BIO-OIL PRODUCTION FROM PYROLYSIS OF PALM OIL WASTES

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SUPERVISOR DECLARATION

“I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the Bachelor in Chemical Engineering (Gas Technology)

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I hereby declare that the work in this thesis entitled “Bio-oil production from pyrolysis of palm oil wastes” is the results of my own research accept as cited in references. This thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Special dedication to my beloved family and friends for all theirs loves, care, support and believes in me.

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ABSTRACT

Energy demand is increasing rapidly because of the growth of population and industrialization. However, the conventional energy source is depleting. Biomass is abundant but inefficiently utilized. Pyrolysis of biomass is the one of the alternative ways to encounter this problem. The products of pyrolysis are bio-oil, char and gas. In this research, the production of bio oil from the pyrolysis of palm oil fiber (POF) and palm oil empty fruit bunch (EFB) were studied using a small lab scale pyrolysis unit. The objectives of this research are to investigate the effect of sample size and produce bio oil from EFB and POF. Preliminary analysis was conducted using thermo gravimetric analyzer (TGA) to determine the volatility, ash residue and moisture content. From the result of the TGA, it is found that EFB contain more volatile matter in comparison to POF. It can also be concluded that EFB might produced more bio oil than POF. Meanwhile, the effect of sample size towards the yield was also studied. The sample size was varied between < 0.63 mm, 0.63-2 mm and 2-4 mm. The best size, which is < 0.63 mm, was pyrolysed in a reactor at constant temperature of 500 ^{o}C. The general characteristic of the product was investigated by the determination of functional groups present in bio oil using Fourier Transform Infrared spectrometer (FTIR). From the analysis, it is shown that bio oil contains complex compounds mostly functional groups of phenol, alcohol, ketones, aldehydes, carboxylic acid and carbonic structure. Physical properties of the bio oil such as pH and viscosity were also investigated. From the result, the pH for the bio oil is 3.99 and the viscosity value is 34 cP.

ABSTRAK

Permintaan tenaga semakin meningkat kerana pertumbuhan penduduk dan perindustrian. Walau bagaimanapun, sumber tenaga konvensional semakin berkurangan. Biojisim adalah banyak tetapi tidak cekap digunakan. Pirolisis biojisim adalah salah satu cara alternatif untuk menghadapi masalah ini. Produk pirolisis ialah minyak bio, arang dan gas. Dalam kajian ini, pengeluaran minyak bio daripada pirolisis gentian minyak sawit (POF) dan tandan buah kelapa sawit kosong (EFB) telah dikaji dengan menggunakan unit pirolisis makmal kecil. Objektif kajian ini adalah untuk mengkaji kesan saiz sampel dan menghasilkan minyak bio daripada EFB dan POF. Analisis awal telah dijalankan menggunakan termo gravimetrik Analisis (TGA) untuk menentukan bahan meruap, abu dan kandungan kelembapan. Daripada hasil daripada TGA, didapati bahawa EFB mengandungi bahan meruap lebih banyak berbanding dengan POF. Dapat disimpulkan bahawa EFB mungkin menghasilkan lebih banyak minyak bio daripada POF. Sementara itu, kesan saiz sampel ke arah hasil yang juga dikaji. Saiz sampel yang berbeza di antara < 0.63 mm, mm 0.63-2 dan 2-4 mm. Saiz terbaik iaitu < 0.63 mm menjalani proses pirolisis di dalam sebuah reaktor pada suhu malar sebanyak 500 ^{o}C. Ciri-ciri umum produk telah disiasat oleh penentuan kumpulan berfungsi yang hadir dalam minyak bio menggunakan spektrometer inframerah transformasi Fourier (FTIR). Daripada analisis, ia telah menunjukkan bahawa minyak bio mengandungi sebatian kompleks kebanyakannya kumpulan fenol, alkohol, keton, aldehid, asid karboksilik dan struktur karbonik. Sifat fizikal minyak bio seperti pH dan kelikatan juga disiasat. Dari hasilnya, pH untuk minyak bio adalah 3.99 dan nilai kelikatan adalah 34 cP.

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LIST OF SYMBOLS

g - gram
min - minute
^{o}C - degree Celsius
wt% - weight percentage
% - percentage
psi - unit of pressure
mm - millimeter
Mpa - Mega Pascal (unit of pressure)
s - second
CO_2 - carbon dioxide
H_2O - water
CO - carbon monoxide
CH_4 - methane
t_r - reaction time
KBr - potassium bromide

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently, the demand for energy is increasing rapidly due to the growth of population and industrialization. The world community have devoted their industries on coal and petroleum, which were plenty and cheap before the Middle East War in 1973. But with the oil crisis after the war, depletion of natural reserves of coal and oil has attracted great interest to sustainable energy production (Zheng, 2008). Since the fossil fuels reserves gradually deplete, renewable energy is now become very important (Jun et al., 2009). So, renewable energy source such as biomass play an important role in the production of energy. Compared with the use of fossil fuel, the use of biomass can reduce the emission of CO_2 which will cause to global warming and greenhouse effect (Jun et al., 2009).

Biomass is a renewable energy resource which can be changed into electricity and fuels by different processes such as combustion, gasification or pyrolysis. It is also refers to living and recently dead biological material that can be used as fuel or for industrial production. It is also include biodegradable wastes that can be burnt as fuel (Biomass, 2008). Other than that, biomass provides a clean energy that can improve environment. Biomass is grown from several plants included miscanthus, switchgrass, hemp, corn, poplar, willow, sugarcane, palm oil and many more. Biomass such as palm oil empty fruit bunches; fiber and shell are generated every year in Malaysia with an annual increment of 5% (Sukiran et al., 2009).

Malaysia, as the largest producer of palm oil in the world, generates a significant amount of palm oil wastes. Malaysia generates 7.7 million tones of empty fruit bunch (EFB), 6.0 million tones of fiber and 2.4 million tones of palm shell every year as wastes. The fiber wastes are used to produce energy by incinerating the waste for power and fertilizer purposes. Usually, palm oil mills have excess fiber and shell which have to be disposed off separately. There are more than 270 palm oil mills operating in Malaysia that utilize mainly fiber and partly shell in their boilers as fuel to generate power and steam required (Kawser and Nash, 2000).

Figure 1.1: Abundance of oil palm biomass (Ahmad et al., 2009)

Pyrolysis is one of the thermo chemical processes, which convert the biomass into liquid (bio- oil), gas and char. Biomass pyrolysis converts basically 80–95% of the feed material to gases and bio-oil. The pyrolysis process is to optimize the production of liquids which is including tar and bio-oil. The liquid products have high energy density, ease of transportation & storage and have the potential to be upgraded as fuels similar to refined premium-grade fuels (Williams & Bessler, 1996).

1.2 Problem Statement

Production of bio oil is quite challenging to engineering world today. It is a lot more challenging when it comes to the production of high yield of bio oil. In bio oil production, it is well known that biomass can be used to generate bio oil. According to Xu et al. (2011) grape residues, sugarcane residues, palm oil residues and forestry residue can be used as a sample for the pyrolysis processes. Most research has been performed on wood biomass because of its consistency and comparability between tests (Mohan et al., 2006). Palm oil wastes are high potential biomass energy sources that are CO_2 neutral. There is abundance of palm oil waste at Malaysia which is about 90%. Once the type of biomass has been considered, it is realized that another factor that also will contributing to the yield of bio oil is sample size.

1.3 Objective Of Research

The objectives of this research are:

- to investigate the effect of sample size and produce bio oil from Empty Fruit Bunch Fiber (EFB) and Palm Oil Fiber (POF).
- to determine the characterization of the bio oil.

1.4 Scope Of The Study

This research mainly focuses on:

1. parameters that have been evaluated in this study were sample size (< 0.63 mm, 0.63-2 mm, 2-4 mm) and type of biomass.
2. production of bio oil from biomass. Bio oil was obtained from palm oil wastes via pyrolysis at temperature $500^{o}C$.
3. characterized the bio oil that produced from palm oil wastes using Fourier Transform Infrared (FTIR).The pH and viscosity of the bio oil were also determined.

1.5 Rational And Significance

The EFB fiber and POF fiber was chosen to be compared between each other in order to determine which one of them contributes to high yield of bio oil. It is also decided that samples with range of < 0.63 mm, 0.63-2 mm and 2-4 mm size were compared to see how those factors lead to the production of high quality bio oil. This is based on size range suggested by Seebauer et al. (1997) studies. Sample size of 0.1mm to 2mm has been used in his study in order to determine the effect of sample size to the formation of bio oil.

The study of factors that influencing the production of high yield and quality of bio oil is very important to the community. Bio oil can replace fossil fuel that widely used now and known to be finished in less than 100 years from now. It can help s to solve the problems of shortage in supplies of fossil fuel by replacing it with a renewable energy source such as biomass. So, this study is crucial to help sustaining the energy supplies in the future for the sake of our next generations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Concern over the global warming and fossil fuel reserves have led to the realization that a more environmentally friendly is required. Biofuels are seen have a good potential solution for this problem. Biofuels is a type of fuel whose energy is derived from biological carbon fixation. Biofuels include fuels derived from biomass conversion with solid biomass, liquid fuels and various biogases. Biofuels are gaining increased public and scientific attention because of factors such as oil price hikes, concern over greenhouse gas emissions from fossil fuels, and support from government subsidies. In 2010 worldwide biofuel production reached 105 billion liters and biofuels provided 2.7 % of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel (Biofuel, 2012). According to the International Energy Agency, biofuels have the potential to meet more than a quarter of world demand for transportation fuels by 2050.

