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Potential for bio-oil production from biodiesel production residues, with emphasis on African feedstocks.

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Abstract

Utilization of waste products from biomass have been scarcely research on. These wastes have been a major environmental hazard which involves a lot of capital and effort to curb. Thermochemical conversion using the LtL method is one way of producing marketable biofuels and bio based chemicals from these wastes. This project focus on using this method to convert residual biomass to a useful product for its sustainability.

Three materials which are bagasse, eucalyptus and jatropha residues were studied. The solvent used was water and formic acid as the hydrogen donor. There was variation of temperature from 320 to 380°C with heating time of 2-4hrs. GC-MS (gas chromatography and mass spectrometer) was used to analyze the samples.

Analysis of these samples shows an approximate 58%wt of bio oil could be produced from eucalyptus and 45%wt and 35%wt from bagasse and jatropha residue respectively. Some of the chemical compounds generated which are furan, guaiacol, catechol and hydroquinone are useful chemicals in pharmaceutical and petrochemical industries.

Keywords: Biomass, biofuels, bagasse, eucalyptus, jatropha, residues.

Abbreviations

LtL	Lignin to Liquid
wt	Weight
GC-MS	Gas chromatography- Mass spectrometer
$^{\circ}$C	Degree Celsius
%	Percentage
EU	European Union
US	United State of America
p-coumaryl	Para coumaryl
HC	Hydrocarbon
MJ/Kg	Mega joule/kilogram
Nm	Newton meter
mL	Milli liter

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1 Introduction

1.1 Overview

The decline of the fossil oil reserves has led to an interest in alternative means of generating energy. Various ways have been implemented to produce biofuel, some of which are generated from food products and some from non-food products like wood. Attention has been shifted to biomass as a means of generating energy. The energy generated from biomass is sustainable and can be renewed [1]. Energy produced from biomass has over the decades gained global attention because it is a renewable and environmentally friendly fuel. Biodiesel as the main product is a major key component for use in the motor diesel engines today, because of the attractive features of these engines. It can represent a largely closed carbon dioxide cycle (approximately 78%), as it is derived from renewable biomass sources. Bio diesel has lower emissions of pollutants, compare to petroleum diesel, it is biodegradable and enhances the engine lubricity [2]. Different biomass feedstocks have been used to produce bio diesel. The stability of the fuel depends on the feedstocks origin. Feedstocks with a high saturated fatty acids content are more stable as compared to the unstable ones with high unsaturated fatty acid content [3]. Various feedstocks have been used all over the world to produce biofuel. Some examples of these feedstocks are corn, sugarcane, soybeans, palmoil. In the US, corn is the main materials for producing biofuel. Ethanol is the main product. The United States and Brazil produce well over 70% of the ethanol in the world. Vegetable and animal oil are the main feedstocks used in EU. The European Union is the largest producer of biodiesel, about 75% of biodiesl generated in the world is credited to the EU [4]. Most of this biodiesel is generated from transesterification reaction of triglycerides to produce fatty acid methyl ester [5]. Africa use edible and non-edible oil for biodiesel production. Edible oils are used mostly. The only non edible oil currently in use in Africa is the jatropha. Ongoing studies are in place to introduce other non-edible oils.

1.2 Biomass

Biomass can be defined as a non-fossil, energy resource which contains carbon, it is found as land and water based vegetables, municipal solid wastes, agricultural residues, industrial waste and municipal bio solids [6]. It can also be said to include all kinds of materials that are derived directly or indirectly from photosynthesis reactions, vegetable matter and its derivatives such as fuel crops, animal by-products, agro-industrial by-products and wood fuel [7]. Also it could be defined as the composition of organic matter in plant and animal residues expressed in dry weight [8]. It is one of the few renewable, natural resources that can be utilized to reduce the emission of greenhouse gases when fossil fuel is burned or formed during combustion processes. Burning of fossil fuels produces carbon dioxide and because the source is renewable, bioenergy creates what is called net gain of zero [8], this implies that the overall emissions of carbon dioxide to the environment is not increased nor reduced and net emission of carbon dioxide from bioenergy is also zero.

Biomass can be processed to create bioenergy such as fuel, heat and electricity. Bioenergy is the energy stored in biomass or energy associated with biomass while the term biofuel is usually used for liquid fuel. It is mostly used for transportation and it includes corn ethanol, biodiesel, cellulosic ethanol, biomass derived methanol and many more. According to history, biomass is the oldest fuel known to humans in all region of this world [9]. In this current world, biomass is a clean and renewable fuel source whose utilization, if done in a sustainable way, does not have much negative impact on the environment and climate.

There are various reasons for the growth in the use of solid, liquid and gaseous biofuels for energy purposes. This includes environmental benefits such as mitigation of greenhouse gas emission and improvement of soil. Also it reduces dependency on imported oils and there are more job opportunities with biomass fuel than when restricted to coal and oil.

1.3 Sources of Biomass and Feedstocks

Forest based feedstock*:* Forest based feedstock are mostly from wood. Wood is an important source of biomass, trees from forest could be used but due to valuable characteristics of wood after being processed from tree, the residuals such as sawdust, pieces and barks are more used for fuel. It is also more economical for use, and it is the most important source of fuel for cooking and space heating. Woods that are not suitable for sales are used in bioenergy production. Low grade waste from forest for bioenergy could be used, as bark as well as wood chips which can be used as solid fuel or refined and densified into pellets. Its of three different

types, the mill chips which are produced from waste wood, whole tree chips which is produced from low grade trees during forest management activities. Bole chips are also produced like whole tree chips but do not include branches or foliage [7].

Agriculture based feedstocks

Biomass from agriculture products comes majorly from crops that are grown specifically for bioenergy production. Agricultural residue such as stalks from maize, straws from grains and bagasse from sugarcane can be used as fuel. Bioenergy crops used can either be annual crops which are grown yearly or perennial crop which can be grown over years. Most first generation bioethanol was made from feedstocks which is derived from annual crops [10]. These crops include cereal crops, sugar beets, sorghums, cassava and potatoes. However, perennial crops are sources of lignocellulosic biomass, they have long term yield potential and environmental benefit such as water quality improvement, prevention of soil erosion and also enabling environment for wildlife habitat. There are also perennial grasses which is of good use in advanced biofuels. Materials which are left in field after crops have been harvested are good source of cellulosic feedstocks, they are referred to as crop residue.

Waste based feedstock

Waste based materials are leftover materials from industrial processes, solid waste and agricultural liquid and municipal solid wastes. There are many industrial wastes that could be used for bioenergy. There are woody and non-woody wastes, the sources of non-woody waste include black liquor leftover from paper production industry as well as waste paper while the sources of woody wastes include sawdusts and shavings, pallets and many more.

Livestock manure could be used as bioenergy feedstock, the manure is converted to biogas through the process of anaerobic digestion. Municipal waste is another major sources of biomass, this is mainly household waste and this include waste food from kitchen, recyclable materials such as paper and plastic. In addition is construction waste, which consists of plastic, wood which can be used for power production [10].

1.3.1   Bio Energy Feedstocks

There are three main types of material from which bioenergy feedstocks can be derived from: lipids which are water insoluble such as fats and oil. It can be derived from non woody material or algae. We also have sugar/ starch which can be found in food crops such as corn, and the cellulosic biomass which can be found in leaves and steam of plants. The materials could also

be categorised according to plant production which is woody and non-woody [10], as shown in figure 1.1.
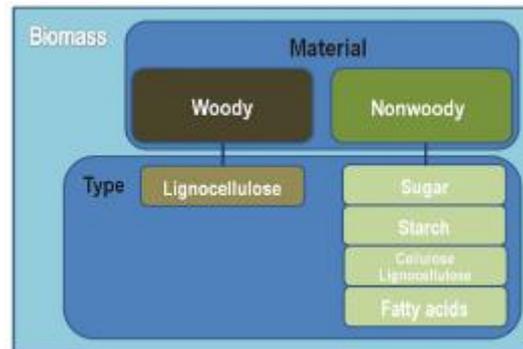
Figure 1.1: Biomass category [10]

Most biomass used for bioenergy feedstock are from three main sources, which are agriculture, waste and forests. Biomass product from agriculture and waste can provide woody and non-woody biomass

1.4   Plant Biomass Composition

Biomass can be categorised into various categories. Biomass consisting of grass and leaves are classified as fresh biomass. Lignocellulosic biomass is composed of straw, wood and grasses. Some biomass are found in the marine world, these are classified as aquatic biomass and they are made up of microalgae, seaweeds and aquatic plants. These biomasses are quantied based on their components. Lignocellulosic biomass composed mainly of lignin, cellulose and hemicellulose. These compositions vary from one plant to the other. The major components of aquatic biomass are proteins and oils. Sugars and fibers are the main constituents of fresh biomass [11].

1.4.1   Hemicellulose

Hemicellulose is polysaccharides with a smaller molecular weight as compared to other polysaccharides. It is basically classified as a complex carbohydrate. It is covalently bonded with lignin, and hydrogen bonds exist between its molecules and cellulose molecules. Hemicellulose serves as an intermediary connecting lignin to cellulose fibers. They are hetro polysaccharides with different monomers of sugar like xylose, mannose, galactose, glucose and uronic acid. Hemicellulose molecules are easily attached to other molecules making it extremely amorphous compared to other polysaccharides. They are available in most plant biomass, but vary depending on the biomass compositions. In the case of sugar cane bagasse

for example, the main hemicellulose is arabinoxylan containing mainly xylose and less of arabinose [12].

1.4.2 Cellulose

Cellulose is a linear polymer found in plant fibres. It consist of D-anhydroglucopyranose units bonded by β-1,4-glycosidic linkages. Cellulose can generally be classed as 1,4- β-D glucan [12, 13]. The properties of cellulose are determined by its molecular structures. Every cellulose is distinguished by its geometrical cells which tells the mechanical properties. Cellulose is formed in crystalline and amorphous forms. It structures consist of long chain of glucose connected to a glycosidic bonds. Figure 1.2 illustrate this. It is hydrolysed to water soluble sugars by acid and resistant to oxidising agents and strong alkali [12].
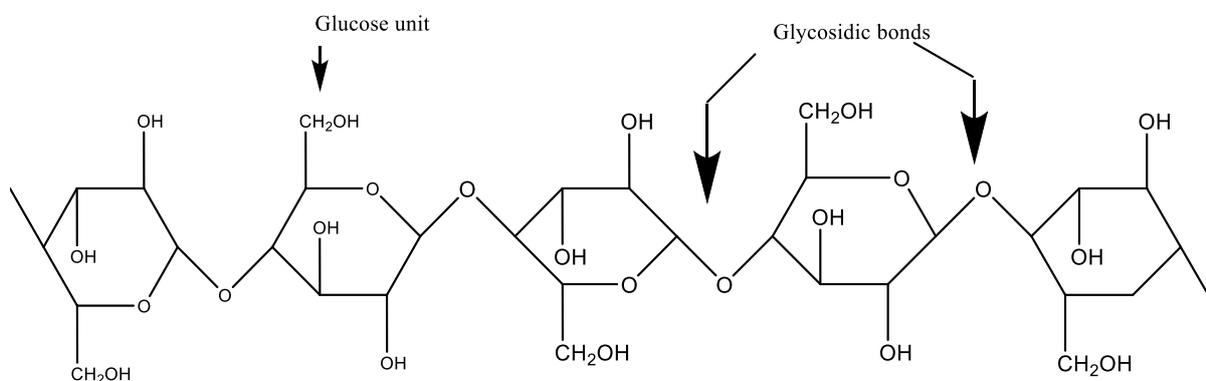
Figure 1.2: Cellulose chain

1.4.3 Lignin

Lignins consist of different aliphatic and aromatics hydrocarbon polymers. They are complex monomer units of different phenyl propanes substituted ring. Lignin is both amorphous and hydrophobic and has a lower strength compare to cellulose. Lignin is classified as the brain behind plants firmness and exists as a thermoplastic polymers with temperature of $90^{\circ}C$ and $170^{\circ}C$ as the melting temperature [14, 15]. Lignins are condensed easily with phenol, cannot be hydrolysed in acids. They are easily oxidised, and readily soluble in high temperate alkali [15]. Lignin units comprises coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. Figure 1-3 illustrates the lignin units.
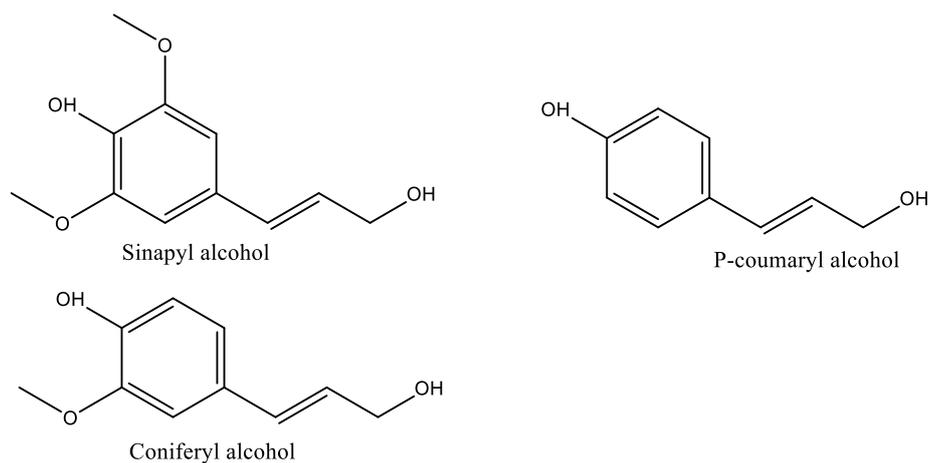
Figure 1.3: Lignin units

1.5 Chemical and Biochemical Conversions of Biomass

Biomass has a great advantage over fossil fuels in terms of sustainability, renewability, regional economic benefit and carbon neutrality. It occurs in different forms and varying composition. Due to diverse origin of the biomass and varying feedstock composition, there is need for process treatment of biomass conversion and utilization technologies.

The processing of biomass to bio-fuels can take several forms, some of these may involve the use of chemicals, mechanical and thermal transformation. The two major biomass conversion process are biochemical and thermochemical conversion. Biochemical conversion involves the transformation of biomass to useful fuels and chemicals using biological means like enzymatic process and application of microorganisms. Thermochemical processing on the other hand involves the use of heat and at times with catalysts to convert biomass into useful fuels and chemicals [16]. When there is biomass with high molecular weight and oxygen, it needs to be converted to lighter form through some chemical reaction such as partial oxidation, gasification, reformation, hydrolysis, hydrocracking, fermentation, liquefaction and many more. Some of the processes involved in processing biomass are discussed as follow.

