in the wood hydrolysate by paper chromatography showed the presence of various sugars such as glucose, xylose and arabinose.

Enzymatic hydrolysis uses enzymes produced by bacteria and fungi, which include cellulases such as glucanase, hemicellulases such as xylanase and lignases such as lignin peroxidase to hydrolyze lignocellulosic biomass. Due to enzyme specificity, it yields less degradation products than acid hydrolysis (Centi, 2009). A well established bioethanol production process using lignocellulosic biomass as the feedstock involves: (i) the use of separate hydrolysis/saccharification and fermentation steps (SHF) and (ii) simultaneous saccharification and fermentation (SSF), which combines the hydrolysis and fermentation steps in a single reactor (Hari *et al.*, 2001; Centi, 2009). The advantages of using the SHF process include the production of a few residues in the reactor and ease of removal of the inhibitors (Dien *et al.*, 2006).

2.1.2.3 Fermentation of sugars

Lignocellulosic biomass decomposes into a mixture of hexose and pentose sugars upon pre-treatment (Badger, 2002). After hydrolysis, the resulting sugar molecules must be fermented into alcohol. Current ethanol production uses mainly strains of micro-organisms such as

baker's yeast (*Saccharomyces cerevisiae*), which are highly adapted to industrial processes of converting feedstocks such as corn and sugarcane into ethanol. *S. cerevisiae* ferments glucose rapidly and efficiently to ethanol due to its high ethanol-production capacity and inhibiting properties. However, it is not capable of fermenting xylose, which is the major component of hemicellulose and other components such as arabinose and rhamnose (Badger, 2002; Hahn-Hägerdal *et al.*, 2007). Yeasts such as *Candida shehatae*, which can ferment xylose to ethanol, however, have a low ethanol tolerance and slow rates of fermentation (Jeffries and Jin, 2004; Liu *et al.*, 2008). While xylose can be converted to xylulose using the enzyme xylose isomerase and *S. cerevisiae* to ferment it to ethanol, the process is, however, not cost-effective (Centi, 2009).

Liu *et al.* (2008) considered some major challenges for sustainable and cost-effective conversion of lignocellulosic biomass to ethanol to include the heterogeneous sugar utilization and capital and production costs. Other challenges are to ferment all the hexoses and pentoses at high rates and yields and lack of techniques for the removal of toxic hydroxylates as well as high capital and production costs. These could, however, be overcome through the development of effective pre-treatment techniques and highly efficient enzymatic hydrolysis processes (Jarvis, 2005). Simultaneous saccharification and fermentation (SSF) process ferments all the sugars released from lignocellulosic biomass during hydrolysis. SSF reduces the inhibition of glucose during the hydrolysis of lignocellulosic biomass by removing it (Jarvis, 2005; Dien *et al.*, 2006; Liu *et al.*, 2008).

2.2. Environmental benefits of biofuel use

Emission of GHG from fossil fuels contributes to global warming. One of the major reasons for the use of biofuels is to reduce GHG emissions (Weeks, 2006). In contrast to fossil fuels such as gasoline and diesel oil, biofuels burn cleaner and with a greater efficiency since they emit less CO₂, NO₂ and SO₂ into the atmosphere. Thus, they contribute little to the GHG effect. The emission of CO₂ from biofuels has been reported to be 85% lower than that from fossil fuels (Puppán, 2002; Demain *et al.*, 2005; Weeks, 2006; Abbasi and Abbassi, 2010). According to the U.S. Department of Energy (2010), cellulosic ethanol reduces GHG emissions by 90 % when compared to fossil gasoline.

The production and use of bio-oil as an alternative energy source to conventional fossil fuels for transportation and stationary engine applications is currently being promoted globally due to increasing levels of global GHG emissions as a result of rapid socio-economic and industrial development. Bio-oil production technology has a number of environmental advantages, i.e. low sulphur oxide (SO₂) and nitrogen oxide emission. As a renewable fuel, bio-oil is carbon-neutral in terms of global warming potential. Steele *et al.* (2012) reported GHG emissions reduction by the substitution of bio-oils for fossil fuels. They estimated a reduction of CO₂ emissions by 0.075 kg/CO₂ per MJ of biofuel combustion or a 70% reduction over gasoline or diesel oil based on the relative carbon emissions of the two fuels when bio-oil is substituted for diesel oil.

CHAPTER THREE

3.0 MATERIALS AND METHODS

This chapter gives an account of materials and methods, which were employed to achieve the four objectives of this work. Sub-chapter 1 looks at the characterization of selected major lignocellulosic biomasses using proximate, ultimate and compositional analyses, and the determination of HHVs. Sub-chapter 2 looks at the investigation of the effect of temperature on pyrolytic product distribution during fast pyrolysis. Sub-chapter 3 looks at the characterization of the bio-oils for energy purposes using physical characteristics, elemental analysis and the determination of HHVs. Conclusions are drawn from the results of these analyses, which form the basis for the development of a scheme for bio-oil production from the selected lignocellulosic biomasses using fast pyrolysis.

3.1 Characterization of major lignocellulosic biomass

This sub-chapter looks at materials and methodologies employed for the characterization of the selected biomass samples. The methodology consisted of proximate, ultimate, chemical composition and x-ray fluorescence (XRF) analyses and determination of thermal values.

3.1.1 Materials and methodology

Seven lignocellulosic biomasses, which were collected from various parts of Ghana were used for this study. Biomass characterization consisted of proximate and ultimate analyses and chemical composition according to ASTM 5152-02 and ASTM D 5291-92 and determination of heating values. All the biomass samples were air-dried and ground below 1.0 mm. Sand and fines were removed by washing.

3.1.1.1 Materials

Biomass is the major energy source in Ghana contributing about 64% of Ghana's primary energy supply (Duku *et al.*, 2011).

An assessment of the availability of biomass in the Western, Central, Ashanti, Brong-Ahafo and Eastern regions of Ghana, covering agricultural crop residues, forest and wood processing residues, urban wastes and animal wastes showed that the available biomass resources in the Western region were 451,578 tonnes/year. There were 276,400 tonnes/year in the Central region, 474,228 tonnes/year in the Eastern region, 407,589 tonnes/year in the Ashanti region and 641,240 tonnes/year in the Brong-Ahafo region.

Agricultural residues included those generated from sugarcane, maize, rice, cocoa, oil palm and coconut. Maize residues constitute the largest available biomass resource (47%), followed by cassava residues (17%) and cocoa residues (16%). The least available residues are sugarcane bagasse and rubber residues. The large availability of unutilized biomass residues in the Western region and some nearby regions, gives Ghana high potential for thermal energy generation (Appendix 4 refers) (Hagan and Duku, 2012).

The lignocellulosic biomass samples used in this study were agricultural crop residues (rice straw and its husk, corn stalk and its cob, cocoa pod husk and sugar cane bagasse), which were obtained from various commercial farms of Ghana, namely the Western, Central, Eastern and Greater Accra regions (Figure 3.1 refers) and wood residue (e.g. *Triplochiton scleroxylon* (wawa) sawdust obtained from Accra in the Greater Accra region. Rice husks were obtained fresh from a rice mill at the Dawhenya Rice Project as processing residue,

while the rice straw was obtained from the Aveyieme Rice Farms in the Eastern region as harvesting residue. The rice straw was collected six weeks after harvesting. Fresh cocoa pod husks were obtained from a commercial farm at Enchi in the Western region as harvesting residue. Sugar cane bagasse and corn stalk were obtained fresh from Gomoa Adawukwaa Co-operative farm, near Winneba in the Central region. Wawa sawdust was obtained from the Timber market in Accra in the Greater Accra region.

The lignocellulosic biomass samples were air-dried and then separated from physical impurities such as sand and fine fractions. They were then ground through a 1-mm screen in a Wiley mill. Each prepared sample was closely stored in zipped plastic containers.

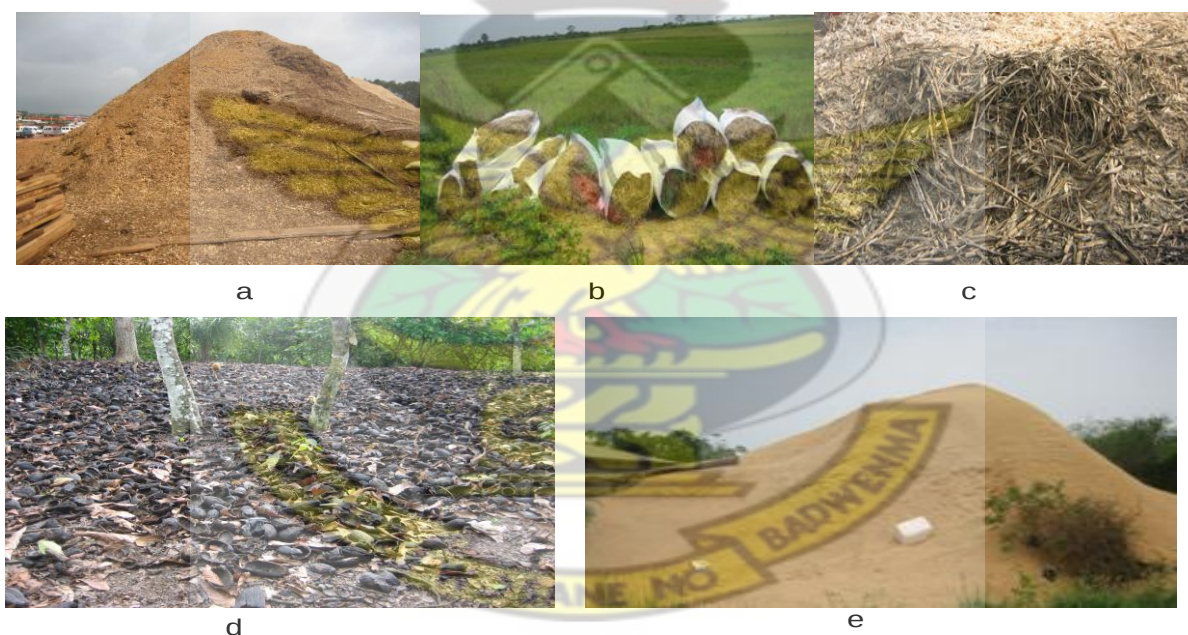


Figure 3.1: Some of the types of lignocellulosic biomass used for the study (a) Sawdust dumped at Ofankor Timber Market in Accra; (b) Rice straw bagged at Aveyieme in the Eastern region); (c) Sugarcane bagasse heaped at a Sugarcane Processing Mill at Gomoa Adawukwaa in the Central region; (d) Cocoa pod husks spread on a Cocoa Farm at Omanpe-Enchi in the Western region; (e) Rice husk heaped at a Rice Processing Mill at Dawhenya Rice Project in the Eastern region.

3.1.1.2 Proximate and Ultimate Analyses and Determination of Heating Values

Proximate and ultimate analyses of the feedstocks were conducted according to ASTM 5152–02 and ASTM D 5291–92 respectively.

The proximate analysis of the matter is performed to know the nitrogen (protein), oil (fat), mineral, ash content, etc. to have an idea about the energy contained in that matter. The proximate analysis gives moisture content (MC), volatile matter content, consisting of gases and vapours driven off during pyrolysis (when heated to 950 °C), the fixed carbon content, the ash content (the inorganic residue remaining after combustion of the sample) and the higher heating value (HHV) based on complete combustion of the sample to carbon dioxide and liquid water.

Experiments were conducted to determine the moisture content, fixed carbon content, ash content and volatile matter content of air-dried biomass samples ground to particle size below 1.0 mm. MC and fixed carbon content were determined by heating 10 g each of the biomass samples at 105 °C in an oven for 3 h (ASTM Standard, 1998).

The moisture content (MC) of biomass is defined as a quantity of water in material as a percentage of the material either in its wet or dry basis.

MC on wet basis (MC_{wb})

$$MC_{wb} = W(H_2O) / (W_{(dry\ biomass)} + W(H_2O)) \dots\dots\dots \text{Equation 2}$$

on dry basis (MC_{db})

$$MC_{wb} = W_{(H_2O)} / (W_{(dry\ biomass)}) \dots\dots\dots \text{Equation 3}$$

where

$W_{(H_2O)}$ is the weight of inherent water and

$W_{dry\ biomass}$ is the weight of dry biomass.

Volatile matter is any matter in a substance that has the tendency to vaporize, given the right condition. It is the portion of the biomass sample that vaporized when they were heated in the absence of oxygen. A substance's volatility is measured by its vapour pressure, the point at which a substance turns from solid to a gas or vice-versa. Volatile matter test typically involves heating a specific amount of the matter to a specific temperature for a specific amount of time. The test is performed in a vacuum. The inorganic mineral content in the biomass that remains in oxidized form after complete combustion is called ash.

Ash content was obtained by heating 10 g each of the biomass samples at 650 °C in air to a constant mass in a muffle furnace. The ash composition was analyzed using an X-ray Fluorescence (XRF) Spectrometer (Spectro X-Lab 2000) SPECTRO Analytical Instruments Inc. X-LAB 2000) (Figure 3.3 refers) for its mineral content using 10 g of the ash of each biomass sample.

Fixed carbon was the remains after the biomass samples had been completely vapourized. Its content was estimated by determining the difference between 100 %wt. and the sum of moisture content, volatile matter content and ash content.

Ultimate analysis gives the composition of the biomass in weight percent (wt.%) of carbon, hydrogen and oxygen (the major components) as well as sulphur and nitrogen, if any. The

ultimate analysis of the biomass samples was performed at MEDAC Laboratories Ltd. (Surrey, UK) using an Elemental Analyzer (Thermo FlashEA 1112) according to ASTM–D 5291–92 (Figure 3.3 refers).

Oxygen content was estimated by the difference between 100 % and the sum of carbon, hydrogen, nitrogen and sulphur contents. The technique used for the determination of CHNOS is based on the quantitative “dynamic flash combustion” method.

The biomass samples were put in a tin capsule and placed in a vertical quartz tube. They were then combusted at 900 °C in a furnace heated using helium stream with pure oxygen. The resulting mixture of gases was passed over a catalyst layer (copper) to remove any excess oxygen and to reduce the nitrogen oxides to elemental nitrogen. It was then sent to the chromatographic column where the individual components were separated and identified with an automatic Elemental analyser - EAGER300 (Figure 3.3 refers).

The HHVs of the biomass samples were determined with a PAAR bomb calorimeter using ASTM-D 4809 method. 20 g of each biomass sample was combusted in the calorimeter using pure oxygen. HHV is defined as the quantity of heat generated by complete combustion in a bomb calorimeter of a unit mass of biomass sample in an oxygen atmosphere, assuming that both the water contained in the sample and that generated from the combined hydrogen remains in liquid form.



Figure 3.2. X-ray Fluorescence Spectrometer (SPECTRO Analytical Instruments Inc. X-LAB 2000) (1: Access to the spectrometer; 2: Synoptic panel; 3: Sample container)



Figure 3.3: Thermo FlashEA 1112 Elemental Analyzer at MEDAC Laboratories Ltd. (Surrey, UK) used for elemental analysis (1: Access to the furnace; 2: Synoptic Panel; 3: Access to the Thermostatic Chamber).

3.1.1.3 Determination of Chemical Composition

The chemical composition of the biomass samples was analyzed at Aston University, Birmingham, UK. This included an analysis of cellulose, hemicellulose and lignin content using the detergent system sequential analysis by difference according to ASTM 170 220 (Van Soest, 1967).

Sulphuric acid (72%) was used to dissolve cellulose and isolate the crude lignin and ash. A neutral detergent solution is used to dissolve the easily digested pectins. The values of uronic

anhydride, galactan and arabinan, decline more or less steadily as the cell in the biomass matures. These compounds constitute the pectic complex.

Total cell wall was defined as the neutral detergent fibre (NDF) value. Lignin, acid detergent fibre (ADF), NDF and total ash were determined. A 16 h Soxhlet extraction with acetone was conducted to remove unwanted compounds such as extractives from the biomass samples. NDF was the organic matter that did not dissolve after 1 h reflux in the neutral detergent solution, which consisted of sodium laurylsulphate amylase at 98 °C. It was filtered, washed with hot water and dried with acetone. It was composed of hemicellulose, cellulose, lignin and ash.

Acid detergent fibre (ADF), the fibrous component represents the least digestible fibre portion of the forage or other roughage. ADF was the organic matter that did not dissolve after 1 h under reflux in an acid detergent solution. It was made up of cellulose, lignin and ash.

Lignin is the organic substance binding the cells, fibres and vessels, which constitute wood and the lignified elements of plants, as in straw. It is an amorphous polymer related to cellulose that provides rigidity and together with cellulose forms woody cells of plants and cementing materials. Acid detergent lignin (ADL), the lignin in the residue was determined following extraction in the acid detergent. It was the organic matter that did not dissolve after 3 h of extraction with sulphuric acid (72%).

The hemicellulose content was obtained by subtracting the value of ADF from that of NDF. Cellulose content was obtained by the difference between ADF and lignin (ADL). This is summarized by the equations below.

$$H = NDF - ADF \dots\dots\dots \text{Equation 4}$$

$$C = NDF - ADL \dots\dots\dots \text{Equation 5}$$

$$L = ADL - A \dots\dots\dots \text{Equation 6}$$

where

H = hemicelluloses; C = Cellulose; L = Lignin; A = Ash; NDF = Neutral Detergent Fibre; ADF = Acid Detergent Fibre; ADL = Acid Detergent Lignin.

3.2 Investigate the effect of temperature on fast pyrolysis product distribution

This sub-chapter looks at the second objective, which was to investigate the effect of temperature on product distribution of fast pyrolysis. It gives a brief description of the fluidized-bed reactor that was used. Bubbling fluidized-bed pyrolyzer was used in this work because the technology is well understood. It is also easy to control the temperature within the reactor. Moreover the pyrolyzer has been used for several years and high bio-oil yields can be obtained. It is also easy to scale-up the pilot plant.

3.2.1 Materials and Methodology

3.2.1.1 Materials

The materials used for the determination of the effect of temperature on pyrolytic product distribution were six agricultural crop residues and wood processing waste. These were characterised to determine their suitability as feedstocks for pyrolysis in sub-chapter 3.1.

3.2.1.2 Methodology

Fast pyrolysis was carried out in a pilot bubbling fluidized-bed of quartz sand at temperatures in the 400–700 °C range using the selected biomass samples described in sub-chapter 3.1. The apparatus consisted of a 45-mm-diameter fluidized-bed reactor with a height of 390 mm, carbon filters placed in series for gas clean-ups, and a series of two condensing canisters (vapour condensers) that were cooled by a dry ice/water bath and a gas storage (Figures 3.4 and 3.5 refer). Nitrogen gas was used as the inert gas for the process. The reactor was heated by a carborundum heater with a power of 8 kW. Temperature and pressure measurements were respectively carried out using thermocouples and a pressure transducer. Heating rate was maintained at 200 °C/min. Temperature readings in the reactor were taken at three points (T_1 , T_2 and T_3) and the averages computed.

5 g each of the biomass samples was determined and placed in the feeding system before it was connected to the reactor. When the temperature of the reactor reached 400 °C, the feeding system was connected to the reactor through valve 2. The flushing flow using nitrogen gas was initially allowed to run for about 1 min to remove all the oxygen from the system in order to ensure an inert atmosphere (nitrogen gas) in the reactor tube. Then, the valve 1 was closed while second valve (valve 2) was opened to enable the biomass sample move up to the heated reactor by the feeding flow.

As each of the biomass samples was pyrolyzed inside the reactor, streams composed of volatiles and bio-char residues passed through the carbon filters where the bio-char residues were separated. The purified volatile streams then flowed through the condensers where they condensed into bio-oils. The first condenser, which contained a mixture of water and ice was used to cool the hot volatile streams initially to 50 °C. It then passed through the second

condenser where the bio-oils were condensed by the mixture of dry ice and acetone at -10° C. The condensed volatiles were finally collected in a spiral circular tube. The liquid yield was calculated as the difference between the weight of the pyrolyzed liquid and the weight of the feedstock multiplied by 100 percent.

$$r_1 = w_1 \times 100 / w_2 \text{Equation 7}$$

where r_1 is the liquid yield and

w_1 is the weight of the liquid product and w_2 is the weight of the fed feedstock.

After each run, the bio-char obtained as a co-product was separated from the bed and the carbon filters to determine its yield by dis-assembling the carbon filters. The amount of char produced was determined by calculating the weight difference of the carbon filters. The non-condensable gas, together with the carrier gas (nitrogen) was collected by gas sample bags and analysed by gas chromatography (GC) Agilent MicroGC 3001A. Its yield was determined by the difference between the biomass sample and the sum of bio-oil and bio-char.

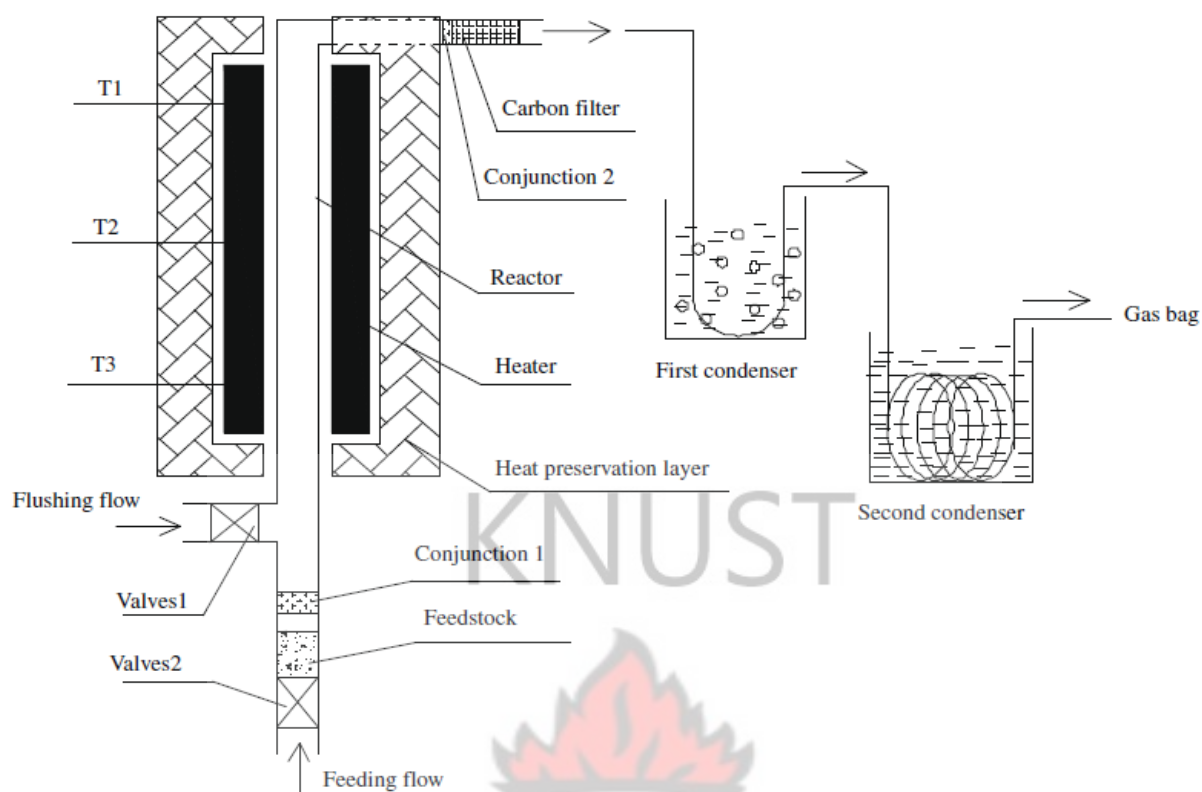


Figure 3.4: Schematic representation of the fluidized-bed fast pyrolysis reactor set-up for the biomass pyrolysis and volatiles condensation system.