2.2 Biomass

Biomass is the word used for all organic material originating from plants, trees and crops and is essentially the collection and storage of the sun's energy through photosynthesis. Biomass energy is the change of biomass into valuable forms of energy such as heat, electricity and fuels. It is comes either directly from the land or from residues generated in the processing of crops for food or other products such as pulp and paper from the wood industry. The biomass to bioenergy system can be considered as the management of flow of solar generated materials, food, and fiber in society. These interrelationships are shown in Figure 2.1, which presents the various resource types and applications, showing the flow of their harvest and residues to bioenergy applications.

Not all biomass is directly used to produce energy but rather it can be converted into intermediate energy carriers called biofuels. This includes charcoal (higher energy density solid fuel), ethanol (liquid fuel) or producer-gas (from gasification of biomass) (Antonia et al., 2000).

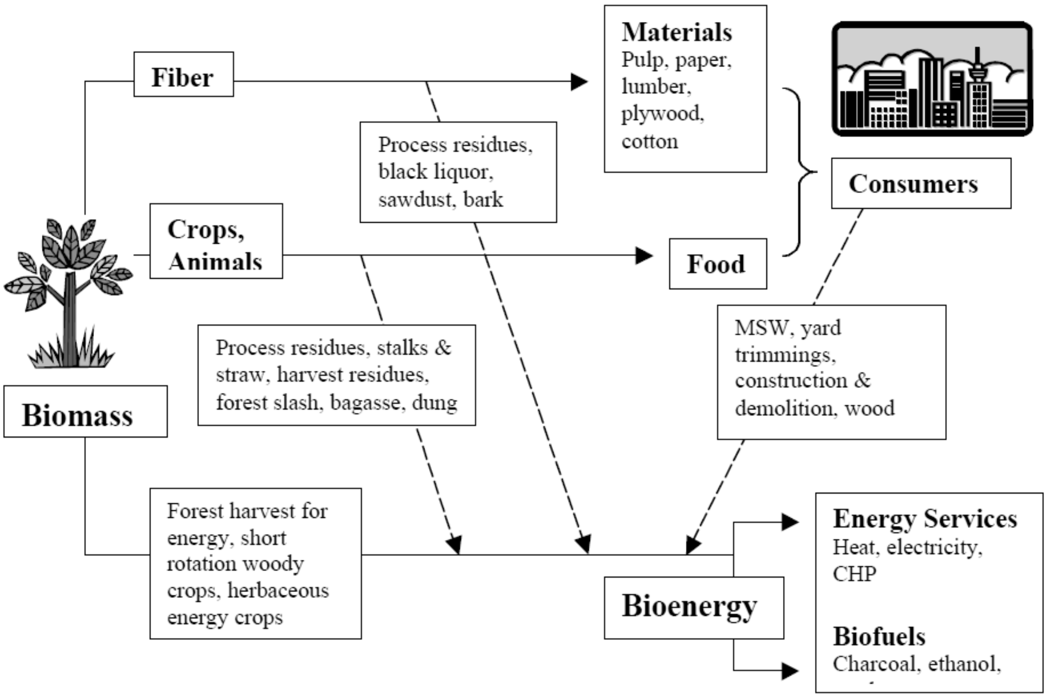

Figure 2.1: Biomass and Bioenergy flowchart (Antonia et al., 2000)

2.3 Type of Biomass

Biomass comes from a variety of sources as shown in table 2.1

Group Biomass	Subclassifications	Examples
Virgin	Terrestrial biomass	Forest biomass
		Grasses
		Energy crops
		Cultivated crops
	Aquatic biomass	Algae
		Water plant
Waste	Municipal waste	Municipal solid waste
		Biosolids, sewage
		Landfill gas
	Agricultural solid waste	Livestock and manures
		Agricultural crop residue
	Forestry residues	Bark, leaves, floor residues
	Industrial wastes	Demolition wood, sawdust
		Waste oil or fat

Table 2.1: Two major groups of biomass and their sub classifications (Basu, 2010)

Virgin biomass comes directly from plant and animals which are include wood, plants, leaves, crops and vegetables. Waste includes solid and liquid waste, sewage, animal and human waste, gases derived from land filling and agricultural wastes (Basu, 2010).

2.4 Resource of biomass

Biomass can be obtained from different sources such as wastes, standing forest and energy crops. The wastes categories comprise waste from agricultural production, process waste from agro industries, crop residues and many more. Standing forest consist of different intermediate products and residuals wastes of different nature. An energy crop includes various edible and non-edible crops (Saxena et al., 2009). Biomass resources can be categorized into modern biomass and traditional biomass. Modern biomass involves large scale uses and use to substitute for conventional energy sources. Meanwhile traditional biomass involves small scale uses and use to developing countries.

2.5 Biomass utilization

Biomass has always been a main source of energy for mankind from early. Currently, it contributes around 10–14 % of the world’s energy supply (Putun, et al., 2001). Biomass can be converted into three main types of products:

- Electrical or heat energy.
- Fuel for transport sector.
- Feedstock for chemicals.

Conventionally, biomass had been utilized through direct combustion. Pollutants with dust and the acid rain gases such as sulfur dioxide and nitrogen oxides will produce when the biomass is burned. But, the sulfur dioxide produced is 90 % less than that is produced by burning coal (Saxena et al., 2009). The quantities of atmospheric pollution produced are insignificant compared to other pollution sources. Biomass usage as a source of energy is of interest due to the following envisaged benefits:

- Biomass is a renewable, potentially sustainable and environmentally friendly source of energy.
- A gigantic range of diverse materials, frequently stereo chemically defined, are available from the biomass giving the user many new structural features to develop (Joseph, 1999).
- The increased use of biomass would avoid diminishing crude oil supplies.
- Biomass fuels have small sulfur content and the amount will not contribute to sulfur dioxide emissions that cause acid rain.

- The combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive on farms and many more.
- The combustion of agricultural, forestry residues and municipal solid wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal.
- Biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities (Othmer, 1980).
- Biomass usage could be a way to prevent more carbon dioxide production in the atmosphere.

Biomass can be used in several ways to obtain energy. Most of the biomass energy is consumed in domestic purposes and by wood-related industries. It is burned by direct combustion to produce steam that drives the turbine or generator to produce electricity. Gasifiers are used to convert biomass into a combustible gas which is then used to drive a high efficiency, combined cycle gas turbine. Biomass is converted to pyrolysis oil by heating. Pyrolysis oil is easier to store and transport than solid biomass material and is burned like petroleum to generate electricity (Saxena et al., 2009).

2.6 Biomass components

The significance of particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. The chemical structure and major organic components in biomass are important in the development of processes for producing fuel and chemicals. Biomass contains varying amounts of cellulose, hemicellulose, lignin and a little of extractive (Bridgewater, 1999). Cellulose is a glucose polymer containing linear chains of (1, 4)-D-glucopyranose units, in which the units are linked 1–4 in the alpha configuration, with an average molecular weight of around 100,000 (Saxena et al., 2009). Alpha cellulose is a polysaccharide having the general formulae ($C_6H_{10}O_5$). Hemicelluloses are complex polysaccharides that are present in association with cellulose in the cell wall. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methlyglucoronic and galaturonic acids (Saxena et al., 2009). Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain biomass and are often adjacent to cellulose fibers to form a lignocellulosic complex (Ana-Rita & Ian, 1996). In biomass, cellulose is generally the largest fraction, about 40–50 % by weight and hemicellulose about 20–40 % (McKendry, 2002).

2.7 Biomass conversion

The bulky of biomass is a major difficulty to a rapid shift from fossil to fuels.Biomass is hard to handle, transported and stored. So, this problem gives an idea for the conversion of solid biomass into liquid and gaseous fuel. The biomass conversion can be achieved through biochemical route and thermochemical route as shown in Figure 2.2 below.