1.5.1 Pyrolysis of Biomass

Pyrolysis involves the breaking down of heavy molecules, in this case biomass into lighter molecules. Some of the molecules which are gaseous in form are CO, CO_2, liquid products are bio oils and char represent solid products. Pyrolysis occurs in the absence of oxygen [17]. Pyrolysis can be represented with equation 1.

$$C_nH_mO_p + Heat \rightarrow \sum_{liquid} C_aH_bO_c + \sum_{gas} C_xH_yO_z + \sum_{solid} C \qquad (1)$$
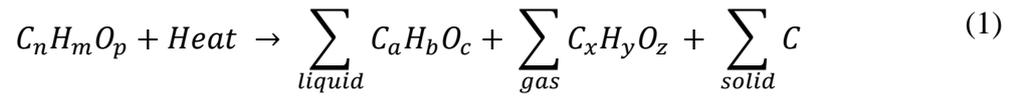
1.5.2   Gasification of Biomass

Gasification is a thermochemical process that involves oxidizing biomass with steam, air or oxygen. It is classified as a complex organic reactions of breaking down heavy hydrocarbon through steam reforming, flash evaporation and at times by pyrolytic process [18]. The gas products from gasification are CO_2, H_2O, CH_4, CO, CHs (gaseous HCs). Solid products from gasification process are char, tars, ash, inorganic products. The schematic diagram in figure 1.3, shows a typical gasifier where biomass is fed at the top and air is injected from the bottom.
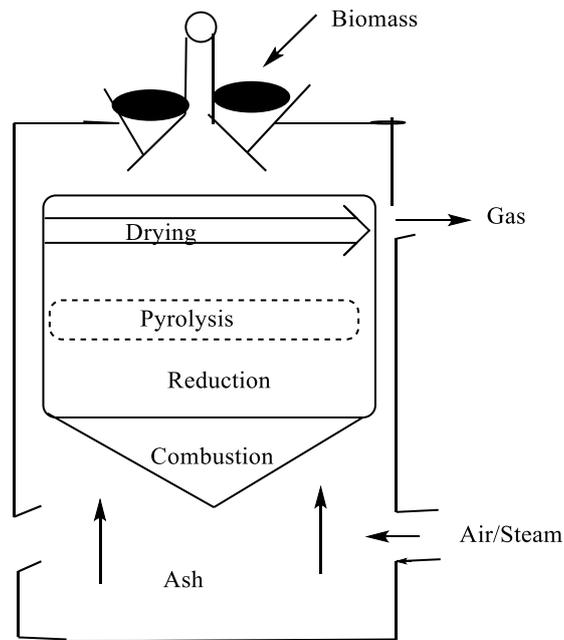
Figure 1.4: Biomass gasifier [Adapted from [18, 19]]

1.5.3   Liquefaction of Biomass

Biomass liquefaction can be categorised as a thermochemical process of converting biomass to liquid. In terms of lignin, this method is called LtL (lignin to liquid) [20]. This process occurs at a temperature of around 300 to 350ºC and high pressure between 5 and 20MPa. When catalysts are introduced alongside hydrogen, this process is referred to as catalytic liquefaction. Liquefaction can also be carried out in the absence of catalyst, this process is called direct liquefaction. The products from biomass liquefaction vary from solid, liquid and gas. The variation has to do with the reaction conditions [21]

1.5.4   Process of biomass combustion

Combustion is one of the process used for converting biomass into usable energy. The combustion process can be divided into several processes such as drying, pyrolysis and combustion. Starting combustion can be difficult but once ignition has taken place and there is sufficient air, combustion will proceed. Drying is the evaporation of moisture contained in the biomass and its uses heat released by the combustion processes. Biomass particles may contain water in different forms but when it enters combustion system, it undergoes conduction, convection and radiation. When the temperature of the particle rises above 100℃, it evaporates the water in the particles.

 On the other hand, pyrolysis is the process of heating up the fuel, by thermal decomposition process. Pyrolysis is also known as devolatilization [22]. It can occur without extra energy,

thereby referred to as exothermic process. For thermal cracking of compounds to occur, devolatilization of solid biomass starts at a temperature above 200℃, while formation of tars, liquids and gaseous products occurs at temperature of about 600℃. Tars are complex hydrocarbons with an organic structure similar to base fuel, they evaporate from the biomass at temperatures between 400 to 600℃ and condenses at a temperature below 200℃ and forms sticky layers on equipment it is used on. When the temperature goes above 600℃, solids intermediates is being converted into char and this results to split of carbon monoxide and hydrogen. Due to high volatile matter content of biomass, the pyrolysis stage lasts a relatively long period when compared to coal.

In addition, comes the combustion of volatile matter or char. The combustion of volatile matter is basically determined by high reaction rates. Concentration of volatile components decreases with increase in distance of biomass particle, this is as result of volatile particles which diffuses into bulk gas. When volatile matter is released from the particle and the porous structure such as carbon and ash is referred to as char. When the reaction rate of combustion of volatile matter is compared to combustion of char, it is observed that the orders of magnitude of char is lower, hence the total combustion time is therefore determined by the rate of char combustion [22].

1.5.5   Thermal conversion of biomass

Essential properties relating to thermal conversion of biomass include Bulk density, Moisture content, Heating value, Ash content, Elemental composition.

Bulk density is the weight of material per unit of volume. Biomass bulk densities shows variation but the bulk density is majorly expressed on an oven dry weight basis where the moisture content is equal zero percent. There is low bulk density of biomass and high bulk density. Low bulk density means the material has low energy density and otherwise for greater bulk density. To have a condensed feedstock, pressure may be applied to process to create solid. When biomass is densified into pellets, this process is called pelletisation and this process is used to increase bulk density of biomass [23].

Heating value of a fuel has to with energy chemically bounded in the fuel with reference to a standardized environment. The Standardization in this aspect referred to temperature, state of water as well as combustion products. The standards are essential in measurements of heating values. Heating value and bulk density determine the energy density [23], that is, the potential

energy available per unit volume of biomass. The energy density of biomass of is approximately one-tenth of fossil fuels generation [23].

Moisture content has to do with the quantity of water in the material. This has a great effect on the value of the biomass, and for reference purpose the basis of which the moisture content is measured must be stated. The moisture content for forest residues is about 50 to 70percent and that of grains and cereals is less than 10percent [23].

Ash Content can also be expressed in the same way as moisture content, but generally it is expressed on a dry basis. The ash content and chemical composition in biomass are important as this affect the behaviour depending on temperatures of combustion and gasification.

Elemental composition of biomass is relatively uniform. It consist of carbon, oxygen and hydrogen as major components. Most biomass also contains relatively small proportion of nitrogen.

1.5.6   Fermentation

Fermentation of biomass can be described as the process of breaking down the glucose in the biomass to produce ethanol. Ethanol has been adopted to power automobiles. Fermentation mostly occurs in the absence of oxygen thereby classified as anaerobic process. Some biomass used for bio ethanol production are agricultural wastes, wheat, bagasse [21]. Most lignocellulosic biomass contains lignin in addition to cellulose and hemicellulose. This lignin cannot be fermented. In other to ferment biomass, the process entails adding yeast as a form of catalyst that converts sugars to ethanol. A simple chemical equation for fermentation process is given in equation 2.

$$C_6H_{12}O_6 \ \rightarrow 2C_2H_5OH + 2CO_2 \tag{2}$$

1.6 Products from Biomass Conversion

Various products are derived from the processing of biomass. This project is focus on the production of bio oil as the main product from biomass conversion. Some common biofuels are discussed below.

1.6.1 Ethanol from Biomass

Ethanol (C_2H_5OH) can be produced from biomass in various ways through its components such as sugar, cellulosic and starch. Fermentation is one of the common process in which yeast is converted to ethanol [24]. The type of sugar or starch determines the generation classification of ethanol. Ethanol from feedstocks which contain larger quantities of sugar is referred to as first generation while the second generation comes from lignocellulosic biomass. Above all, the most abundant renewable resource in the world is plant cellulose [24]. The process of converting starch and cellulosic biomass into ethanol requires that microbes break down the starch components into sugars and the sugar is converted to ethanol by fermentation of yeast. Cellulosic biomass requires hydrolysis to produce sugars before fermentation. First generation biomass can easily be fermented while lignocellulosic biomass requires chemical to ferment. Figure 1.5 shows ethanol production from biomass.
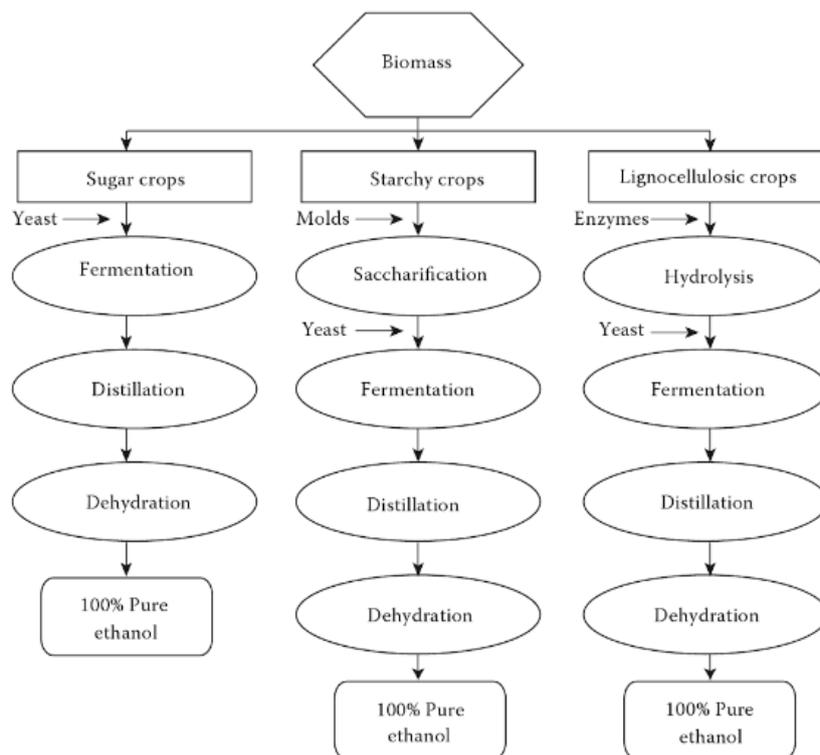

Figure 1.5: Ethanol production from various biomass components[24]

Another alternative approach for producing ethanol from lignocellulosic is by biomass gasification process and this involves burning of biomass in a regulated process to produce synthetic gas and conversion of the synthetic gas to ethanol. Synthetic gas can also be referred

to as syngas and it can be converted to ethanol by two main approaches, one is by using microorganisms as biocatalysts to convert syngas to ethanol while the second approach is by using a metal based catalyst to produce ethanol from syngas[25]. This is shown in figure 1.6
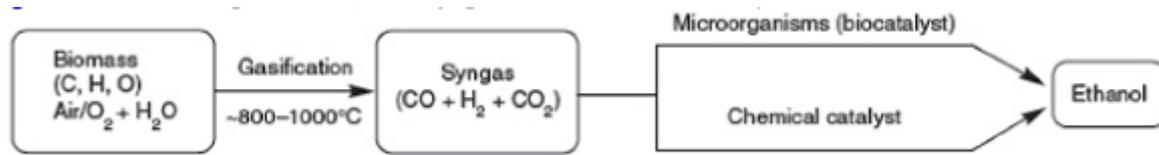

Figure 1.6:Biomass gasification process, syngas to ethanol conversion[25]

1.6.2   Biogas and Biodiesel from Biomass

Biogas can be referred to as flammable gases of different composition mainly generated when organic material undergoes anaerobic decomposition, that decomposition in absence of oxygen[26]. The organic material could be food, sewage sludge, plant debris, animal manure and many others. When this material undergoes decomposition in the absence of oxygen, it generates gas such as methane, carbondioxide and others.

Due to high demand of diesel fuel and the pollution problems caused by its usage, a renewable fuel was encouraged and this was biodiesel. It consists of monoalkyl esters of long chain fatty acids derived from animal fats or vegetable oil. It is the alkyl ester of fatty acids made by the transesterification of oils or fats derived from plant or animal[27].

1.7 Bio Oil Production in Africa and Feedstocks

Africa with a population of over 885 million, with a diversified socio cultural backgrounds has a well rich land mass bigger than other continents in the world. The energy resources in Africa is not evenly distributed. Of the 53 countries in the continent, only about 4 countries, Algeria, Nigeria, Angola and Egypt have a self-sustained energy resources [28]. The other countries depend on importation of their energy resources, which results into spending a high percentage of their budget on sourcing for energy. As a results of this, the need to produce a sustainable fuel locally is of utmost important. Biodiesel and other biofuels from biomass is a better alternative to the dire need of Africa scarce energy than importing oil. At the moment, jatropha oil is mostly used in producing biodiesel in Africa. Vegetable oil and animal fats will be an alternative in years to come [29]. The use of edible vegetable oil will pose a challenge to the sustainability considering the fact that Africa energy demand will rise to about 60 to 80% in 2030 according to world bank statistics [28]. The use of non-edible feedstocks will be a good advantage for biodiesel production in Africa. The continent has a huge land mass over 1 billion

hectares of land which is fertile to yield biodiesel feedstocks but only about less than one fourth is being actively cultivated. Ethanol and biodiesel in the form of liquid biofuel is produced in small quantities in Africa as a results of limited policies in place. The production of large quantities is underway due to high fuel prices and the investors interest in biofuel exportation [30]. Some potential feedstocks that could be used to produce biofuel are highlighted below:

Jatropha Oil

Jatropha oil is commonly found in Africa and Asia continent. Over the past years, it has been used for biodiesel production. It is renewable because it has a high seed yield which can be continuously produced for 30–40 years and the oil content is approximately 30–40% by weight. Biodiesels produced from jatropha seeds is subject to oxidative instability due to its predominantly presence of unsaturated fatty acid. The free fatty acid content in jatropha oil is high compared to some other bio oil plants. In Jatropha oils, the main acids present are oleic and linoleic acids with almost 74.2% [31]. [3] studied the oxidation stability of biodiesel synthesised from jatropha oil of African origin. The fatty acid composition produced from jatropha oil methyl ester is rich in unsaturated fatty acid (77.5%) with only 22.4% saturated fatty acid methyl esters.

Bagasse

It is a fibrous residue from sugarcane after crushing it into the mill. Sugarcane produces a number of industrial feedstocks such as molasses and bagasse. Bagasse from sugarcane can be used to produce electricity, heat and biochemical products. Biofuel could be made from sugarcane bagasse but it requires a thermochemical treatment. Production of ethanol from sugarcane bagasse requires pre-treatment such as physical and chemical treatment or combination of both to enhance enzymatic hydrolysis. The pre-treatment helps to remove structural and compositional barrier of lignocellulosic materials which helps improve the rate of hydrolysis [32].

Eucalyptus

Eucalyptus species are excellent commercial crops which grows in a wide range climatic conditions. Different parts of the plant such as the leave, bark, flower and even oil generated can serve different purpose. The tree can be process to biofuel.

Trisperma oil

Trisperma oil seeds (Aleurites trisperma). This is a potential oil seeds for biodiesel production in that, it has one of the highest oil content of about 62% by weight. [33], investigated that at 65°C, 95% of biodiesel yield with density of 887kg/m^3 and flash point of 148°C can be gotten using trisperma oil as feedstock. Trisperma seeds have a very high polyunsaturated fatty acid, making it a poor choice for biodiesel production.

Jojoba Oil

Jojoba oil is another very viable substitute for fossil fuel. It contains a long chain monounsaturated liquid wax esters. Jojoba oil is different from trigycerides structurally. Recent researches have shown that it is more efficient, the combustion is clean, it does not pollute the environment, most importantly, and it releases more energy than fossil fuel. It is also a stable compound. Studies show that jojoba oil can withstand the high temperatures from an engine without changing its form. Jojoba oil as a potential feedstock for biodiesel is eco-friendly due to its low carbon ratio when compared with fossil fuel, as a result of this, the emission of the pollutant from the exhaust pipe will be minimal [34]. The content of sulphur in the oil is zero, meaning that the emission of sulphur oxide is very minute which reduces the exposure to acid rain from the environment. All these factors make jojoba oil a better option to run the engines, thereby providing long lasting automobile engines.

Country like Egypt has started planting this plant for biodiesel production. It can excel in a harsh dry land. It is easy to cultivate and can produce nuts continuously throughout its entire life. The only set back in using jojoba seed is the huge amount that will be require to cultivate it in a large scale and fund necessary to finance the desert like land for its planting [35].

Rubber Seeds

Rubber seed is also a non-edible feedstock for biodiesel production. The raw feedstocks from biodiesel production account for 60-80% of the overall production cost. Producing biodiesel from non-edible feedstocks will reduce the production cost and consequently the biodiesel price. At present, about 251million rubber trees are in Sub Sahara Africa. These trees have the capacity to produce well over 16,000 tons of biodiesel. Rubber seeds contain 40 to 52% of the kernels by weight and 35% shell by weight. The moisture content is 20- 25%wt [36].

Croton Tree

Croton tree commonly called C. Megalocarpus is a potential feedstock for biodiesel in Africa in time to come. It is mostly found in east Africa. The seeds contain 40-45% oil.

C. Megalocarpus is much similar to other biodiesel feedstocks in terms of chemical and compositions. It has approximated cetane number of 40. [37] Research carried out by [37] indicate that the calorific value of croton tree is 43.6MJ/kg. The by product of this oil is useful for animals and birds' feeds.

Moringa Oleifera

Moringa oleifera is another important feedstocks plant used for biodiesel production. It is commonly found in India, Asia, African and South America. [38] investigated that Moringa seeds contain between 35% and 40% weight of vegetable oil. The oil is similar to olive oil with excellent qualities. Moringa contain oleic acid which account for about 71% of the oil. This high acid makes moringa suitable for biodiesel production [39]. Moringa could yield about 20 metric tonnes of pods per hectare in one year. This amount can be used to produce 3000 to 4000 liters of biodiesel.