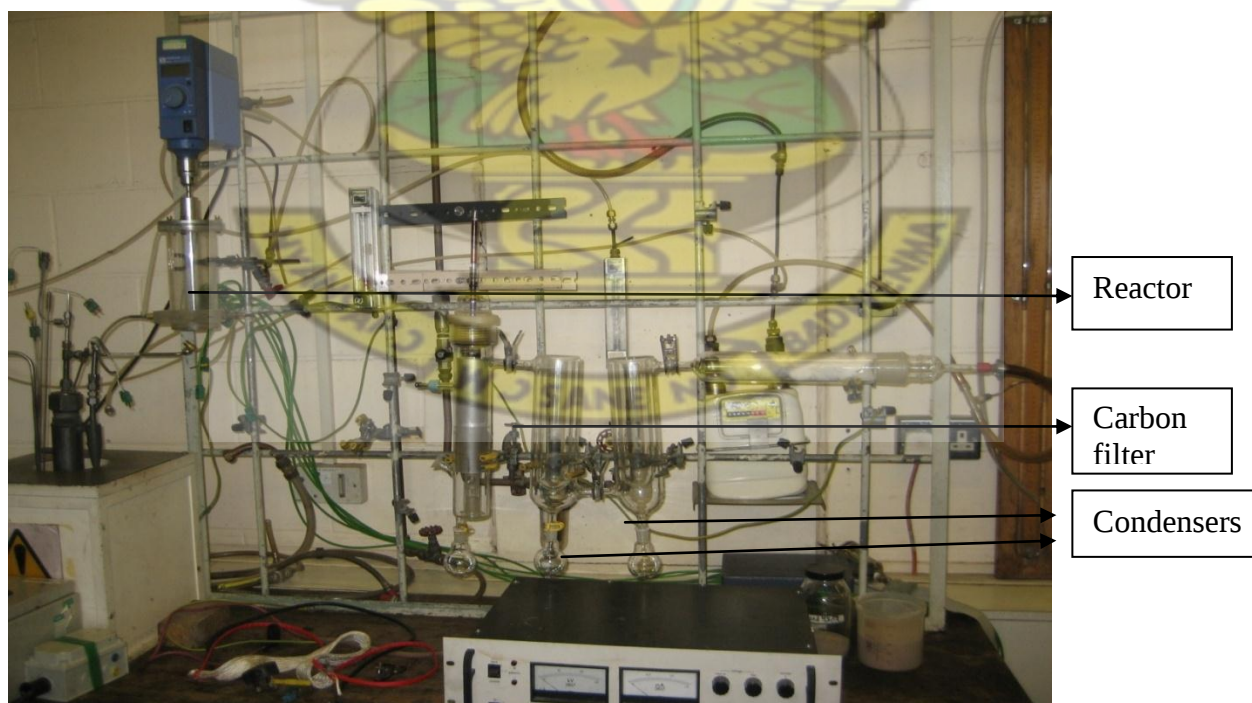


Figure 3.5: The fast pyrolysis pilot plant at Aston University in the UK used to conduct the study.

3.3 Characterize the bio-oils for energy using different analytical techniques

This sub-chapter looks at the physical and ultimate characterisation of the bio-oils obtained in sub-chapter 3.2 from fast pyrolysis of the selected lignocellulosic biomasses. Physical characterisation was carried out for fuel physical properties. A two-way analysis of variance (ANOVA) was used to test the significance of the differences in the results.

3.3.1 Materials and Methodology

The physical characteristics of the bio-oils included water content, density, heating value, pH and ash content. Elemental analysis of the total C, H, N and O of the bio-oils obtained as maximum yields was also carried out.

3.3.1.1 Analysis of the physical properties of the bio-oils

The water content of the bio-oils was determined by Karl Fisher titration using ASTM D-1744. 5 ml of each bio-oil sample was measured and titrated with a Karl Fischer reagent. The end point of the solution was shown by an intense colour change from yellow to brown. Information on the water content can be useful in predicting the quality and performance characteristics of the bio-oils.

The viscosity was measured with a Cannon–Fenske up–flow viscometer. A sample (20 ml) of each of the bio-oils was placed in the viscometer and the flow was observed at 22 °C. Density is a basic physical property that can be used together with other properties to characterize the bio-oils. The determination of the density of bio-oils is important for the conversion of measured volumes at standard temperatures. Density was measured using a 10 ml picnometer according to ASTM D-369. 10 ml of the bio-oil samples were measured and weighed at 25

°C. The density was then calculated as the weight of the bio-oils per unit volume. The procedure was repeated.

Ash content was determined by burning 5 ml sample of the bio-oils in air in a Muffle furnace. In order to evaluate the corrosive property of the bio-oils, the pH was measured using a digital pH-meter (Model–HI 8424). The electrode was dipped directly into 30 ml of the bio-oil sample.

The heat of combustion is a measure of energy available from the bio-oils. The heating value of the bio-oils is important when considering the energy content and heating efficiency of fuels for energy production. Two different approaches can be used in the determination of this value, i.e. using a bomb calorimeter and by simple calculation. A Parr bomb calorimeter was used to measure the heating values of the bio-oils according to ASTM D-4809. The test procedure consisted of placing a weighed sample of the bio-oils, approximately 0.3–0.5g in the cup, installing a cotton firing thread and charging the bomb calorimeter with oxygen to approximately 30 bars.

3.3.1.2 Ultimate analysis of the bio-oils

The purpose of this test was to determine the elemental composition in the bio-oils. This was determined using an Elemental Analyzer (Thermo FlashEA 1112), according to the ASTM-D 5291 method. 5 ml of each bio-oil sample were put in a tin capsule and placed in a vertical quartz tube. They were then combusted at 900 °C in a furnace heated using helium stream with pure oxygen. The resulting mixture of combustion gases was passed over a catalyst layer (copper) and sent to the chromatographic column where the individual components were

separated and identified with an automatic EAGER30. Oxygen content was estimated by the difference between 100% and the sum of the other contents.

3.3.1.3 Statistical analysis of the results

A two-way analysis of variance (ANOVA) was used to test the significance of the differences in proximate, ultimate and chemical composition and heating values of the biomass samples and their effect on the pyrolytic product yields. Standard deviation, mean and range for the HHVs of the biomass samples were calculated for the bio-oils. The relationship between bio-oil yields from the biomass samples and temperature as well as that of the ultimate analyses of the biomass samples and bio-oils obtained were also analysed using correlation coefficient (r) and coefficient of determination (r^2).

3.4 Develop a scheme for bio-oil production from the selected lignocellulosic biomass using fast pyrolysis

This sub-chapter looks at the development of a scheme for bio-oil production from the selected lignocellulosic biomasses based on the results and conclusions drawn from sub-chapters 3.1–3.3.

3.4.1 Materials and methodology

A scheme for bio-oil production using fast pyrolysis has been proposed based on the results obtained from objectives 1, 2 and 3. It is also based on the large availability of lignocellulosic biomasses in the country. Logging and wood processing residues in Ghana were respectively estimated to be 72,000 m³ and 256,000 m³, while agricultural crop residues amounted to 48,216 tonnes in 2008 (Duku *et al.*, 201; Hagan and Duku, 2012).

The proposed scheme is composed of (i) biomass collection and preparation, including drying and grinding, (ii) biomass fast pyrolysis at 500 °C, high heating rate (100 °C/min) and short residence time of 1–2 s, (iii) bio-char separation from pyrolysis products, using cyclones or carbon filters, (iv) use of bio-char as an energy-source for the pyrolytic process, (v) application of bio-char in agricultural soils as soil amendment to increase soil fertility and hence improve crop productivity or for climate change abatement, (vi) crude bio-oil collection and storage, (vii) crude bio-oil use in stationary engines such as turbines, (viii) upgrading of crude oil using processes such as de-oxygenation and (ix) application of up-graded bio-oil as fuels for transportation.

The proposed scheme provides a cost-effective approach for maximum utilization of the selected lignocellulosic biomasses using fast pyrolysis for bio-oil production. This is to serve as alternative source for fossil fuels for transportation and other applications. It also considers the utilization of the co-products, namely bio-char and non-condensable gas, as well as process parameters, particularly temperature, which could result in maximum bio-oil yields from the selected biomasses at different temperatures.

CHAPTER FOUR

4.0 RESULTS

This chapter looks at the results of the analyses carried out to achieve the four objectives. It consists of four sub-chapters, namely: (i) biomass characterization, (ii) fast pyrolysis in a fluidized-bed reactor to determine the effect of temperature on product distribution and (iii) characterization of the bio-oils obtained as maximum yields for energy in terms of physical and ultimate characteristics, and potential applications of the products of fast pyrolysis. Finally, it presents and discusses a scheme for bio-oil production using the selected lignocellulosic biomasses. Conclusions are then drawn from the results of the analyses.

4.1 Characterization of the biomass samples

This sub-chapter looks at results of proximate, ultimate, ash composition by XRF and chemical composition analyses, and the determination of heating values to determine their suitability as feedstocks for the production of bio-oils.

4.1.1 Proximate analysis

The results of proximate, ultimate and chemical composition analyses of the biomass samples (rice straw and husk, corn straw and cobs, sugarcane bagasse, cocoa pod husks and wawa sawdust (*Triplochiton scleroxylon*)) are shown in Tables 4.1–4.3 and Figures 4.1–4.2. The higher heating values (HHVs) are also shown in Table 4.4 and Figure 4.3.

Table 4.1. Proximate analysis of the biomass samples

Biomass	Weight percentage (%wt. dry basis)			
	Moisture	Volatile	Ash	Fixed carbon ^a
Corn stalk	9.15	75.02	6.13	9.70
Corn cobs	8.72	80.72	2.96	7.60
Rice straw	7.23	45.68	45.76	1.33
Rice husk	8.59	58.22	24.71	8.48
Cocoa pod husk	10.29	68.47	10.81	10.43
Sugarcane bagasse	8.59	79.45	3.91	8.12
Wawa sawdust	6.03	80.48	1.48	12.01

^a. Calculated by difference of 100 %wt – sum of moisture, volatile and ash content.

Moisture contents of the biomass samples ranged from 6.03 %wt. for the wawa sawdust to 10.29 %wt. for the cocoa pod husk. The corn stalk had a relatively higher moisture content of 9.15 %wt. than the corn cobs (8.72 %wt.), while it was lower (7.23 %wt.) in the rice straw than in the rice husk (8.59 %wt.).

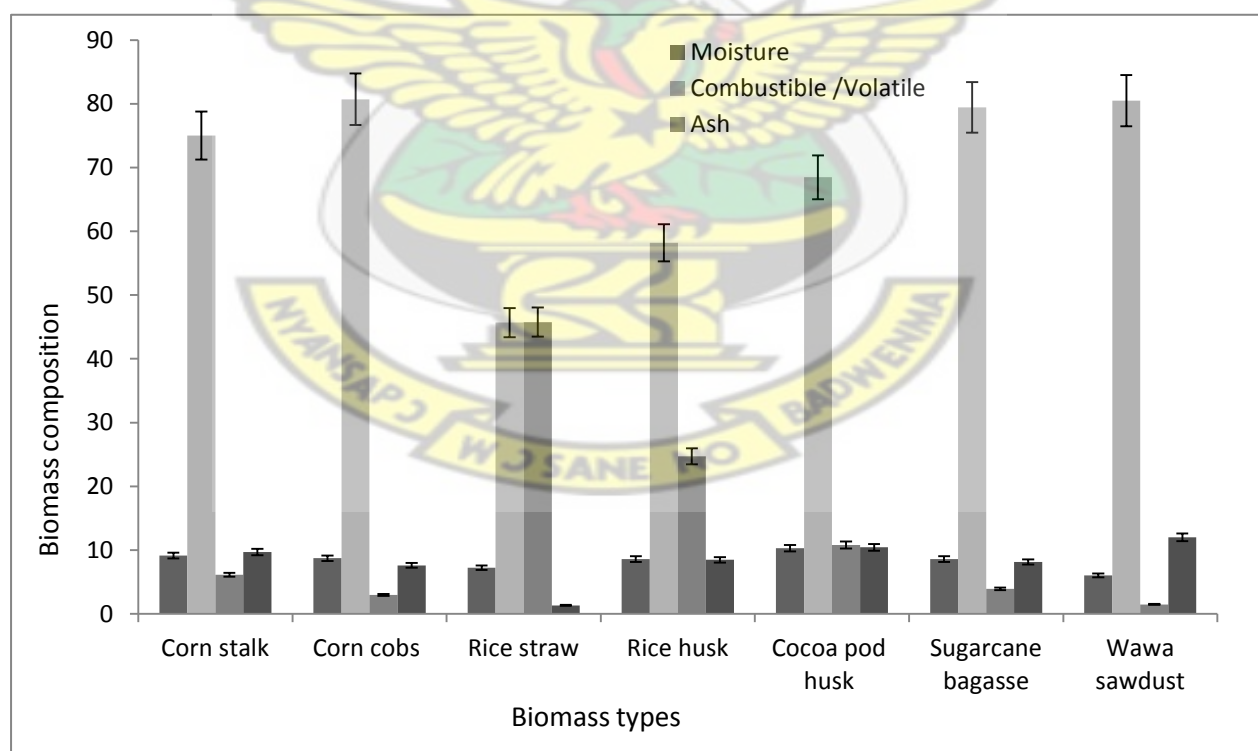


Figure 4.1: Proximate analysis of the biomass samples showing volatile matter, moisture, fixed carbon and ash contents.

The volatile matter was the portion of the biomass samples that turned into vapour when they were heated without oxygen. It was high in all the biomass samples, and ranged from 45.68 %wt. for the rice straw to 80.72 %wt. for the corn cobs. It was lower in the corn stalk (75.02 %wt.) than in the corn cobs (80.72 %wt.). The rice straw had a lower volatile matter (45.68 %wt.) than the rice husk (58.22 %wt.). The cocoa pod husk, sugarcane bagasse and wawa sawdust had volatile matter of 68.47 %wt., 79.45 %wt. and 80.48 %wt. respectively. Ash was the remains after complete combustion of the biomass samples. It was high in the rice husk (24.71 %wt.), rice straw (45.76 %wt.) and cocoa pod husk (10.81 %wt.). However, it was low in the wawa sawdust (1.48 %wt.), corn cobs (2.96 %wt.) and sugarcane bagasse (3.91 %wt.). High volatile matter in biomass results in high tar or bio-oil formation. Fixed carbon was the remains after complete vaporization of the biomass samples. It was high in all the biomass samples and ranged from 7.60 %wt. for corn cobs to 12.01 %wt. for wawa saw dust except for the rice straw, which had a very low value of 1.33 %wt. The wawa sawdust had the highest fixed carbon, followed by the cocoa pod husk with a value of 10.43 %wt.

4.1.2. Ultimate analysis

Ultimate analysis gave carbon content ranging from 26.73–44.37 %wt. for rice straw and wawa sawdust, hydrogen content (4.05–6.02 %wt) for rice straw and corn cob and oxygen content (47.30–66.57 %wt) for cocoa pod husk and rice straw. Sulphur and nitrogen levels were below 1.0 %wt. for all the biomass samples (Table 4.2 and Figure 4.2). The cocoa pod husk showed the highest nitrogen level of 2.23 %wt. while the rice straw and husk had low values of 1.02 %wt. and 0.31 %wt. respectively.

Table 4.2. Ultimate analysis of the biomass samples

Biomass	Percentage by weight (%wt.)					
	Carbon	Hydrogen	Oxygen^a	Nitrogen	Sulphur	Chlorine
Corn stalk	42.65	5.57	49.16	1.49	<0.10	1.05
Corn cob	43.32	6.02	49.37	0.93	<0.10	0.27
Rice straw	26.73	4.05	66.57	1.02	0.56	1.09
Rice husk	34.90	5.15	59.00	0.31	0.64	<0.01
Cocoa pod husk	43.87	5.82	47.30	2.23	0.57	0.23
Sugarcane bagasse	44.31	5.73	49.11	0.63	<0.10	0.13
Wawa sawdust	44.37	5.77	49.23	0.34	0.10	0.19

^a Calculated by the difference between 100 %wt. and the sum of the carbon, hydrogen, nitrogen, chlorine and sulphur contents.

Hydrogen content in the biomass samples ranged from 4.05 %wt. for the rice straw to 6.02 %wt. for corn cobs. Carbon contents were high except in the rice straw (26.73 %wt.) and husk (34.90 %wt.). It was 44.31 %wt. for the sugarcane bagasse, 43.90 %wt. for the cocoa pod husk, 43.32 %wt. for the corn cobs and 42.65 %wt. for the corn stalk. The oxygen content was high in all the biomass samples and ranged from 47.30 %wt. for the cocoa pod husk to 66.57 %wt. for the rice straw. Chlorine levels in the rice straw and corn stalk respectively were 1.09 and 1.05 %wt. It was below 0.1 %wt. in the corn cobs, sawdust, cocoa pod husk and sugarcane bagasse.

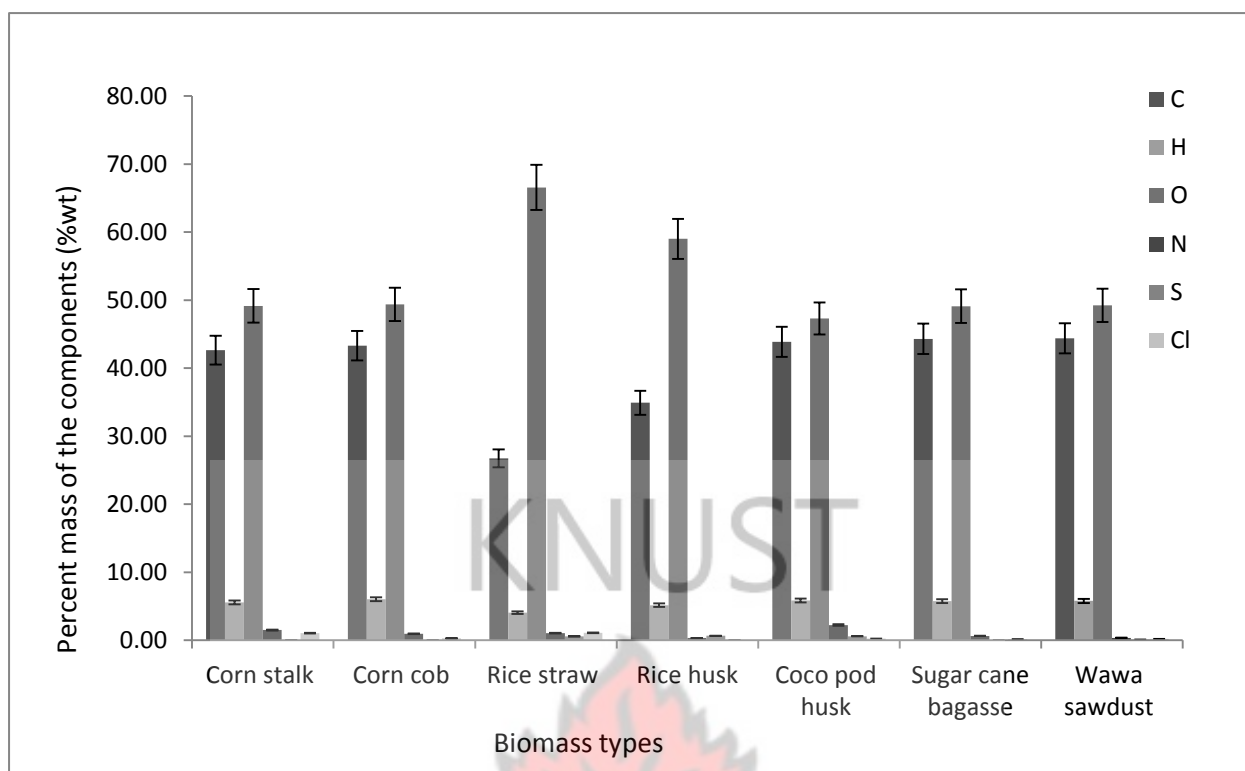


Figure 4.2: Ultimate analysis of the biomass samples.

4.1.3. Minerals content in the ash

The XRF analysis of the ash (Table 4.3 refers) showed high silica content in both the rice straw (16.3 %wt.) and the rice husks (22.38 %wt.) and high potassium oxide content (5.03 %wt.) in the cocoa pod husks. Potassium oxide was the most abundant inorganic fraction in the cocoa pod husk (5.03 %wt.). It was 2.10 and 1.00 %wt. in rice straw and corn stalk respectively. Silica was the most abundant oxide in both the rice straw and husks, and measured 16.3 and 22.38 %wt. respectively. It was low in the rest of the biomass samples including the corn stalk and sugarcane bagasse. The high silica content in the rice husk and straw may have resulted in their high ash content (Tables 4.1 and 4.3 refer). Phosphorus levels were below 0.50 %wt. in all the biomass samples except in the corn stalk (1.6 %wt.).

Table 4.3 Composition of the ash in the biomass samples determined by XRF (%wt.)

Biomass type	(%wt. of ash, dry basis)											
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	S	Cl	K ₂ O	CaO	TiO	MnO	Fe ₂ O ₃
Corn stalk	0.87	0.58	0.18	1.60	0.25	0.01	0.92	1.20	0.26	-	0.01	0.06
Rice straw	0.54	0.45	0.24	16.30	0.19	0.03	0.62	2.10	0.37	0.02	0.20	0.08
Rice husk	0.27	0.52	0.42	22.38	0.32	0.03	0.08	0.39	0.09	0.02	0.03	0.12
Wawa saw dust	0.12	0.12	0.10	0.17	0.06	0.00	0.01	0.22	0.30	-	-	0.01
Cocoa-pod husk	0.28	0.70	0.14	0.25	0.37	0.00	0.04	5.03	0.59	-	0.01	0.01
Sugarcane bagasse	0.66	0.29	0.16	1.64	0.23	0.00	0.40	0.74	0.10	-	0.01	0.06

4.1.4. Higher heating values

The higher heating values (HHVs) of the biomass samples are presented in Table 4.4 and Figure 4.3. They ranged from 12.26 MJkg⁻¹ for the rice straw to 18.61 MJkg⁻¹ for the wawa sawdust and are the averages of three readings obtained.