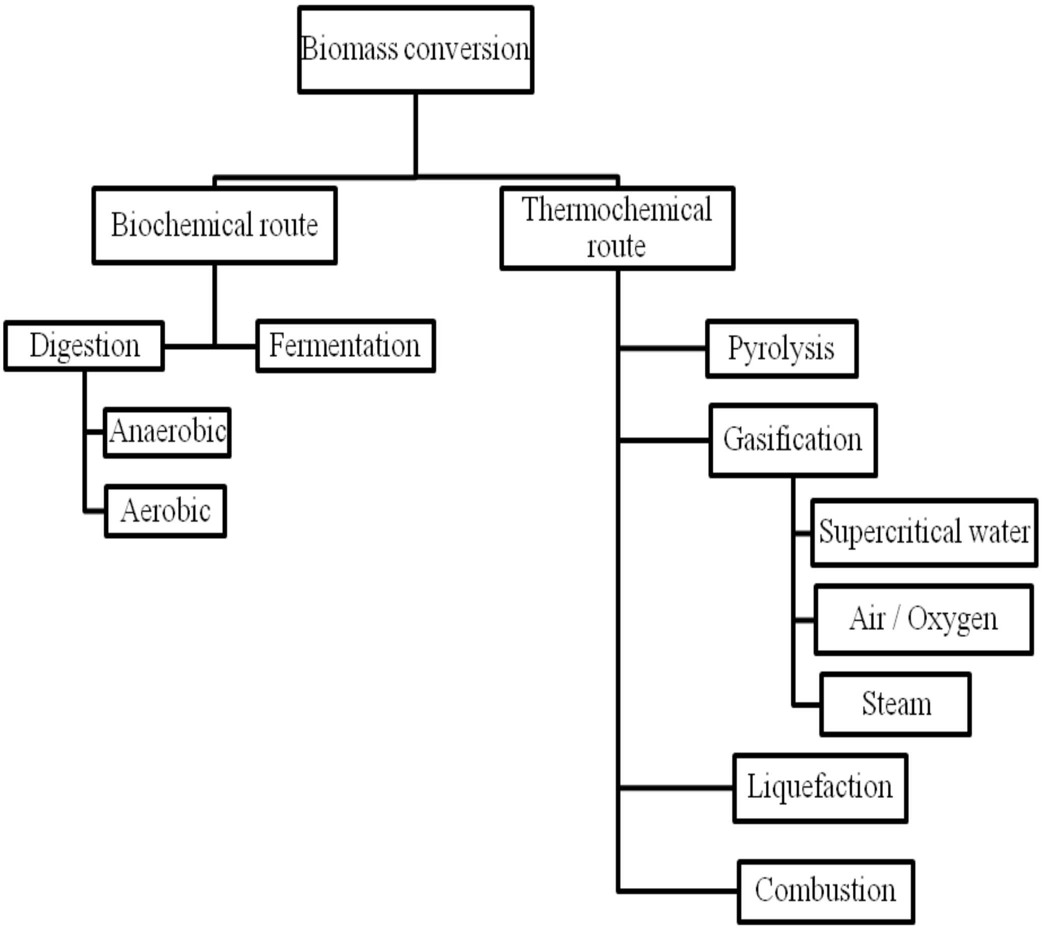

Figure 2.2: Biomass conversion (Basu, 2010)

2.8 Thermochemical conversion

Biomass is converted into gases in thermochemical conversion. The gases is then synthesized into the desired chemicals or used directly as shown in Figure 2.3 below. There are four main processes in thermochemical conversion which are combustion, gasification, liquefaction and pyrolysis.

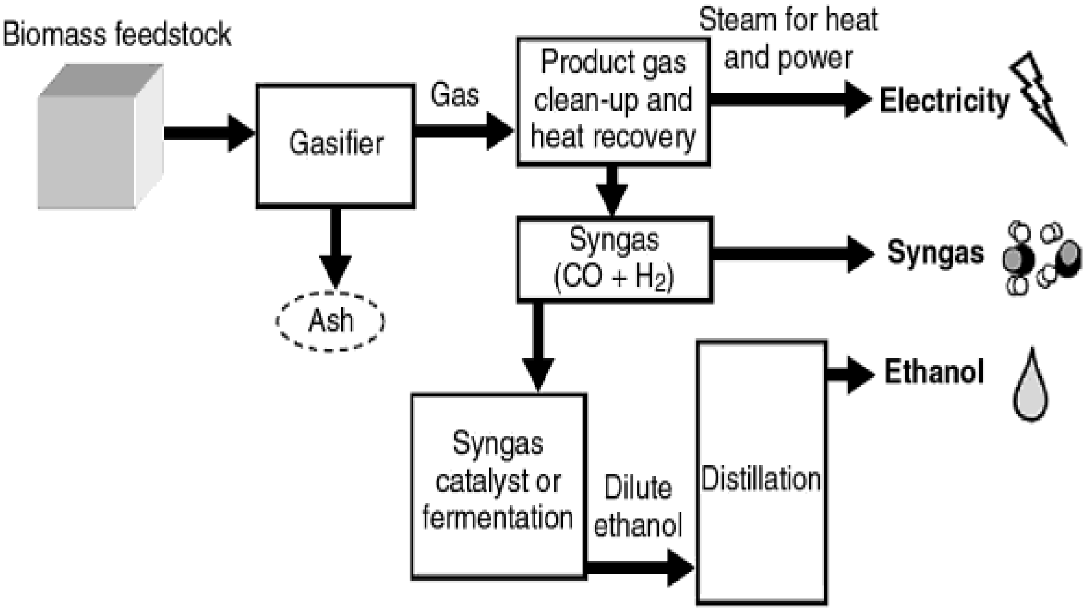

Figure 2.3: Thermochemical route for production of energy, gas and ethanol (Basu, 2010)

Combustion involves high temperature conversion of biomass in excess air. The products of combustion are carbon dioxide and water. Gasification involves a chemical reaction in insufficient oxygen environment. Pyrolysis takes place in the total absence of oxygen. For liquefaction, the large feedstock molecules are decomposed into liquids having smaller molecules.

Process	**Temperature (^oC)**	**Pressure (Mpa)**	**Catalyst**	**Drying**
Liquefaction	250 – 330	5 – 20	Essential	Not required
Pyrolysis	380 – 530	0.1 – 0.5	Not required	Necessary
Combustion	700 – 1400	> 0.1	Not required	Not essential
Gasification	500 – 1300	> 0.1	Not Essential	Necessary

Table 2.2: Comparison of four main thermochemical conversion processes (Demirbas, 2009)

2.8.1 Combustion

Combustion is the oldest utilization of biomass. Combustion is an exothermic reaction between oxygen and hydrocarbon of the biomass (Basu, 2010). The biomass will be converted into two major compounds which are H_2O and $CO_{2.}$ Heat and electricity are two principal forms of energy obtained from biomass. Biomass provides heat for cooking and warmth especially in countryside areas. Industrial heating is also produced by steam generated in biomass fired boilers. Pellet stoves or log fired fireplaces is also a direct source of warmth in many cold weather country. Electricity, the foundation of all modern economic activities may be generated using from biomass combustion. The most ordinary practice involves the generation of steam by burning biomass in a boiler and the generation of electricity through a steam turbine. In some places, electricity is produced by burning combustible gas derived from biomass through gasification.

2.8.2 Gasification

Biomass gasification is a process that converts carbonaceous biomass into combustible gases such as H_2, CO, CO_2 and CH_4. It requires gas or supercritical water as a medium for reaction. Gaseous medium can be air, oxygen, subcritical steam or its mixture. For production of synthetic gases, gasification of fossil fuels is more common than non fossil fuels such as biomass. Gasification is important because of to increase the heating value of the fuel by rejecting noncombustible components like nitrogen and water, to remove sulfur and nitrogen to avoid burnt nitrogen and sulfur from released to the atmosphere and to reduce the carbon to hydrogen (C/H) mass ratio in the fuel.

The higher the hydrogen contain in a fuel, the lower vaporization temperature (Basu, 2010). So, the probability of the fuel being in a gaseous state is higher. Gasification increases the relative hydrogen content (H/C ratio) in the product through direct, indirect and pyrolysis.

- Direct: Direct exposure to hydrogen at high pressure
- Indirect: Exposure to steam at high pressure and temperature where hydrogen as an intermediate product is added to the product. This process also includes steam reforming.
- Pyrolysis: Reduction of carbon by rejecting it through solid char or CO_2 gas (Basu, 2010).

Biomass provides two important benefits that make it a possible feedstock for syngas production. They are not make any net contribution to the atmosphere when burnt and it use reduces dependence on nonrenewable and often imported fossil fuel. Biomass gasification into CO and H_2 provides a good base for production of liquid transportation such as gasoline and methanol. Gasification is generally carried out in moving bed, fluidized bed and entrained flow. Downdraft and updraft are two common types of moving bed gasifier. Downdraft gasifier is the most common use in Europe, United Stat and Canada which is 75 % uses (Knoef, 2000).

2.8.3 Liquefaction

Liquefaction of solid biomass into liquid fuel can be done through pyrolysis, gasification and hydrothermal process. In the liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. Direct liquefaction of wood by catalyst was carried out in the presence of K_2CO_3 (Ogi et al., 1985). The heavy oil obtained from the liquefaction process was a viscous tarry lump and sometimes caused problems during handling. So, some organic solvents were added to the reaction system. Among the organic solvents tested, propanol, butanol, acetone, methyl ethyl ketone, and ethyl acetate were found to be effective on the formation of heavy oil having low viscosity (Demirbas, 2000).

2.9 Pyrolysis

Pyrolysis is one of the most promising thermo chemical conversion routes to recover energy from biomass. Pyrolysis is the process heating biomass in the absence of air and oxygen. The initial product of pyrolysis is made of condensable gases and solid char. The condensable gas may break down further into non condensable gases such as CO, CO_2, H_2 and CH_4, liquid and char. The yields of end products of pyrolysis and the composition of gases are dependent on the several parameters including temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration.

Pyrolysis is a thermal degradation of the organic matrix in absence of oxygen to obtain an array of solid, liquid and gas (Serdar yarman, 2003). Pyrolysis utilized heat either directly or indirectly in order to decompose waste material. Pyrolysis is usually endothermic reaction and also occurs at high temperatures.