The oxidative stability of Moringa oleifera oil was studied by [3] in eastern part of Africa. The study reveal that Moringa oil methyl ester is rich in 68.5% oleic acid methyl esters and 13.5% palmitic acid methyl esters with lower polyunsaturated fatty acid methyl esters (2.5%). The antioxidants were doped to increase the oxidation stability of Moringa oil methyl ester. Pyrogallol and propylgallate antioxidants are more effective than butylated hydroxyanisole antioxidate. Moringa oil methyl ester has a high cetane number of about 62.3. This is as a results of the high fatty acid in the plant. This cetane number rank among the highest in biodiesel from plants as feedstocks. Biodiesel produced from moringa oil is also thermally stable, recording the onset temperature of 237.05 °C.

1.8 Biofuel classification

Biofuel are classified into two major categories which are first and second generation biofuels. These classifications are based on the type of feedstocks and the process technologies that is applied. First generation biofuel refers to fuel derived from biological sources such as sugar, starch, vegetable oil and animal fats. They are also known as conventional biofuels as they are produced from cereal crops, sugar crops, and oil crops using different technology for production. Typical types of first generation biofuel include conventional biodiesel, bio alcohols, vegetable oil and biogas [9].

Second generation biodiesel are derived from lignocellulosic feedstock, they are produced from non food crops such woody material and perennial grasses. This feedstock a times produces more biofuel and also require less chemical and energy input for production and harvesting. However raw material from second generation biofuel is considered sustainable than first generation biofuel. Second generation biofuels can also be referred to as advanced sustainable biofuels and advanced research are still on going on this biofuel generation. Biofuels from this generation include algae fuel, biomethanol, bio-methylether, cellulosic ethanol [9] and many more.

Biofuel refers to solid, liquid and gas fuels. Two major forms of biofuel are biodiesel and bioethanol. The main usage of solid fuels is for space heating during combustion while liquid and gases are used for transportation and industrial processes. They are produced through the process of fermentation, torrefaction, gasification and more. Figure 1-7 represents energy products and the end uses.
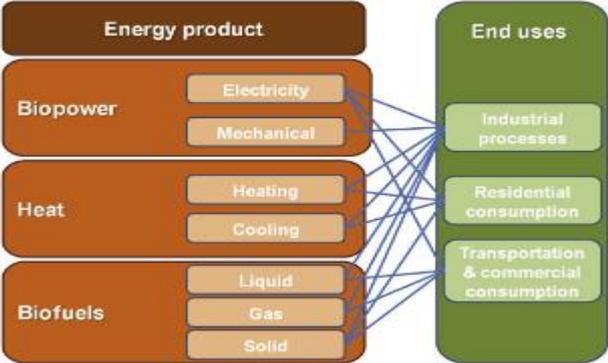

Figure 1.7: Energy product and end uses [10]

1.9 Biorefinery

Biorefinery is defined as a sustainable concept of integrating biomass into a useful and marketable products. The products derived from biorefinery process depends on the biomass used. Major products from biorefinery process are power, heat, fuels and chemicals. The process is similar to petroleum refinery [40]. Figure 1-8 depicts a simple biorefinery process.
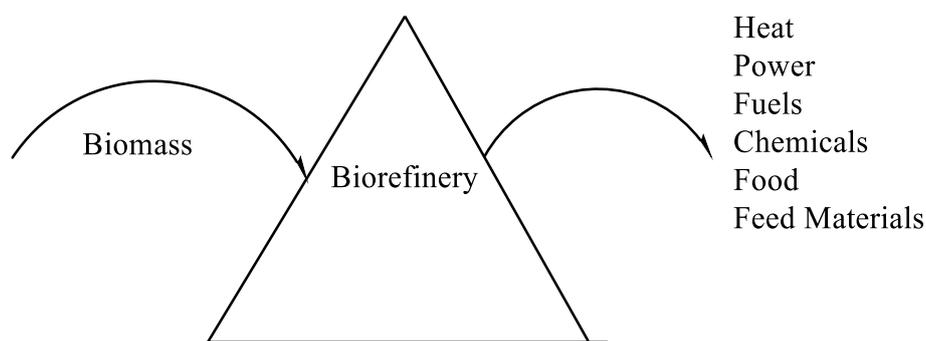
Figure 1.8: Biorefinery process and products

Biorefinery process should produce a spectrum of useful products and energy. During bio refining, oils are being crushed out of the biomass and these oils are later refined to fuels and energy. The residues from the biomass after oil extraction can also be converted to fuel.

1.10 Aim and Objectives

The aim of this work is to use the method of thermochemical LtL process with water as solvent and formic acid as hydrogen donor to depolymerise the plants residues after oil had been extracted out, to produce bio oil. The focus of this project is to maximise bio refinery process by making use of the residues from the process to further produce fuel, energy and chemicals by LtL through depolymerisation of the molecules.

The objectives are:

- Literature survey of potential bio plants materials
- Perform screening experiment on plants residues using LtL methods, and find the maximum oil yield.
- Analyse the oils with GC-MS to identify the major compounds in the products

2 Methodology

This chapter describes the technique applied for carrying out the experiments. Some parameters outlined in this chapter are, the reaction conditions such as solvent, temperature, time duration, and the values of feedstocks used for the pyrolytic process.

2.1 Pyrolytic Process of Residual Feedstocks

The feedstocks used for this project are eucalyptus, bagasse, and jatropha residues. The pyrolytic processes adopted for the three feedstocks were similar except for the variations in conditions. Highlighted below is the process involved.

- Oven is adjusted to the desired temperature
- The solvent was prepared as ratio (9:1 ethyl acetate: tetrahrofuran).
- 75mL reactor is thoroughly washed with solvent.
- Measured feedstocks, water and formic acid are mixed and transfer to the reactor.
- The reactor is then tightened according to Mikel methods (See appendix) which stepwise is stated below: start at 7Nm, then increase the tork to 13.5Nm and 20.5Nm. The reactor is then tightened three times at 20.5Nm with the bolts waxed at every steps.
- The reactor is then weighed.
- The reactor is thereafter transfer to the oven and heated at stipulated temperature.
- Take out the reactor and cool it overnight.

The work up procedures are stated below:

- The cooled reactor is then weighed to see if no leakage.
- Open the reactor in a fume hood to let out gas.
- The evaporated gas was then weighed, the difference between the initial weight of reactor and the final
- The solution in the reactor was transferred to a beaker with a pipet, the remaining content was then extracted from the reactor with solvent.
- The water was separated from the oil and the water weight was recorded
- Little amount of sodium sulphate was mixed with the oil and stirred for 2hrs.
- The solution is then filtered under vacuum.
- The separated oil and solvent was transferred to a round beaker and to a rotorvapor.

- The oil and solvent was then evaporated with the rotavapor.
- The oil was then weighed and rinse with the solvent.
- Mixture of oil and solvent was transferred and dried under nitrogen.

2.2 Pyrolysis of Eucalyptus

The eucalyptus used was produced at biorefinery demo plant (BDP) in Örnsköldsvik, Sweden. It originated from Thailand.

A varying weight (0.5-1.54g) of eucalyptus powder was mixed with different proportion of water (4-15g) and (0.9 -2g) of formic acid in a 75mL reactor. The reactor was placed in an oven for 2hrs at a temperature of (320-380°C). The table 2-1 shows the values of feedstocks used for the experimental work:

Table 2-1: Feedstocks Input for eucalyptus pyrolysis

Experiment No.	Eucalyptus (g)	Temperature (°C)	Time (h)	Water (g)	Formic acid (g)	Total input mixture (g)
1	0.8	300	2	8	1.5	10.3
2	1.54	320	2	15	2	18.54
3	1.54	340	2	15	2	18.54
4	0.5	340	2	4	0.92	5.42
5	1.54	360	2	15	2	18.54
6	1.54	380	2	15	2	18.54

Table 2-1 shows the values inputs for the pyrolysis of eucalyptus. The experiments were carried out at a constant time duration and all other parameters were varied.

2.3 Pyrolysis of Bagasse Residues

Bagasse is the fibrous biomass residue remnants gotten from pressed sugarcane fluid. Bagasse can be said to be classified as a second generation cellulosic biofuels feedstocks.

Dried untreated bagasse was used for this experiment. The bagasse contains dried stem and leafs. It was gotten from Karl Weyland, Bergen University College. There were no initial pre-treatments on the bagasse. The composition for 100g basis dried bagasse is given in table 2-2:

Table 2-2: 100g Bagasse Compositions [41]

Components	Chemical Compositions
Polysaccharides	56.16 ± 0.80
Glucan	41.34 ± 0.49
Xylan	13.21 ± 0.17
Arabinan	1.61 ± 0.14
Lignin	20.66 ± 0.51
Acid insoluble lignin	19.59 ± 0.51
Acid soluble lignin	1.07 ± 0.00
Others	17.88 ± 0.81
Ash	6.76 ± 0.47
Extractive	11.12 ± 0.34
Solid residues	94.70 ± 2.12

The process was repeated using bagasse as the feedstock with a varying amounts and different process conditions of temperatures ranging from 320 to 380°C, formic acids (1-2g), time is kept constant at 2hrs and the solvent water was varied from 5 to 15g.

Table 2-3 shows the feedstocks and compositional inputs of pyrolysis of bagasse.

Table 2-3: Bagasse pyrolysis at varying temperatures.

Experiment No.	Bagasse (g)	Temperature (°C)	Time (hr)	Water (g)	Formic acid (g)	Total inputs (g)
1	1.54	320	2	15	2	18.54
2	1.54	340	2	15	2	18.54
3	1.54	360	2	15	2	18.54
4	1.54	380	2	15	2	18.54

The amounts of bagasse used was later varied, also the solvent, formic acid and temperature were also varied from 320 to 380°C. Table 2-4 illustrates the values of these variations.

Table 2-4: Bagasse pyrolysis at varying conditions

Experiment No.	Bagasse (g)	Temperature (°C)	Time (hr)	Water (g)	Formic acid (g)	Total input (g)
1	0.5	320	2.0	5.0	1.0	6.5
2	0.5	340	2.0	5.0	1.0	6.5
3	1.0	320	2.0	10.0	1.6	12.6
4	1.0	340	2.0	10.0	1.6	12.6
5	1.54	320	2.0	15.0	2.0	18.54
6	1.54	340	2.0	15.0	2.0	18.54
7	1.54	360	2.0	15.0	2.0	18.54
8	1.54	380	2.0	15.0	2.0	18.54

2.4 Extraction of Oil from Jatropha Seeds

Jatropha seeds can be applied for different purposes. The viscous oil in this plant is about 50% wt which is used in the industries for producing several household utilities ranging from soaps, candles and also as diesel additives [42]. Jatropha plant has numerous species which are mostly America native. The jatropha seeds used for this project is the jatropha curcas which was supplied by Dr Jorge Marchetti of the Norwegian University of life sciences. The oil in the jatropha is extracted using the Soxhlet methods. An approximate 40% of fat was extracted from the jatropha curcas using this method with dichloromethane as the solvent.

The procedures for this method is stated below.

- Jatropha seeds were blended into powdering form using mortal.
- The apparatus was set up as shown in figure 2-1. The apparatus was washed with dichloromethane and run for about 2hrs.
- The powder jatropha curcas was weighed and poured into the thimble and then covered with cotton wool.
- The equipment is set up and run for 24hrs.
- The thimble was then collected from the distillation flask and dried in an oven for about 6hrs.
- The jatropha residues left in the thimble were the weighed.
- The extracted fat from the jatropha curcas which was mixed with dichloromethane in the still flask was evaporated using a rotorvapour instrument.
- The dichloromethane was evaporated further with nitrogen gas.
- The fat was then weighed.

Figure 2.1: Soxhlet apparatus set-up

2.5 Pyrolysis of Jatropha Residues

The jatropha nuts residues gotten after fat extraction was made to undergo pyrolytic Ltl reaction in a 75mL reactor. The reaction conditions were varied. The temperature ranges from 320 to 380°C, time was at 2hrs for first experimental sets and 4hrs thereafter, solvent (water) was at 15g, formic acid at 2g. Table 2-5 shows the first experimental sets, the second experiment is illustrated in table 2-6. Figure 2.2 shows a raw jatropha seeds.

Figure 2.2: Jatropha seeds

Table 2-5: First Jatropha Experimental set.

Experimental No	Jatropha (g)	Temperature (ºC)	Time (hr)	Water (g)	Formic acid (g)
1	1.54	320	2	15	2
2	1.54	340	2	15	2
3	1.54	360	2	15	2
4	1.54	380	2	15	2

Table 2-6: Second Jatropha Experimental set

Experimental No	Jatropha (g)	Temperature (ºC)	Time (hr)	Water (g)	Formic acid (g)
1	1.54	320	4	15	2
2	1.54	340	4	15	2
3	1.54	360	4	15	2
4	1.54	380	4	15	2

2.5.1   Data Analysis

In the course of this project, some calculations, formulas are employed to analyse the data. The products gotten from the various synthesis were calculated in relations to the amounts of feedstocks used. The oil yields were analysed in g/g of the lignin used, same to the char and gas yields were analysed based on the amount of formic acid used. The mass balance analysis was based on the ratio of the percentage difference between the input and output. The loss

was accounted for by considering the initial difference between the weight of the loaded reactor before and after applying heat.

Ratio of Oil yield in feedstocks (g/g) = Oil produced (g)/ lignin(g)

Ratio of char yield in feedstock (g/g) = Char produced (g)/ lignin(g)

Ratio of gas yield in feedstock (g/g) = Gas evaporated (g)/ formic acid (g)

Mass balance = 100 – [(total input – total output)/ total input) x 100].

2.6 Analytical Techniques Used

The products gotten from the synthesis of the feedstocks were analysed using gas chromatography and mass spectrometer (GC-MS). The instrument was used to analyse the compounds from the yields.

2.6.1 Gas Chromatography and Mass Spectrometer

This instrument was used to detect the various compounds present in the products samples. It was used with the combination of gas chromatography and mass spectrometer. The conditions that was considered in using this instrument are the delay time, the initial temperature, final temperature, the injection temperature and heating rate.

Initial temperature: 40°C

Hold time 5min

Heating rate 1: 6°C/min

Final temperature1: 280°C

Hold time: 0min

Final temperature 2: 300°C

Hold time: 5min

Heating rate 2: 40°C/min

Injection temperature: 280°C

Mass spectrometer temperature: 250°C

Delay valve set time: 4.6mins

3 Results

This chapter describes the outcomes of the experiments conducted. The results include the yields and compounds from GCMS.

3.1 Yields of Eucalyptus Pyrolysis

Table 3.1 shows the amounts of products generated from the pyrolytic reaction in table 2-1.

Table 3-1: Products of pyrolytic reaction from table 2-1

Experiment No.	Oil yield (g)	Ratio of oil to input (g/g)	Percentage oil yield (%)	char (g)	Gas evaporated (g)	Aqueous (g)	Total output (g)
1	0.4320	0.540	54.0	0.063	1.20	7.940	9.635
2	0.7998	0.519	51.9	0.351	1.80	14.967	17.918
3	0.8870	0.576	57.6	0.320	1.75	14.857	17.814
4	0.2424	0.481	48.1	0.050	0.90	4.150	5.322
5	0.8910	0.579	57.9	0.448	1.80	14.924	18.063
6	0.8965	0.582	58.2	0.410	1.82	15.025	18.152

The oil yield as shown in table 3-1 varies depending on the temperature and amount of eucalyptus added to the reactor. Figure 3-1 shows the plot of yield and temperature from table 3-1.
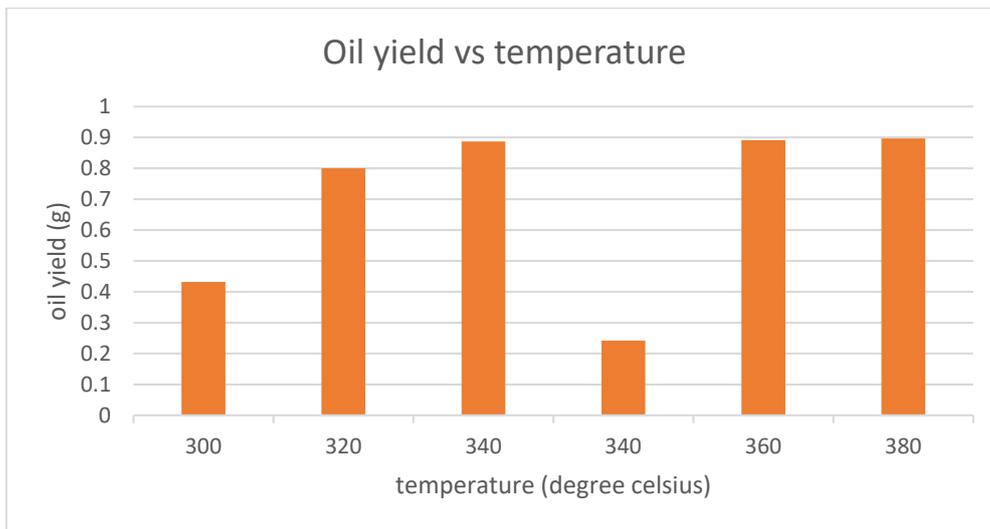
Figure 3.1: Oil yield vs Temperature for Eucalyptus

The charts in figure 3-1 shows the variation of temperature and the oil yields in the eucalyptus pyrolytic synthesis.