Table 4.4. Higher heating values of the biomass samples

Biomass type	Heating value analysis (MJ kg ⁻¹) (mega joules)
Corn stalk	16.24
Corn cob	16.99
Rice straw	12.26
Rice husk	14.08
Cocoa pod husk	17.93
Sugar cane bagasse	16.88
Wawa sawdust	18.61

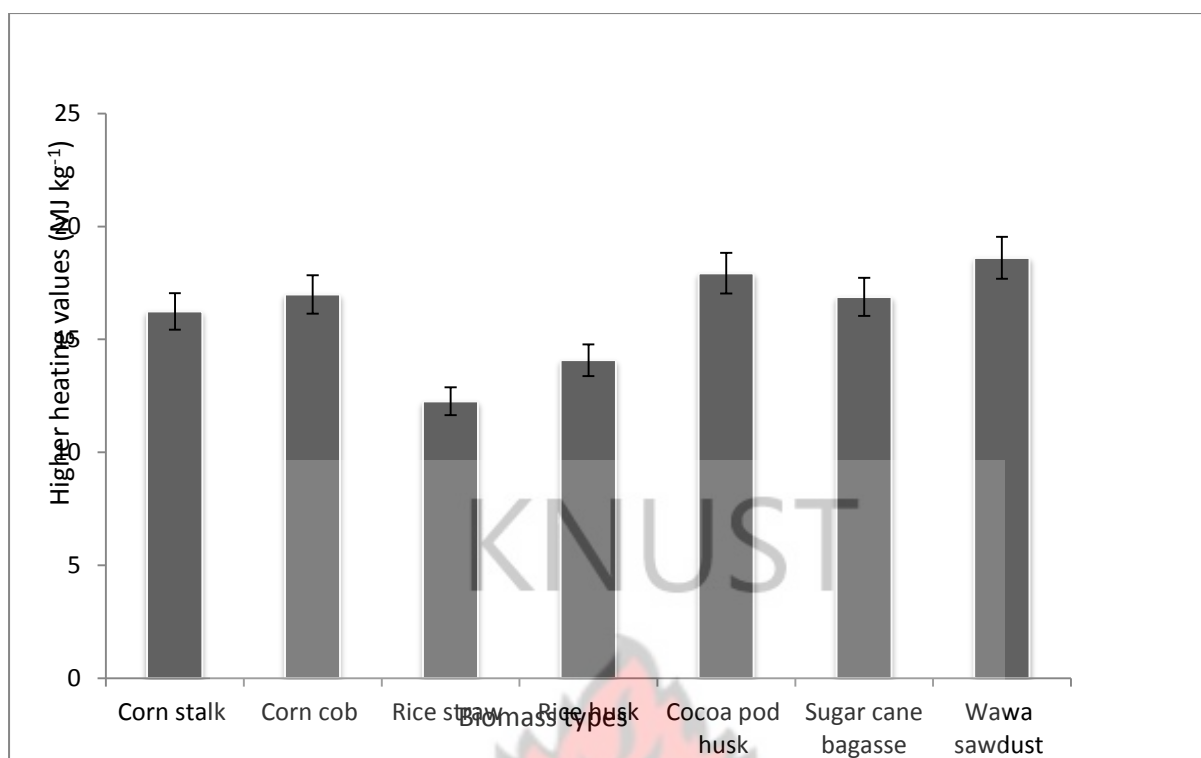


Figure 4.3: Higher heating values of the biomass samples

4.1.5. Chemical composition analysis

The results of chemical composition analyses of the biomass samples are shown in Table 4.5 and Figure 4.4. Cellulose content was high in all the biomass samples, and ranged from 30.41 %wt. for the cocoa pod husk to 44.40 %wt. for the wawa sawdust. It was higher in the corn stalk (43.82 %wt.) than in the corn cobs (38.20 %wt.). The rice straw and husk and sugarcane bagasse respectively had cellulose content of 31.84, 37.3 and 42.86 %wt. Hemicellulose content was high in the corn cobs and stalk and the sugarcane bagasse. It was 46.59, 24.39 and 22.45 %wt. respectively. The rice straw, cocoa pod husk and wawa sawdust respectively were, however, characterized by low hemicellulose contents of 7.29, 11.97 and 15.5 %wt. Lignin content was high in the rice husk (41.08 %wt.) but low in the corn cobs (7.16 %wt.). It was 33.97 and 28.39 %wt. for the cocoa pod husks and the rice straw respectively.

Table 4.5. Chemical composition analysis of the biomass samples

Biomass type	Percentage by weight (%wt. (dry matter))		
	Cellulose ^a	Hemicellulose ^b	Lignin
Corn stalk	43.82	24.39	9.03
Corn cob	38.26	46.59	7.16
Rice straw	31.84	7.29	28.39
Rice husk	37.34	10.07	41.08
Cocoa pod husk	30.41	11.97	33.97
Sugarcane bagasse	42.86	22.45	15.39
Wawa sawdust	44.40	15.50	31.70

a Cellulose measured as Neutral Detergent Fiber (NDF) – Lignin

b Hemicellulose measured as NDF–Acid Detergent Fiber (ADF)

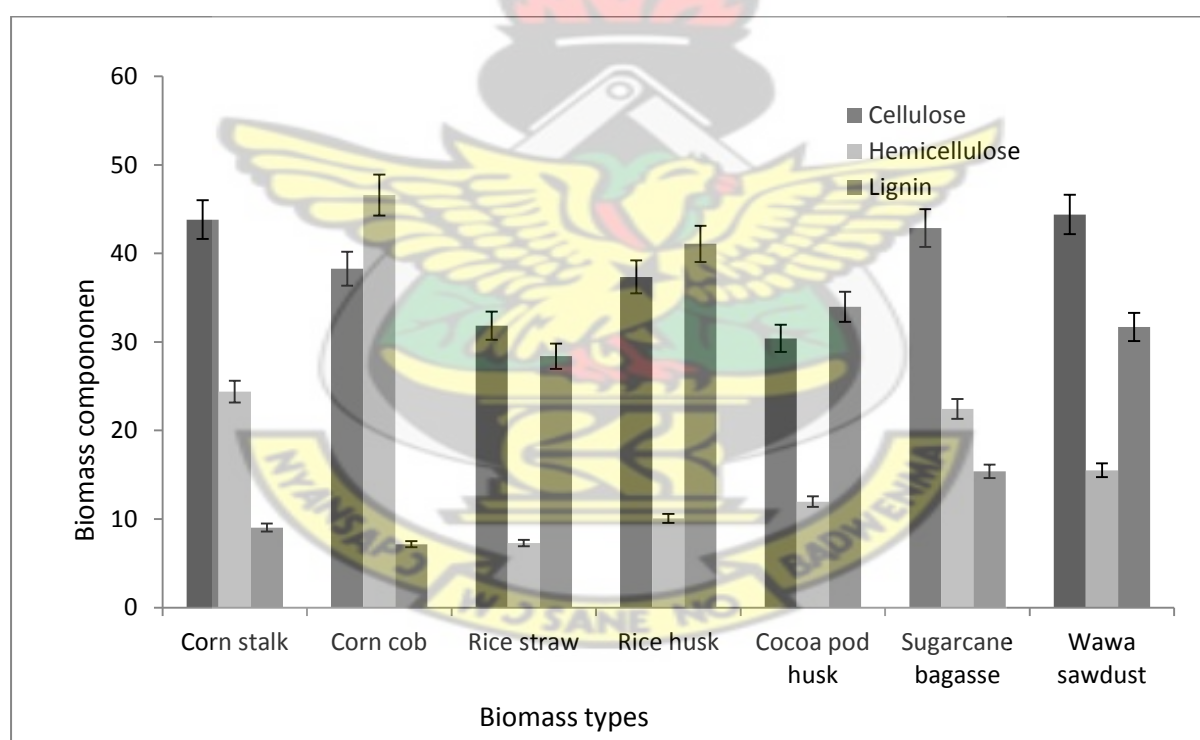


Figure 4.4: Chemical composition analysis of the biomass samples

4.2 Effect of temperature on product distribution of fast pyrolysis

This sub-chapter looks at how product yields from fast pyrolysis of the biomass samples varied with temperature increase. It reports bio-oil, bio-char and non-condensable gas yields as temperature increased for the biomass samples from 400 to 700 °C.

4.2.1 Fast pyrolysis parameters monitored

Table 4.6 shows the parameters monitored in this study for fast pyrolysis of the various biomass samples in a fluidized-bed reactor. They included a heating rate of 300 °C/s, temperature range of 400–700 °C, biomass with a particle size (1.0 mm), vapour residence time (0.5 s) and vapour condensation temperature (-10 °C).

Table 4.6: Parameters monitored for the fast pyrolysis of the biomass samples

No.	Pyrolysis parameter monitored	Values
1	Heating rate	300 °C/min.
2	Pyrolysis temperature	400– 700 °C
3	Particle size of biomass	<0.50 mm
4	Holding/residence time	1 s
5	Condensation temperature	-10 °C
6	Gas flow rate	4 l/min

Product yields of fast pyrolysis of the biomass samples are shown in Tables 4.7–4.14. Figures 4.5–4.12 represent the product distribution with temperature of the fluidized-bed reactor. All the product yields are reported on the basis of the dry biomass feedstock, and are the averages of duplicate analyses. As the temperature increased from 400 to 700 °C, bio-oil yields increased and reached a maximum value at 450 to 500 °C. It then decreased as the temperature increased to 700 °C for all the biomass samples. The maximum bio-oil yields obtained varied with the type of biomass sample and at different temperatures. The NCG

yields also increased as the temperature increased from 400 to 700 °C. Char yield, however, decreased as the temperature increased within the same range.

4.2.2 Fast pyrolysis of corn cobs

Table 4.7 and Figure 4.5 show the effect of temperature on the product yields from the fast pyrolysis of corn cobs, namely bio-oil, char and NCG. From Table 4.7, it was observed that the bio-oil yield first increased from 48.2 %wt. at 400 °C to a maximum of 57.0 %wt. at 550 °C. It then decreased to 52.0 %wt. as the temperature increased to 700 °C. The gas yield also continuously increased from 12.0 to 25.0 %wt. as the temperature increased from 400 to 700 °C. The char yield, however, decreased from 39.8 to 23.0 %wt. as the temperature increased from 400 to 700 °C. The maximum char and gas yields were 39.8 and 25.0 %wt. respectively for the corn cobs.

Table 4.7: The yields of bio-oil, char and non-condensable gas from fast pyrolysis of corn cobs

Product yield (%wt.)	Temperature (°C)					
	400	500	550	600	650	700
Liquid (bio-oil)	48.2	54.4	57.0	56.4	55.0	52.0
Non-condensable gas (NCG)	12.0	13.6	14.0	15.6	19.0	25.0
Char	39.8	32.0	29.0	28.0	26.0	23.0

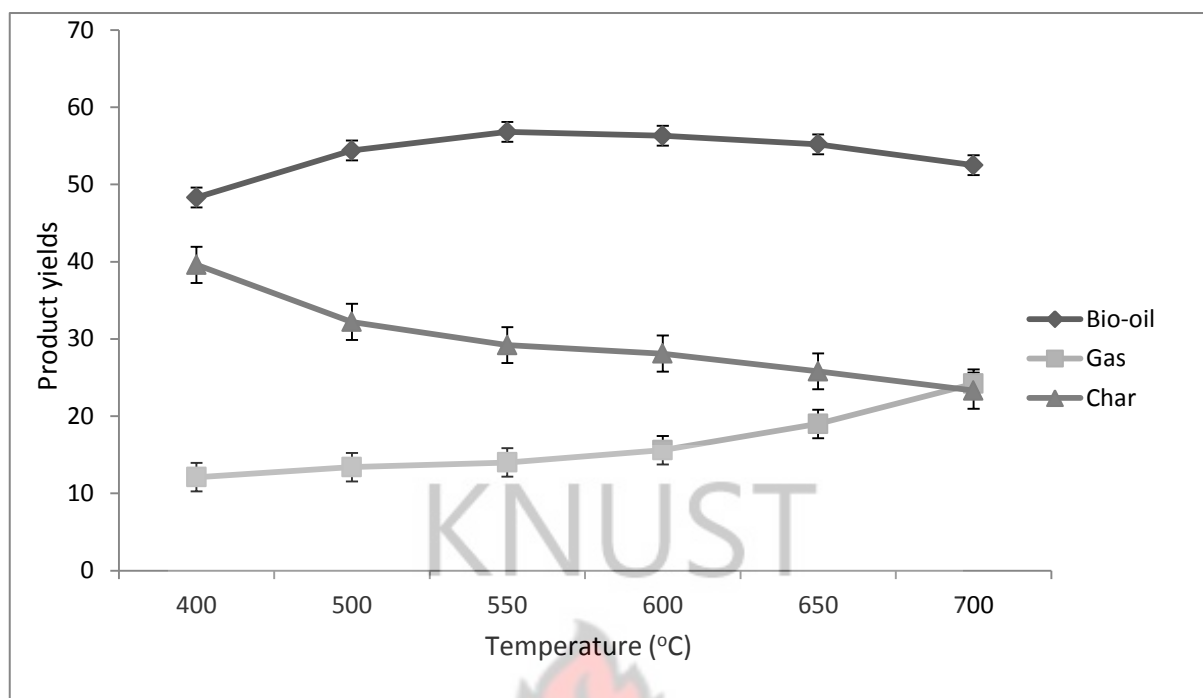


Figure 4.5: Effect of temperature on product distribution of corncobs fast pyrolysis

4.2.3 Fast pyrolysis of corn stalk

The product yields of fast pyrolysis of corn stalk are shown in Table 4.8 and Figures 4.6 and 4.7. The results showed that the bio-oil yields first increased from 60.0 to 66.0 %wt. when the temperature increased from 400 to 500 °C. It then decreased to 62.0 %wt. when the temperature increased further to 700 °C. The maximum bio-oil yield was 66.0 %wt. at 500 °C. The NCG yield also increased continuously from 10.0 to 27.0 %wt. as the temperature increased from 400 to 700 °C. The yield of char, however, decreased from 30.0 to 10.9 %wt. as the temperature increased from 400 to 700 °C.

Table 4.8: The yields of bio-oil, NCG and char from fast pyrolysis of corn stalk

Product (%wt.)	Temperature (°C)				
	400	500	550	600	700
Liquid (bio-oil)	60.0	66.0	65.0	63.5	62.0
NCG	10.0	15.0	16.0	25.5	27.0
Char	30.0	18.0	14.0	11.0	11.0

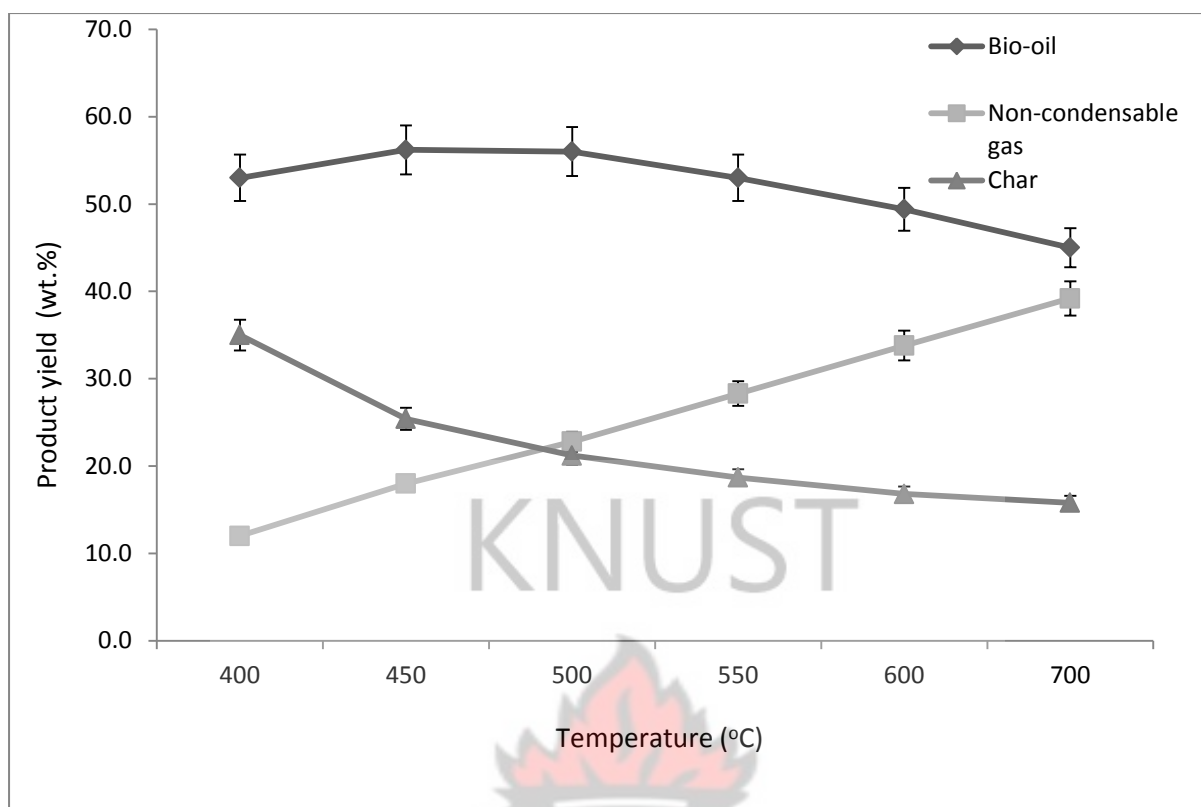
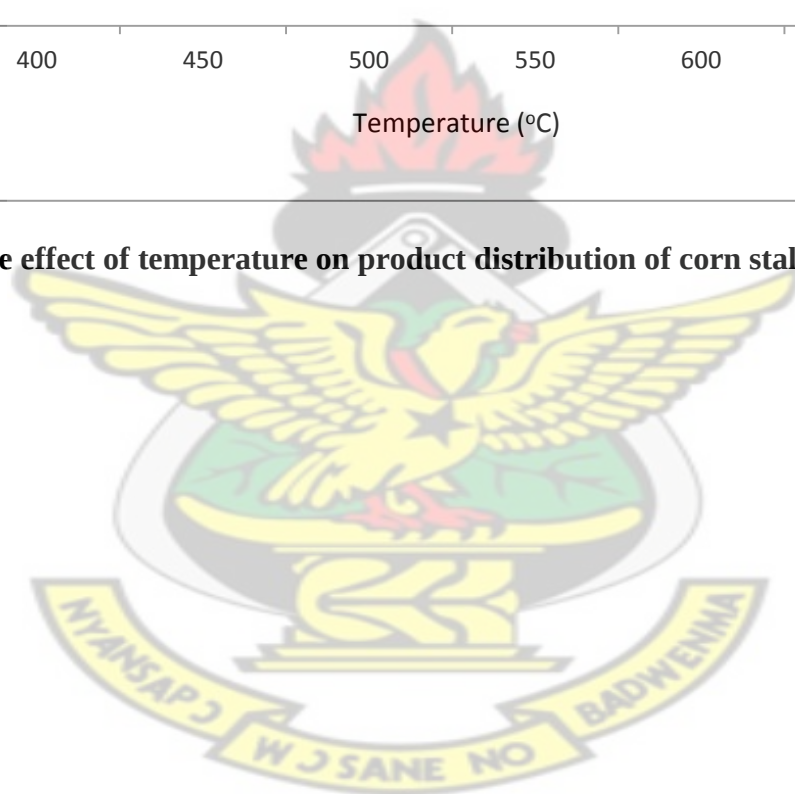


Figure 4.6: The effect of temperature on product distribution of corn stalk fast pyrolysis



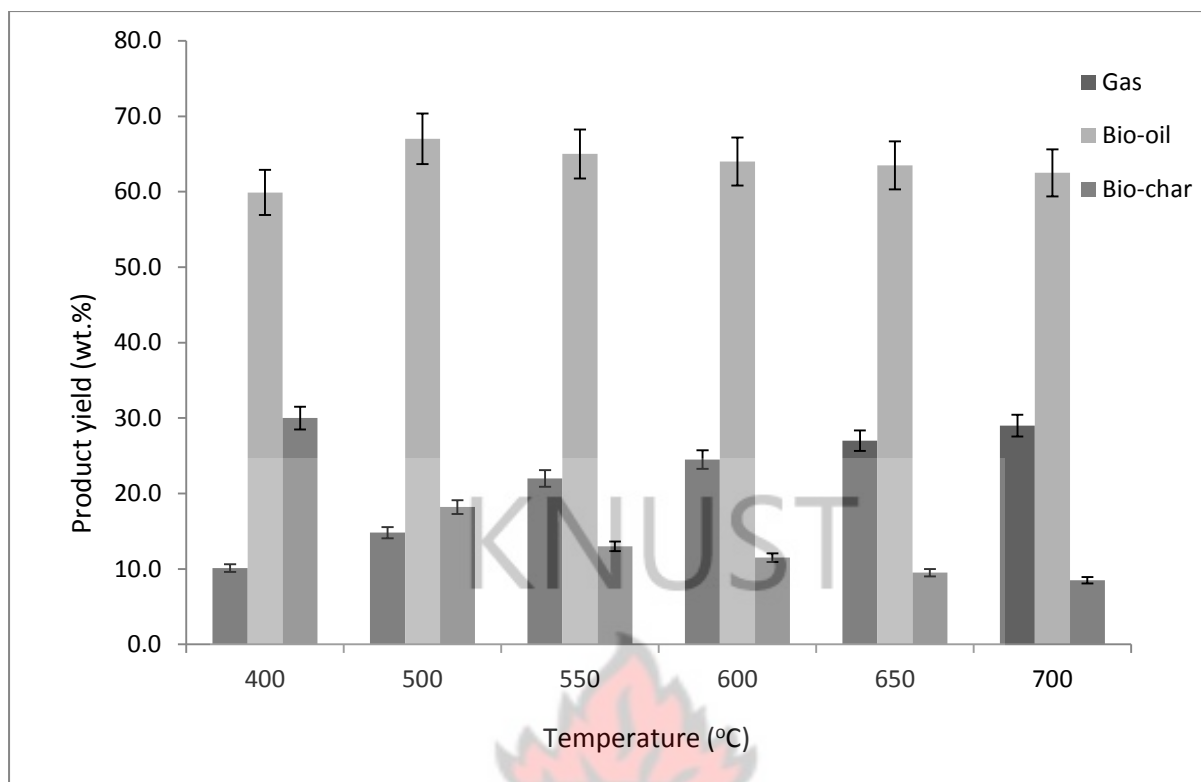


Figure 4.7: Effect of temperature on product distribution of fast pyrolysis of corn stalk

4.2.4 Fast pyrolysis of rice straw

The yields of products of fast pyrolysis of the rice straw are shown in Table 4.9 and Figure 4.8. Liquid yields first increased from 53.2 to 60.0 %wt. as the temperature increased from 400 to 550 °C, and then decreased to 50.5 %wt. as the temperature increased to 700 °C. The maximum liquid yield of 60.0 %wt. was obtained at 500 °C. The NCG yield also increased as the temperature increased from 400 to 700 °C. Char yield, however, decreased as the temperature increased from 400 to 700 °C.

Table 4.9: The yields of bio-oil, NCG and char from fast pyrolysis of rice straw

Product yield (%wt.)	Temperature (°C)				
	400	500	550	600	700
Liquid (bio-oil)	53.2	60.0	59.0	54.6	50.5
NCG	8.2	13.2	19.8	26.8	32.5
Char	38.6	26.8	21.2	18.4	17.2

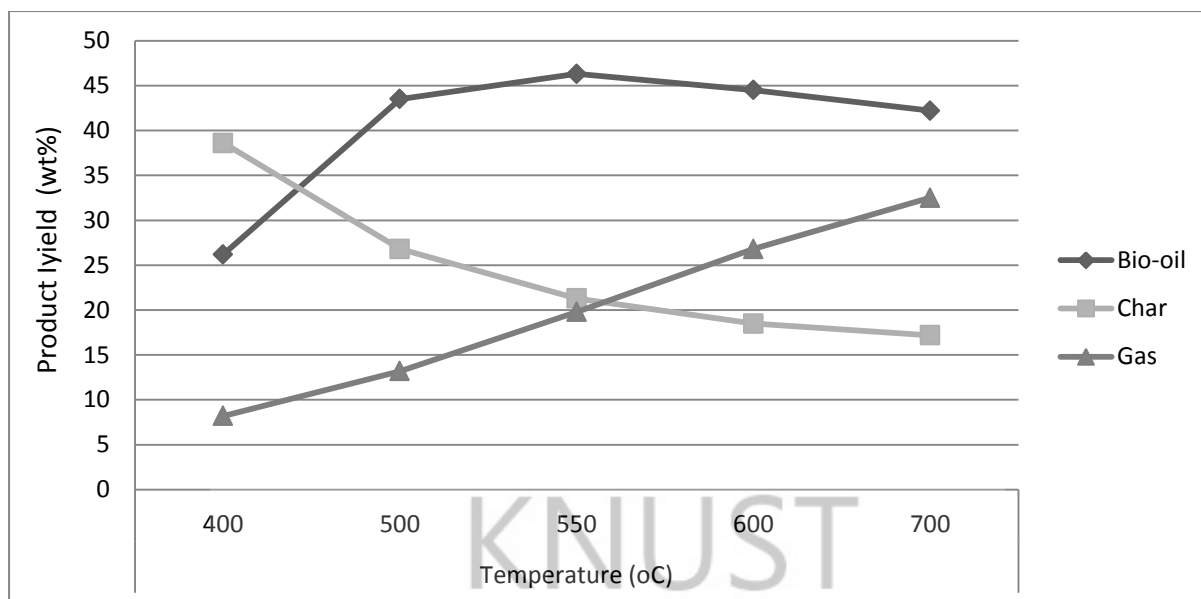


Figure 4.8: Effect of temperature on product distribution of fast pyrolysis of the rice straw

4.2.5 Fast pyrolysis of rice husk

The product yields of the pyrolysis of the rice husk are shown in Table 4.10 and Figure 4.9 respectively. The bio-oil yield first increased from 53.0 %wt. at 400 °C to 56.0 wt.% at 500 °C. It then decreased to 45.0 %wt. when the temperature further increased to 700 °C. The maximum bio-oil yield for the rice husk of 56.0 %wt. was obtained at 500 °C. The NCG yield also increased continuously from 12.0 to 39.2 %wt. as the temperature increased from 400 to 700 °C. However, the char yield decreased from 35.0 to 15.8 %wt. as the temperature increased from 400 to 700 °C.