2.9.1 Types of Pyrolysis

Pyrolysis may be classified as slow and fast based on heating rate. For the slow pyrolysis, the time heating ($t_{heating}$) required to heat the fuel to the pyrolysis temperature is much longer than the characteristic pyrolysis reaction time (t_r). Usually, slow and fast pyrolysis are carried out in the absence of medium. Meanwhile, for the hydrous pyrolysis and hydropyrolysis both carried out in the medium. Hydrous pyrolysis carried out in H_2O while hydropyrolysis carried out in the H_2. These two types are mainly for the production of chemical.

In slow pyrolysis, the residence time of vapor in the pyrolysis zone is on the other of minutes or longer. Usually this process is used for char production and is broken down into carbonization and conventional. But, in fast pyrolysis the vapor residence time is on the order of seconds or milliseconds. Primarily this type of pyrolysis is for the production of bio oil.

Pyrolysis Process	**Residence Time**	**Heating Rate**	**Final Temperature (^{o}C)**	**Products**
Carbonization	Days	Very low	400	Charcoal
Conventional	5 – 30 min	Low	600	Char, bio oil, gas
Fast	< 2s	Very high	~ 500	Bio oil
Flash	< 1s	High	< 650	Bio oil, chemicals , gas
Ultra-rapid	< 0.5s	Very high	~ 1000	Chemical, gas
Vacuum	2 – 30s	Medium	400	Bio oil
Hydropyrolysis	< 10s	High	< 500	Bio oil
Methano-pyrolysis	< 10s	High	>700	Chemicals

Table 2.3: Characteristic of some pyrolysis process (Basu, 2010)

Table 2.3 is the comparison between the characteristics of different pyrolysis processes. The table shows that carbonization is the slowest process while ultra-rapid is the fastest process. Fast pyrolysis process target production is mainly liquid.

2.9.1.1 Slow Pyrolysis

Carbonization is a slow pyrolysis process. The primary production of this process is charcoal. It is the oldest form of pyrolysis that has been use for thousand years. The biomass is heated slowly in the absence of oxygen to a relatively low temperature (~400 ^{o}C) over an extended period of time. Carbonization allows sufficient time to for the condensable vapor to be converted into char and non condensable gases.

Conventional pyrolysis involves all three types of pyrolysis product which are gas, liquid and char. It heats the biomass at a moderate temperature (~600 ^{o}C). The product residence time is on the order of minutes.

2.9.1.2 Fast Pyrolysis

In the 1980s, researchers establish that the liquid product yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly. The main objective of fast pyrolysis is to maximize the production of liquid or bio oil. The biomass is heated rapidly that it reaches the peak temperature before it decomposes. The heating rate of fast pyrolysis can be high as 1000 to 10 000 ^{o}C/s but the peak temperature should be below 650 ^{o}C if bio oil is the needed product. However, the peak temperature can be up to 1000 ^{o}C if gas is the needed product.

Four important features of the fast pyrolysis that help in increase the bio oil yield are very high heating rate, reaction temperature within the range of 425 – 600 ^{o}C, short residence time and rapid quenching of product gas.

2.9.1.3 Flash Pyrolysis

In flash pyrolysis, biomass is heated rapidly in the absence of oxygen to a relatively temperature range of 450 – 600 ^{o}C. The product containing condensable and non condensable gas will leaves the pyrolyzer within a short residence time of 30 – 1500 ms (Bridgewater, 1999). The condensable vapor is then condensing to liquid which is known as bio oil. A typical yield of bio oil in flash pyrolysis is 70 – 75 % of the total pyrolysis product.

2.9.1.4 Ultra-Rapid Pyrolysis

Ultra-rapid pyrolysis involves extremely fast mixing of biomass with a heat carrier solid that will resulting in a very high heat-transfer and also heating rate. A rapid quenching of the primary product follows the pyrolysis that occurring in its reactor. A gas-solid separator separates the hot heat carrier solids from the non condensable gases and primary product vapors and returns them to the mixture. Then, they are heated in separate combustor. A non oxidizing gas transports the hot solids to the mixture. An accurately controlled short uniform residence time is an important factor of ultra –rapid pyrolysis. To maximize the product yield of gas the temperature is around 1000 ^{o}C for gas and 650 ^{o}C for liquid (Basu, 2010).

2.9.2 Effect of Particle Size to Pyrolysis Product yield

The composition, size, shape and physical structure of the biomass use some influence on the pyrolysis product through their effect on heating rate. Finer biomasses particles offer less resistance to the escape of condensable gases which therefore escape relatively easily to the surroundings before undergo secondary cracking. This leads to higher liquid yield. Meanwhile, larger particles facilitate secondary cracking due to the higher resistance they offer to the escape of the primary pyrolysis product. So, older methods of charcoal production used stacks of large size wood pieces in a sealed chamber (Basu, 2010).

The effect of particle size on the product yields is given in Figure 2.4 at a pyrolysis temperature of 500 ^{o}C at heating rate of 30 ^{o}C/ min. The smallest biomass particle size of <91 µm produced a bio-oil yield of 33 wt% with a char yield of 28 wt% and gas yield of 39 % wt%. Largest particle size of 126-250 µm produced a bio-oil yield of 31 wt% with a char yield of 28 wt% and gas yield of 41 wt%. The maximum bio-oil yield was obtained with particle size of 91-106 µm about a 35 wt% with a char yield 25 wt% while the lowest bio oil yield was obtained with particle size 107-125 µm which is 30wt% and gas yield of 43 %. (Sukiran et al., 2009).

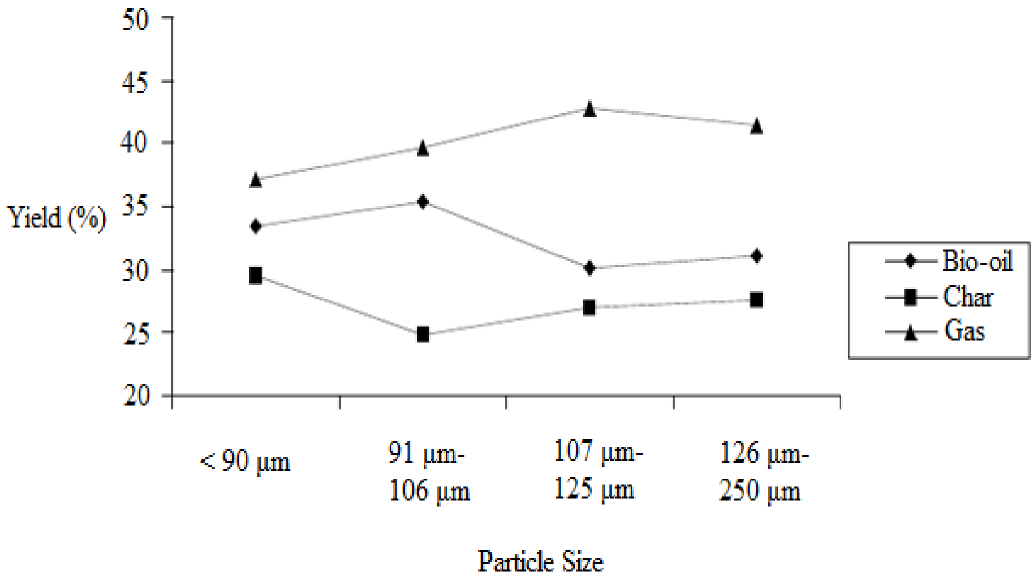

Figure 2.4: Yield of pyrolysis product at various particle sizes with a final temperature 500 °C and a heating rate of 30°C/min (Sukiran et al., 2009)

From the previous study of who pyrolysed cardoon (*Cynara cardunculus L.*), an increase in particle size causes greater temperature gradients insides the particle so that at any given time the core temperature is lower than that of the surface which possibly gives rise to an increase in the char yields and a decrease in the yield of liquids and gases (Encinar et al., 2000). Particle size is known have influence pyrolysis product yields. If the particle size is sufficiently small it can be heated uniformly (Seebaur et al., 1997).

2.9.3 Physical Aspect of Pyrolysis

Pyrolysis process can be divided into four stages:

1. Drying (~100 °C)

During the initial phase of biomass heating at low temperature, the free moisture is released and evaporates. Then, the heat is conducted into biomass interior.

2. Initial Stage (100 – 300 °C)

At the initial stage, exothermic dehydration of the biomass is occur with discharge of water and low molecular weight gases like CO and CO_2.

3. Intermediate Stage (> 200 °C)

At this stage, primary pyrolysis is occurring at the temperature range of 200 °C - 600 °C). Most of the vapor to bio oil is produced at this stage. Large molecules of biomass particles decompose into char, condensable gases and non condensable gases.

4. Final Stage (~300 – 900 °C)

The final stage of pyrolysis involves secondary cracking of volatile into char and non condensable gas. If they reside in the biomass long enough, relatively large molecular weight condensable gases can crack and yielding additional chars and gases. Usually, this stage occurs at temperature above 300 °C (Reed, 2002). Higher pyrolysis temperature favors production of hydrogen which increases quickly above 600 °C.