The amounts of oil produced from the biomass (eucalyptus) used and temperature is shown in figure 3-2.
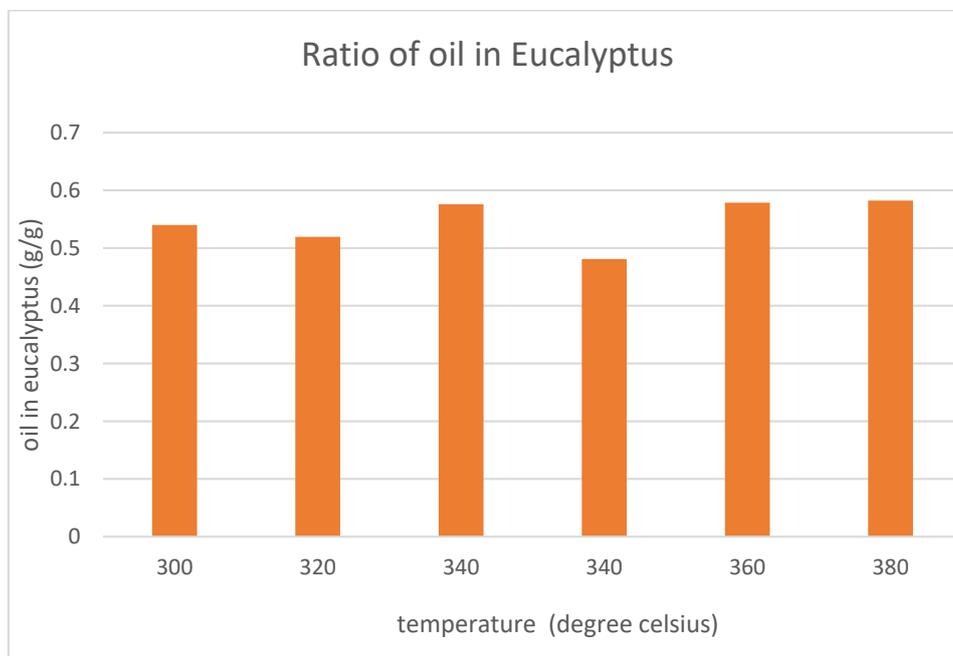
Figure 3.2: plots of Oil in eucalyptus vs Temperature

In the pyrolytic process, the amounts of char produced and gas given off in the process are illustrated in figure 3-3 and figure 3-4 respectively.
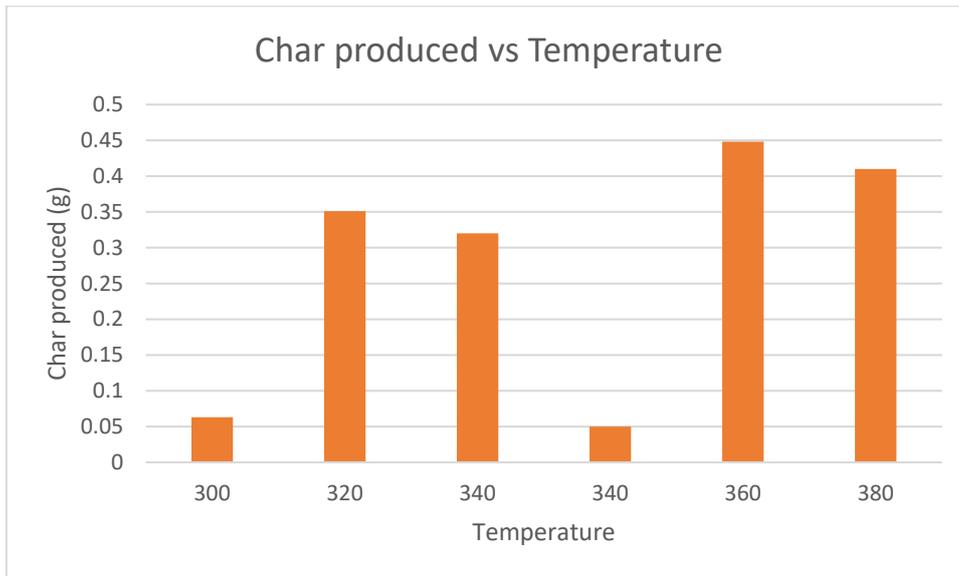
Figure 3.3: Char produced from eucalyptus pyrolysis
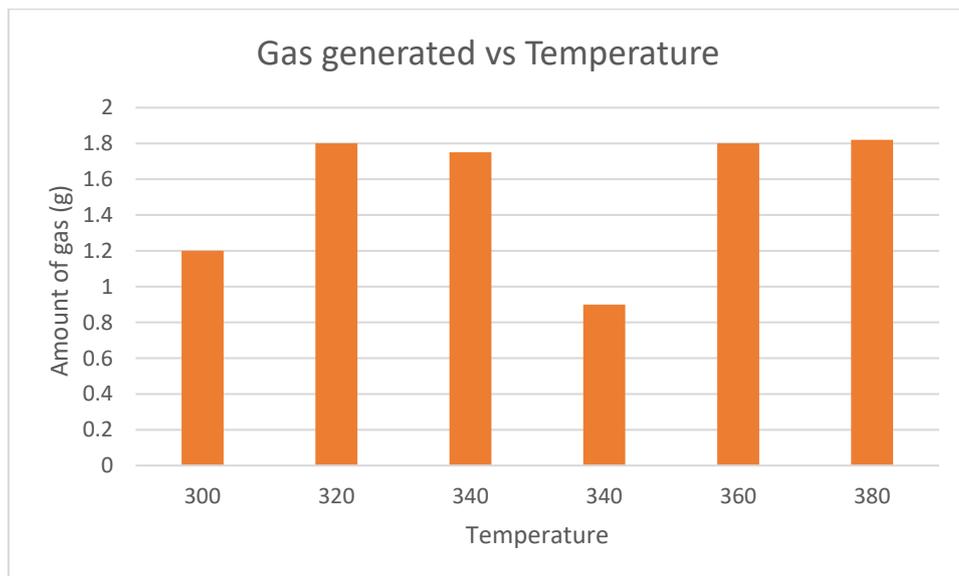
Figure 3.4: Amount of gas generated from eucalyptus pyrolysis

The mass balance from table 2-1 and table 3-1 is shown in table 3-2

Table 3-2: Mass balance of eucalyptus pyrolysis from table 2-1 and table 3-1

Total inputs (g)	Total output (g)	Loss from reactor(g)	Mass balance (%)
10.3	9.635	0.000	94
18.54	17.918	0.000	97
18.54	17.814	0.013	96
5.42	5.322	0.120	98
18.54	18.063	0.000	97
18.54	18.152	0.110	98

The least mass balance was over 94% and the highest was below 99%.

The loss is the difference between the weight of reactor before and after heating.

3.2 Probable Compounds in Eucalyptus Pyrolysis

The table 3-3 shows the compounds from pyrolysis of eucalyptus. The solvent used was dichloromethane and concentration of 10mg oil/10ml solvent. The compounds are represented based on the temperature condition. A, B, C and D indicates temperature 320, 340, 360 and 380ºC respectively. The percentage probability of the identification occurrence of these compounds are also shown.

Table 3-3: GCMS Compounds derived from eucalyptus pyrolysis

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	% probability	A	B	C	D
1	Isobutyl acetate $C_6H_{12}O_2$	5.251	116	116, 73, 56	91.9	x			
2	2-Cyclopenten-1-one, 2-methyl- C_6H_8O	9.916	96	96, 67, 53	85.1	x			
3	2(3H)-Furanone, dihydro-5-methyl- $C_5H_8O_2$	10.708	100	100, 85, 56	77.3	x			
4	2-Cyclopenten-1-one, 3-methyl- C_6H_8O	11.004	96	96, 81, 67	64.6	x			
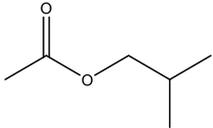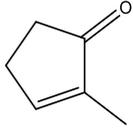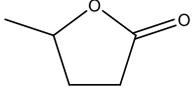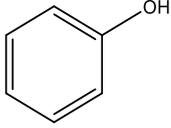
5	Phenol C_6H_6O 	11.752	94	94, 66, 55	73.0	x			
6	Phenol, 2-methoxy- $C_7H_8O_2$ 	14.691	124	124, 109, 81	78.3	x			
7	Creosol $C_8H_{10}O_2$ 	17.438	138	138, 123, 95	66.3	x	x		
8	Catechol $C_6H_6O_2$ 	17.564	110	110, 92, 64	85.8	x	x		
9	1,2-Benzenediol, 3-methoxy- $C_7H_8O_3$ 	19.108	140	140, 125, 97	76.4	x			
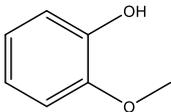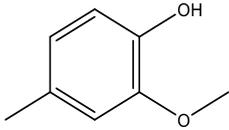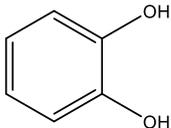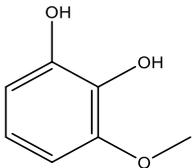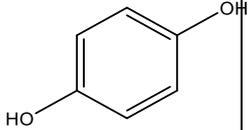
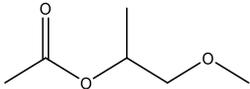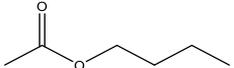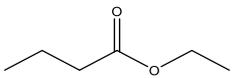| 10	Hydroquinone $C_6H_6O_2$	19.384	110	110, 81, 53	72.5	x	x	x	x
11	Phenol, 4-ethyl-2-methoxy- $C_9H_{12}O_2$	19.559	152	152, 137, 122	79.8	x			
12	1,2-Benzenediol, 4-methyl- $C_7H_8O_2$	19.756	124	124, 107, 78	70.6	x			
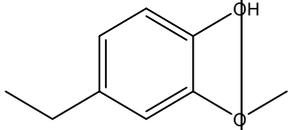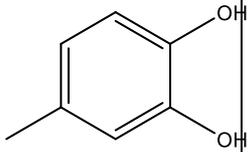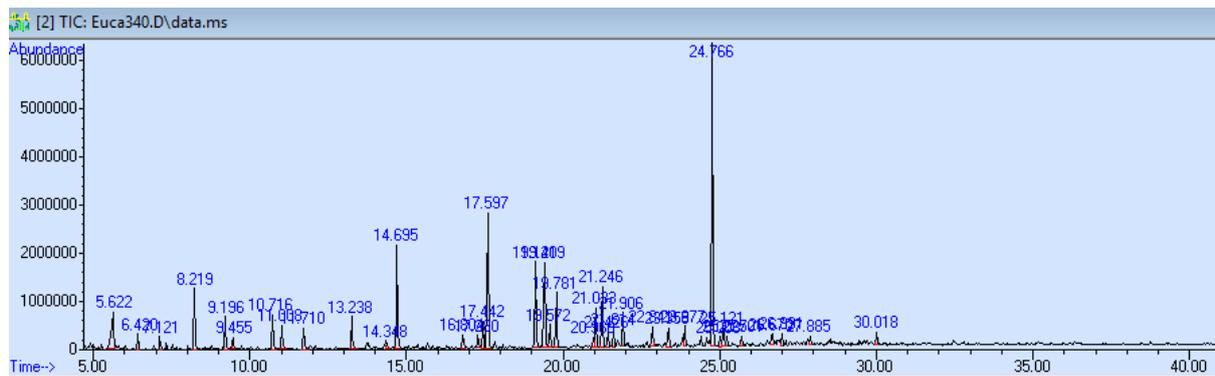
Figure 3.5: Eucalyptus analysis peaks at 340ºC

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	Percentage probability	A	B	C	D
13	1-Methoxy-2-propyl acetate $C_6H_{12}O_3$	8.219	132	87, 72, 58	97.8			x	
14	2-Cyclopenten-1-one, 2-methyl- C_6H_8O	9.209	96	96, 67, 53	83.6			x	
15	Phenol, 2-methoxy- $C_7H_8O_2$	14.695	124	124, 109, 81	68.3			x	
16	Catechol $C_6H_6O_2$	17.572	110	110, 92, 81	89.9	x	x	x	
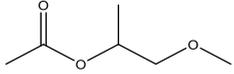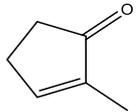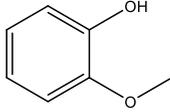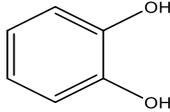
17	Hydroquinone $C_6H_6O_2$	19.363	110	110, 81, 53	72.0	x	x	x	
18	Phenol, 2,6-dimethoxy- $C_8H_{10}O_3$	21.234	154	154, 139, 111	64.7			x	
19	4-Ethylcatechol $C_8H_{10}O_2$	21.902	138	138, 123, 110	63.7	x	x	x	
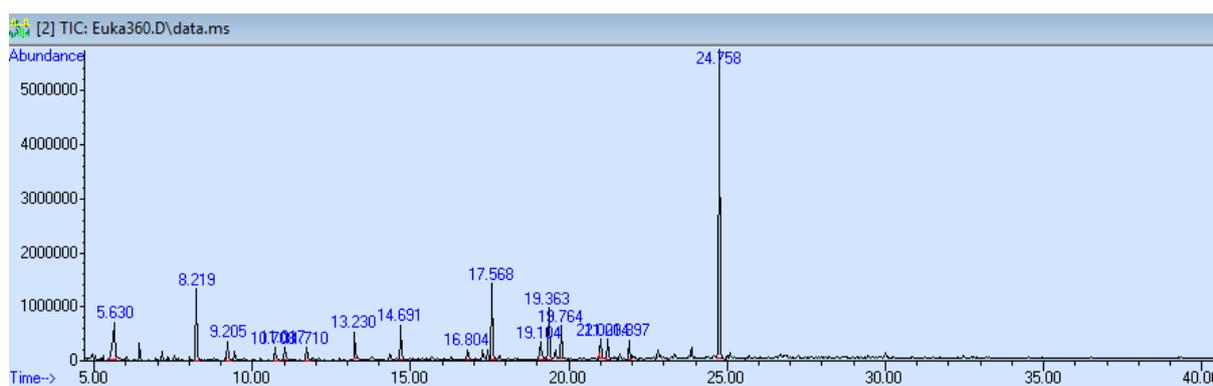
Figure 3.6: Eucalyptus pyrolysis peaks at 360ºC

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	Percentage probability	A	B	C	D
20	Isobutyl acetate $C_6H_{12}O_2$	5.276	116	107, 73, 56	92.5				x
21	Methoxy-2-propyl acetate $C_6H_{12}O_3$	8.219	132	87, 72, 58	85.4				x
22	Acetic acid, butyl ester $C_6H_{12}O_2$	6.428	116	73, 61, 56	95.5				x
23	Butanoic acid, ethyl ester $C_6H_{12}O_2$	6.027	116	88, 71, 62	85.1				x
24	Catechol $C_6H_6O_2$	17.572	110	110, 92, 81	89.1	x	x	x	x
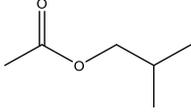
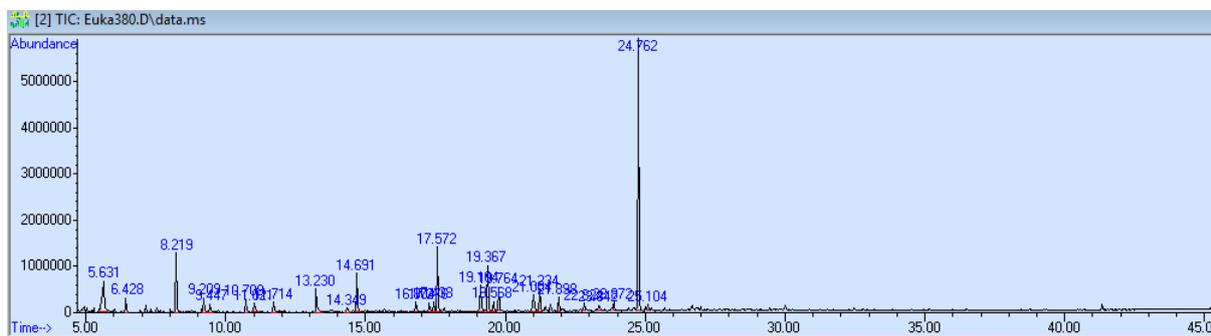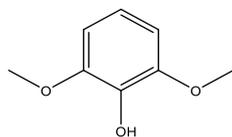| 25	Phenol, 2,6-dimethoxy- $C_8H_{10}O_3$	21.234	154	154, 139, 123	70.7				x

Figure 3.7: Peaks representing eucalyptus at 380ºC

3.3 Yields of Pyrolysis of Bagasse residues

The products derived from bagasses residual pyrolysis is shown in table 3-4. These values are from the inputs from table 2-3.