Table 4.10: The yields of bio-oil, NCG and char from fast pyrolysis of rice husk

Product yields (%wt.)	Temperature (°C)					
	400	450	500	550	600	700
Liquid (bio-oil)	53.0	56.2	56.0	53.0	49.4	45.0
NCG	12.0	18.0	22.8	28.4	33.8	39.2
Char	35.0	25.8	21.2	18.6	16.8	15.8

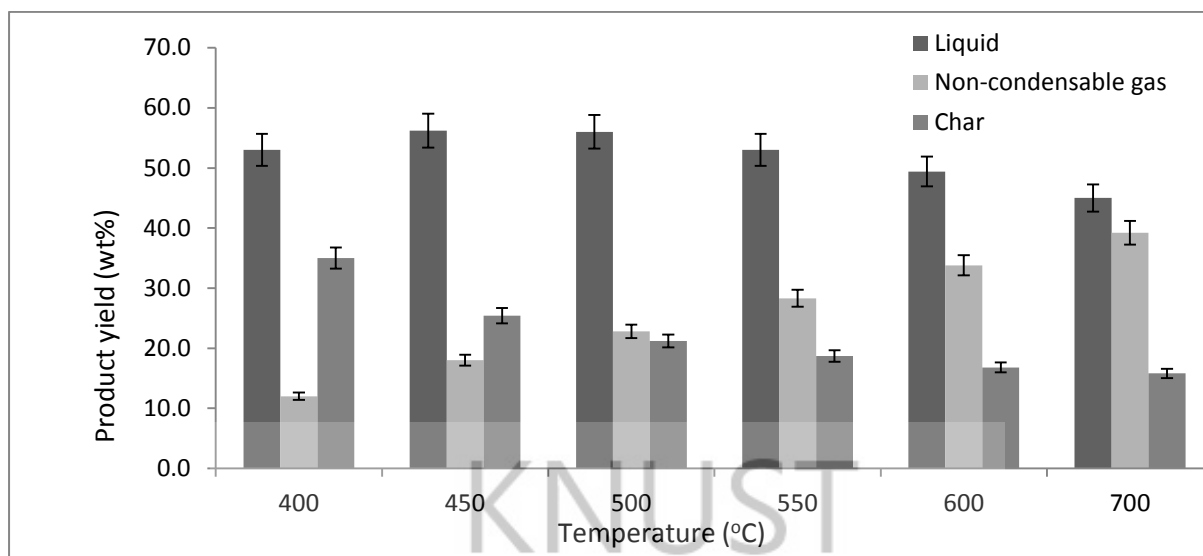


Figure 4.9: Effect of temperature on product distribution of the fast pyrolysis of the rice husk

4.2.6 Fast pyrolysis of sugarcane bagasse

The products yields of fast pyrolysis of the sugarcane bagasse are shown in Table 4.11, while Figure 4.10 represents the effect of temperature on the distribution of the products. As the temperature increased from 400 °C, the bio-oil yield first increased from 35.0 to 61.0 %wt. at 500 °C and then decreased to 40.0 %wt. as the temperature further increased to 700 °C. The maximum bio-oil yield of 61.0 %wt. was obtained at 500 °C. The NCG yield also increased continuously from 12.0 to 35.0%wt. as the temperature increased from 400 to 700 °C. However, the char yield decreased from 45.0 to 14.0 %wt. as temperature increased from 400 to 700 °C.

Table 4.11: The yields of bio-oil, NCG and char from fast pyrolysis of sugarcane bagasse

Product yield (%wt.)	Temperature (°C)					
	400	450	500	550	600	700
Liquid (bio-oil)	35.0	48.0	61.5	56.0	50.0	40.0
NCG	12.0	23.8	21.0	22.0	26.0	35.0
Char	45.0	28.2	18.0	17.0	15.0	14.0

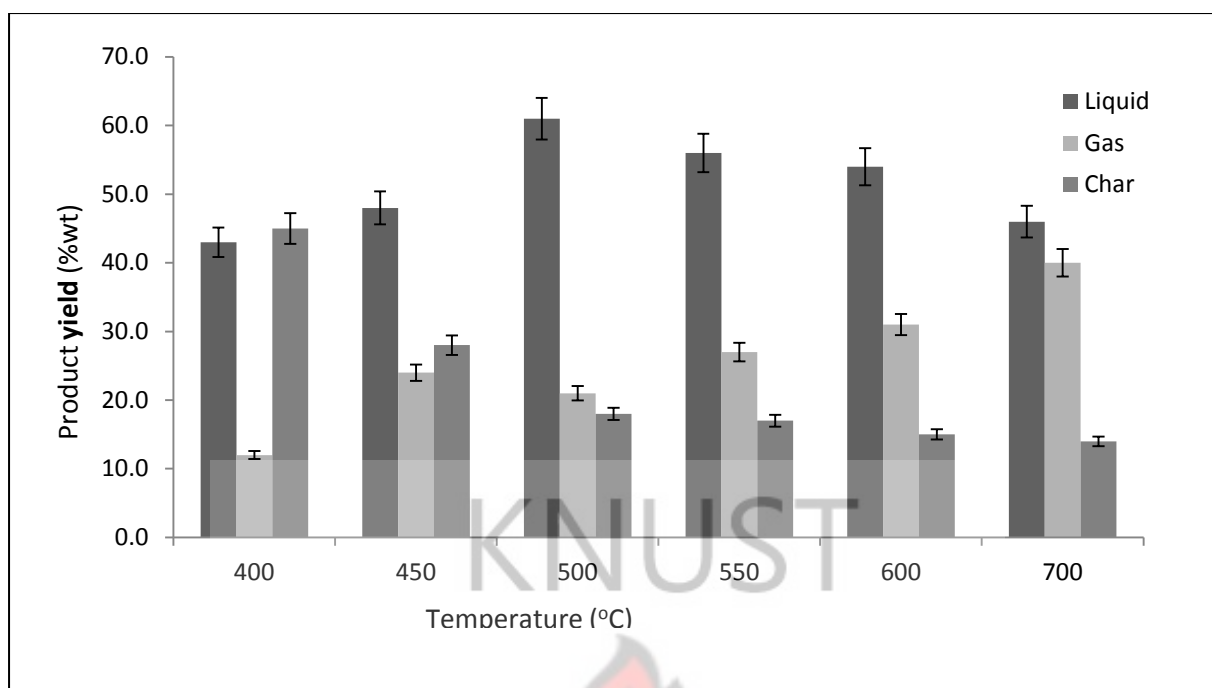


Figure 4.10: Effect of temperature on product distribution of sugarcane bagasse pyrolysis

4.2.7 Fast pyrolysis of cocoa pod husk

The product yields of the fast pyrolysis of cocoa pod husks are shown in Table 4.12 and Figure 4.11. The bio-oil yield from fast pyrolysis of the cocoa pod husks first increased from 50.0 to 53.0 %wt. as the temperature increased from 400 to 500 °C, and then decreased to 46.5 %wt. as it further increased to 700 °C. The maximum bio-oil yield of 53.0 %wt. was obtained at 500 °C. The NCG yield also increased continuously from 12.0 to 37.0 %wt. as the temperature increased from 400 to 700 °C. However, the char yield decreased from 38.0 to 16.4 %wt. as the temperature increased from 400 to 700 °C.

Table 4.12: The yields of bio-oil, NCG and char from fast pyrolysis of cocoa pod husks

Yield (%wt.)	Temperature (°C)					
	400	450	500	550	600	700
Liquid (bio-oil)	50.0	52.4	53.0	52.0	49.6	46.5
NCG	12.0	18.0	22.8	28.4	32.0	37.0
Char	38.0	29.6	24.2	19.6	18.4	16.5

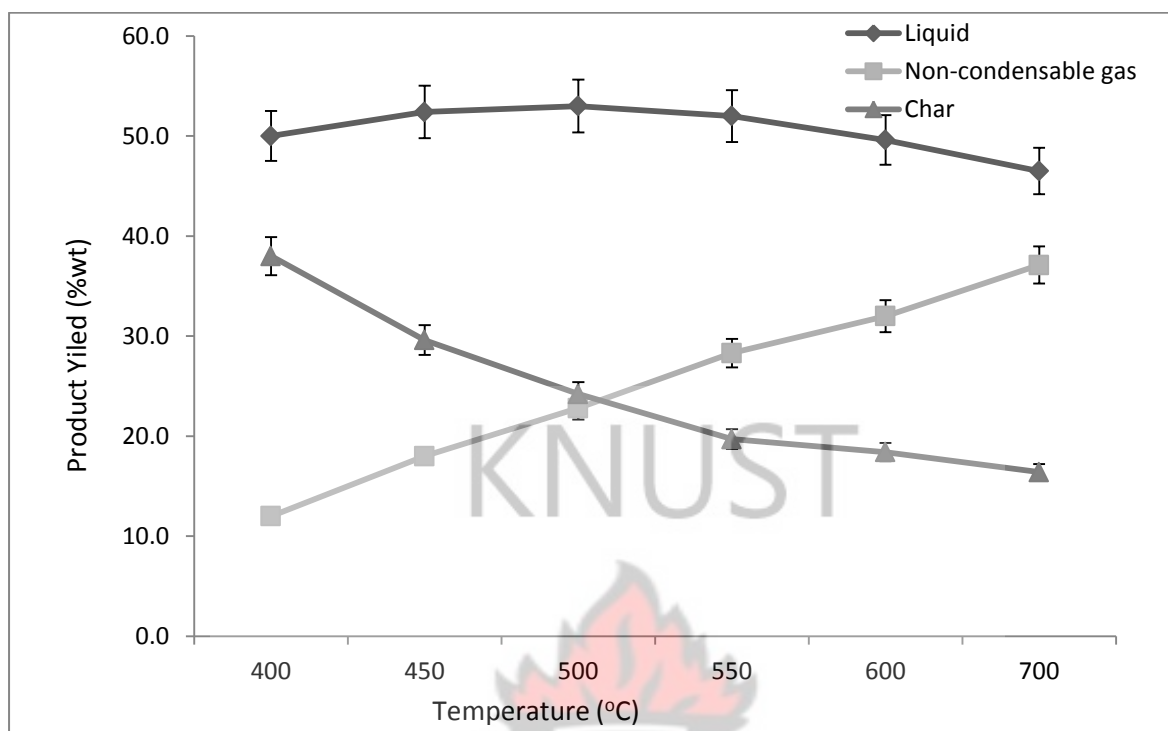


Figure 4.11: Effect of temperature on product distribution of fast pyrolysis of the cocoa pod husk.

4.2.8 Fast pyrolysis of wawa sawdust

The product yields of fast pyrolysis of the wawa sawdust are shown in Table 4.13, while Figure 4.12 represents the products distribution. As shown on Figure 4.12, the bio-oil yield increased from 58.0 to 62.0 %wt. as the temperature increased from 400 to 500 °C, and then decreased to 49.0 %wt. at 700 °C. The maximum bio-oil yield for the wawa sawdust of 62.0 %wt. was obtained at 500 °C. The NCG yield also increased from 10.0 to 36.0 %wt. as the temperature increased from 400 to 700 °C. However, the char yield decreased from 32.0 to 15.0 %wt. as the temperature increased from 400 to 700 °C.

Table 4.13: The yields of bio-oil, NCG and char from fast pyrolysis of wawa sawdust

Product yield (%wt.)	Temperature (°C)					
	400	450	500	550	600	700
Liquid (bio-oil)	58.0	61.0	62.0	58.0	55.0	50.0
NCG	10.0	13.0	17.0	25.0	30.0	35.0
Char	32.0	26.0	21.0	17.0	15.0	15.0

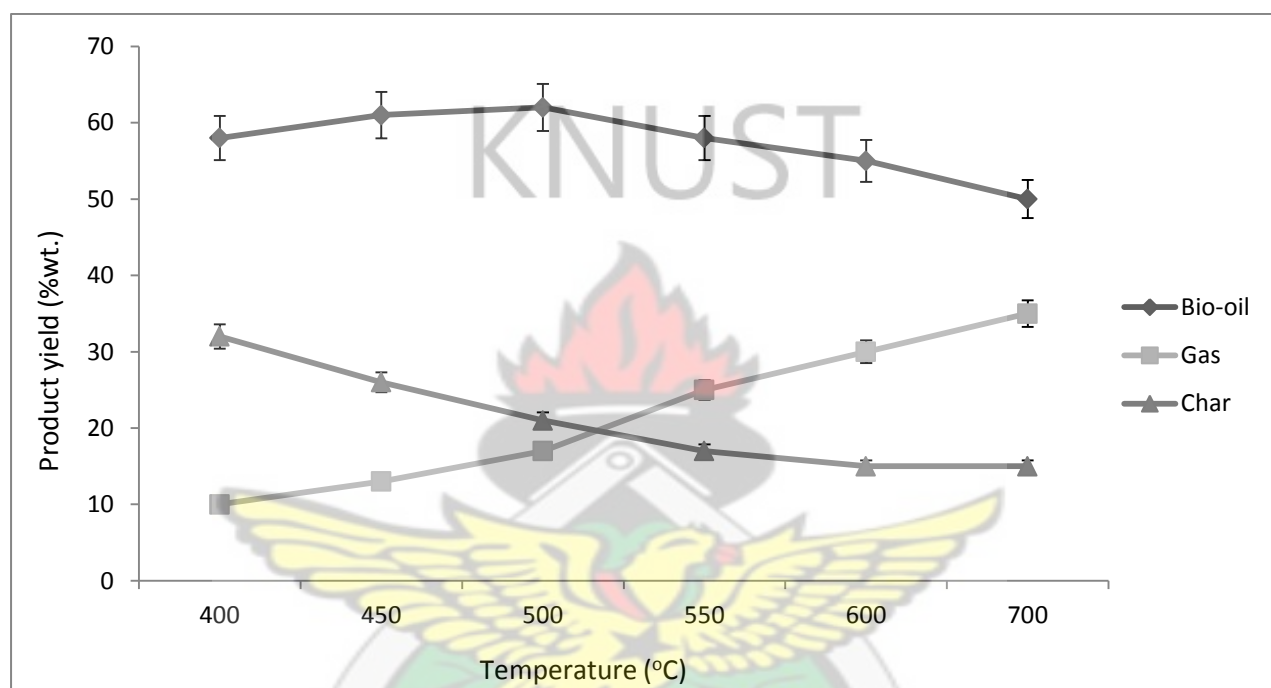


Figure 4.12: Effect of temperature on product distribution of fast pyrolysis of sawdust

4.3 Characterization of the bio-oils for energy purpose

This sub-chapter reports the results of the analyses carried out to characterize the bio-oils obtained as maximum yields. Conclusions are also drawn from the results discussed.

4.3.1 Physical characteristics

Table 4.14 shows some of the physical characteristics of the bio-oils obtained as maximum yields from the biomass samples. Physical fuel characteristics included higher heating values, density, viscosity and pH. Maximum bio-oil yields obtained for the rice husk and corn stalk respectively ranged from 56.0 to 66.0 %wt.

Table 4.14: Characteristics of the bio-oils obtained from fast pyrolysis

Characteristics	Rice husk	Rice straw	Corn cob	Corn stalk	Sugarcane bagasse	Cocoa pod husk	Wawa Sawdust
Bio-oil yields (%wt.)	56.0	60.0	57.0	66.0	61.5	53.0	62.0
Calorific value (MJkg ⁻¹)	17.42	18.43	16.80	19.60	23.30	17.20	17.40
Moisture content (%wt.)	25.2	26.0	22.9	22.5	12.0	26.7	24.0
Density (kgm ⁻³)	1190	1180	1180	1220	1150	1155	1180
Viscosity (mm ² s ⁻¹)	128	126	140	138	139	156	240
pH	2.80	2.89	2.80	3.20	2.60	2.60	2.10

For the rice straw and husk, and corn stalk and its cobs, maximum bio-oil yields respectively were 60.0, 56.0, 66.0 and 57.0 %wt. The bio-oils were acidic in nature with pH of 2.8 for the rice husk, rice straw and corn cobs bio-oils. The corn stalk bio-oil had a pH of 3.2, while the sugarcane bagasse and cocoa pod husk bio-oils had pH of 2.6. A high pH value of 2.1 was obtained for the wawa sawdust bio-oil. The moisture contents of the bio-oils were high, and ranged from 12.0 %wt. for the sugarcane bagasse to 26.7 %wt. for the cocoa pod husk. The corn stalk, corn cobs and wawa sawdust bio-oils had moisture content of 22.5, 22.9 and 24.5 %wt. respectively. The viscosity of the bio-oils ranged between 128 and 240 mm²s⁻¹ at 20 °C. Corn cobs and stalk bio-oils respectively had viscosity of 140 and 139 mm²s⁻¹.

4.3.2 Ultimate analysis

Ultimate analysis of the bio-oils is presented on Table 4.15. Carbon and hydrogen contents were higher than those of the biomass samples. Carbon contents ranged from 41.7 %wt. for the rice husk bio-oil to 65.7 %wt. for the rice straw bio-oil while it ranged from 26.73 to 44.37 wt% for rice straw and wawa sawdust. There was, however, a decrease in oxygen content in the bio-oils compared to the biomass samples. There was also a slight increase in

nitrogen levels of the bio-oils over the biomass samples. Oxygen contents were high in all the bio-oils, which ranged from 25.6 %wt. for the rice straw bio-oil to 50.3 %wt. for the rice husk bio-oil.

Carbon-to-oxygen (C:O) and hydrogen-to-carbon molar ratios (H:C) for the bio-oils obtained in this study are shown in Table 4.15 and Figure 4.13. The H:C and C:O molar ratios for the bio-oils respectively ranged from 1.40 to 2.22 and 0.76 to 3.42. C:O and H:C ratios respectively indicate acidity and heat content of the bio-oils. High C:O lowers the heat content of the biomass or bio-oil. Compared to water, the bio-oils produced in this study were denser. The densities ranged from 1,180 to 1,220 kgm⁻³ for the corn cob and the corn stalk bio-oils. The HHVs ranged from 16.8 to 23.3 MJ kg⁻¹ respectively for the corn cob to sugarcane bagasse bio-oils. The differences in density and HHV could be due to differences in elemental constituents and biomass composition. The reduction in ash content and increased carbon and hydrogen contents of the bio-oils obtained may have resulted in an increased HHV compared to those for the original biomass.

Table 4.15: Elemental analysis of the bio-oils obtained from fast pyrolysis of the biomass samples

Composition	Rice husk	Rice straw	Corn cob	Corn stalk	Sugarcane bagasse	Cocoa pod husks	Wawa Sawdust
C (%wt.)	41.70	65.68	51.9	44.3	45.77	46.5	53.5
H (%wt.)	7.70	7.66	7.00	6.30	7.86	7.30	6.40
O (%wt.)	50.30	25.58	40.30	47.50	46.19	49.80	40.20
N (%wt.)	0.30	1.08	0.80	0.60	0.18	0.20	0.20
S (%wt.)	0.20	-	-	0.30	-	0.10	0.10
H/C molar ratio	2.22	1.40	1.62	1.71	2.06	1.88	1.44
C/O molar ratio	1.11	3.42	1.72	1.24	0.76	1.24	1.77

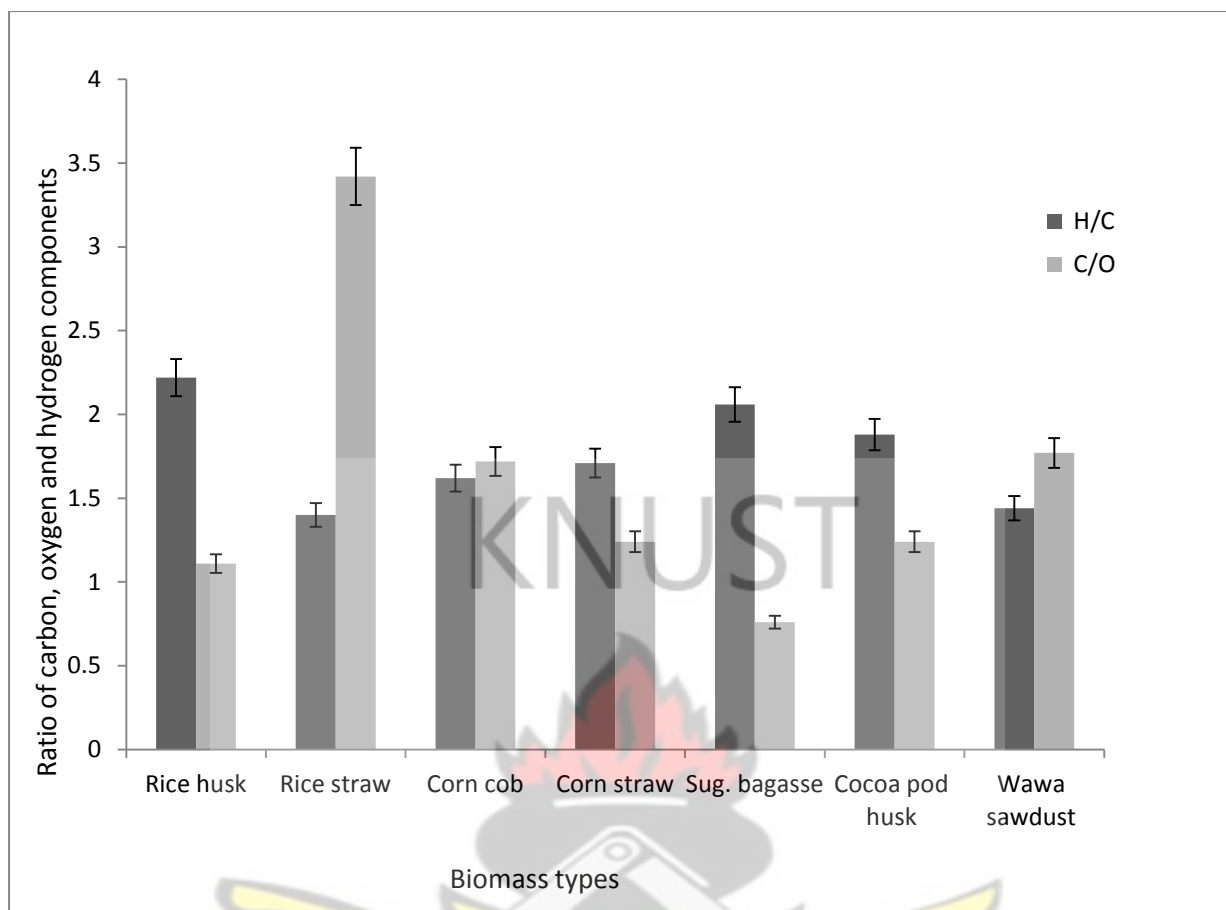


Figure 4.13: Hydrogen-to-carbon (H:C) and carbon-to-oxygen (C:O) molar ratios of the bio-oils obtained from the biomass samples

Table 4.16: Composition of the NCG obtained from fast pyrolysis of corn cob and stalk

NCG component	% by volume	
	Corn cobs	Corn stalk
Carbon monoxide	41.0	51.5
Carbon dioxide	51.4	40.4
Methane	6.4	6.1
Hydrogen	1.2	2.0

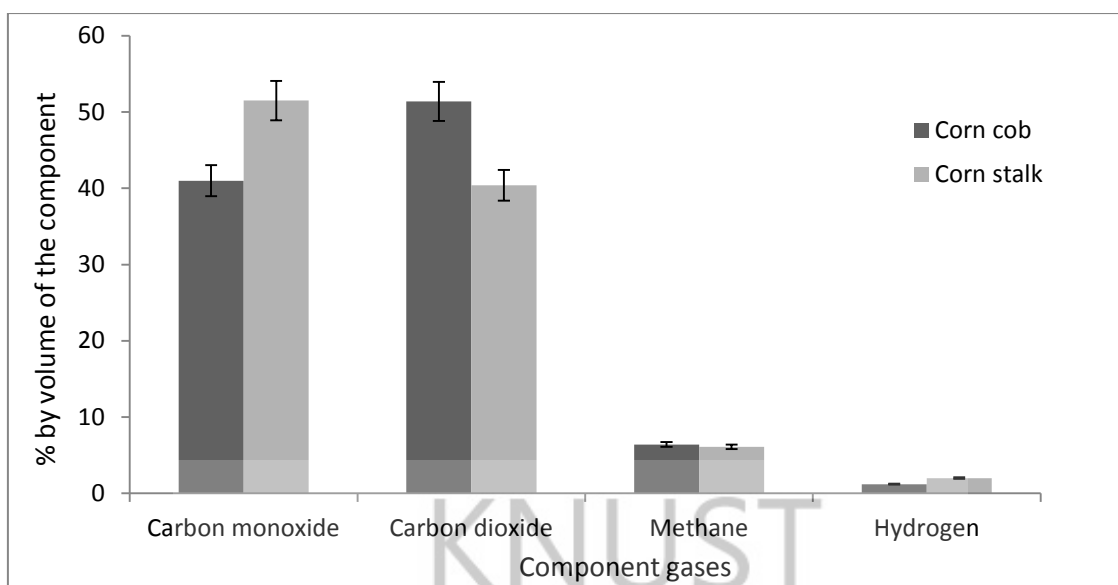


Figure 4.14: Yields of NCG components of fast pyrolysis of corn cob and stalk

4.4. Scheme for bio-oil production system from lignocellulosic biomass

This sub-chapter looks at a scheme, which has been developed for bio-oil production based on the literature review, results obtained from fast pyrolysis experiments and conclusions drawn from the analyses. It discusses the various aspects considered in the proposed scheme such as process design and potential utilization of fast pyrolysis products, namely, bio-oil, bio-char and non-condensable gas.