Temperature has a major influence on the product of pyrolysis. The carbon dioxide yield is high at low temperature and the yield is decrease at higher temperature. The release of hydrocarbon gases peak at around 450 °C and then starts decreasing above 500 °C boosting the generation of hydrogen (Basu, 2010).

2.10 Pyrolyzers Types

2.10.1 Fixed Bed

Heat for the thermal decomposition of biomass is supplied from an external source. One of the disadvantage of this pyrolyzer is the product may flow out from pyrolyzer because of volume expansion while char remains in the reactor. There is some design where sweep gas is used to remove the gas product from the reactor. The main product of this pyrolyzer is char due to the relatively slow heating rate and long residence time.

2.10.2 Bubbling Fluidized Bed

Biomass that has been crushed with 2 – 6 mm is fed into a bubbling bed of hot sand. The bed is fluidized by an inert gas. Recycled flue gas is also can be use as a fluidized. Usually sand is used as intense mixing of inert bed solids. It will give good and temperature control and also provides high heat transfer to biomass solids. The residence time of the solid is higher than gas in pyrolyzer.

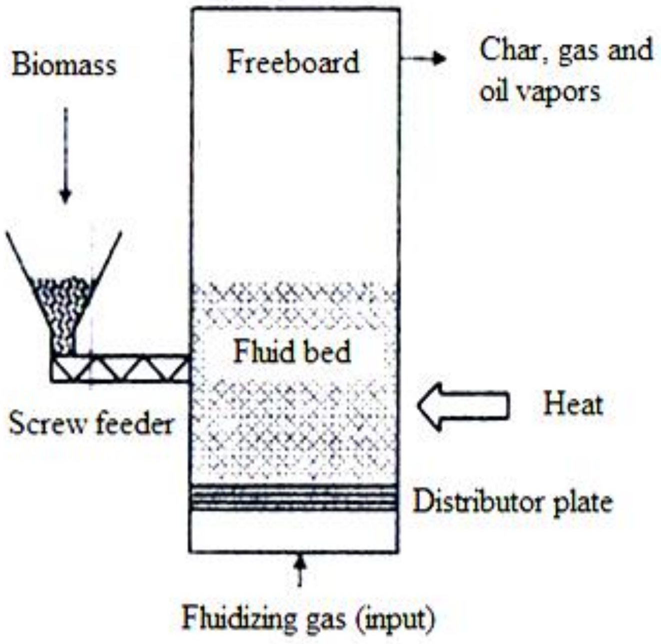

Figure 2.5: Bubbling fluidized bed (Basu, 2010)

The heat required for the pyrolysis is provided by burning a part of gas in the bed or by burning the char in a separate chamber and transferring the heat to the bed solids as shown in Figure 2.5.The pyrolysis product contain about 70 – 75 % liquid. As shown in the figure, the char in the bed solid act as a vapor cracking catalyst. So, its separation through elutriation or otherwise is important if the secondary cracking need to be avoided to maximize the liquid product. Char is separated from product gas using single or multistage cyclones. An advantage of using bubbling fluidized bed is it is easy to scale up.

2.10.3 Circulating Fluidized Bed

The principle is same as bubbling fluidized bed. The different are for the circulating fluidized bed, the bed is highly expanded and solids continuously recycle around an external loop comprising a cyclone and loop seal. The bed operates in a hydrodynamic regime which is known as fast bed (Basu, 2010). It provides good temperature control. The superficial gas velocity in a CFB is significantly higher than bubbling bed. High velocity combined with excellent mixing allows CFB to have large throughputs of biomass. Then, gas and solids move up to the reactor with some degree of internal refluxing. So, the residence time of average biomass particles is longer than gas. The advantage of this system is char entrained from the reactor is easily separated and burn in an external fluidized bed. The combustion heat is transferred to the inert bed solids that are recycled to the reactor by means of a loop seal.

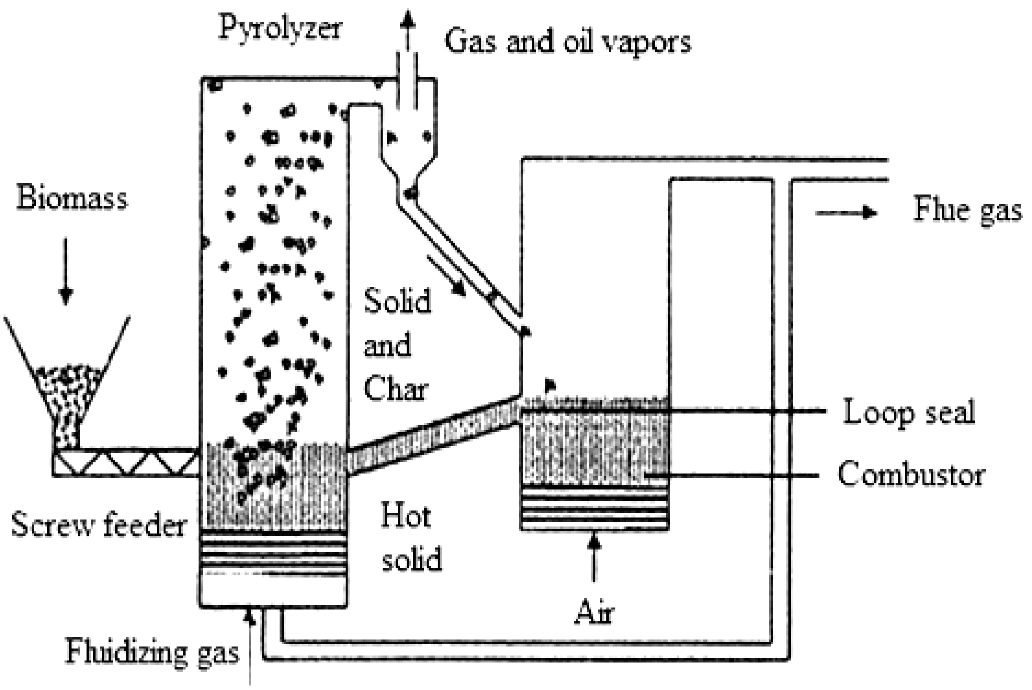

Figure 2.6: Circulating fluidized bed (Basu, 2010)

2.10.4 Ultra-Rapid

To obtain high liquid yield, high heating rate and short residence time must have in the pyrolysis. The ultra-rapid pyrolyzer that is developed by University of Western Ontario provides extremely short mixing (10 – 20 ms), reactor residence (70 – 200 ms) and quench (~20 ms) times. The reactor temperature is low which is ~650 ^{o}C. So, it can achieve a liquid yield as high as 90 % (Hulet, 2005). Gas nitrogen is heated 100 ^{o}C above the reactor temperature and injected at very high velocity into the reactor to bombard a stream of biomass injected in the reactor. The reactor can use a heat carrier solid such as sand that is heated externally and bombarded on a biomass stream through multiple jets. High velocity in the reactor cause high heating rate. The pyrolysis product leaves the reactor from the bottom and is quickly cooled to cracking of the oil vapor. This process is able to maximize liquid yield during pyrolysis.

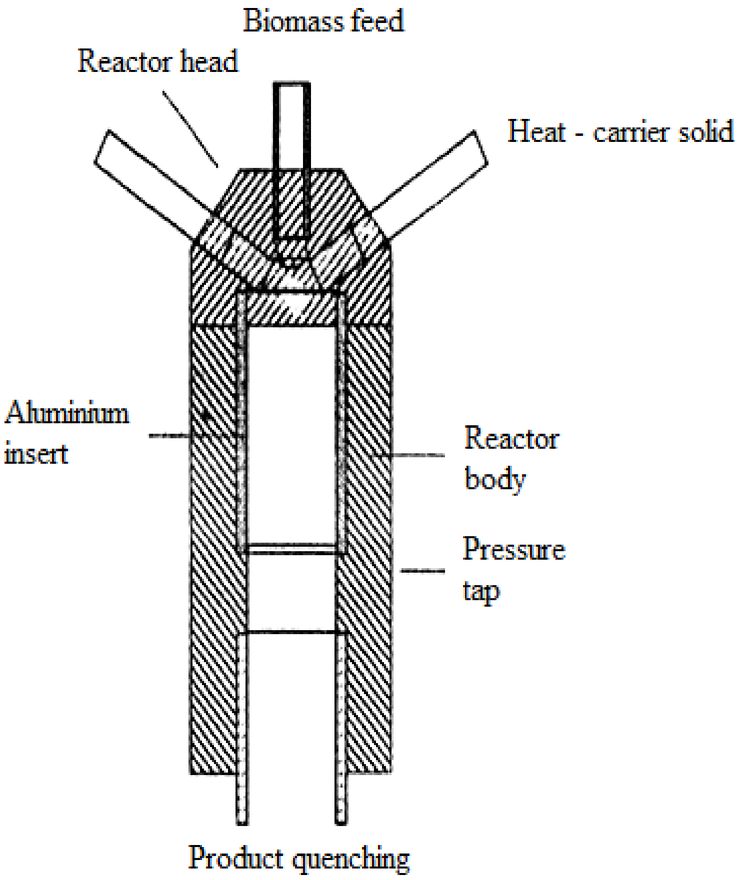

Figure 2.7: Ultra-rapid (Basu, 2010)

2.10.5 Ablative

This type of pyrolyzer involves creation of high pressure between a biomass particle and a hot reactor wall. This allows uninhibited heat transfer from the wall to the biomass that will cause liquid product to melt. The biomass sliding against the wall leaves behind a liquid film that evaporates and leaves the pyrolysis zone which is the interface between biomass and wall. As a result of high heat transfer and short gas residence time, the production of liquid yield is as high as 80 % (Diebold & Power, 1988). The pressure between biomass and wall is produced by mechanical means or by centrifugal force. In a mechanical system a large piece of biomass is pressed against a rotating hot plate.