Table 3-4 Yields from bagasse pyrolysis

Experiment No.	Oil yield (g)	Ratio of oil to input (g/g)	Percentage oil yield (%)	char (g)	Gas evaporated (g)	Aqueous (g)	Total output (g)
1	0.665	0.4316	43.2	0.601	1.80	14.89	17.956
2	0.668	0.4336	43.4	0.581	1.80	14.92	17.969
3	0.670	0.4351	43.5	0.565	1.81	15.04	18.085
4	0.687	0.4461	44.6	0.520	1.83	14.85	17.887

The oil yield in the case of bagasse defers based on the temperature and the gas evaporated depends on the hydrogen donor; the formic acid. The charts representing the temperature, oil yields and char is shown in figure 3-8.
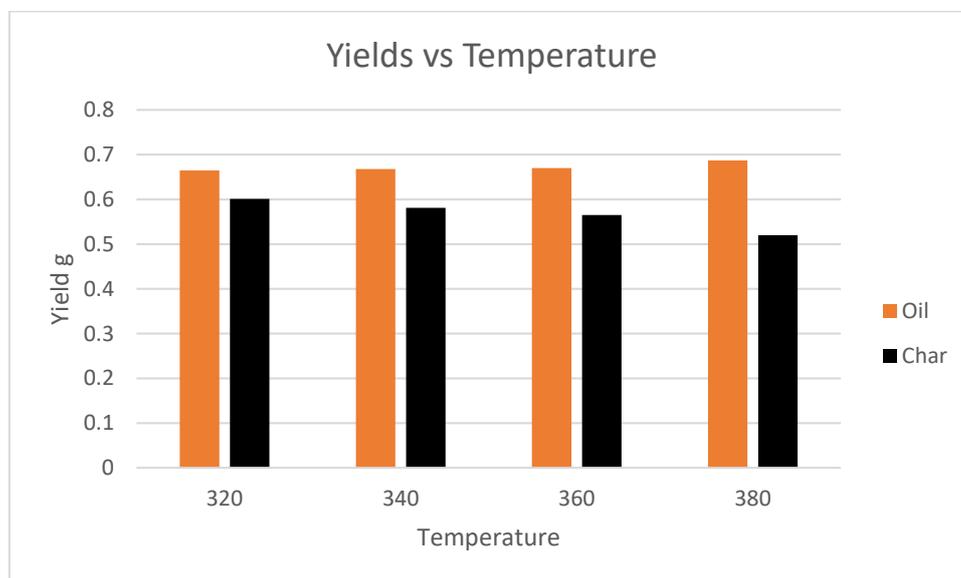
Figure 3.8: Oil and Char Yields

The chart shows how the oil yields increases as the temperature was varied from

320 to 380°C and the char produced decreases. Varying the formic acid, water, bagasse contents and temperature from table 2-4 above gives the results in table 3-5.

Table 3-5: Products from Pyrolysis of Bagasse with Varying conditions from table 2-4

Experiment No.	Oil yield (g)	Ratio of oil in bagasse (g/g)	Percentage oil yield (%)	char (g)	Gas evaporated (g)	Aqueous (g)	Total output (g)
1	0.172	0.344	34.4	0.094	0.70	4.94	5.91
2	0.196	0.392	39.2	0.075	0.75	4.96	5.98
3	0.379	0.379	37.9	0.239	1.43	9.68	11.73
4	0.423	0.423	42.3	0.214	1.46	9.81	11.70
5	0.665	0.432	43.2	0.604	1.80	15.02	18.09
6	0.668	0.434	43.4	0.584	1.80	14.85	17.90
7	0.670	0.435	43.5	0.572	1.81	14.91	17.96
8	0.687	0.446	44.6	0.531	1.83	14.78	17.83
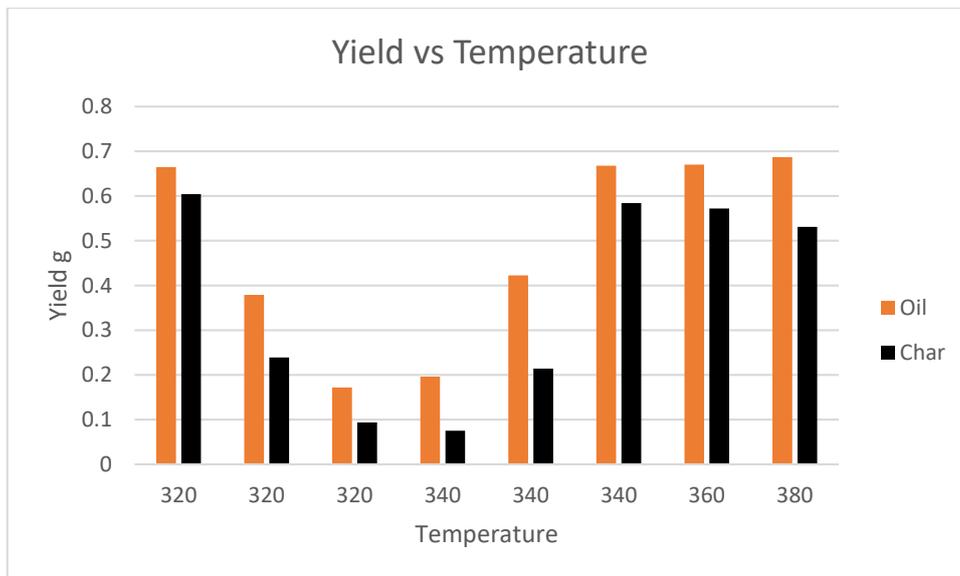
Figure 3.9: Bagasse Yields from vs temperature

The feedstocks used from table 2-4 to produce the results in table 3-5 shows some varying proportions of products based on the amounts of water and formic acid used and also the variations in temperatures. The mass balance can be analysed to deduce the inputs and outputs of the materials.

3.3.1   Mass Balance of Bagasse

The mass balance of bagasse pyrolysis in table 3-6 was analysed based on the values in table 2-4 and table 3-5.

Table 3-6: Mass balance of bagasse pyrolysis

Total inputs (g)	Total output (g)	Loss from reactor(g)	Mass balance (%)
6.5	5.91	0.000	91
6.5	5.98	0.000	92
12.6	11.73	0.000	93
12.6	11.70	0.100	93
18.54	18.09	0.000	98
18.54	17.90	0.120	97
18.54	17.96	0.000	97
18.54	17.83	0.021	96

As shown in table 3-6, the percentage of mass balance is below 90 and the highest accuracy is 98. The focal products, that is the oil, char and gas were calculated based on the feedstocks used in g/g as given in table 3-7.

Table 3-7: Yields g/g at varying temperatures

Temperature	Oil (g/g)	Gas (g/g)	Char (g/g)
320	0.344	0.70	0.19
340	0.392	0.75	0.15
320	0.379	0.89	0.24
340	0.423	0.91	0.21
320	0.432	0.90	0.39
340	0.434	0.90	0.38
360	0.435	0.91	0.37
380	0.446	0.92	0.35

The yields from the pyrolysis of bagasse at a temperature increase from 320 to 380°C, constant amount of water and formic acid at 2hrs heating is shown in the graph in figure 3-10 to figure 3-12.
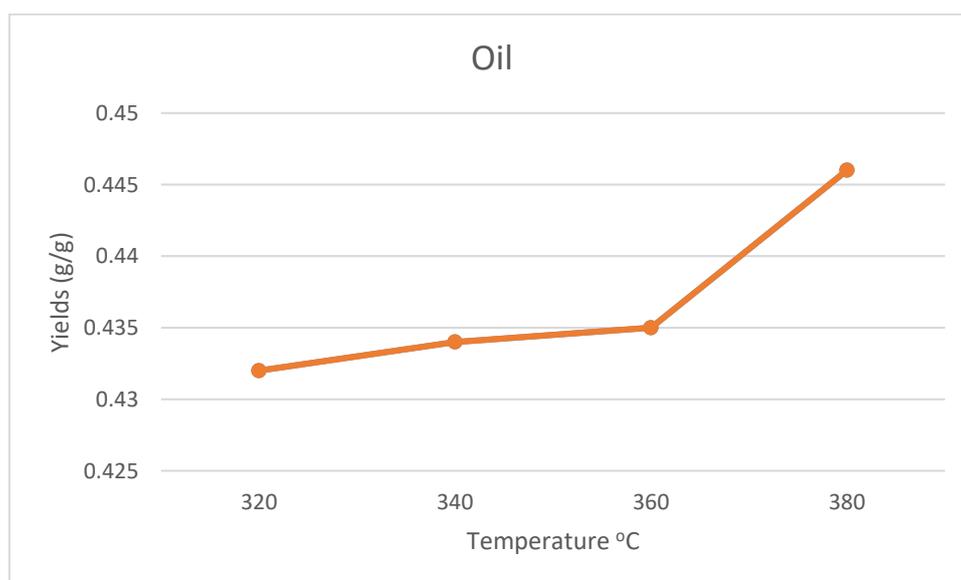
Figure 3.10: Oil yields in Bagasse content
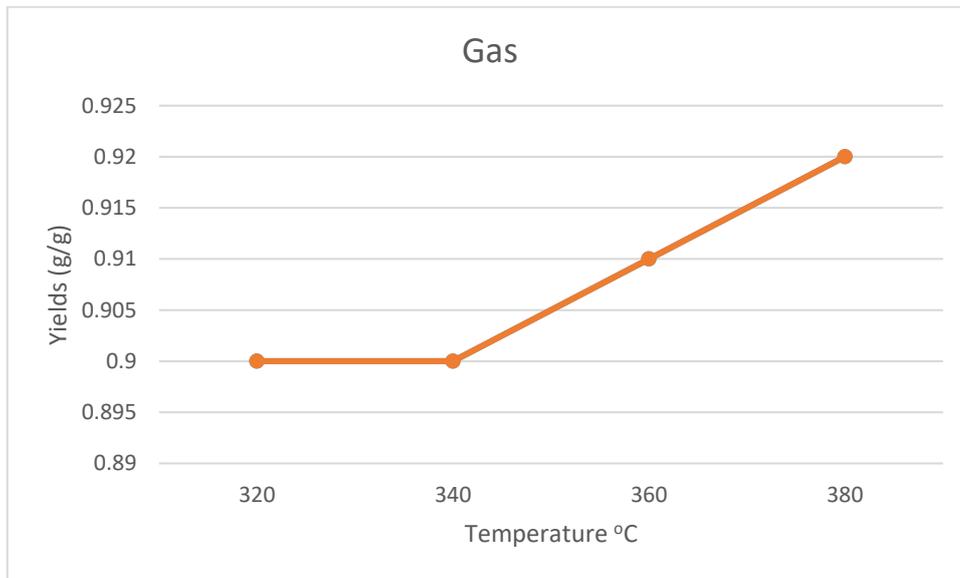
Figure 3.11: Gas evaporated at a varying temperatures
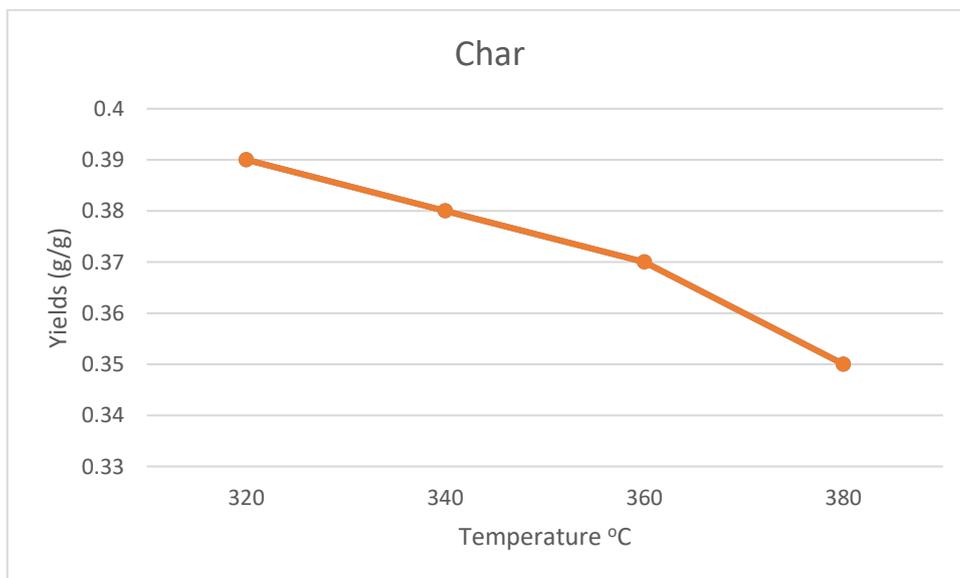
Figure 3.12: Char produced at a varying temperature

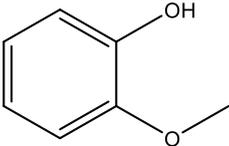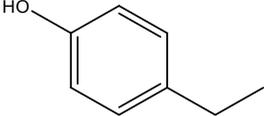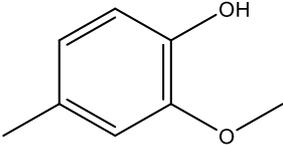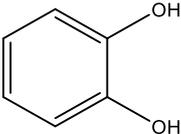Oil was found to have a maximum yield at the highest temperature of 380ºC, this temperature also generates the lowest char and maximum evaporation of gas.
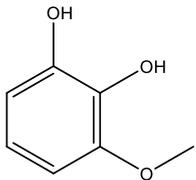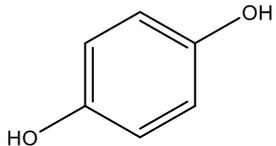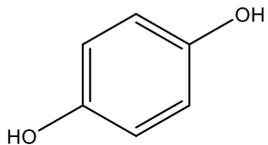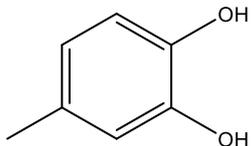
3.4 Compositions of Compounds from Bagasse Pyrolysis

The compounds from the pyrolysis of bagasse were gotten from the GC-MS instrument. The organic compounds with oil samples at temperature of 320, 340, 360 and 380°C, water as solvent, formic acid as the hydrogen donor at 2hrs heating interval are given in table 3-8.