4.4.1 Proposed process design for biomass fast pyrolysis

Fast pyrolysis could be of immense interest nationally due to the large availability of different types of lignocellulosic biomass at the national level and its potential to contribute to the solution of current fuel crisis, GHG emissions and sustainable development. An assessment of the availability of biomass in the Western, Central, Ashanti, Brong-Ahafo and Eastern regions of Ghana, covering agricultural crop residues, forest and wood processing residues, urban wastes and animal wastes showed that the available biomass resources in the Western region were 451,578 tonnes/year. There were 276,400 tonnes/year in the Central region,

474,228 tonnes/year in the Eastern region, 407,589 tonnes/year in the Ashanti region and 641,240 tonnes/year in the Brong-Ahafo region. Agricultural crop residues included those generated from sugarcane, maize, rice, cocoa, oil palm and coconut. Maize residues constituted the largest available biomass resource (47 %), followed by cassava residues (17 %) and cocoa residues (16 %) (Hagan and Duku, 2012).

The proposed scheme consists of process stages, which include (i) lignocellulosic biomass collection (mainly wood processing residues and agricultural crop residues analyzed in this study), (ii) biomass preparation such as drying and grinding, (iii) fast pyrolysis reactor configuration, (iv) heat supply and heat transfer, (v) fast pyrolysis at 450–500 °C, heating rate of 100 °C /min, a short vapour residence time of 1–2 sec and pressure of 5 KPa., (vi) separation of bio-char from pyrolysis vapours using cyclones, (vii) crude bio-oil recovery and storage, (viii) utilisation of the crude bio-oil in stationary engines, (ix) up-grading of the crude bio-oil by dehydroxygenation and its utilisation as a fuel for transportation, (x) utilisation of bio-char as an energy source for the pyrolytic process and other applications such as soil amendment and climate change abatement due to its high stability in soils and (xi) utilisation of the non-condensable gas as an energy source for the pyrolytic process due to its high energy content. Flow sheets of the pyrolytic process are provided on Figures 4.15 and 4.16, as well as Appendix 4.

Lignocellulosic biomass such as wood processing residues and selected agricultural crop residues would be collected respectively from major wood processing firms and commercial farms in various parts of the country. The biomass types considered are mainly those analyzed in this study. Biomass handling and drying equipment consists of tractors, conveyors, grinders and dryers. Pre-treatment of the biomass includes drying in a dryer and

grinding using a grinder. Drying reduces the moisture content of the biomass to 8–10 %wt on dry basis, while the evaporated water is flashed. The dried biomass is passed below a magnetic separator to remove un-wanted materials such as metals before it is transferred using a set of conveyors to a milling area. The milled biomass is then sieved using mechanically vibrating screens with openings (1–2 mm) to produce biomass with particle sizes ranging between 1 and 2 mm. It is then sent to storage bins equipped with rotary feeders to ensure regular and steady feed to the pyrolyzer.



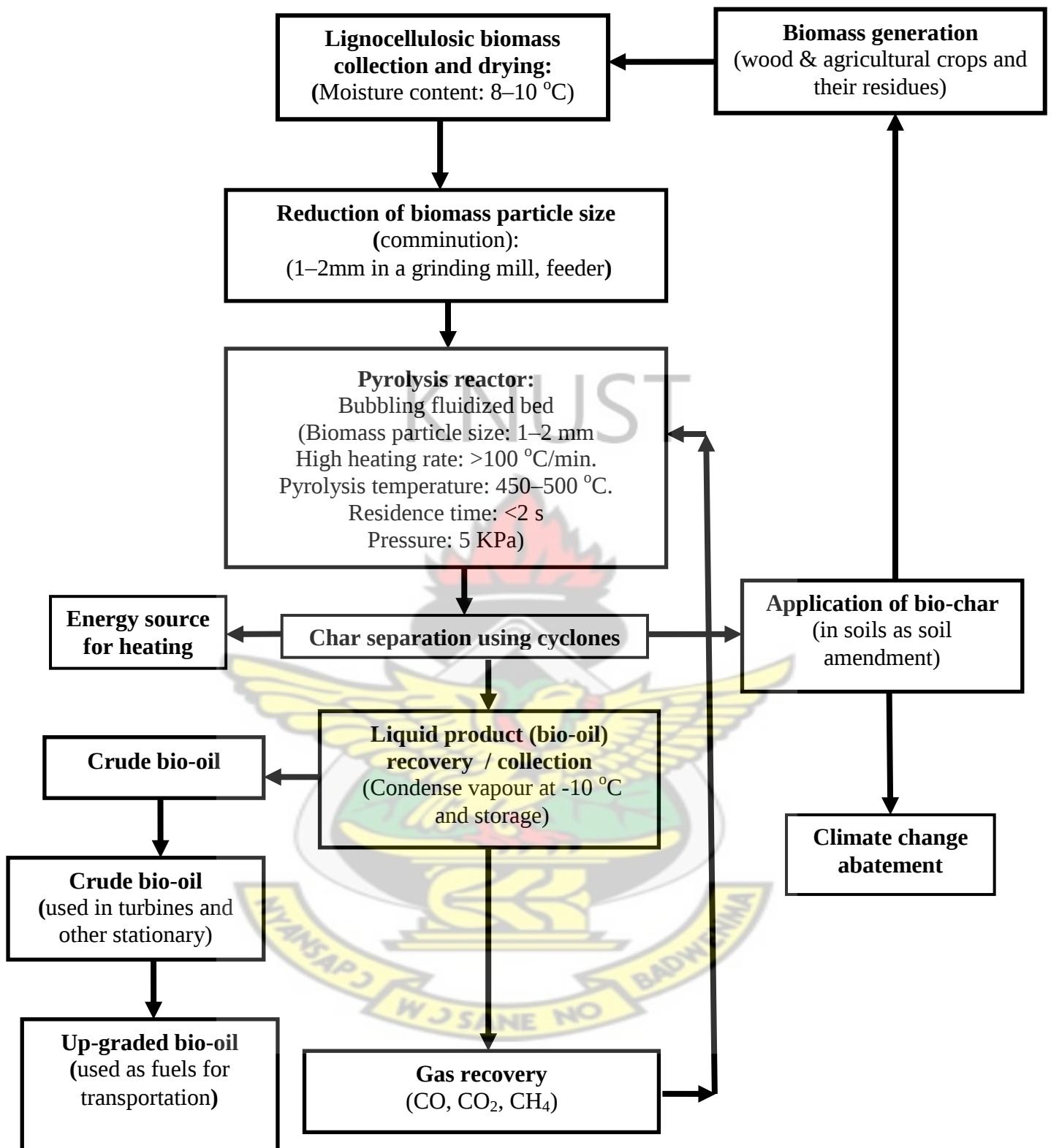


Figure 4.15. Proposed scheme for bio-oil production from lignocellulosic biomass using fast pyrolysis and the utilization of products

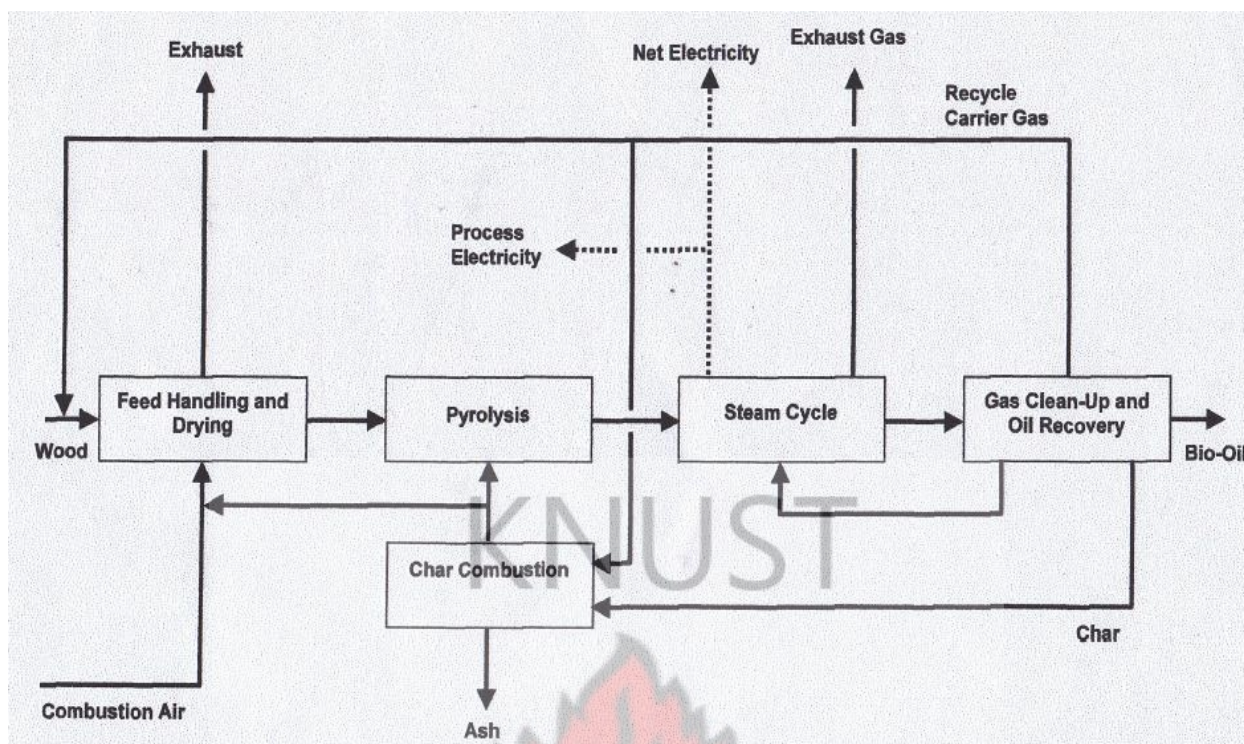


Figure 4.16: Process flowsheet of the proposed pyrolysis facility.

A bubbling fluidized-bed reactor is recommended for the commercial facility since it gives high bio-oil yields. Moreover, it has been used widely for a long time commercially and is easy to operate. A production unit, which processes 200 ton/day of lignocellulosic biomass is recommended for use. The production capacity has been selected based on demonstration commercial facilities for bio-oil production from lignocellulosic biomass reported by some authors (Garcia-Perez *et al.*, 2007).

The bubbling fluidized-bed reactor contains a bed of silica sand with particle sizes ranging between 1–2 mm, which is fluidized using an inert gas such as nitrogen (N₂). The milled biomass is introduced at the bottom of the fluidized-bed reactor where it is mixed with the hot agitated sand particles. The fluidized silica sand, which can withstand a temperature of 1.500 °C and is in a state of continuous turbulence or fluid, promotes fast and homogeneous heat

transfer to the biomass particles. This ensures a high efficiency of the pyrolytic process coupled with a rapid removal of the vapours produced.

Fast pyrolysis involves heating the dried biomass-gas mix in the pyrolysis reactor fluidized using nitrogen gas (N_2) at 450–500 °C using heat from the bio-char combustor at a heating rate of 100 °C/min and residence time of 1–2 s. Subsequent fluidization is carried out using re-cycled NCG at 200 °C in a 2.75:1 gas-to-feedstock ratio.

Fast pyrolysis converts the lignocellulosic biomass to three (3) basic phases, namely:- (i) condensable vapours which, constitute the crude bio-oil constituents (e.g. $C_2H_4O_2$) and water, (ii) a solid phase comprising small carbon particles and ash (also known as bio-char) and (iii) a non-condensable gas, composed mainly of CO , CO_2 and H_2 .

The mix of solids, liquid and gases are sent to carbon filters where the solids such as ash and bio-char are separated from the non-condensable gases and bio-crude vapours. The bio-char is temporarily stored before being directed to a combustor using a pneumatic conveyor.

At 500 °C, the pyrolysis reaction is rapidly quenched within 1-2 s and the condensable gases (bio-crude vapours) are condensed in a series of two condensers. The condensable vapours are cooled initially to about 100 °C in the first condenser, followed by further condensation in the second condenser using chilled water at 4 °C to form the bio-oil. Crude bio-oil obtained is stored in a storage tank. The first condenser is used to generate a high pressure of about 5 KPa. of steam, which is stored in a steam drum, while the second condenser is used as the cooling medium. The resulting gases and residual vapours are cleaned in a scrubber and wet

electrostatic precipitators (ESP) and re-cycled as fluidizing medium for the pyrolytic process.

The proposed scheme could be employed for the production of bio-oil as the major product, char and non-condensable gas as co-products simultaneously from lignocellulosic biomass. Maximum bio-oil yields are expected to range between 53.0 and 66.0 %wt. of the dry weight of the lignocellulosic biomass at 500 °C. Maximum bio-oil yields for corn cobs, rice straw, cocoa pod husk, corn stalk and wawa sawdust respectively are projected as 57.0, 60.0, 53.0, 66.0 and 62.0 %wt. at 500 °C. Bio-char and NCG yields are respectively expected to range between 18.0–26.8 %wt and 13.0–22.8 %wt (Tables 4.17, 4.18 and 4.19 refer).

The proposed scheme provides a cost-effective approach for maximum utilization of lignocellulosic biomass using fast pyrolysis for bio-oil production. Biomass fast pyrolysis is of rapidly growing interest globally as it offers significant logistical and hence economic advantages over other thermal conversion processes such as combustion. This is because the liquid product (bio-oil) can be stored until required. It can also be readily transported to places where it can be most effectively utilised.

The crude bio-oil could be used as a substitute or replacement to fossil fuels such as diesel oil in stationary engines, for example turbines since it has a high energy content. Sulphur and nitrogen levels were also found to be very low, making its use as a fuel environmentally friendly. Low levels of emissions of SO₂ and NO₂ will be expected on combustion.

However, crude bio-oil can be up-graded using processes such as hydrodeoxygenation and the upgraded bio-oil, known as green gasoline and green diesel oil used as a substitute or

replacement to either gasoline or diesel oil for transportation purposes. This will contribute to climate change mitigation through reduced GHG emissions. Hydrodeoxygenation of the bio-oils can be either by hydro-cracking or hydrotreatment. Hydrocracking is conducted without the use of catalysts. Hydrotreatment is, however, carried out in the presence of catalysts such as Co–Mo, Ni–Mo, their oxides and Al₂O₃ (Appendix 2 refers).

Bio-char can be used as an energy-source for the pyrolytic process since it has a high energy content. It is combusted at about 1600–1800 °C and the hot gases are used for heating the pyrolyzer. Bio-char can be applied to agricultural soils primarily to improve soil fertility and consequently improve crop productivity or for carbon sequestration. This is to serve as an option for climate change abatement, since its carbon content is very stable (Garcia-Perez *et al.*, 2007).

Table 4.17 Proximate, ultimate, ash composition, chemical composition and heating values

Type of Analysis		Lignocellulosic biomass						
		Corn stalk	Corn cob	Rice straw	Rice husk	Cocoa pod husk	Sugarcane Bagasse	Wawa sawdust
Proximate Analysis	Moisture	91.50	8.72	7.23	8.59	10.29	8.59	6.03
	Volatile	75.02	80.72	45.68	58.22	68.47	79.45	80.48
	Ash	6.13	2.96	45.76	24.71	10.81	3.91	1.48
	Fixed carbon	9.70	7.60	1.33	8.48	10.43	8.12	12.01
Ultimate Analysis	Carbon	42.65	43.32	26.73	34.90	43.87	44.31	44.37
	Hydrogen	5.57	6.20	4.05	5.15	5.82	5.73	5.77
	Oxygen	49.16	49.37	66.57	59.00	47.30	49.11	49.23
	Nitrogen	1.49	0.93	1.02	0.31	2.23	0.63	0.34
	Sulphur	<0.10	<0.10	0.56	0.64	0.57	<0.10	0.10
	Chlorine	1.05	0.27	1.09	<0.01	0.23	0.13	0.19
Heating values		16.24	16.99	12.26	14.08	17.93	16.88	18.61
Chemical Composition	Cellulose	43.84	38.26	31.26	37.34	36.44	42.86	44.40
	Hemicellulose	24.39	46.59	7.29	10.07	11.92	22.45	15.50
	Lignin	9.03	7.16	28.39	41.08	33.97	15.39	31.70

Table 4.18 Product distribution of fast pyrolysis of the biomasses with temperature

Biomass type	Product yield (%wt.)	Temperature (°C)						
		400	450	500	550	600	650	700
Corn cobs	Bio-oil	48.2		54.4	57.0	56.4	55.0	52.0
	NCG	12.0		13.6	14.0	15.6	19.0	23.0
	Char	39.8		32.0	29.0	28.0	26.0	23.0
Corn straw	Bio-oil	60.0		66.0	65.0	63.5		62.0
	NCG	10.0		15.0	16.0	25.5		27.0
	Char	30.0		18.0	14.0	11.0		11.0
Rice straw	Bio-oil	53.2		60.0	59.0	54.6		50.5
	NCG	8.2		13.2	19.8	26.8		32.5
	Char	38.6		26.8	21.2	18.4		17.2
Rice husk	Bio-oil	53.0		60.0	53.0	49.4		45.0
	NCG	12.0		22.8	28.4	33.8		39.2
	Char	35.0		21.2	18.6	16.8		15.8
Sugarcane bagasse	Bio-oil	35.0	48.0	61.5	56.0	50.0		40.0
	NCG	12.0	23.8	21.0	22.0	26.0		35.0
	Char	45.0	28.2	18.0	17.0	15.0		14.0
Cocoa pod husk	Bio-oil	50.0	52.4	53.0	52.0	49.0		46.5
	NCG	12.0	18.0	22.8	28.4	32.0		37.0
	Char	38.0	29.6	24.2	19.6	18.4		16.5
Wawa sawdust	Bio-oil	58.0	61.0	62.0	58.0	55.0		50.0
	NCG	10.0	13.0	17.0	25.0	30.0		35.0
	Char	32.0	26.0	21.0	17.0	15.0		15.0

Table 4.19. Key design parameters for bio-production using fast pyrolysis

Parameter	Value
1. Feedstock	
Type	Lignocellulosic biomass (wood residue such as wawa sawdust), agricultural crop residues including sugarcane bagasse, corn cob and stalk, rice straw and husk and cocoa pod husk).
Moisture content	8–10 %
Throughput	200 ton /day
Particle size	1–2 mm
2. Pyrolysis design	
Pyrolysis type	Bubbling fluidized bed reactor
Pyrolysis temperature	450–550 °C (500 °C)
Pressure drop across the reactor	5 KPa
Input pressure	30 KPa
Retention/residence time	1–6 s
Feed	800 kg/h
Feed ground particle size	1–2 mm
3. Gas	
Carrier gas (Nitrogen gas)	2.75 kg/kg feed
Bed material	Silica sand
Particle size diameter	1 mm
Density	3.4 g/cm ³
4. Yield (% dry wt)	
Bio-oil	53–66
Bio-char	18–27
Non-condensable gas	13–23
Water and others	12–27

NB. Nitrogen gas is used for process start up. For the steady state operation, recycled clean flue gases are to be used in the fluidized bed pyrolyzer.

CHAPTER FIVE

5.0 DISCUSSION

This chapter presents a discussion on the results of the analyses carried out in Chapter 3. It is categorized into four sub-chapters. The first sub-chapter discusses the results of the characterization of the selected biomasses. The second sub-chapter discusses the results of fast pyrolysis, while the third sub-chapter discusses the results of the characterization of the bio-oils, which were obtained as maximum yields for energy purposes. The last sub-chapter presents and discusses a scheme for bio-oil production using the selected lignocellulosic biomasses. Finally conclusions are drawn based on the results discussed in this chapter.

5.1 Characterization of the lignocellulosic biomass samples

Characterization of the biomass samples is discussed under the following sub-chapters: proximate analysis, ultimate analysis, chemical composition analysis, mineral ash composition and HHVs. The characteristics of a particular type of biomass provide useful information in the evaluation of its suitability as biofuel feedstock in various thermochemical applications. The chemical composition provides information on cellulose, hemicellulose and lignin content, potential yields of bio-oils and the composition of chemical compounds in the bio-oils.

5.1.1. Proximate Analysis

The proximate analysis characterizes biomass and bio-oils in terms of their moisture content, volatile matter, fixed carbon and ash content. Table 4.1 shows the results of the proximate analysis obtained on a dry and ash free (daf) basis. The characteristics of a particular type of biomass provide useful information in the evaluation of its suitability as biofuel feedstock in various applications. The ultimate analysis and determination of HHVs are particularly

important in the evaluation of the feedstock in terms of its heating value and potential technical problems such as reactor slagging and pollution (Renew Fuel, 2003; Ji-lu, 2007).

The moisture content (MC) of the biomass can have different effects on pyrolysis product yields. All the biomass samples had high MC, which ranged from 6.0 to 10.3 %wt. respectively for wawa sawdust to cocoa pod husk. Fast pyrolysis is, in general, conducted using a dry biomass feedstock with MC around 10 %wt. Water plays a major role in the pyrolytic process by influencing the final MC of the bio-oil. During pyrolysis water is produced as a major portion in the liquid product. Together with the water in the biomass, they constitute the water content of the bio-oil produced.

All the lignocellulosic biomass samples showed high values for volatile matter, which ranged from 45.68 to 80.72 %wt and fixed carbon contents, which ranged from 1.33 to 12.01 %wt. The wawa sawdust showed a high amount of volatiles of 80.48 %wt. Fixed carbon content was also high in both the wawa sawdust and cocoa pod husk, due possibly to the high lignin content of these samples. The rice straw, however, had a low fixed carbon content of 1.33 %wt. Garcia-Perez *et al.* (2010) reported fixed carbon content of sugarcane bagasse to be 11.9 %wt. Prolonged drying in the oven, however, can result in loss of the volatile constituents due either to decomposition, distillation or oxidation of the biomass. Since biomass rapidly absorbs moisture, dry biomass has to be stored carefully in closed vessels (Renew. Fuel, 2003).