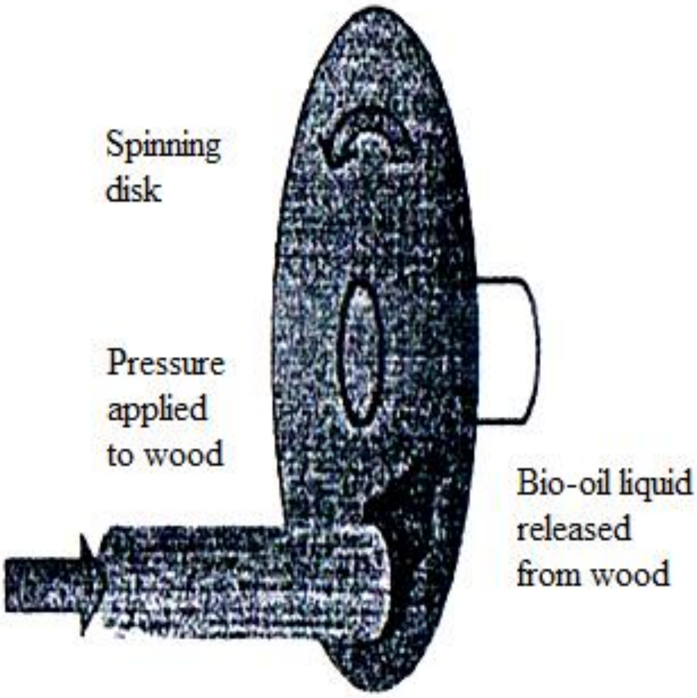

Figure 2.8: Ablative (Basu, 2010)

2.10.6 Rotating Cone

In this system, particles of biomass are fed into the bottom of a rotating cone about 360 - 960 rev/min together with an excess of heat carrier solid particles. The particles are transported spirally upward along the wall when centrifugal force pushes the particle against the hot wall. The biomass undergoes rapid heating which is 5000 K/s and is pyrolyzed within the small annular volume. The product gas containing bio oil vapor leaves through another tube while solid char and sand spill over the upper rim of rotating cone into a fluidized bed surrounding it. The combustion of char in the fluidized bed will helps heat the cone as well as the solids that are recycled to it to supply heat for pyrolysis. The advantage of this reactor is very short residence time and don’t need a carrier gas. These typically provide a liquid yield of 60 % to 70 % on dry feed (Hulet, 2005).

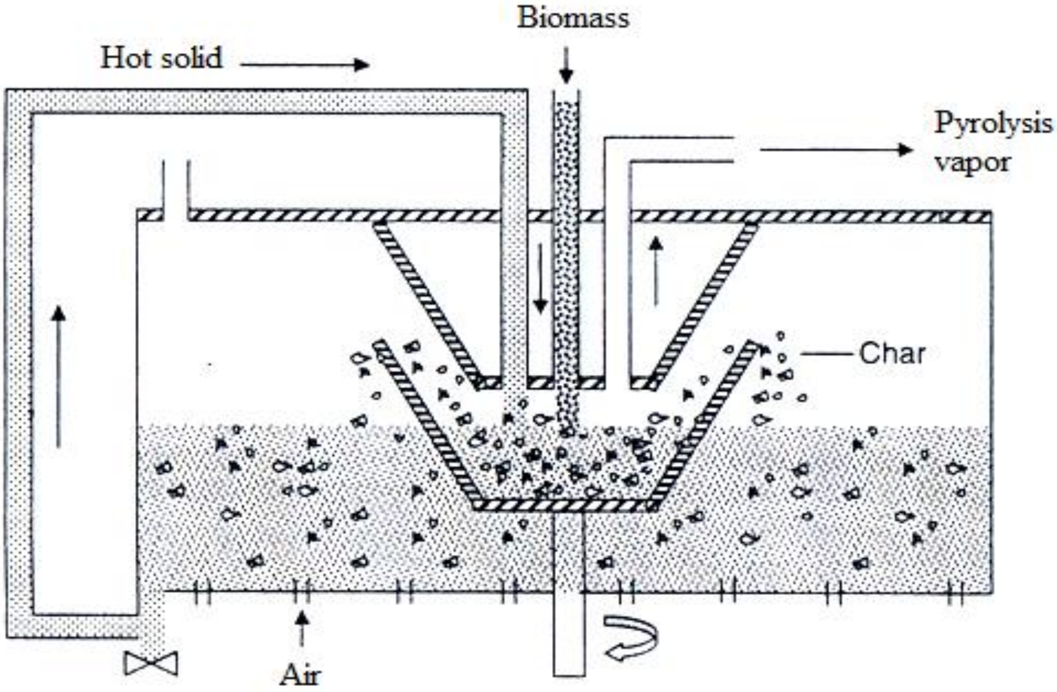

Figure 2.9: Rotating Cone (Basu, 2010)

2.10.7 Vacuum

Vacuum pyrolyzer comprises a number of stacked heated circular plates. The top plate is about 200 °C and the bottom one is about 400 °C. Biomass is fed at the top plate drops into successive lower plates by means of scrapers. The biomass undergoes drying and pyrolysis while moving over the plates. vacuum pyrolyzer not need a carrier gas. Only char is left when the biomass reaches the lowest plate. Because the heating rate of the biomass is relatively slow, the residence time of the vapor in the pyrolysis become short. The liquid yield in the process is only about 35 % to 50 % with a high char yield. The design of this pyrolyzer is complex.

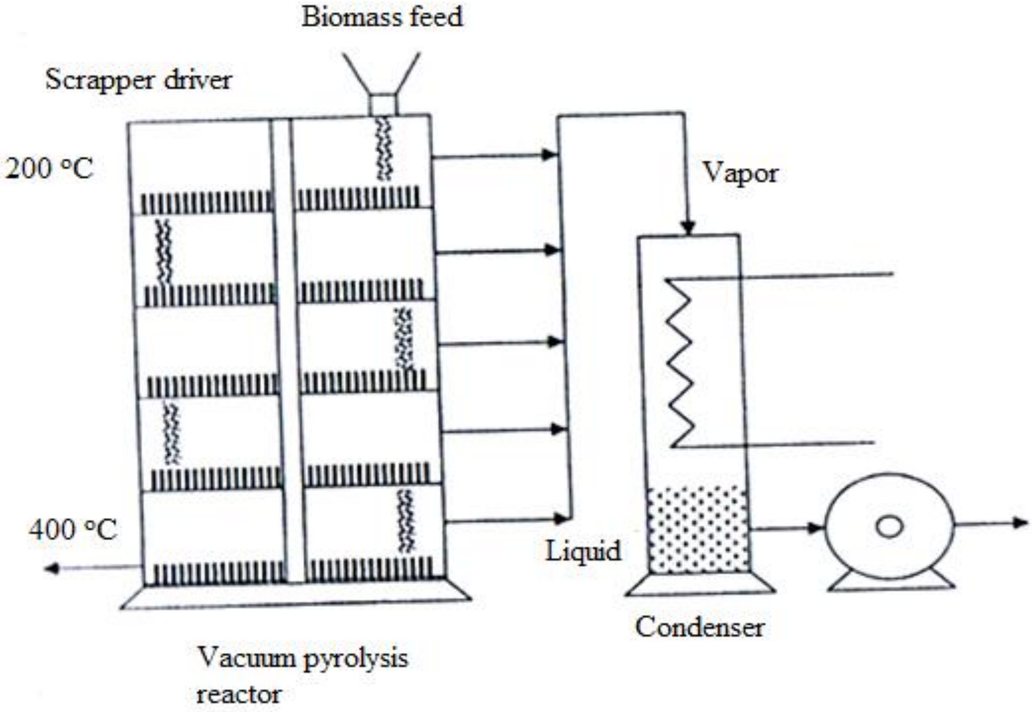

Figure 2.10: Vacuum (Basu, 2010)

2.11 Distinct Characteristic of Biomass

In comparison to fossil fuels, biomass fuels have comparatively low heating values. This can be explained by two of their distinct characteristics that are high moisture and high oxygen contents (Jenkins et al., 1998; Demirbas, 2007).

The high moisture content is one of the most disadvantageous features of using biomass as a fuel. Although the combustion reactions are exothermic, the evaporation of water is endothermic. To maintain a self-supporting combustion process, the moisture content (on wet basis) of biomass fuels cannot be higher than 65 % (Jenkins et al., 1998). In addition, the heating value of the fuel is negatively related with the relative amount of water even when the moisture content is within the maximum acceptable limit (Jenkins et al., 1998; Demirbas, 2007; Quaak et al., 1999).