A, B, C and D signify 320, 340, 360 and 380°C. The peaks from the instrument showing the retention time is given in figure 3-13, 3-14 and 3-15 respectively

Table 3-8: Chemical Compounds from GCMS

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	Percentage probability	A	B	C	D
1	2(3H) Furanone, dihydro-5-methyl- $C_5H_8O_2$	10.7241	100	100, 85, 56	73.7	x			
2	Phenol C_6H_6O	11.726	94	94, 66, 63	75.5	x	x	x	x
3	Phenol, 2-methoxy- $C_7H_8O_2$	14.687	124	124, 109, 81	65.8	x			
4	Phenol, 4-ethyl- $C_8H_{10}O$	16.791	122	122, 107, 71	66.5	x			
5	Creosol $C_8H_{10}O_2$	17.438	138	123, 107, 95	51.1	x			
6	Catechol $C_6H_6O_2$	17.584	110	110, 92, 64	89.3	x			x
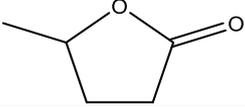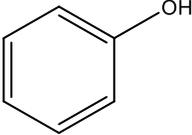
7	1,2-Benzenediol, 3-methoxy- $C_7H_8O_3$	19.100	140	140, 125, 97	71.4	x			
8	Hydroquinone $C_6H_6O_2$	19.401	110	110, 81, 53	76.4	x	x	x	x
9	Phenol, 4-ethyl-2-methoxy- $C_9H_{12}O_2$	19.563	152	152, 137, 122	80.5	x		x	x
10	1,2-Benzenediol, 4-methyl- $C_7H_8O_2$	19.764	124	124, 107, 78	66.1	x		x	
11	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl- $C_{23}H_{32}O_2$	39.688	340	340, 284, 177	97.4	x			
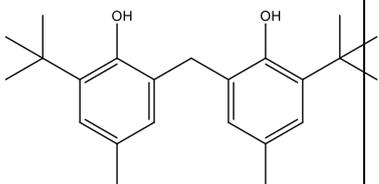
Some compounds like phenol and its derivatives, catechol and creosol are found in the analyses. These compounds have a high tendency of occurrence.
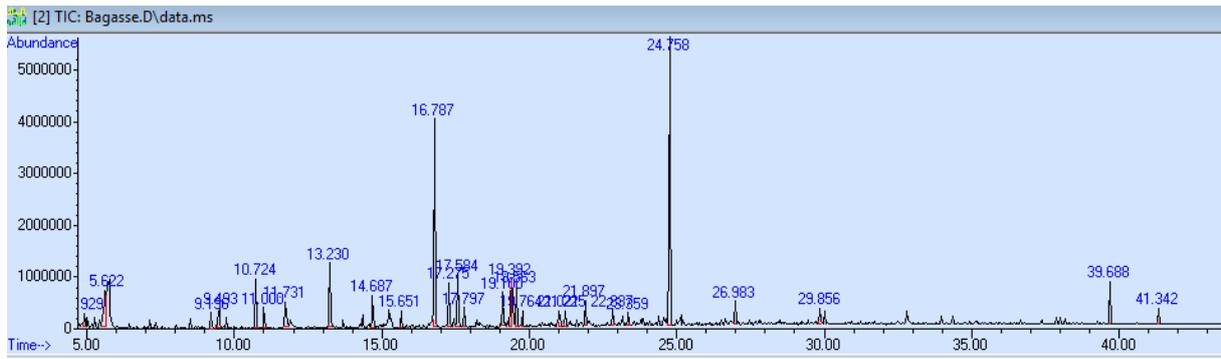
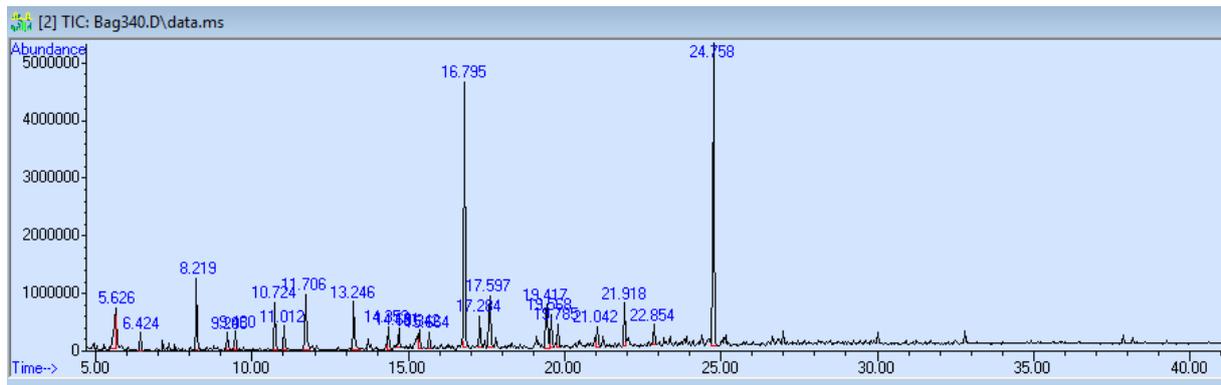*Figure 3.13: Peaks showing retention time of bagasse pyrolysis at 320ºC*
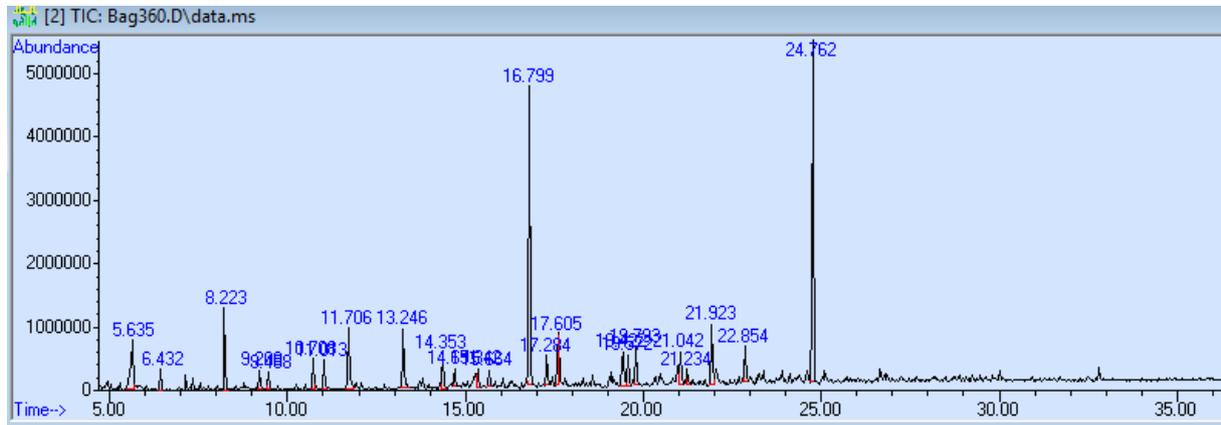

Figure 3.14: Bagasse pyrolysis peaks at 340ºC

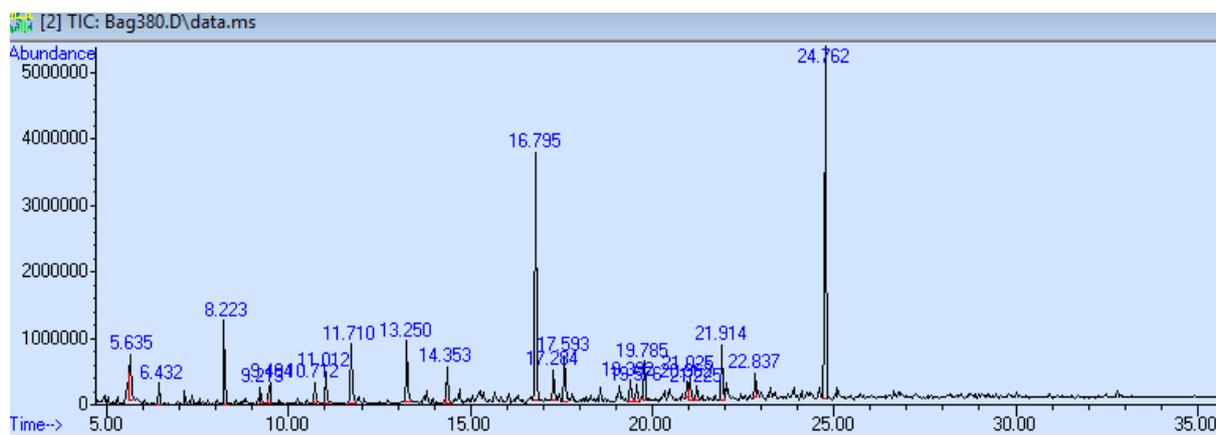*Figure 3.15: Pyrolysis of bagasse peaks at 360ºC*

Figure 3.16: Peaks showing retention time at 380ºC

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	Percentage probability	A	B	C	D
12	Isobutyl acetate $C_6H_{12}O_2$	5.276	116	86, 73, 56	88.7		x		
13	Acetic acid, butyl ester $C_6H_{12}O_2$	6.428	116	73, 61 ,56	96.6		x	x	x
14	Butanoic acid, 2-methyl-, ethyl ester $C_7H_{14}O_2$	7.539	130	130, 115, 106	93.9		x		x
15	1-Methoxy-2-propyl acetate $C_6H_{12}O_3$	8.223	132	87, 72, 58	97.5		x	x	x
16	2-Cyclopenten-1-one, 2-methyl- C_6H_8O	9.209	96	96, 67, 53	86.0		x	x	x
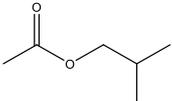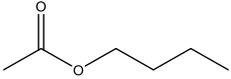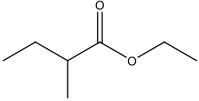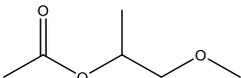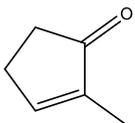
#	Compound								
17	2(3H)-Furanone, dihydro-5-methyl- C$_5$H$_8$O$_2$	10.720	100	100, 85, 71	71.0		x	x	
18	Phenol C$_6$H$_6$O	11.714	94	94, 78 ,66	76.1	x	x	x	x
19	Catechol C$_6$H$_6$O$_2$	17.597	110	110, 81, 64	84.7	x	x		
20	Hydroquinone C$_6$H$_6$O$_2$	19.417	110	110, 81, 53	76.9	x	x		
21	2-Pyrrolidinone, 1-methyl- C$_5$H$_9$NO	13.259	99	91, 84, 67	70.9			x	x
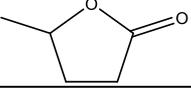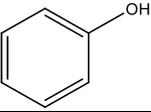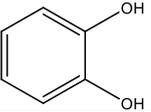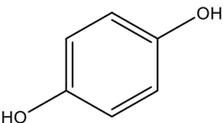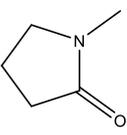
3.5 Yields of Jatropha Residues

The oil from the jatropha seeds was extracted by the Soxhlet methods. The residues left were made to undergo Ltl process using pyrolysis method. Temperature used was from 320 to 380°C, the solvent used was water which was kept constant at 15g and the amount of formic acid acting as the hydrogen donor was 2g. The time was at 2hrs and 4hrs. Table 3-10 illustrates the yields from table 2-6.

Table 3-9: Yield from Jatropha pyrolytic process

Experiment No.	Oil yield (g)	Ratio of oil in lignin (g/g)	Percentage oil yield (%)	char (g)	Gas evaporated (g)	Aqueous (g)	Total output (g)
1	0.499	0.32	32	0.34	1.9	14.65	17.39
2	0.464	0.30	30	0.17	1.7	15.60	17.93
3	0.486	0.32	32	0.22	1.8	15.45	17.96
4	0.542	0.35	35	0.21	2.0	15.07	17.82

The table 3-10 shows that oil was produced more at temperature of 380°C and at 320°C. The relationship between these conditions are depicted in figure 3-17.
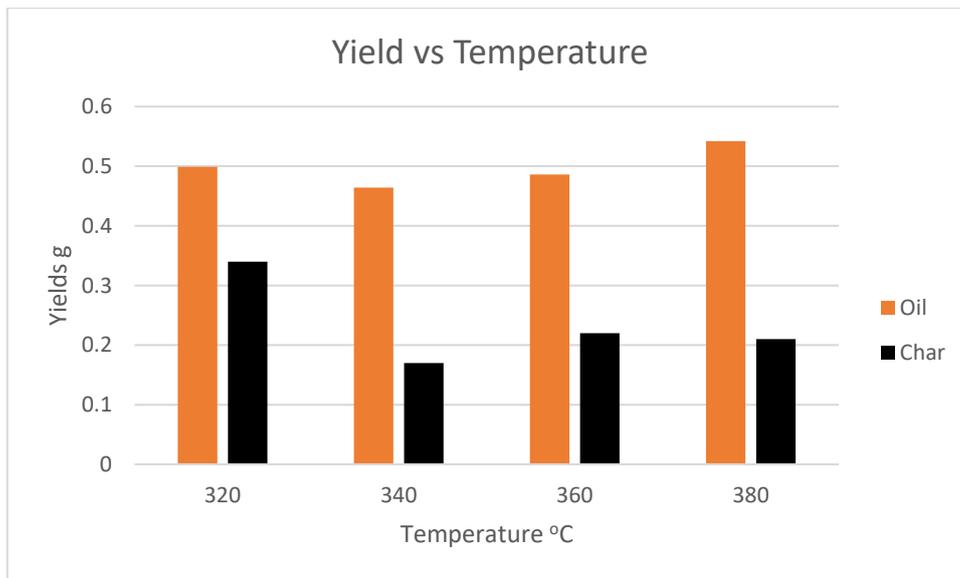
Figure 3.17: Jatropha Residual Yields and Temperature

The amount of char generated was more at 320°C, compare to others. The amount of yields in g/g is given in table 3-11.

Table 3-10: Yields in g/g from Jatropha pyrolysis

Temperature	Oil (g/g)	Gas (g/g)	Char (g/g)
320	0.324	0.95	0.221
340	0.301	0.85	0.110
360	0.316	0.90	0.143
380	0.352	1.0	0.136

Figure 3-18, 3-19 and 3-20 depict the graphs of the yields produced in g/g.
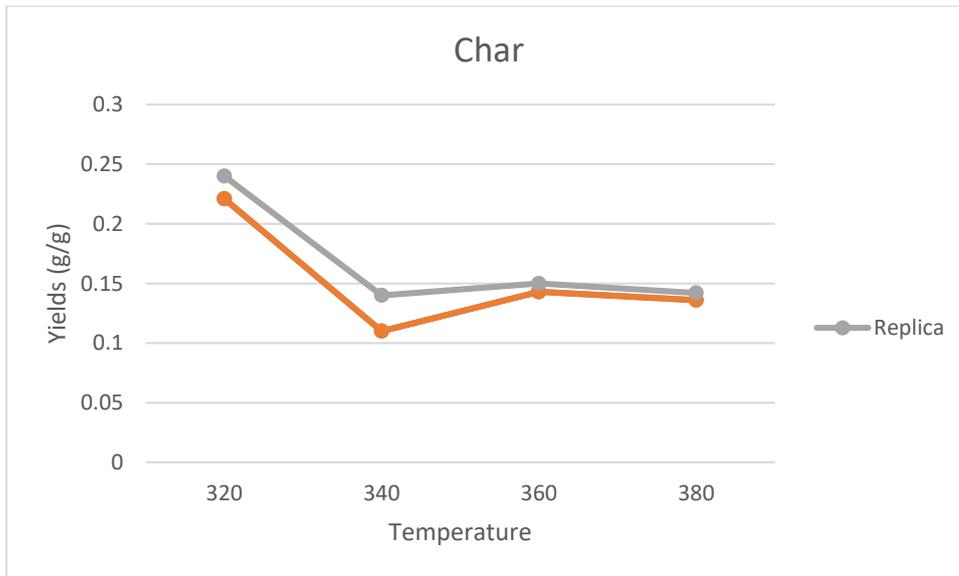
Figure 3.18: *Char yields (g/g)*
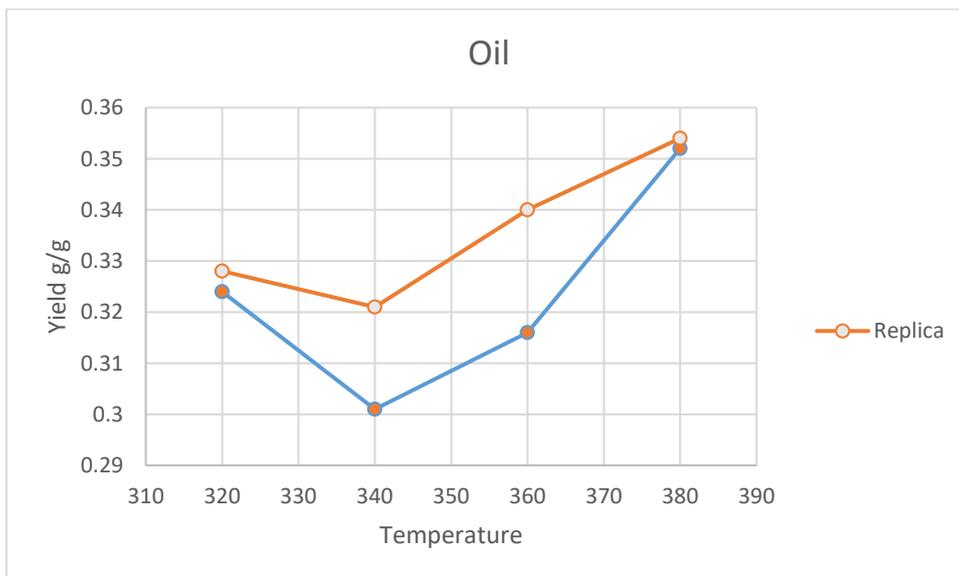
Figure 3.19: Oil yields g/g
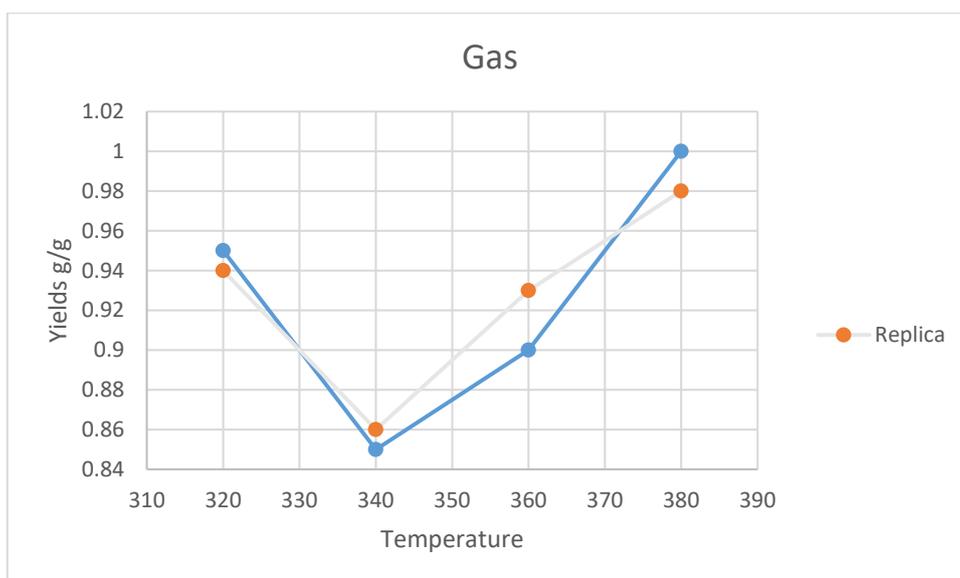
Figure 3.20: Gas yields g/g

The production of oil was evaluated by varying the time from 2hrs to 4hrs. Table 3-12 illustrate these changes. The inputs are shown in table 2-6.