5.1.2 Ultimate Analysis

The ultimate analysis of the lignocellulosic biomass samples gives an indication of the elemental carbon (C), hydrogen (H), nitrogen (N), chlorine and sulphur (S) contents. Oxygen content was obtained by calculating the difference between 100% and the sum of C, H, N and S contents (Zanzi *et al.*, 2002; Mullen *et al.*, 2011; Zhu and Lu, 2010). The ultimate analysis showed that all the lignocellulosic biomass samples had high oxygen and carbon contents, but low nitrogen, sulphur and chlorine levels (Figure 4.2). The cocoa pod husk showed the highest nitrogen level of 2.23 %wt. while the rice straw and husk had low nitrogen levels of 1.02 and 0.31 %wt. respectively.

The high oxygen content, which ranged from 47.30 to 66.57 %wt respectively for the cocoa pod husk and the rice straw, is expected to yield bio-oils containing many oxygenated compounds and a high moisture content. Hydrogen content ranged from 4.05 to 6.02 %wt. respectively for the rice straw and corn cobs. Carbon content was high in all the biomass samples except in the rice straw and husk. It was 44.31 %wt. for the sugarcane bagasse, 43.90 %wt. for the cocoa pod husk, 43.32 %wt. for corn cobs and 42.65 %wt. for the corn stalk. Tsai *et al.* (2006) and Garcia-Perez (2010), however, reported a higher carbon content for sugarcane bagasse than was obtained in this study.

Chlorine levels were very low in all the biomass samples, except in the rice straw and corn stalk respectively, which were 1.09 and 1.05 %wt. They were approximately 1.0 %wt. in the rice straw and corn stalk, but below 0.1 %wt. in corn cobs, sawdust, cocoa pod husk and sugarcane bagasse. Sulphur contents in the rice straw and husk respectively were 0.56 and 0.64 %wt. However, they were below 0.10 %wt. in corn cobs and sugarcane bagasse. The low sulphur and nitrogen levels in the biomasses indicated that low sulphur and nitrogen

levels would be expected in the bio-oils, and low SO₂ and NO₂ emissions on their combustion (Mullen *et al.*, 2010).

5.1.3 Ash composition

The mineral matter was composed mainly of Si, Ca, K, Na and Mg together with small amounts of S, P, Fe, Mn and Al. It varied with the type of lignocellulosic biomass and occurred as oxides, silicates, sulphates, chlorides and phosphates (Raveendran *et al.*, 1995) (Table 4.3). This was confirmed in this analysis. High ash content could affect the yields of bio-oil during fast pyrolysis since it catalyses the formation of char. Silica was the most abundant oxide in both the rice straw and husk, and measured 16.3 and 22.38 %wt. respectively. It was, however, low in the other biomasses including the corn stalk and sugarcane bagasse. The high silica content in the rice husk (22.38 %wt.) and straw (16.30 %wt.) reflected their high ash contents. Potassium oxide was the most abundant inorganic compound in the cocoa pod husk, rice straw and corn stalk. It was 5.03, 2.10 and 1.00 %wt. in the cocoa pod husk, rice straw and corn stalk respectively. Phosphorus levels were below 0.50 %wt. except in the corn stalk (1.6 %wt).

5.1.4 Higher heating values

The HHVs of the corn stalk and cobs respectively were 16.24 and 16.99 MJkg⁻¹ were lower than those reported by Mullen *et al.* (2010). The rice husk had a higher HHV than the rice straw. Jung *et al.* (2008) reported the HHV of rice straw to be 16.00 MJkg⁻¹. Ji-lu (2008) also reported an HHV of rice husk to be 13.36 MJkg⁻¹, which was lower than the results obtained in this study. It would imply that the rice husk sample used in this analysis may have higher energy content than that used by this author probably due to the source of origin. Among the biomass samples studied, wawa sawdust had the highest HHV of 18.61 MJ kg⁻¹. It was higher

than that for bamboo sawdust reported by Jung *et al.* (2008), which was 17.7 MJkg^{-1} . The HHVs of the cocoa pod husks and sugarcane bagasse respectively were 17.93 and 16.88 MJkg^{-1} .

5.1.5 Chemical compositional analysis

Cellulose, which was estimated as the difference between acid detergent fibre and lignin was high in all the biomass samples, and ranged from 30.41 to 44.40 %wt. respectively for the cocoa pod husk and wawa sawdust. Since bio-oil yields generally depend mainly on the cellulose content in the lignocellulosic biomass, it is expected that lignocellulosic biomass such as wawa sawdust, which has high cellulose contents will produce high yields of bio-oil.

Hemicellulose content, which was estimated as the difference of the neutral detergent fibre and acid detergent was high in corn cobs (46.59 %wt.), corn stalk (24.39 %wt.) and sugarcane bagasse (22.45 %wt.). Rice straw, cocoa pod husk and wawa sawdust were, however, characterized by low hemicellulose contents, which were 7.29, 11.97 and 15.5 %wt. respectively. The carbohydrate composition of lignocellulosic biomass such as wood and agricultural residues is generally not much different, and could be represented approximately by $\text{C}_6\text{H}_9\text{O}_4$. It may be regarded as a mixture of 50 %wt. carbon with 50 %wt. water (Renew fuel, 2003).

Hemicellulose is thermally less stable than cellulose due to lack of crystallinity but its reaction mechanism during pyrolysis is similar to that of cellulose. Fast pyrolysis of glucomannan in hemicellulose results in products similar to those of cellulose, while products obtained from the pyrolysis of xylan differ from those of cellulose (Zhu and Lu, 2010). Shen

and Gu (2009) proposed a detailed possible routes for the formation of major products from xylan chains (Figure 5.1 refers).

Lignin content was high in the rice husk (41.08 %wt.), the cocoa pod husk (33.97 %wt.) and the rice straw (28.39 %wt.), but low in the corn cobs (7.16 %wt.). Mullen *et al.* (2010) reported low lignin contents of 3.30 %wt. for corn cobs and 6.3 %wt. for corn stover. Zhang *et al.* (2009) reported higher cellulose and lignin contents for corn cobs, but lower hemicellulose content than was obtained in this study. High lignin content may affect bio-oil yields since it promotes secondary reactions which result in char formation.

Primary pyrolysis of lignin begins around 200 °C with softening of the lignocellulosic biomass and results in higher yields of char but lower bio-oil yields than that of cellulose and hemicellulose. The major product is char, most of which is retained during the secondary reactions. The liquid products from the pyrolysis of lignin are classified into three major groups, namely: (i) the large molecular-weight compounds (known as pyrolytic lignin), (ii) low-molecular-weight compounds and (iii) small compounds such as methanol and acetic acid (Shen and Gu, 2009; Garcia-Perez *et al.*, 2010).

According to Garcia-Perez (2007), lignin inhibits the de-polymerization of levoglucosan, which is formed from the pyrolysis of cellulose. It, however, promotes the formation of compounds such as methanol from the decomposition of cellulose. Cellulose, however, inhibits char formation from lignin during secondary reactions but enhances the yields of products such as guaiacol and 4-methyl-guaiacol.

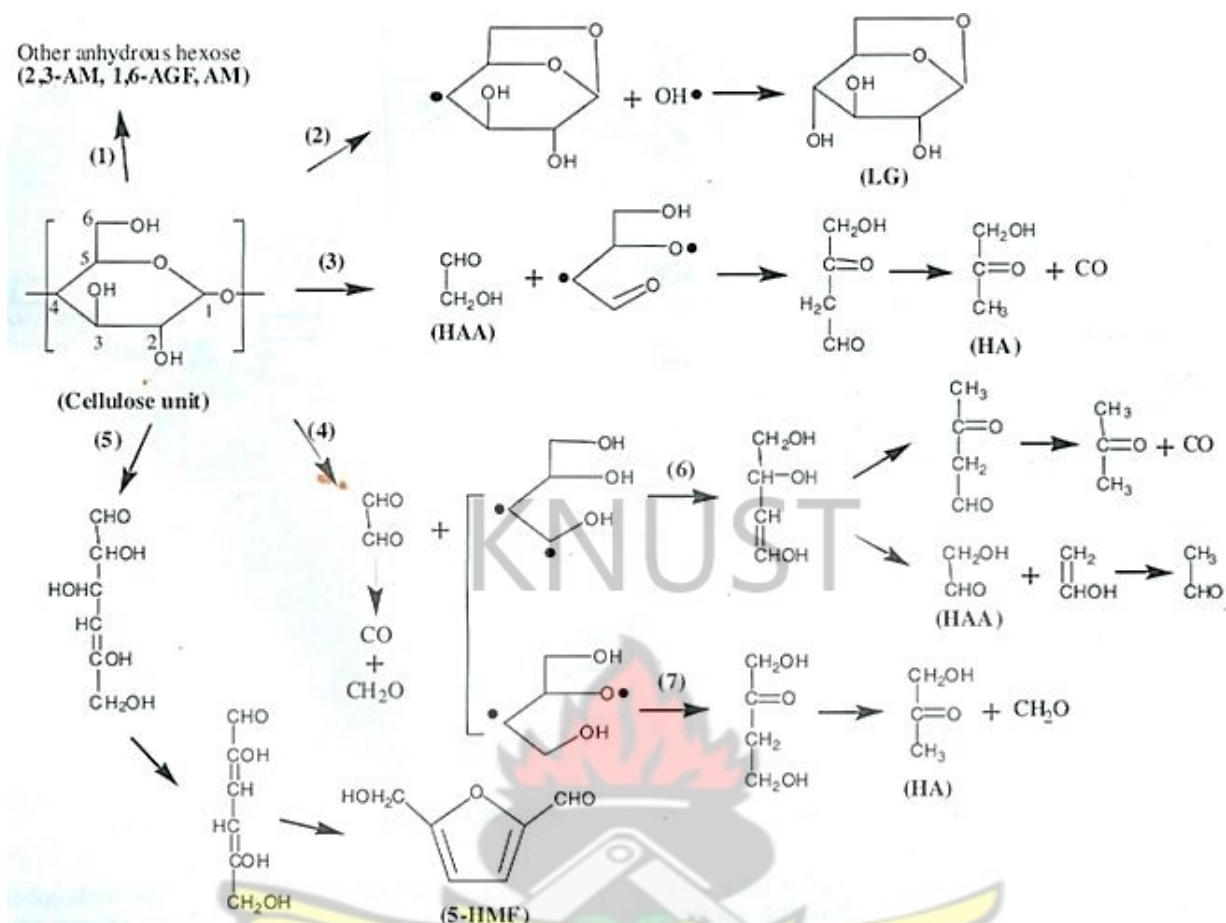


Figure 5.1: Proposed scheme for the degradation of cellulose during fast pyrolysis.
Source: Shen and Gu, 2009.

5.1.6 Significance of the work

Forestry, wood processing and agricultural practices in Ghana and globally generate considerably large amounts of residues and wastes, which either remain in mills or are normally left on farms during harvesting. These residues and wastes offer no significant value but rather pose serious environmental disposal problems. However, they may be considered as potentially sustainable and suitable feedstock for bio-oil production because of their abundance, low-cost nature, the high cellulose and hemicellulose content and the need to identify uses for these problematic wastes and residues. Their utilization as bio-oil feedstock will help tackle problems such as unsustainable availability of biofuel feedstock, high feedstock costs and food security feedstock. The use of lignocellulosic biomass as feedstock

for bio-oil production would reduce potential competition that exists between food, animal feed and biofuels since it is a non-food renewable resource.

This work has many potential benefits at the national level in terms of sustainable supply of bio-oil feedstock and environmental sustainability. It could contribute to current knowledge base on lignocellulosic biomass by providing information on the characteristics such as proximate, ultimate, chemical composition and HHVs of the selected lignocellulosic biomass available in Ghana and their suitability as feedstock for bio-energy production. This would enable bio-oil producers to select suitable types of lignocellulosic biomass as feedstock for bio-oil production. The information on the cocoa pod husk, which constitutes a major harvesting residue in the country would be significant since this residue could be used as a feedstock for biofuel production.

The utilization of these lignocellulosic biomasses as bio-oil feedstock will provide additional income to both local farmers and bio-oil feedstock producers, reduce their poverty levels and promote rural development by the government. It will also reduce the large volume of waste and residues generated by agricultural and wood processing activities in the county and thus have significant economic and environmental benefits for the country.

At the international level, the results of this work provide information on the selected lignocellulosic biomasses available in Ghana, which could be included in the list of global biofuel feedstock. Moreover, their wide and large availability as a renewable resource implies that bio-oil production could be undertaken globally.

5.1.7 Conclusion

Of all the biomass samples characterized, the corn stalk, wawa sawdust and sugarcane bagasse samples proved to possess the most suitable characteristics for bio-oil production due to their high carbon, cellulose and volatile matter contents as well as HHVs and produced the highest bio-oil yields during the fast pyrolysis. The cocoa pod husk and rice husk, however, possessed the least suitable characteristics due to the high silica, low carbon and cellulose contents as well as HHVs and produced the least maximum bio-oil yields of 53.0 and 56.0 %wt. respectively. Bio-oils produced from these biomasses would be expected to generate low SO₂ and NO₂ on combustion.

5.2. Effect of temperature on fast pyrolysis product distribution

This sub-chapter looks at the effect of temperature on product distribution from fast pyrolysis in a fluidized-bed. The yields of each of the major products at different temperatures are also analyzed. The effect of biomass type and composition on product yields is also analyzed.

5.2.1 Fast pyrolysis product distribution

The temperature employed for fast pyrolysis is one of the major parameters, which affect the distribution of products and bio-oil characteristics. The kinetic mechanism for pyrolysis shows that primary reactions occur between 200 and 470 °C, which results in the formation of bio-char. Above 400 °C, the bio-char slowly undergoes various physical and chemical changes to produce bio-oil and non-condensable gas (NCG) (Garcia-Perez, 2010; Mullen *et al.*, 2010) (Figure 2.10).

Generally, maximum yields of bio-oils were obtained between 500 and 600 °C. As the temperature increased, bio-oil yield increased and reached a maximum of 50.0 %wt. at 500

°C. It then decreased considerably at 700 °C. Non-condensable gas (NCG) yields also increased as the temperature increased from 400 to 700 °C. Bio-char yields, however, decreased as the temperature increased from 400 to 700 °C.

The results obtained in this study compared well with those reported on the effect of temperature on fast pyrolysis of corn cobs, straw and stover in fluidized-bed reactors by some authors including Putun *et al.* (2001), Lee *et al.* (2005), Asadullah *et al.* (2008), Zhang *et al.* (2009), Aannidou *et al.* (2009) and Mullen *et al.* (2010). As the temperature increased, secondary reactions such as cracking or breaking-up of the vapours into small unit occurred, which decreased the bio-oil yields.

Mullen *et al.* (2010) reported maximum bio-oil yields from the pyrolysis of corn cobs in a fluidized-bed reactor at 550 °C to be 61.0 %wt. However, Shen and Gu (2009) also reported maximum bio-oil yields from fast pyrolysis of cellulose at 580 °C at a residence time of 0.4 sec. According to these authors, as the temperature increased, NCG yields also increased. However, char yields decreased due to secondary reactions which occurred.

Similar results were reported for the fast pyrolysis of rice straw and husk in a fluidized-bed reactor by some authors including Putun *et al.* (2001), Lee *et al.* (2005), Worasuwannarak *et al.* (2007), Jung *et al.* (2008) and Ji-lu (2008). Bio-oil yields obtained from the rice straw and husk were lower than those from the fast pyrolysis of wood. This was mainly due to the lower cellulose and hemicellulose contents in the rice straw and husk than in wood, and also the high mineral content in the ash of rice straw and husk (Lee *et al.*, 2005).

Tsai *et al.* (2006) reported maximum bio-oil yields of 50.0 %wt. at 600 °C for fast pyrolysis of rice straw in an induction-heating reactor. Bio-oil yield from the rice straw were lower than those obtained from sugarcane bagasse. High yields of NCG were obtained above 700 °C (El Harfi *et al.*, 1999; Ozbay *et al.*, 2001; Fisher *et al.*, 2002). Similar results were obtained for the pyrolysis of cocoa pod husk and wawa sawdust (Tables 4.12 and 4.13, and Figures 4.11 and 4.12). Slight differences in product yields were due mainly to biomass type and composition (Lee *et al.*, 2005; Mullen *et al.*, 2010; Heo *et al.*, 2010).

The ash content in lignocellulosic biomass is important in fast pyrolysis using fluidized-bed since the ash becomes sticky and increases the chance of reactor slagging. Small amounts of ash catalyze the decomposition of both cellulose and hemicellulose during secondary reactions, which result in the formation of bio-char and reduced bio-oil yields. This results also in high yields of hydroxyacetaldehyde (HAA) during both primary and secondary reactions. Since HAA is also formed from the secondary cracking of primary products such as anhydrosugar. It is the most abundant organic compound in bio-oils. High concentrations of char particles in bio-oils affect the performance of combustion systems due to release of ash and alkali metals (Raveendran *et al.*, 1995).

5.2.2 Significance of the work

At the national level, this work would provide relevant information on the fast pyrolysis product yields of the selected lignocellulosic biomasses at different temperatures and pyrolytic characteristics of these lignocellulosic biomasses. Bio-oil producers would use this information to select suitable types of lignocellulosic biomass for bio-oil production. It would also contribute to existing knowledge base of fast pyrolysis

5.2.3 Conclusion

During the biomass fast pyrolysis, bio-oil yields initially increased from 53.0 to 60.0 %wt. for the rice straw as the temperature increased from 400 to 500 °C and then reduced to 50.3 %wt. as the temperature increased further to 700 °C. The non-condensable gas yields such as CO, CO₂, CH₄ and H₂ increased from 8.2 to 32.5%wt. while bio-char yields decreased from 38.6 to 17.2 %wt. as the temperature increased from 400 to 700 °C. The increase in non-condensable yields with increase in temperature results from the conversion of bio-oil to gas mostly from the decomposition of cellulose (Figure 2.13 refers). Similar trends were obtained for the pyrolysis of the other biomasses studied. Thus, product distribution of fast pyrolysis varies differently as the temperature increases and the lignocellulosic biomasses have suitable pyrolytic characteristics, which enable them to be used as feedstocks for fast pyrolysis. Slight variations in product yields may be due to differences in biomass composition.

5.3. Characterization of the bio-oils

This sub-chapter discusses the results obtained from the characterization of the bio-oils in terms of physical and ultimate characteristics using different analytical techniques. The results enable the fuel characteristics of the bio-oils to be compared with light petroleum oil (diesel oil) and their suitability as substitute or replacement fuel to fossil fuels. Conclusions are drawn from the results obtained.

5.3.1. Physical characteristics

Tables 4.14 and 4.15 show the results of physical characterization of the bio-oils, which included the elemental analysis, HHVs, density, viscosity and pH obtained from the different biomass samples at maximum yield temperatures. The bio-oils were acidic with a pH of 2.8 for the rice husk, rice straw and corn cobs bio-oils. The high acidity of bio-oils, would make

them corrosive particularly at high temperatures due mainly to the high content of carboxylic organic acids such as acetic acid and formic acid (Czernik and Bridgwater, 2004; Zhang *et al.*, 2011).

The viscosities of the bio-oils, which ranged from 128–240 mm²/s at 20 °C were similar to those reported by Zhang *et al.* (2009) for corn cobs and stover. Several factors such as temperature, biomass composition and type, water content and ageing affect the viscosity of bio-oils (Zhang *et al.*, 2011). Temperature and the presence of char in bio-oils are some major factors that affect the rate of ageing of bio-oils. High temperatures increase the viscosity of bio-oils. Increases in the viscosity of bio-oils during storage also affect their ability to combust efficiently in turbines and furnaces. Bio-oils with low viscosities are also easier to pump and atomize than those with high viscosities (Diebold, 2002).

5.3.2. Ultimate analysis

The ultimate analysis showed that carbon contents were high, which ranged from 41.7 %wt. for the rice husk bio-oil to 65.7 %wt. for the rice straw bio-oil. Oxygen content was also high, which ranged from 25.6 %wt. for the rice straw bio-oil to 50.3 %wt. for the rice husk bio-oil respectively. The high oxygen content was due to the presence of high concentration of oxygenated compounds. This may have contributed also to the high viscosities of the bio-oils.

The carbon-to-oxygen (C:O) and hydrogen-to-carbon molar ratios (H:C) of the bio-oils respectively were 0.76–3.42 and 1.40–.22 respectively (Table 4.15). C:O molar ratios indicate the carbohydrate content as well as the acidity of the bio-oil whereas C:H ratios give an indication of the energy content. According to Mullen *et al.* (2010), bio-oils generally have higher H:Cs than the original biomasses since most of the water content is removed

during fast pyrolysis. The bio-oil obtained from rice husk had the highest H:C of 2.22. However, the rice straw bio-oil had the lowest H:C value of 1.40. The high C:Os of the bio-oils may be due to loss of oxygen from the biomass during fast pyrolysis (Mullen *et al.*, 2010).

The bio-oils were denser than water with the densities, which ranged from 1,180 to 1,220 kgm⁻³ respectively for bio-oils obtained from corn cob and its stalk. Mullen *et al.* (2010) reported that the energy densities (i. e. the amount of energy per unit volume) of bio-oils obtained from fast pyrolysis of corn residues were higher than those of the original biomass samples. They concluded that it was more efficient and cost-effective to transport them than corn residues.

The HHVs of the bio-oils ranged from 16.8 to 23.3 MJkg⁻¹ respectively for corn cobs and rice straw bio-oils. However, they were lower than that of heavy fuel oil (40.0 MJkg⁻¹). The HHV of the corn stalk bio-oil was slightly higher than that of corn cobs bio-oil probably due to its lower moisture content, but it was higher than those for bio-oils produced from the rice husk and rice straw (Putun *et al.*, 2004).

The bio-oils had high MCs, which ranged from 12.0 %wt. for the sugarcane bagasse bio-oil to 26.7 %wt. for that obtained from cocoa pod husk. The corn stalk, corn cobs and wawa sawdust bio-oils respectively had MCs of 22.5, 22.9 and 24.5 %wt. These values fall within those reported by Mullen *et al.* (2010) for bio-oils obtained from the fast pyrolysis of hardwoods had moisture contents, which ranged from 15.0 to 30.0 %wt. The high MC could be due to the high MC of the biomass and some dehydration reactions, which occurred during

fast pyrolysis. The relatively low HHV of bio-oils, however, is due to the high MC and the presence of many oxygenated compounds (Putun *et al.*, 2001; Zhang *et al.*, 2011).

Generally, sulphur and nitrogen levels in the bio-oils were below 1.0 %wt. The bio-oil obtained from rice straw showed the highest nitrogen level of 1.08 %wt. However, bio-oils obtained from the corn straw had the highest sulphur content of 0.3 %wt. The low nitrogen and sulphur levels make bio-oils environmentally friendly on combustion since they would generate low NO₂ and SO₂ emissions. Inorganic compounds, particularly those derived from potassium and calcium catalyze reactions such as polymerization and condensation within bio-oil during its storage. Therefore, it is necessary to remove them during pyrolysis. This could be achieved by means of either carbon filters (Raveendran *et al.*, 1995; Lee *et al.*, 2005).

Bio-oils are generally composed of many organic compounds, which are derived from the decomposition of cellulose, hemicellulose and lignin. Mullen *et al.* (2010) quantified some compounds found in the bio-oils of corn stover and corn cobs. According to these authors, the compounds, which were most abundant in the bio-oils (other than water) were small water-soluble oxygenated molecules such as levoglucosan, acetic acid and HAA derived from cellulose and hemicellulose in the corn crop residues. Compounds that were directly derived from the decomposition of cellulose included levoglucosan and HAA. According to these authors, these compounds were generally found in higher quantities in bio-oils obtained from corn stover, which indicated high cellulose content in that feedstock.