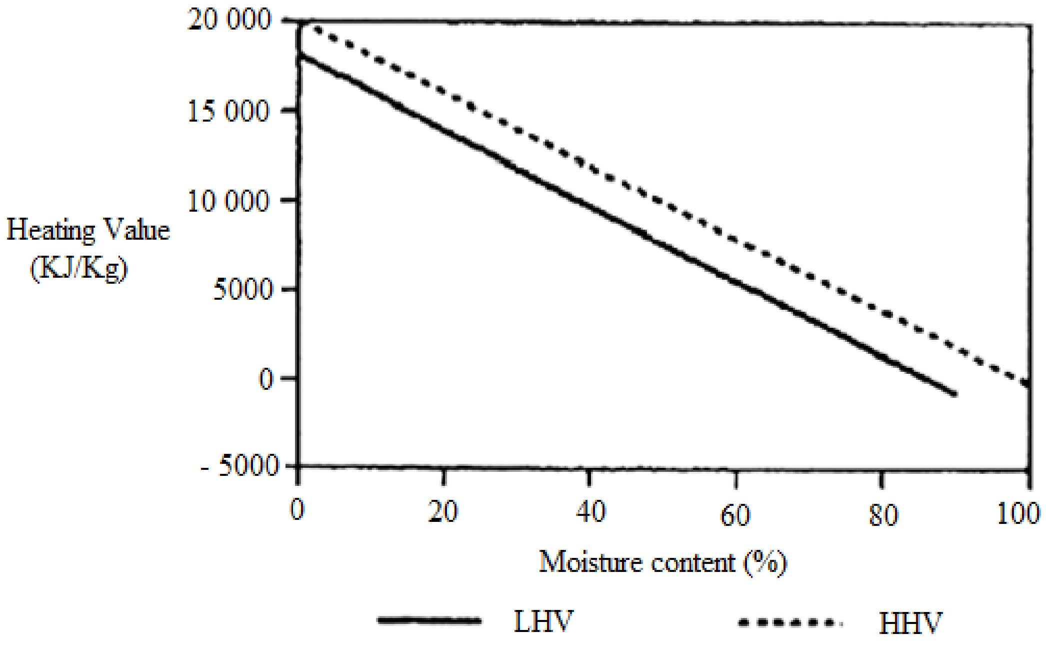

Figure 2.11: Relationship between heating value and moisture content of biomass fuel (Quaak et al., 1999)

Figure 2.11 exhibits the negative linear relationship between the moisture content and the heating value. As the moisture content increases, both the higher heating value (HHV) and lower heating value (LHV) decrease. HHV and LHV are used to describe the heat production of a unit quantity of fuel during its complete combustion. In determining the HHV and LHV values of a fuel, the liquid and vapor phases of water are selected as the reference states. As HHV incorporates the heat of the condensation of water vapor during the combustion, it is not surprising to observe that the curve of the HHV is always above that of the LHV (Quaak et al., 1999).

Another important feature of biomass fuel is its elevated oxygen content. Usually, the oxygen content of biomass is as high as 35 wt%, approximately ten times higher than that of a high-rank coal, which is below 4 wt% (Demirbas, 2007).Fouling and corrosion of the combustor are typical issues associated with biomass combustion. These are considered to be damaging because of the resulting reduction in heat transfer in the combustor. Fouling is commonly associated with the presence of alkali metals and some other elements such as silicon, sulphur, chlorine, calcium and iron in the ash.

With a series of complex chemical reactions, these elements are deposited in the forms of chlorides, silicates or sulphates on the wall of the combustor or the surface of the heat transfer elements. Generally, herbaceous biomass, such as straws and grass with comparatively higher contents of alkali, sulphur, chlorine and etc has a higher potential for the occurrence of ash deposition and corrosion in comparison to woody biomass.

2.12 Applications of Bio Oil

Bio-oil can be a replacement for fuel oil in many static applications including boilers, furnaces, engines and turbines for electricity generation. Liquids products from pyrolysis process can be used for combustion, power generation and chemicals constituents. The most significant changes since then are:

- An appreciation of the potential for fast pyrolysis to be a pre-treatment method for bio-oil to be an effective energy carrier.
- Greater interest in bio-oil as a precursor for second generation biofuels for transport.
- Greater awareness of the potential for fast pyrolysis and bio oil to offer more versatile processes routes to a wider range of products and contribute to bio refinery concept development.
- Considerably greater interest in upgrading bio-oil sufficiently for it to be used for heat, power and other applications with greater confidence by users.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experiment method and procedure for the preparation and characterization throughout the research are summarized. Figure 3.1 shows the flow chart of overall experimental work. The first stage is analyzed the samples with Thermogravimetric Analysis (TGA). The two types of biomasses which are EFB and POF was analyzed first. The analysis followed with the three different samples sizes which are < 0.63 mm, 0.63-2 mm and 2-4 mm. Then, the pyrolysis process was undergone at condition of temperature 500 ^{o}C with heating rate 20 ^{o}C/min. Lastly the bio oil was characterized using Fourier Transform Infrared (FTIR), pH meter and viscometer.

3.2 Research Methodology

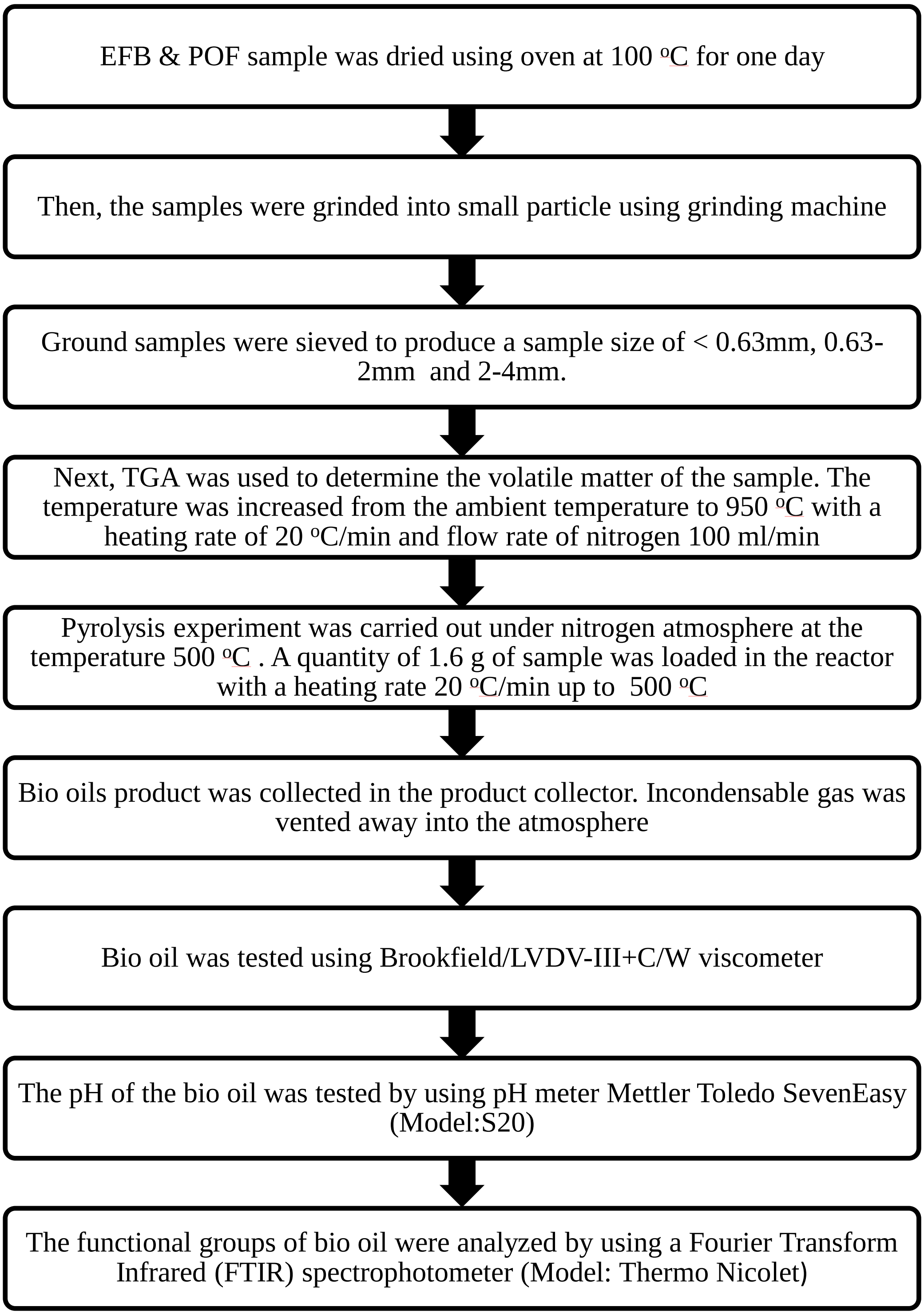

Figure 3.1: Schematic diagram for the flow of experiment

3.3 Materials

Biomass that used in this study was empty fruit bunch fiber (EFB) and palm oil fiber (POF). The sample was obtained from Felda Lepar Hilir 3 which is situated at Pahang. Moisture content is low compared to other biomass residues. The moisture content for the samples was identified by using TGA.