Table 3-11: Output of Jatropha pyrolysis at 4hrs.

Experiment No.	Oil yield (g)	yield of oil on input (g/g)	Percentage oil yield (%)	char (g)	Gas evaporated (g)	Aqueous (g)	Total output (g)
1	0.5180	0.336	33.6	0.321	1.85	14.90	17.59
2	0.496	0.322	32.2	0.340	1.90	15.03	17.77
3	0.5139	0.334	33.4	0.284	1.87	14.88	17.55
4	0.5184	0.337	33.7	0.281	1.90	15.06	17.76

At 4hrs, there are slight increases in the yields, except for 380°C. The gas evaporated was observed to be similar due to the same amount of formic acid used. Figure 3-21 illustrates the relationships between the yields and temperature.
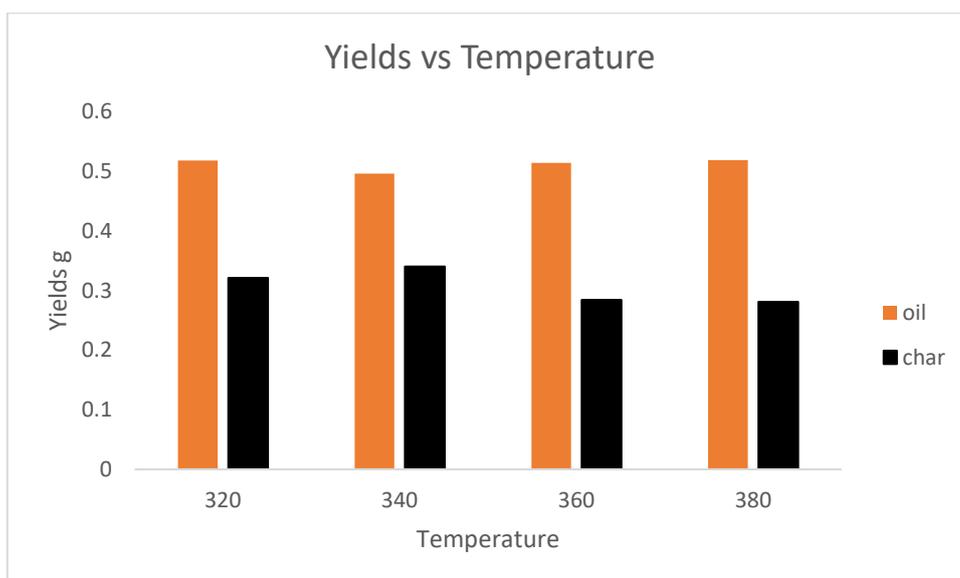
Figure 3.21: Yields vs Temperature at 4hrs

The difference between the char produced for 360 and 380ºC was not very much, compare to 320 and 340ºC. The total yields g/g for the products give a good correlation between the amount of feedstocks and the corresponding outputs. Table 3-13 shows these relationships.

Table 3-12: Yields g/g of Jatropha pyrolysis at 4hrs

Temperature	Oil (g/g)	Gas (g/g)	Char (g/g)
320	0.336	0.925	0.208
340	0.322	0.950	0.221
360	0.334	0.935	0.184
380	0.337	0.950	0.182

The graphs showing the yields trend are illustrated in figure 3-22, 3-23 and figure 3-24 respectively.
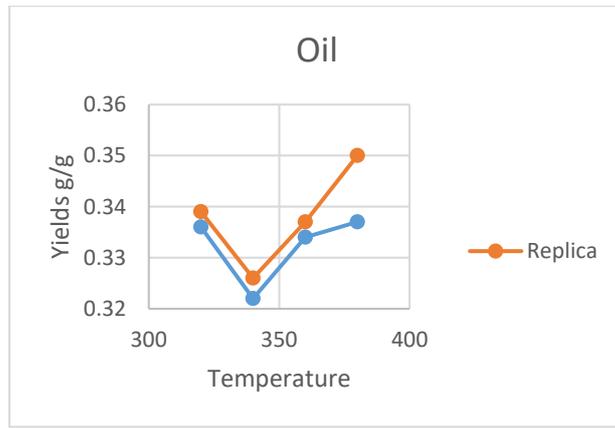
Figure 3.22: Oil yields g/g
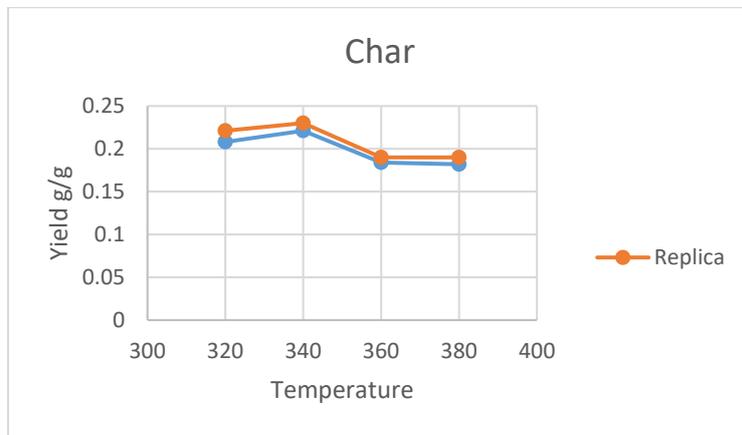
Figure 3.23: Char yields g/g
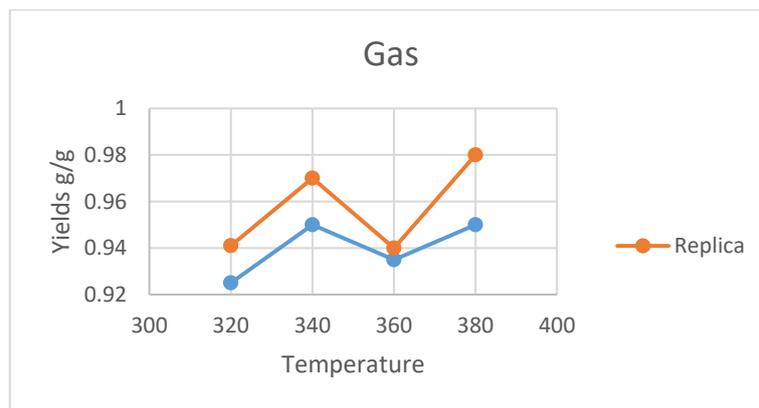
Figure 3.24: Gas yields g/g

The yields of jatropha residue as depicted in figure 3-22 has a maximum oil at 380ºC, with a lower char produced. The yield at 320ºC was also at a higher level but with more char produced. Gas was observed to be given off more at 340ºC.

3.5.1   Mass Balance

The mass balance illustrate the losses, total inputs of the feedstocks and the total outputs. Table 3-16 shows the mass balance of jatropha residues at varying temperatures and feedstocks. The values were calculated from the inputs in table 2-6 and table 3-14.

Table 3-13: Mass balance of Jatropha Residues

Total inputs (g)	Total output (g)	Loss from reactor(g)	Mass balance (%)
18.54	17.59	0.000	95
18.54	17.77	0.012	96
18.54	17.55	0.000	95
18.54	17.76	0.014	96

The values from table 3-16 shows the mass balance with 96% has the maximum accuracy.

3.6 Chemical Compounds from Jatropha Pyrolysis

The compounds from the pyrolysis of jatropha were analysed using the gas chromatography and mass spectrometer instrument. The solvent used was ethylacetate and tetrahydrofuran with a ratio of 9:1.

No	Compounds	Retention time[min]	Molecular weight	Ionic charges	Percentage probability	A	B	C	D
1	2-Pyrrolidinone, 1-methyl- C_5H_9NO	99	99, 83, 70	13.179	89.3	x	x	x	x
2	Pyridine, 3-trimethylsiloxy- $C_8H_{13}NOSi$	167	167, 152, 113	15.935	65.4	x			
3	Phosphonic acid, methyl-, bis(trimethylsilyl) ester $C_7H_{21}O_3PSi_2$	240	240, 225, 205	19.225	67.9	x	x		x
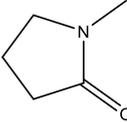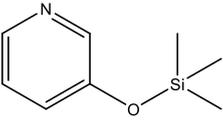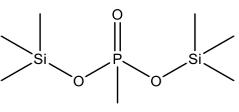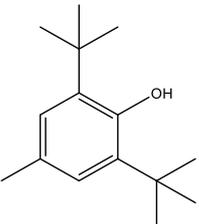
4	Butylated Hydroxytoluene $C_{15}H_{24}O$	220	220, 205, 189	24.732	82.9	x	x	x	x
5	Phenol, 4-ethyl- $C_8H_{10}O$	122	122, 107, 77	16.766	64.4		x	x	x
6	Silane, trimethyl(2-isopropoxyphenoxy)- $C_{12}H_{20}O_2Si$	224	182, 166, 151	17.630	63.8		x		x
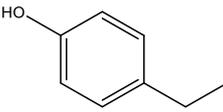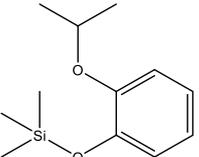
4 Discussion

Biomass pyrolysis is described as the thermochemical depolymerisation of organic matters in the absence of oxygen to produce bio oil, gas and char. Pyrolytic process of three materials were studied. The feedstocks studied were eucalyptus, untreated bagasse and jatropha residues.

4.1 Analysis of Eucalptus Feedstocks

Different weight of eucalyptus was subjected to pyrolytic process; water was used as solvent at different temperatures from 320 to 340°C. Table 2.1 shows the feedstocks input. Table 3-1 depicts the yields. From this table, oil yield was found to be more at the highest temperature of 380°C. The bio char produced from table 3-1, depends on the temperature and the amount of biomass applied. The gas evaporated was observed to depend on the amount of formic acid and the temperature applied. The yields in g/g produced around 58% oil by weight.

Table 3-3, shows the compounds produced from eucalyptus pyrolysis samples after injecting these diluted oil in GC-MS instrument. The compounds contain aromatic, aliphatic and some cyclic aromatics compounds. Some predominant compounds are creosol, phenol and catechol which are found in all the samples. Furanone which a major component in tobacco are found more at a temperature of 320°C from table 3-3. Phenol was found more at temperature of 360°C. This product has a numerous use. Phenol acts as an additive for making plastics. When condensed with acetone, it can be used to produce bisphenol-A which is used for epoxide resins. Phenol could also be condense with formaldehyde to produce phenolic resins, a common example is Bakelite [43]. Hydroquinone which is an aromatic compound was found as one of the predominant compounds at a temperature of 340°C. Hydroquinone is soluble in water and serves as a reducing agent which makes it a major chemical in cosmetics industries. Catechol was another major products from the GC-MS analysis instrument. It was found in all the samples. It is an additive to making fine chemicals used in pharmaceutical companies and perfumes industries due to its flavour. Catechol can produce guaiacol when methylated [44]. Another major products observed in eucalyptus pyrolysis samples after GCMS analysis was cyclopenten and its derivatives. These are cyclic aromatic compounds with numerous use in plastic industries and in acts as an elastomer in the production of polypentenamer [45].

4.2 Analysis of Bagasse Feedstocks

Bagasse used was untreated. It was not washed, no chemical pretreatment. Table 2-2 shows that untreated bagasse contains 22% lignin, 25% hemicellulose and 35% cellulose. Observation from table 3-4 shows that untreated bagasse can actually have up to 45%wt oil yield. The biochar produced was far more. About 40%wt was produced. This could be as a result of the bagasse not washed. It might have attracted dust and sands. Maximum oil yield was found at temperature of 380°C, with less amount of char. At this temperature, gas was found to have the maximum evaporation as shown in figure 3.11. Analysis of the mass balance shows about 99% which is near accuracy with loss of ±0.012.

Just like eucalyptus, some notable compounds were observed in pyrolysis of bagasse when the samples are analysed by GCMS. Among these compounds are phenol, catechol, hydroquinone, pyrrolidinone, cyclopentene, methoxy propyl acetate and acetic acid butyl ester. 2- pyrrolidinone, 1-methyl (C_5H_9NO) is an organic compounds belonging to the dipolar aprotic solvent is used in plastics and petrochemical industries as a solvent. It is applied as a recovery chemicals for HC produced in petrochemical industries. Some major use of this chemical is as a surface treatment for resins, textiles and metals [46]. Methoxy propyl acetate is applied as solvent in resins and dyes. Its cleaning power makes it a good washing agent in electronics industries. It is also applied as a coating coalescent for compounds with polyisocyanates [47].

4.3 Analysis of Jatropha Residue Feedstocks

Jatropha curcas seeds were ground into a fine powdered form with a pestle. Fat was extracted from the seed. An approximate 40%wt of fat was extracted from the jatropha curcas seeds. Pyrolysis of the left over residues shows the production of some reasonable bio oil. Table 3-10 shows that the residues can actually generate up to 35%wt bio oil, with biochar of around 14%wt. Biochar was observed to be produced less at 340°C, which is a good sign that the method can withstand an industrial production scale. A critical look at table 3-11, illustrate that the optimum temperature for bio oil production is at 340°C. This was as a result of the consideration of its gas and biochar yields.

Some useful chemical compounds were produced from the samples of the products using GC-MS. Among these are pyridine 3-trimethylsiloxy ($C_8H_{13}NOSi$), phosphoric acid methyl-bis(trimethylsilyl) ester ($C_7H_{21}O_3Psi_2$), butylated hydroxytoluene ($C_{15}H_{24}O$) and silane

trimethyl (2-isopropoxyphenoxy) ($C_{12}H_{20}O_2Si$). Butylated hydroxytoluene which lipophilic organic compounds is used as food preservatives due to its antioxidant properties. Pyridine and its derivatives are class of heterocyclic organic chemical compounds applied as an adhesive in rubber production, used as an additive in making paints, and insecticides. In medicines, it can be used as an in-vitro synthesis of DNA for the prevention of bacterial and viral infections [48].

This project shows that bio oil can actually be produced from residual plants biomass using LtL method. Comparing the results from this work to some previous research on pyrolysis of lignin feedstocks (Norway spruce, birch) [49], gives a high potential of producing bio oil from Africa residual plants biomass such as jatropha.

5 Conclusion

The potential for bio oil production from residual plants feedstocks has been studied and thermo chemical conversion of these feedstocks using LtL method was employed.

Bio oil yield of 58%wt was generated from eucalyptus and 30%wt biochar This was achievable at a temperature of 380°C.

Bagasse yields are quite different considering the amount of lignin present. Approximately 45%wt bio oil and 40%wt biochar were produced (Figure 3.8, 3.9,3.10 and figure 3.12).