The decomposition of lignin, however, yields many water-insoluble phenolic compounds such as phenol, guaiacol and isoeugenol. The most abundant small phenolic compound

derived from lignin found in the bio-oil obtained from corn cobs was phenol, while that found in the bio-oil obtained from corn stover was isoeugenol (Mohan *et al.*, 2006; Ji-lu, 2007; Mullen *et al.*, 2010).

The high oxygen content and MC of bio-oils require them to be up-graded before they can be used effectively as substitutes or replacement for conventional fossil fuels for transportation. Up-grading processes such as hydro-treating and hydro-cracking using catalysts including zeolites separate the oxygenated organic components from the water phase, raise their HHVs and reduce their corrosiveness (Garcia-Perez, 2001; Ji-lu, 2007; Zhang *et al.*, 2009; Heo *et al.*, 2010; Mullen *et al.*, 2010) (Appendix 2). The non- condensable gas obtained from the fast pyrolysis of corn cobs was composed mainly CO and CO₂ with small amounts of CH₄, H₂, ethane (C₂H₆) and ethene (C₂H₄) (Table 4.16 and Figure 4.14). This compares favourably with those reported for the fast pyrolysis of corn stalk, cob and stover, rice husk and sugarcane bagasse by Ji-lu (2007), Zhang *et al.* (2009), Mullen *et al.* (2010) and Heo *et al.* (2010).

Bio-char is a co-product of fast pyrolysis of biomass. It is a fine-grained, highly porous charcoal. Naturally, it is found in soils as a result of vegetation fires and historic soil management practices, for example, bio-char-rich dark earths in the Amazon (terra preta). The suitability of a particular type of lignocellulosic biomass as a potential feedstock for the production of char depends on various characteristics such as moisture, fixed carbon, oxygen, hydrogen, nitrogen, volatile matter and ash contents as well as high heating values (Duku *et al.*, 2011).

The major characteristics of char include its high soil organic matter, high nutrient and water holding capacities, enhanced soil fertility and stable carbon structure (Lal, 2008). Mullen *et al.* (2010) reported the HHVs of chars produced from corn cobs and corn stalk respectively to be 30.0 and 21.0 MJ kg⁻¹. Nitrogen and sulphur levels were also reported to be 0.5–1.5 %wt. and 0.02–0.15 %wt., which indicated that NO₂ and SO₂ emissions from the combustion of bio-char would be very low. Char can be used as a renewable solid fuel (Glasser *et al.*, 2002; Hansen *et al.*, 2008; Laird, 2008; Mullen *et al.*, 2010).

5.3.3 Significance of the work

The results give information on the characteristics of the bio-oils produced from the selected biomasses and their suitability as a substitute or replacement to fossil fuels for various applications such as furnaces, boilers and transportation, which is significant at the national and international levels.

5.3.4 Conclusion

Characterization of the bio-oils showed that:

All the bio-oils were acidic with the pH ranging from 2.10 to 3.20 for wawa sawdust and corn stalk bio-oils respectively compared to petroleum diesel oil with a pH of 5.7. The high acidity of the bio-oils makes them corrosive and this property could affect the containers used for their storage. Moisture contents, which ranged from 12.0 to 26.0 %wt. respectively for sugarcane bagasse and rice straw bio-oils were extremely high compared to diesel oil and heavy fuel oil with low moisture content of 0.1 %wt.

This, together with the high oxygen content, high pH and high density makes them less suitable since they may have reduced ignition properties and stability compared to petroleum

light oil (diesel oil) and heavy oil. The densities, which ranged from 1150 to 190 kgm⁻³ respectively for sugarcane bagasse and rice husk indicate that the bio-oils are denser than water but less dense than either light petroleum oil (diesel oil) (854 kgm⁻³) or heavy fuel oil (963 kgm⁻³). The viscosity of the bio-oils, however, varies with temperature since they are unstable and also age with time.

The HHVs ranged from 16.8 to 23.30 MJkg⁻¹ for the rice straw and wawa sawdust bio-oils respectively, lower than those of light petroleum oil and heavy fuel oil, which are 42.9 and 40.7 MJkg⁻¹. Carbon contents, which ranged from 41.7 to 65.68 %wt. respectively for the rice straw and its husk are lower than those of light petroleum oil and heavy fuel oil, which are 86.3 and 86.1 %wt, respectively. The low sulphur and nitrogen contents indicate that they would emit low or less SO₂ and NO₂ during combustion than either light petroleum oil or heavy fuel oil, which have sulphur contents of 0.9 and 2.1 %wt. respectively.

These fuel characteristics indicate that the bio-oils have lower fuel properties compared to light petroleum oil. However, they could be up-graded by hydrodeoxygenation or catalytic means to remove high water and oxygen contents and used as a substitute or replacement fuel for transportation. The low sulphur and nitrogen content in the bio-oils, however, gives them an advantage over light petroleum oil since they would emit low SO₂ or NO₂ during combustion.

5.4. Proposed scheme for the production of bio-oil from lignocellulosic biomass

This sub-chapter looks as a scheme, which has been developed for bio-oil production from the selected lignocellulosic biomasses using fast pyrolysis. The scheme is based on the results and conclusions of the preceding two chapters. It aims to add value in a cost-effective manner

to large quantities of residues and waste, which are sustainably generated from the activities of forestry, wood processing and agriculture.

5.4.1 Scheme for bio-oil production from the selected lignocellulosic biomasses

A scheme has been developed for sustainable and cost-effective production of bio-oil from the selected lignocellulosic biomasses based on the results of this study including the characterization of the selected lignocellulosic biomasses, product distribution during fast pyrolysis at different temperatures and the characterization of the bio-oils for energy (Figure 4.15; Tables 4.17 and 4.18 refer). Product distribution depends on temperature, biomass type and composition.

The production and application of the products of fast pyrolysis are of immense interest due to the large availability of many types of lignocellulosic biomass both at the national and global level. Therefore, this scheme has a high potential to contribute significantly to reduce the dependence on fossil fuels, reduce GHG emissions and promote sustainable development. The use of bio-oils as a replacement energy source to major transportation fuels and stationary fossil fuels in the country and globally could result in lower fuel prices compared to that of crude fossil fuel, reduced dependence on fossil fuels, reduced GHG emissions, job creation and rural income generation.

Since lignocellulosic biomass is a widely available renewable resource, bio-oil production could be undertaken globally. As a result of some undesirable characteristics of bio-oils such as high moisture and oxygen content and high acidity, there is a need to up-grade them if they are to be used as alternative sources to fuels for transportation.

5.4.2 Significance of the work

This scheme would enable bio-oils to be produced locally from a low-cost, non-food resource. This will help to tackle problems such as unsustainable availability of biofuel feedstock, feedstock costs and food, animal-feed and fuel competition faced by biofuel manufacturers, feedstock producers and government. Lignocellulosic biomass will provide also an additional source of income to farmers and feedstock producers and help them reduce poverty. It could also be used by government to promote rural development. Bio-oil production using these lignocellulosic biomasses in Ghana will contribute to global biofuel production and supply. It will contribute to global food security. Bio-oils can be used as a substitute or replacement to fossil fuels for transportation to reduce dependence on fossil fuels. Their use will also result in GHG emissions reduction. The char can be used to enhance soil fertility at both the national and global level. It could also be applied in soils to contribute to global climate change mitigation.

5.4.3 Conclusion

The proposed scheme for bio-oil production re-uses the co-products of fast pyrolysis as process heat to reduce production cost and would result in cost-effective and maximum utilization of the selected lignocellulosic biomasses, which currently offer little value but rather pose serious environmental disposal problems in the country and globally. Clearly, bio-oils are of immense interest at both the national and international levels since they could be used as a substitute or replacement to light petroleum oils in many applications. The large availability of different types of lignocellulosic biomass in Ghana and globally gives this scheme a high potential to contribute to the solution of the current high cost of transportation fuels, need for GHG emission reduction, climate change mitigation and sustainable development.

CHAPTER SIX

6.0. GENERAL CONCLUSION AND RECOMMENDATIONS

This chapter summarizes the conclusions that were drawn throughout the thesis and the novelties made from this work. Finally, recommendations are made for future work in the field of fast pyrolysis.

6.1. Conclusion

This study focused on bio-oil production from lignocellulosic biomass using fast pyrolysis in a fluidized-bed reactor as replacement or substitute energy source to reduce dependence on imported and expensive fossil fuels for transportation and stationary engine applications. Characterization of seven lignocellulosic biomasses, namely agricultural crop residues and wood processing waste collected from various parts of Ghana shows that:

The proximate analysis gave a high moisture content ranging from 6.03 to 10.29 %wt. respectively for the wawa sawdust and the cocoa pod husk, a high volatile matter ranging from 45.68 to 80.72 %wt. respectively for rice straw and corn cobs, high fixed carbon contents of 10.43 and 12.01 %wt. respectively for the cocoa pod husk and wawa saw dust as well as high ash contents of 45.76 and 24.71 %wt. for rice straw and its husk.

The high moisture contents indicate that the moisture content of the bio-oils that would be produced would be high. Furthermore, the biomasses with high volatile matter and fixed carbon contents would be expected to give high bio-oil yields during the biomass fast pyrolysis.

The XRF analysis gave low content below 1.0 %wt of inorganic oxides such as sodium oxide, iron oxide and phosphorous oxide for all the biomasses except the cocoa pod husk with potassium oxide content of 5.03 %wt. and rice straw and its husk, which had high silica contents of 16.30 and 22.38 %wt. respectively. Since silica catalyzes the biomass fast pyrolysis, especially during the secondary reactions, the high silica content in rice straw and its husk would be expected to reduce bio-oil yields but increase char yields. The low ash contents also indicate that very little slagging would be expected to occur during the fast pyrolysis.

The ultimate analysis gave a high carbon content ranging from 41.7 to 65.7 %wt. respectively for the rice husk and its straw as well as a high oxygen content ranging from 47.30 to 66.57 %wt. respectively for the cocoa pod husk and the rice straw. Thus, bio-oils obtained from these biomasses would be expected to contain some oxygenated organic compounds such as acids and aldehydes. The low sulphur content below 1.00 %wt. given for all the biomass samples and nitrogen levels of 1.49 and 2.23 %wt. for the corn stalk and cocoa pod husks, however, indicate that low nitrogen and sulphur contents would be expected in the bio-oils that would be obtained.

The chemical analysis gave a high cellulose content ranging from 30.40 to 44.40 %wt. for the rice straw and wawa sawdust respectively, a high hemicellulose content of 46.59 %wt. for the corn cobs and a high lignin content of 41.08 %wt. for the rice husk. The HHVs ranged from 12.26 to 18.61 MJ.kg⁻³ for the rice straw and the wawa sawdust. Thus, all the seven biomasses could be considered as suitable feedstocks for biomass fast pyrolysis due to the favourable chemical composition such as high carbon, cellulose and volatile matter contents and would be expected to give high bio-oil yields with high calorific values.

Of all the biomasses characterized corn stalk, wawa sawdust and sugarcane bagasse gave the best characteristics such as high volatile matter, carbon and cellulose contents as well as high heating values, which make them suitable for use for bio-energy production. Cocoa pod husk and rice husk, however, proved to have the least suitable characteristics for bio-energy production.

During the biomass fast pyrolysis in a fluidized bed reactor, bio-oil yields initially increased to maximum values of 60.0 and 66.0 %wt. respectively for the rice straw and corn stalk as the temperature increased from 400 to 550 °C and then reduced to 50.5 and 62.0 %wt. respectively as the temperature increased further to 700 °C. Maximum bio-oil yields ranging from 53.0 to 66.0 %wt. respectively were obtained for the cocoa pod husk and corn stalk at 550 °C. The non-condensable gas yields increased from 8.2 to 32.5 %wt. while bio-char yields decreased from 38.6 to 17.2 %wt. as the temperature increased from 400 to 700 °C for the rice straw. Similar trends in product distribution were obtained for the pyrolysis of the other biomasses. This indicates that the product yields obtained during the biomass fast pyrolysis varied differently as the temperature increased. Slight differences in maximum bio-oil yields obtained from the various biomasses could be due to different compositions such as proximate, ultimate and chemical.

Characterization of the bio-oils showed that:

The bio-oils obtained had pH ranging from 2.10 to 3.20 for wawa sawdust and corn stalk bio-oils respectively indicating that they are more acidic than light petroleum oil with a pH of 5.7. This could be due to the presence of acids such as acetic acid and formic acid. This characteristic makes them corrosive and thus could affect metallic storage containers.

The moisture content ranging from 12.0 to 26.0 %wt. for the sugarcane bagasse and the rice straw respectively were higher than petroleum diesel and heavy fuel oils, which have low moisture contents of about 0.1 %wt. This could be due to the high water content of the original biomasses and the large amount of water released during the biomass fast pyrolysis. The densities of sugarcane bagasse and rice husk bio-oils ranging from 1,150 to 1,190 kgm⁻³ respectively indicated that they are denser than either light petroleum oil (diesel oil) or heavy fuel oil with densities of 854 and 963 kgm⁻³ respectively. The viscosities ranging from 126 to 240 mm²s⁻¹ for rice straw and wawa sawdust bio-oils indicated that they were more viscous than light petroleum oil but less viscous than heavy fuel oil with values of 80 and over 400 mm²s⁻¹ respectively.

The HHVs also ranging from 16.8 to 23.30 MJkg⁻¹ respectively for rice straw and wawa sawdust bio-oils were lower than those of light petroleum and heavy fuel oils, which are 42.9 and 40.7 MJkg⁻¹ respectively. This indicates that the bio-oils have lower energy contents than petroleum fuels. The carbon contents ranging from 41.7 to 65.68 %wt. for the bio-oils obtained from rice straw and its husk respectively were also lower than light petroleum oil and heavy fuel oil with values of 86.3 and 86.1 %wt. respectively.

Thus, the bio-oils obtained have lower fuel properties than both petroleum light oil (diesel oil) and heavy oil. However, their low sulphur and nitrogen contents compared to light and heavy fuel oils of 0.9 and 2.1 %wt. respectively give them an advantage over these conventional fuels since they would emit less SO₂ and NO₂ during combustion.

While the characteristics of the bio-oils indicate that they could be used as fuels directly for combustion in stationary engines for power and heat generation, upgrading would improve

their fuel properties such as oxygen and moisture contents and, thus, their ignition temperature, acidity and stability. Upgrading would convert them to either green gasoline or green diesel oil depending on the process employed, making them suitable for use as alternative fuels for transportation and stationary engine applications.

Bio-oil production based on the proposed scheme would be cost-effective since it would use lignocellulosic biomass, which currently offers little value and also re-use some of the co-products, i.e. char and non-condensable gas as process heat. Moreover, the large availability of lignocellulosic biomass would give bio-oil production a high potential. The utilization of lignocellulosic biomass as a bio-oil feedstock would reduce the large volume of waste and residues generated by agricultural and wood processing activities in the country and thus, have economic and environmental benefits.

This work would contribute to both national and international development in terms of reducing the dependence on imported and expensive fossil fuels, providing a suitable bio-oil biomass feedstock option and ensuring environmental sustainability. At the national level, it would contribute to current knowledge base by providing relevant information on the characteristics of major lignocellulosic biomasses available in Ghana and their suitability as feedstock for bio-energy production.

The results of this work would also provide information on the pyrolytic characteristics of some lignocellulosic biomasses and further give an indication of the country's bio-oil production potential. Bio-oil producers could use this information to select suitable lignocellulosic biomasses and appropriate process parameters particularly temperature for bio-oil production. The results are very encouraging for the development of the biofuel

industry and it is a step forward in the development of bio-oil as a viable alternative source to fossil fuels.

6.2 Recommendations

The results of this work indicate that biomass characteristics and the temperature employed for fast pyrolysis are among the major factors that affect the distribution of products as well as the characteristics of the bio-oils obtained. Therefore, the following recommendations are made to ensure high bio-oil yields namely: (a) selection of lignocellulosic biomass as feedstock based on its characteristics, (b) selection of appropriate temperature for fast pyrolysis to optimize bio-oil yields, (c) improvement of the properties of the bio-oils obtained as a fuel for use as an alternative source to fossil fuels for transportation and stationary engine applications and (d) adoption of the proposed scheme for bio-oil production using lignocellulosic biomass.

A. Selection of lignocellulosic biomasses as feedstock for fast pyrolysis

1. The selection of any biomass as feedstock for bio-oil production using fast pyrolysis should be based on some key characteristics such as carbon, hydrogen, oxygen, cellulose, hemicellulose and lignin contents as well as their heating values. Wawa sawdust, sugarcane bagasse and corn stalk were found to possess the most suitable characteristics to be used for bio-energy production. Therefore, bio-oil production could be based on these biomasses if high yields of bio-oil are required to be achieved. However, a combination of biomasses for bio-oil production could be investigated to determine the effect of mixing different biomasses.

2. The presence of silica in biomass could affect bio-oil yields since it promotes char formation during fast pyrolysis particularly the secondary process. Since rice straw and its husk have high silica contents, relatively lower bio-oil yields would be expected to be obtained from using them compared to other biomasses such as cocoa pod husk and corn cobs with no silica content. Therefore, it is recommended that appropriate measures should be taken to remove or reduce the high silica content in rice residues before using them as feedstock in fast pyrolysis. This could be achieved by demineralization, which involves treating the biomass with 10% hydrochloric acid (HCl) at 60 °C for 48 h followed by treatment with aqueous 5% sodium hydroxide (NaOH) for 1 h at 90 °C.
3. Cocoa pod husks, which constitute a major harvesting waste in the country should provide a vast opportunity for bio-energy production on a large-scale. It would have been expected that the bio-oils produced from them would have contained a high level of nitrogen due to the high nitrogen content of 2.23 %wt. in the crop residue and that this would be released in the form of NO₂ during combustion. However, the ultimate analysis of the bio-oil gave a low nitrogen content of 0.20 %wt. Therefore, it is recommended that cocoa pod husks could also be considered as suitable feedstocks for bio-energy production. This would have significant economic benefits for the country.

B. Optimization of bio-oil yields during fast pyrolysis

1. Since the bio-oil yields obtained increased as the temperature increased from 400 to 550 °C and decreased as the temperature further increased to 700 °C, it is recommended that in order to obtain maximum bio-oil yields, fast pyrolysis should be

carried out preferably at 500 °C. Above this temperature, bio-oil yields would decrease, while bio-char yields would rather increase.

2. Since fast pyrolysis is emerging as an important technology for energy production in both academic and industrial research, characterization of other potential lignocellulosic biomasses and determination of appropriate process parameters to maximize bio-oil yields should be carried out. Future work should expand this work to include a database of other fuel properties such as flash point, pour point and miscibility as well as the characteristics of other lignocellulosic biomasses, which have not yet been studied.

C. Improvement of the quality of bio-oils for use as a substitute or replacement to fossil fuels

1. Since the bio-oils have some undesirable characteristics such as high acidity and high oxygen and water contents, which lower their fuel properties, i.e. ignition temperature and stability compared to light petroleum and heavy fuel oils, therefore, there is the need to improve these properties using processes such as catalytic hydro-treating or steam reforming if the bio-oils are to be used as a substitute or replacement for transportation and stationary engine applications.

D. Adoption of the proposed scheme for bio-oil production

1. The large availability of lignocellulosic biomass should provide a huge opportunity for their use as feedstock for bio-oil production. Moreover, the use of lignocellulosic biomass, which is cheap or low cost and the re-use of the co-products during the biomass fast pyrolysis would make the process cost-effective. Utilization of

lignocellulosic biomass would reduce the large volume of wastes and residues generated by agricultural and wood processing activities in the country, they would thus, have economic and environmental benefits.

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APPENDICES

APPENDIX 1

Analysis of Variance using the 2-way ANOVA computation

Using the 2 factor ANOVA model, denote biomass as Factor A; Denote mass of CHON as Factor B.

Appendix 1.1 Test for biomass (Factor A) main effect: Proximate analysis

ANOVA Table for proximate analysis of the biomass samples

Source of variation	Sum of squares (s.s)	Degree of freedom (d.f)	Mean squares (m.s)	F*
SSA	21.43	6	3.57	1.37
SSB	292.85	3	97.6	37.5
SSE	46.75	18	2.59	
SST (Total)	361.02	27		

Hypothesis: $H_0 : \alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = \alpha_6 = \alpha_7 = \alpha_0$

Level of significance $\alpha = 0.05$

Test statistic $F^* = MSA/MSE \sim F(6, 18) = 3.22$

$F^* = 3.57/2.59 = 1.37$

Decision rule: If $F^* < 3.22$, accept H_0 . If $F^* > 3.22$, accept H_1

Since $F^* < 3.22$, the null hypothesis is accepted.

Conclusion: It is concluded that the type of biomass has no effect on amount of moisture, volatile matter, ash or fixed carbon content.

Appendix 1.2 Test for moisture, volatiles, ash and fixed carbon content main effect (Factor B)

Hypothesis: H_0 . $\beta_1 = \beta_2 = \beta_3 = \beta_4 = 0$. H_1 . Not all $\beta_j = 0$

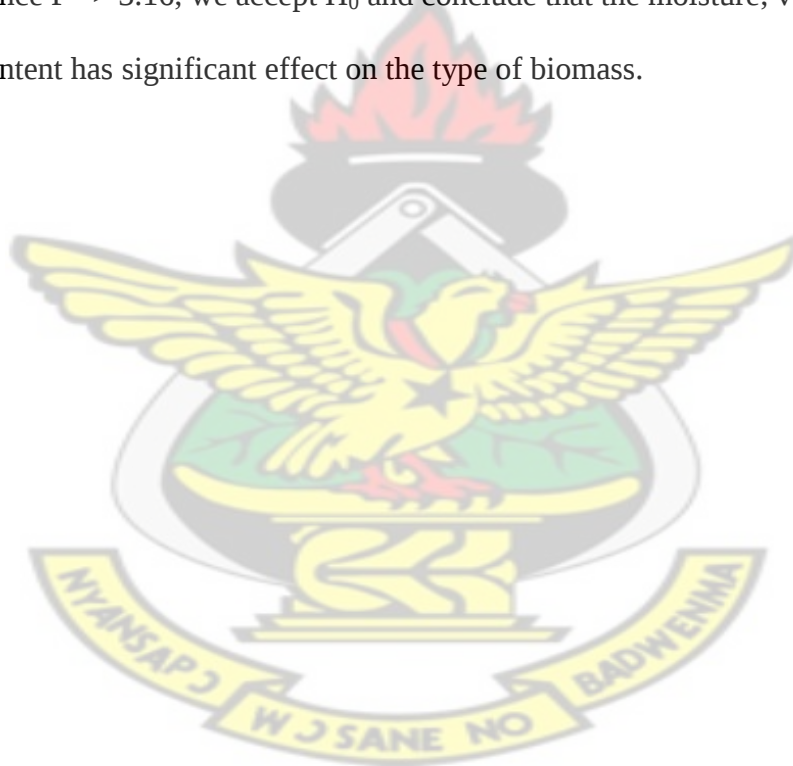
Level of significance $\alpha = 0.05$

Test statistic $F^* = \frac{MSB}{MSE} = \frac{97.6}{2.6} = 37.5$

F $(0.95, 3, 18) = 3.16$

Decision rule: If $F < 3.22$, accept H_0 . If $F^* > 3.22$, accept H_1

Conclusion: Since $F^* > 3.16$, we accept H_0 and conclude that the moisture, volatile ash and fixed carbon content has significant effect on the type of biomass.



Appendix 1.3 Test for proximate analysis

ANOVA Table for test for proximate analysis

Source of variation	Sum of squares (s.s)	Degree of freedom (d.f)	Mean squares (ms)	F*
SSA	14.28	6	2.38	0.29
SSB	2.14	5	0.43	0.04
SSE	258.90	30	8.63	
SST (Total)	275.39	41		

Hypothesis

$$H_0 \quad \beta_1 = \beta_2 = \beta_3 = \beta_4 = 0$$

$$\text{Test statistic } F^* = MSA/MSE = 2.38/8.63 = 0.29$$

Decision rule

Reject H_0 if $F^* < F_{(0.05, 6, 30)}$

$$F_{(0.05, 6, 30)} = 2.42$$

Since $F^* < 2.42$ we accept H_0 .

Conclusion: It is concluded that the type of biomass used in the analysis has no effect on CHON yield.

Appendix 1.4 Test for CHON (Factor B) effect

ANOVA Table for test for ultimate analysis

Source of variation	Sum of squares (s.s)	Degree of freedom (d.f)	Mean squares (ms)	F*
SSA	14.28	6	2.38	0.29
SSB	2.14	5	0.43	0.04
SSE	258.90	30	8.63	
SST (Total)	275.39	41		

Hypothesis

$$H_0 = \beta_1 = \beta_2 = \beta_3 = \dots = \beta_6 = 0$$

$$H_1 = \text{Not all of } \beta_1 = 0$$

$$\text{Test statistic } F^* = \text{MSB/MSE} = 0.43/8.63 = 0.04$$

Decision rule

Retain H_0 if $F^* < F_{(0.05, 5, 30)}$

Reject F^* if $F^* > F_{(0.05, 5, 30)}$

$$F^* = 0.04, F_{(0.05, 5, 30)} = 2.53$$

H_0 is accepted.

Conclusion: It is concluded that the yield of CHON has no effect on the type of biomass used.

Appendix 1.5 Test for ultimate analysis

ANOVA Table for biomass ultimate characterization

Source of Variation	SS	Df	MS	F	P-value	F crit
Treatments	166.8065	6	27.80109	0.154845	0.984214	2.99612
Components	1349.119	2	674.5596	3.75712	0.054073	3.885294
Error	2154.5	12	179.5417			
Total	3670.426	20				

KNUST



APPENDIX 1.6 Analysis of bio-oil yields from fast pyrolysis

ANOVA Table for fast pyrolysis product yields

Source of Variation	SS	Df	MS	F	P-value	F crit
Rows	3706.617	2	1853.3	19.6	0.000825	4.45
Error	756.336	8	94.542			
Total	4462.953	14				

KNUST



Appendix 1.7 Analysis of bio-oils from corn stalk

ANOVA Table for bio-oil yields from corn stalk

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6921.436	2	3460.72	85.02	8.21E-08	3.88
Within Groups	488.468	12	40.71			
Total	7409.904	14				

KNUST



Appendix 1.8 Analysis of bio-oils from rice straw

ANOVA Table for bio-oil yields from rice straw

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	32.374	4	8.0935	0.057224	0.99198	5.192168
Within Groups	707.175	5	141.435			
Total	739.549	9				

KNUST



Appendix 1.9. Analysis of bio-oil yield in corn cobs and rice straw samples using correlation coefficient and coefficient of determination.

This analysis of bio-oil yields from fast pyrolysis of corn cobs and rice straw was analyzed using correlation coefficient (r) and coefficient of determination (r^2). The determination of the degree of correlation between the yields of bio-oil from corn was carried out as follows: Temperature ($^{\circ}\text{C}$) was denoted with X while bio-oil yields were denoted with Y, where Y is the independent variable.

Rice straw bio-oil yields

Correlation table for the analysis of yields of bio-oil from fast pyrolysis of rice straw

X	Y	X ²	Y ²	XY
400	53.2	160,000	2,830.24	21,280
500	60.0	250,000	3,600.00	30,000
550	58.9	302,500	3,469.21	32,395
600	54.7	360,000	2,992.09	32,820
650	52.1	422,000	2,714.41	33,865
700	50.2	490,000	2,520.04	35,140
3,400	329.1	1,759,500	18,125.99	185,500

The correlation coefficient (r) was calculated to be 0.54 as shown below:

$$r = \frac{5934}{10933.8} = 0.54$$

Conclusion: The value of r so obtained indicates a positive relationship between temperature as an independent variable and yield of bio-oil using rice straw as biomass sample for fast pyrolysis. It is, therefore, concluded that the yield of bio-oil from fast pyrolysis of rice straw depends on the temperature employed.

The coefficient of determination (r^2) was calculated to be 0.29, i.e. $r^2 = (0.54)^2 = 0.29$.

Conclusion: The value of r^2 indicates that approximately 29% of the variation of the yield of bio-oil from rice samples is accounted for by changes in temperature.

Correlation table for the analysis of yields of bio-oil from fast pyrolysis of corn cobs

X	Y	X ²	Y ²	XY
400	48.3	160,000	2,332.89	19,320
500	54.3	250,000	2,948.49	27,150
550	56.8	302,500	3,226.24	31,240
600	56.3	360,000	3,169.69	33,780
650	50.2	422,000	2,520.04	32,630
700	52.5	490,000	2,756.25	36,750
3,400	318.4	1,759,500	16,953.60	180,870

The correlation coefficient

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}}$$

$$r = \frac{5587}{5698.58} = 0.98$$

The value of r so obtained indicates a positive relationship between temperature and yield of biooil. The coefficient of determination, $r^2 = (0.98)^2 = 0.96$. The conclusion is that 96% of the variation in the yield of bio-oil using corn as biomass is explained by temperature changes.

Appendix 1.10 **Table of analysis of products of fast pyrolysis**

No.	Product yields	Mean absolute deviation	Margin of error (%)
1	Bio-oil	0.44	± 0.44
2	Char	0.56	± 0.56
3	Non-condensable gas	2.25	± 2.25

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Appendix 1.1 Higher heating values (HHV) of the bio-oils

No.	Parameter	Value
1	*Range for HHV	6.35 MJ kg ⁻¹ .
2	Mean (average HHV of samples)	16.14 MJ kg ⁻¹ .
3	Variance	9.15
4	Standard deviation	3.02
5	Extent / degree of variability of HHVs of all the biomasses	3.0

*Range for HHV = 18.61-12.26 MJ kg⁻¹ = 6.35 MJ kg⁻¹.

The degree of variability of the various HHVs of all biomass samples was 3.0.



Appendix 1.12 Mean absolute, deviations of bio-oil, char and non-condensable gas yields

Dimension	Value
Mean absolute deviation of bio-oil yield	0.44
Margin of error	$\pm 0.44\%$
Mean absolute deviation of char yield	0.56
Margin of error	$\pm 0.56\%$
Mean absolute deviation of NCG yield	2.25
Margin of error	$\pm 2.25\%$

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Appendix 1.13. Correlation table for the analysis of characteristics of the biomasses and bio-oils obtained

The correlation of biomass characteristics and bio-oil characteristics was analyzed using correlation coefficient (r) and coefficient of determination (r^2). The determination of the degree of correlation between biomass characteristics and bio-oil characteristics was carried out as follows: biomass characteristics were denoted by X while bio-oil characteristics were denoted by Y, where Y is the independent variable.

CORN STALK										
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	42.65	1819.02	44.30	1962.49	1889.40	15115		14552.2		
H	5.57	31.02	6.30	39.69	35.09	280.73		248.199		
O	49.16	2416.71	47.50	2256.25	2335.10	18681		19333.6		
N	1.49	2.22	0.60	0.36	0.89	7.152		17.7608		
S	0.10	0.01	0.30	0.09	0.03	0.24		0.08		
Cl						0		0		
HHV	16.24	263.74	19.60	384.16	318.30	2546.4		2109.9		
MC	9.15	83.72	22.50	506.25	205.88	1647		669.78		
TOTAL	124.36	4616.44	141.10	5149.29	4784.69	38278	17547	36931.5	20730.3	21466.1
CORN COB										
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	43.32	1876.62	51.90	2693.61	2248.31	17986		15013		
H	6.02	36.24	7.00	49.00	42.14	337.12		289.923		
O	49.37	2437.40	40.30	1624.09	1989.61	15917		19499.2		
N	0.93	0.86	0.80	0.64	0.74	5.952		6.9192		
S	0.10	0.01	0.00	0.00	0.00	0		0.08		
Cl						0		0		
HHV	16.99	288.66	16.80	282.24	285.43	2283.5		2309.28		
MC	8.72	76.04	22.90	524.41	199.69	1597.5		608.307		
TOTAL	125.45	4715.83	139.70	5173.99	4765.92	38127	17525	37726.7	20602	21989
RICE STRAW										
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	26.73	714.49	65.68	4313.86	1755.63	14045		5715.94		
H	4.05	16.40	7.60	57.76	30.78	246.24		131.22		
O	1.02	1.04	25.54	652.29	26.05	208.41		8.3232		
N	0.56	0.31	1.08	1.17	0.60	4.8384		2.5088		
S	0.56	0.31	0.00	0.00	0.00	0		2.5088		
Cl						0		0		
HHV	12.26	150.31	18.43	339.66	225.95	1807.6		1202.46		
MC	7.23	52.27	26.00	676.00	187.98	1503.8		418.183		
TOTAL	52.41	935.14	144.33	6040.75	2226.99	17816	7564	7481.15	10251.6	24734.34

	RICE HUSK									
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	34.90	1218.01	41.70	1738.89	1455.33	11643		9744.08		
H	5.15	26.52	7.70	59.29	39.66	317.24		212.18		
O	59.00	3481.00	50.30	2530.09	2967.70	23742		27848		
N	0.30	0.09	0.30	0.09	0.09	0.72		0.72		
S	0.64	0.41	0.20	0.04	0.13	1.024		3.2768		
Cl						0		0		
HHV	14.00	196.00	18.43	339.66	258.02	2064.2		1568		
MC	8.59	73.79	25.20	635.04	216.47	1731.7		590.305		
TOTAL	122.58	4995.82	143.83	5303.10	4937.39	39499	17631	39966.6	21868.4	24940.7
	COCOA POD HUSK									
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	43.87	1924.58	46.50	2162.25	2039.96	16320		15396.6		
H	3.82	14.59	7.30	53.29	27.89	223.09		116.739		
O	49.11	2411.79	49.80	2480.04	2445.68	19565		19294.3		
N	0.63	0.40	0.20	0.04	0.13	1.008		3.1752		
S	0.10	0.01	0.10	0.01	0.01	0.08		0.08		
Cl						0				
HHV	17.93	321.48	17.20	295.84	308.40	2467.2		2571.88		
MC	10.29	105.88	26.70	712.89	274.74	2197.9		847.073		
TOTAL	125.75	4778.74	147.80	5704.36	5096.79	40774	18586	38229.9	22188.5	22416.8
	SUGARCANE BAGASSE									
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	44.31	1963.38	45.77	2094.89	2028.07	16225		15707		
H	5.73	32.83	7.86	61.78	45.04	360.3		262.663		
O	49.11	2411.79	46.19	2133.52	2268.39	18147		19294.3		
N	0.63	0.40	0.18	0.03	0.11	0.9072		3.1752		
S	0.10	0.01	0.00	0.00	0.00	0		0.08		
Cl										
HHV	16.88	284.93	19.60	384.16	330.85	2646.8		2279.48		
MC	8.59	73.79	12.00	144.00	103.08	824.64		590.305		
TOTAL	125.35	4767.13	131.60	4818.38	4775.54	38204	16496	38137	21708.3	22424.4
	WAWA SAWDUST									
PROPERTY	X	X ²	Y	Y ²	XY	n(Σxy)	(Σx)(Σy)	n(Σx ²)	n(Σxy)- (Σx)(Σy)	n(Σx2)- (Σx)2
C	44.37	1968.70	53.50	2862.25	2373.80	18990		15749.6		
H	5.77	33.29	6.40	40.96	36.93	295.42		266.343		
O	49.23	2423.59	40.20	1616.04	1979.05	15832		19388.7		
N	0.34	0.12	0.20	0.04	0.07	0.544		0.9248		
S	0.10	0.01	0.10	0.01	0.01	0.08		0.08		
Cl						0		0		
HHV	18.61	346.33	17.40	302.76	323.81	2590.5		2770.66		
MC	6.03	36.36	24.00	576.00	144.72	1157.8		290.887		
TOTAL	124.45	4808.40	141.80	5398.06	4858.38	38867	17647	38467.2	21220	22979.4

Appendix 1.13 (contd). Correlation table for the analysis of characteristics of the biomasses and bio-oils obtained

Biomass type	$n(\sum x^2) - (\sum x)^2$	$n\sum y^2 - (\sum y)^2$	$[n(\sum x^2) - (\sum x)^2][n\sum y^2 - (\sum y)^2]$	$\text{SQRT}([n(\sum x^2) - (\sum x)^2][n\sum y^2 - (\sum y)^2])$	r	r^2
Corn stalk	21466	21285	456909066	21375.43	0.970	0.9406
Corn cob	21989	21876	481026801	21932.32	0.939	0.8824
Rice straw	24734	27495	130169793	11409.20	0.899	0.8074
Rice husk	24941	21738	542155321	23284.22	0.939	0.8821
Cocoa pod husk	22417	23790	533297423	23093.23	0.961	0.9232
Sugarcane bagasse	22424	21228	476036563	21818.26	0.995	0.9899
Wawa sawdust	22979	23077	530301311	23028.27	0.921	0.8491

The values of r so obtained which ranged from 0.899 to 0.995 indicate a positive relationship between biomass characteristics and those of the bio-oils obtained. The coefficient of determination, $r^2 = 0.849 - 0.990$. The conclusion is that 85-99 % of the variation in the characteristics of the bio-oils obtained is explained by the characteristics of the biomass samples.



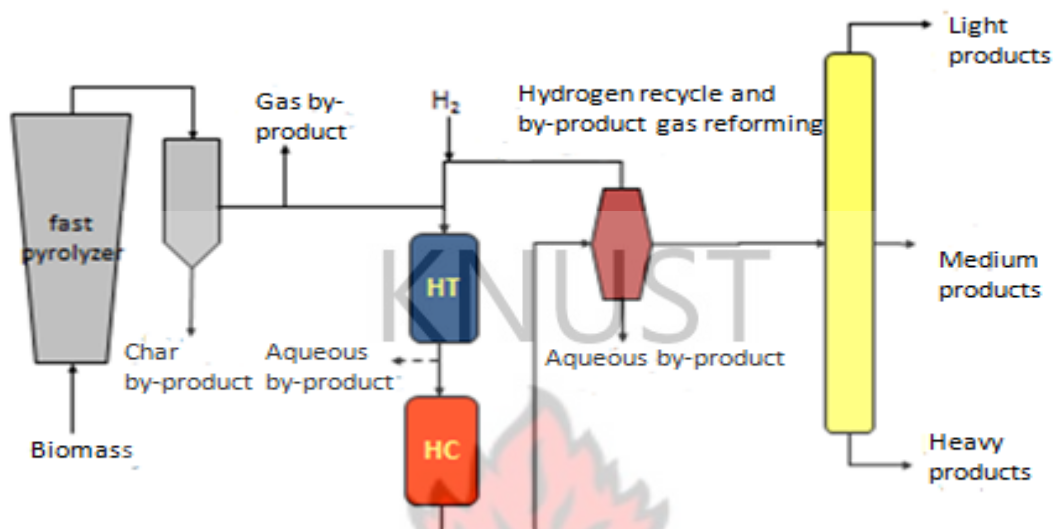
Appendix 1.14. Financial analysis of bio-oil production from lognocellulosic biomass using fast pyrolysis

	Year 0	Year 1	Year 2	Year 3	Year 4	Year 5
Production						
Daily throughput (tons)		100	100	100	100	100
Annual throughput (tons) (180 days)		18,000	18,000	18,000	18,000	18,000
Output annual (tons)						
Bio-oil (55% yield)		9,900	9,900	9,900	9,900	9,900
Bio-oil (65% yield)		11,700	11,700	11,700	11,700	11,700
Bio-char (23% yield)		4,140	4,140	4,140	4,140	4,140
Bio-oil (kg) 55% yield		9,900,000	9,900,000	9,900,000	9,900,000	9,900,000
Bio-oil (kg) 65% yield		11,700,000	11,700,000	11,700,000	11,700,000	11,700,000
Bio-oil in litres (55% yield)		8,250,000	8,250,000	8,250,000	8,250,000	8,250,000
Bio-oil in litres (65% yield)		9,750,000	9,750,000	9,750,000	9,750,000	9,750,000
Revenue/Income (55%) @ US\$0.13/l	0	1,072,500	1,072,500	1,287,000	1,072,500	1,072,500
Revenue/Income (65%)v at US\$0.13/l	0	1,267,500	1,267,500	1,267,500	1,267,500	1,267,500
Expenditure (US\$)	(449,500)	(498,500)	(498,500)	(498,500)	(498,500)	(498,500)
Net income (US\$)	(449,500)	769,000	769,000	769,000	769,000	769,000
Net Present Value (NPV)	2,790,307					
Internal Rate of Return (IRR)	170%					
Price of raw materials US\$35/ton						
Price of bio-oil (US\$0.13/litre)						

The NPV indicates that the production of bio-oil from lignocellulosic biomass using fast pyrolysis is viable.

APPENDIX 2

Hydro-treating of bio-oils

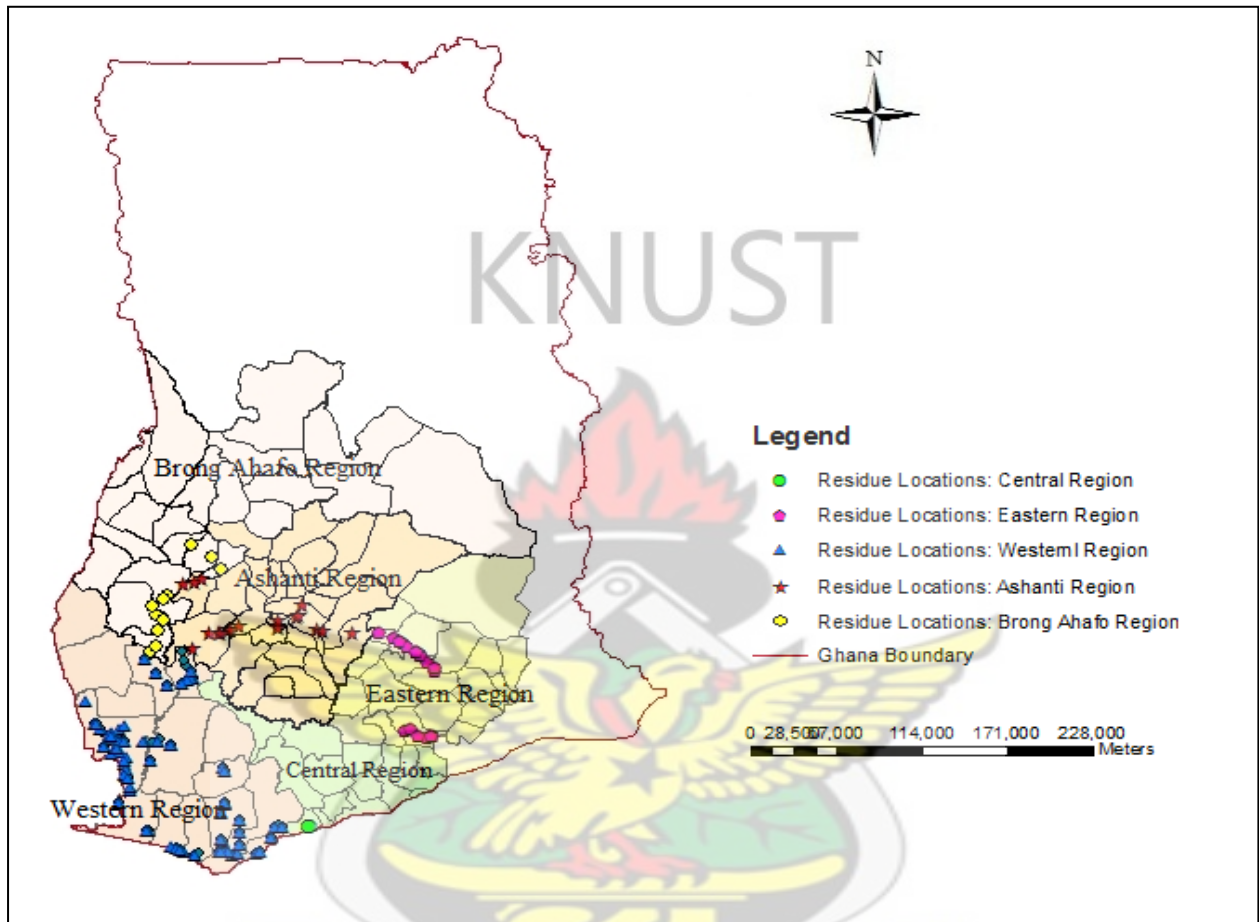


Hydrodeoxygenation consists of two processes namely, hydro-cracking and hydrotreatment. Hydrocracking is carried out without catalysts. However, hydrotreatment is carried out in the presence of catalysts, which include Co–Mo, Ni–Mo, their oxides and Al₂O₃. Oxygen is removed as H₂O and CO₂, while the energy density of the bio-oils is increased. Temperature and pressure conditions for hydro-cracking are higher than those for hydrotreatment. The process is expensive, complex and expensive and may also result in the reactor getting clogged.

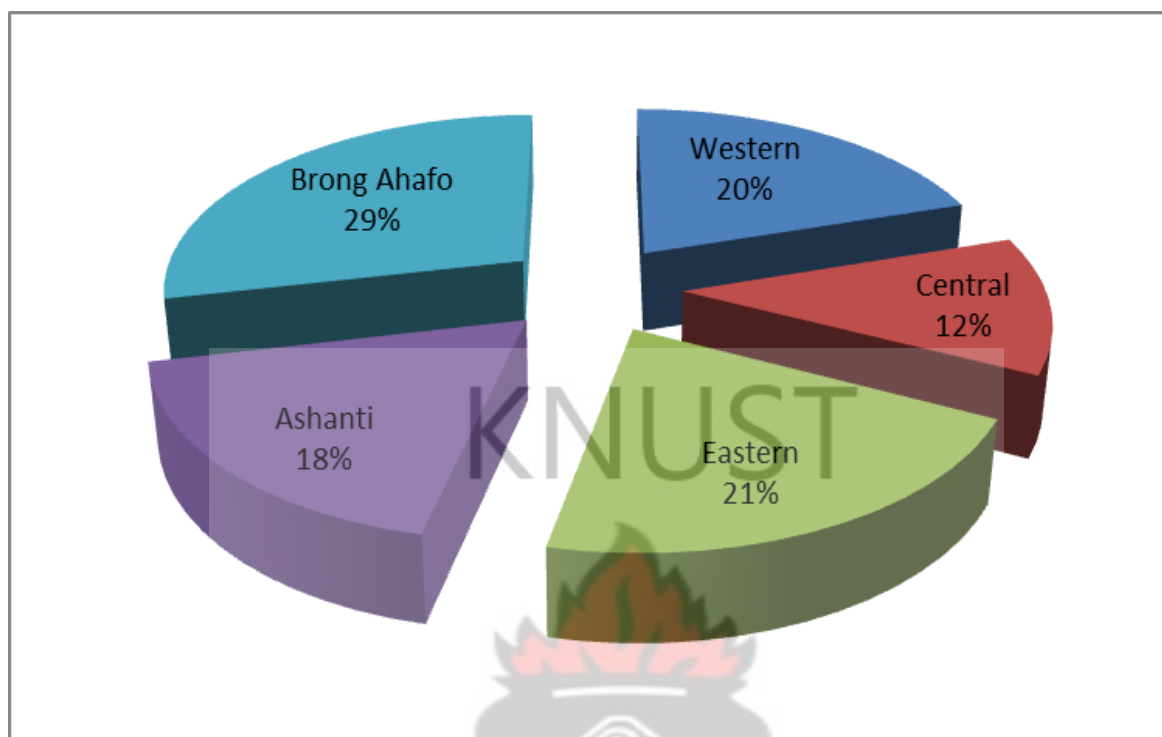
APPENDIX 3

Biomass resource mapping

Appendix 3.1. Locations of available biomass residue in the 5 regions in Southern Ghana. Source: Hagan and Duku, 2012.



Appendix 3.2. Share of the 5 regions in available biomass resources.
Source: Hagan and Duku, 2012.



APPENDIX 4

Typical flow diagramme of fast pyrolysis of biomass