The high amount of biochar yield however, could be caused by some factors such as dust, sands as a results of harvest and its untreated condition.

Jatropha residues show a remarkable yield of about 35%wt bio oil at 380°C, and bio char of 13%wt (figure 3.18 and 3.19). However, at 4hrs, the oil produced was 32%wt and biochar was 22%wt at 340°C. This increase in the amount of char and drop in oil yield was due to prolong heating which might have broken down the lignin molecules.

The organic compounds generated from the GC-MS are similar to bio oil compounds which are applied as some useful additives in chemical, pharmaceutical and petroleum industries.

6 Proposals for Further Work

In the course of this master thesis, some areas can be looked into for future research and also to improve oil yield.

- Elemental compositions of the feedstocks and sample products can be looked into for the proximate and ultimate analysis, thereby calculating the exact mass balance.
- Particle sizes of the plants residues can be calculated to have a finer particle which can improve yields.
- The bio oil yields may be improve on by introducing catalysts.
- The introduction of solvent such as ethanol can be compare with water in future research
- Improve reaction conditions of temperature and heating rate may be considered in the future.

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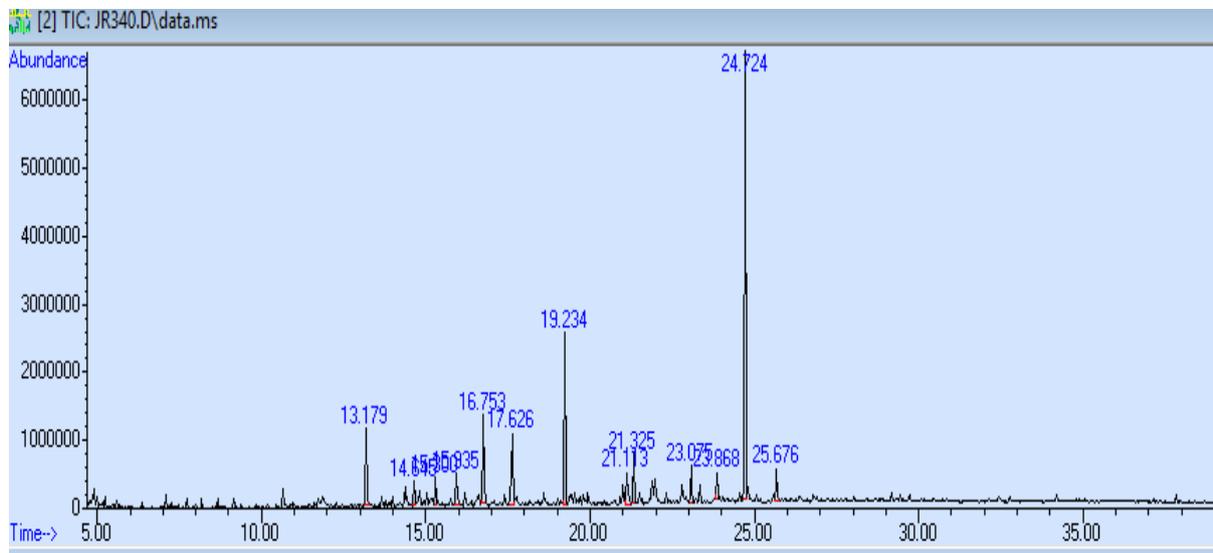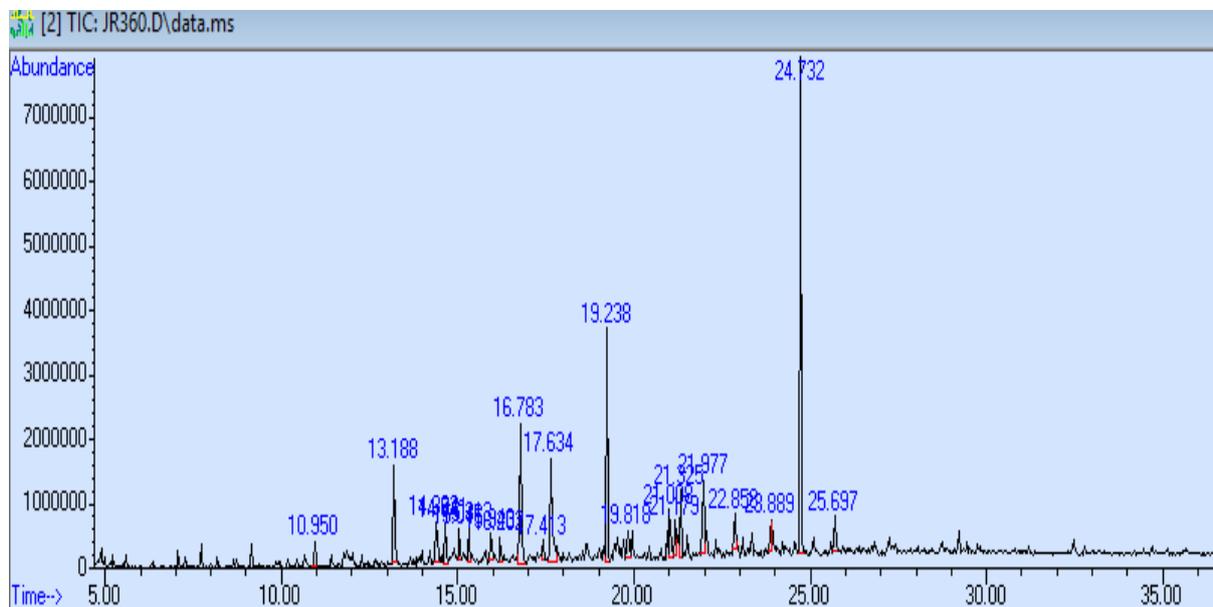# Appendix 1: Peaks of Jatropha Fat and Oil
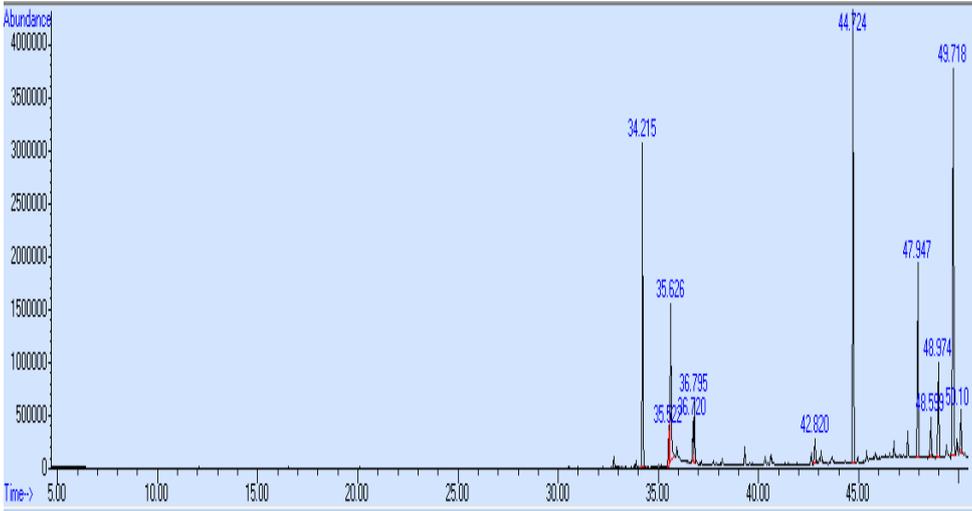
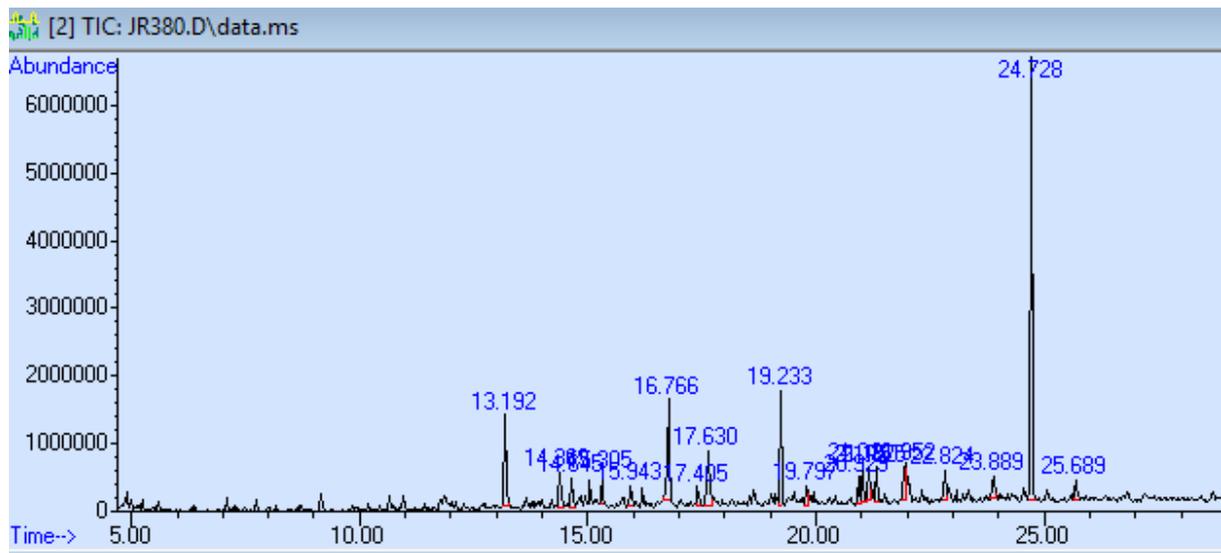*Appendix 1.1: Jatropha fat peaks with retention time*
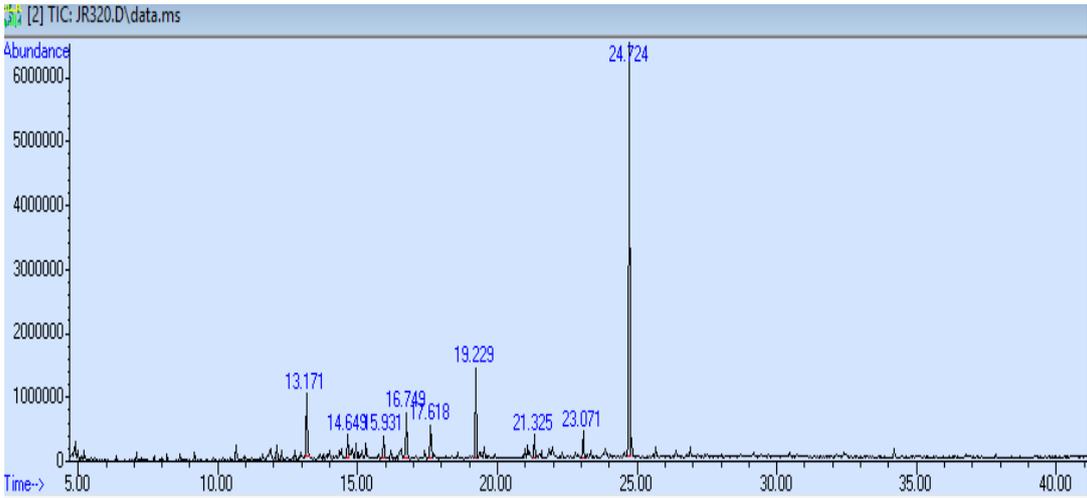
Appendix 1.2: Jatropha residue peaks at 320ºC

Appendix 1.3: Jatropha residue peaks at 340ºC

Appendix 1.4: Jatropha residue peaks with retention time at 360ºC

Appendix 1.5: Jatropha residue with retention time at 380ºC

Appendix 2: GC-MS Instrument

Appendix 2.1: GC-MS Instrument image

Appendix 3: Experimental Procedure

Department of Chemistry, UiB

7. September 2012

Procedure Lignin-to-Liquid. (v1 10.09.12)

Mikel, with in

Part 0. Lignin pretreatment

1. **Grind the lignin (use the mechanic grinder)**
2. **Sieve the lignin (decide which sieve to use)**

Part 1.

1. First: put the catalyst and the lignin in the drying oven for at least 24 h.

Take the catalyst out and put it in a desiccator.

2. Set oven to temperature wanted.

3. Clean reactor with spatula and acetone.

4. Weight the lignin and put in reactor.

5. Weight catalyst. Put in reactor, mix.

6. Weight the water.

7. Mix.

Mix the lignin, catalyst and water with a spatula.

8. Weight acid and put it in the reactor (remember to keep some acid to rinse residual lignin/catalyst off the spatula).

9. Wax on the reactor edge (just to make it easy to open without using too much force)

10. Close reactor.

    a. After waxing close the reactor first with tork-wrench. REMEMBER THERE IS A FIXED PROCEDURE TO CLOSE THE REACTOR (start with one screw, then bolt the opposite one,… ASK IF YOU HAVE ANY QUESTION)

    b. About the force, do it stepwise (Remember the torque is in Nm):

        -Start at a force of 5 Ft-lbs (7 Nm)

        -Then at 10 Ft-lbs (13,5 Nm)

        -Finally at **15 Ft-lbs** (20,5 Nm)

    c. Tighten it 3 times at the final force, to make sure that is completely tightened (with the same force and using the same closing order)

    d. Remember to wax the bolts every 2 times.

12. Weigh reactor.

13. Put in into the oven, take out "on time", and put it on an air stream.

14. Weigh reactor closed (not more than 0,3 g gas difference)

Part 2. Work-up

Weigh the reactor before opening (less than 0,3 g difference)

1. Pre-weight the syringe (glass), filters, pipets and vials (both 20 ml and GC vials).
    a. It is recommended to brake a pipet so when doing the extraction this doesn't plug due to the char.
2. Open the reactor carefully!

    Hear a weak ssss, take it to the fume, open stepwise. Weigh after ventilation (constant weight – with and without reactor top). If any oil goes up through the valve, you have a big product loss

3. Take the water out with a pipet. Once most of the water is taken out and put into the syringe, add some EtAc:THF in the reactor. Take the rest of the water out (probably you will also take some of the oil) and put it on the syringe.
   a. Filter the water.

4. Add a little more of EtAc:THF and take a small sample of "crude" product for GC-MS before work-up (remember to weigh and add the amount to "total product")
5. Extract all the content of the reactor with EtAc:THF and filter it. Use glass syringes.

   a. Use pipette to "stir" in the reactor, dissolve with EtAc:THF, transfer oil to the syringe.
   b. Everytime you see that the filter might be plugged do the following:
      i. Was the filter twice with approximately 5 ml of EtAc:THF
      ii. Change the filter
   If too much char in the reactor is expected, the filtration procedure changes. After you have done step 3-4 (extract and filter the water, and take the GC sample), put a pre-weighted paper filter in the syringe. This will prevent the plastic filter of plugging so fast.

6. Wash the reactor until the solution is clear.

7. Separate oil and water phase. Water phase bottom (blue)/ oil phase top (clear).

   a. Collect the water in a preweighted vial and **check the pH of the water.**
   b. Collect the oil in an erlermeyer. Was the flask with EtAc:THF
8. Extract and decant the water phase 3 times.
   a. Add some EtAc:THF to the water vial and mix it.
   b. Decant it and separate it.
      i. Oil to the Erlenmeyer
      ii. Water back to the same vial
   c. After the last extraction put the water in a new vial a weight it. Put it in the fridge.

9. Dry Oil phase: add 2 spoons with sodium sulfate (Na sulfate) to the Erlenmeyer with the oil, add a magnetic stirrer and sealed it with parafilm.
   a. Stirred it for aprox. 1 h.
   b. Check that the sodium sulfate is still a "free" powder. If it looks like a paste, that means that there is still water in the oil.

10. Filter Oil under vacuum.

    Wash everything with DCM.

Be aware of the solids in the filtered phase. When transferring to the "rundkolbe", use a pipette to avoid taking any solids (If any solids, filter again)

11. Take a sample of the filtered oil before rotarvaporing it and analyse it in the GC-MS.

12. Rotovapor.

   Waterbath 40°C

   (turn on waterflow, fasten bottle, hold, turn on vacuum 700 mbar, start   rotating)

   Pressure; start at 350 mbar, reduce slowly to 250 mbar (slow intervals).

13. Transfer the oil to a pre-weighted vial. Dissolve it in EtAc: and fume 2-3 days, then weight.
   a. After 3 days, weight the vial
   b. Put it under nitrogen for 1 night and the seale it with parafilm and put it in the fridge.

14. After at least 2 days, weight the syringe and filters when they are dried and calculate the char quantity (remember to subtract the amount of catalyst)