Figure 3.2: Empty Fruit Bunch Fiber (EFB)

Figure 3.3: Palm Oil Fiber (POF)

3.4 Sample Preparation

The sample was dried using oven at 100 ^{o}C for one day. Then, the samples were grinded into small particle using grinding machine (Figure 3.4) which is located at FKKSA laboratory. The smaller samples has larger surface for heat to contact. This is due to heat transfer principle. After that, ground samples were put into sieve shaker as shown in Figure 3.5 to get the sample size that was needed. The smallest sample left at the bottom of the tray. The mesh tray sizes were 0.63 mm, 2 mm and 4 mm. Therefore, the sample size that produced were < 0.63 mm, 0.63 - 2mm and 2 - 4mm.

Figure 3.4: Grinding Machine

Figure 3.5: Sieve Shaker

3.5 Pyrolysis Unit

Tubular furnace is the most important part in pyrolysis unit. It provides heat using electric energy. The tubular furnace was controlled by controllers which were set desired temperature, ramping time and heating rate of the tubular furnace. The sample was filled in the reactor and was placed in the tubular furnace for heating purpose. Nitrogen gas was used for purging and acts as a carrier gas. Liquid product was collected inside the vial bottle which placed in beaker. The beaker was filled with tap water. Tap water is use for cooling medium for the cooling process to condense pyrolysis gas into liquid product.

Figure 3.6: Pyrolysis Unit

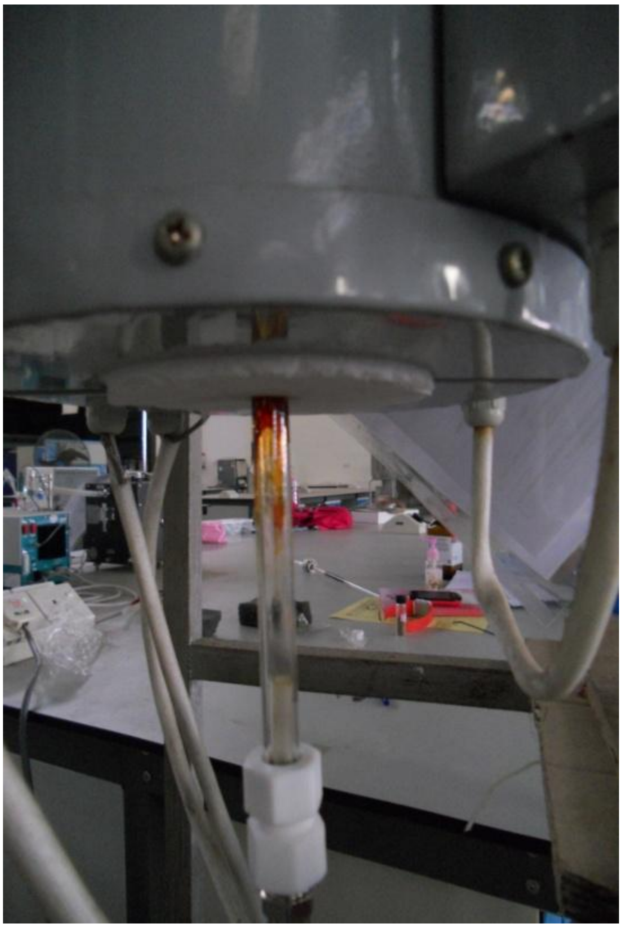

Figure 3.7: During pyrolysis process

3.6 Experimental Set Up

3.6.1 Blank Test

The purpose of the blank test is to make sure if there any leakage on any connection that have been made. Nitrogen was used as a medium. In this test, nitrogen was flow through the system for about 15 minutes at 11 psi. Bubble is needed to determine any leakage of the set up. There is no leakage if the pressure gauge at the pyrolysis system has same reading with the pressure gauge at the nitrogen regulator.

Figure 3.8: Tubular furnace with reactor

3.6.2 Purging

Purging is the first procedure that must be made before starting the experiment. This is to make sure there in no air in the system. The purging process is done for 10 minutes at 11 psi. The flow of Nitrogen will replace the air in the reactor.

3.7 Experimental Procedures

Pyrolysis experiment was carried out under nitrogen atmosphere at the temperature 500 ^{o}C because this temperature was found to be the optimum condition for maximum liquid product yield (Kawser and Nash, 2010). A quantity of 1.6 g of EFB was loaded in the reactor with a heating rate 20 ^{o}C/min up to desired temperature. The study was carried out using glass reactor at FKKSA Gas Lab Engineering.

Bio oils product was collected in the product collector. Incondensable gas was vented away into the atmosphere.

3.8 Analysis

Analysis procedure consists of two stages. The first analysis was used TGA. The bio oil product was analyzed using FTIR. Viscosity and pH of the bio oil were also been determined.

Figure 3.9: Bio oil

3.8.1 Thermogravimetric Analysis (TGA)

For the proximate analysis, TGA analysis of EFB and POF was carried out by using TGA Q500 V6.4 instrument as shown in Figure 3.8. This analysis was performed to determine moisture content, volatility and ash content of the sample. The sample of about 3 mg POF and 3 mg EFB was placed in a standard platinum pan. For the EFB, the experiment was continued with different size of the sample which are < 0.63 mm, 0.63-2 mm and 2 - 4mm. The TGA experiments were performed under the flow of nitrogen with a flow rate 100 ml/min. The temperature was increased from the ambient temperature to 950 ^oC with a heating rate of 20 ^oC/min.

Figure 3.10: TGA Q500 V6.4 instrument

3.8.2 Viscosity

Viscosity is a measure of a resistance of the liquid to flow. The viscosity of the fuel is important because of its effect on pumping and injecting of the fuel. Bio oil was tested using Brookfield/LVDV-III+C/W viscometer. Firstly, the suitable vane spindles have been chosen. Vane spindles are for use with paste like materials, gels & fluids where suspended solids migrate away from measurement surface of standard spindles. The small spindle has been chosen to be submerged in the bio oil. Then, the motor was rotating the spindle and viscosity of the bio oil was determined.

Figure 3.11: Brookfield/LVDV-III+C/W viscometer

3.8.3 pH

The pH of the bio oil was tested by using pH meter Mettler Toledo SevenEasy (Model: S20). Firstly, the cap was removed from the electrode. Electrode was placed in pH 7 buffer and stir. Then, calibrate button was pressed and the electrode was rinsed with H_2O. If performing 2-3 point calibration, buffer was adjusted and repeated. Cal must be pressed after each reading. Read button was pressed for auto endpoint and hold for manual endpoint. Next, electrode was placed in bio oil and read button was pressed. When done, electrode was removed and rinsed. The electrode was placed in appropriate filling solution and recap. The electrode was immersed within the bio oil until the reading of pH meter become stable.

Figure 3.12: pH meter Mettler Toledo SevenEasy (Model: S20)

3.8.4 Fourier Transform Infrared (FTIR)

The functional groups of bio oil were analyzed by using a Fourier Transform Infrared (FTIR) spectrophotometer brand of Thermo Nicolet as shown in figure 3.11. In this study, a small droplet of the bio oil was poured on Potassium Bromide (KBr) pressed disk and the spectrum was acquired via transmission infrared (IR) spectrometry. Pure spectrum of bio oil was obtained since KBr contains no absorption bands in the IR region. IR vibration frequencies characterized the presence or absence of functional group of hydrocarbon. The result of FTIR is illustrated where the functional groups were determined base on the peak value on the graph.

Figure 3.13: Fourier Transform Infrared (FTIR) brand Thermo Nicolet

CHAPTER 4

RESULT & DISCUSSION

4.1 Thermogravimetric Analysis (TGA)

4.1.1 Effect of Type of Biomass

The main purpose of the Thermogravimetric Analyzer is to determine the moisture content, volatility and ash content of the sample. The sample was decreased as the temperature increased due to the degradation of sample components. Figure 4.1 and 4.2 illustrate the analysis result of POF and EFB respectively. Three different regions can be distinguished from the analysis result. The first stage indicates water content from the sample. Determining the moisture content is very important as it influences moisture content in bio oil. It can be seen in the figure that the moisture content for POF and EFB were 10.88 wt% and 11.31 wt% respectively.

Devolatilization is the major step in all thermochemical process including biomass. The second stage shows the decreasing of dry sample as the sample become volatile. This result indicates the amount of the bio oil that might produce in pyrolysis process. The higher percentage of volatile matter typically produce higher yield of bio oil. It is found that the volatile matter of POF is 62.5 wt% and volatile matter of EFB is 66.96 wt%. Since EFB has higher volatile matter than POF, thus, EFB is used as a sample for the next analysis on sample size. The end of the curve was the ash residue. It can be seen that ash for POF is 17.77 wt% and ash for EFB is 19.82 wt%.

According to Isha and Wiliams (2011), the liquid yield of POF is 55.4 wt%. Meanwhile the char and gas yield are 27.7 wt% and 16.9 wt% respectively. While Abdullah et al. (2010) found that in the fast pyrolysis of empty fruit bunch, the liquid yield of EFB is 50.6 wt%. Meanwhile the char and gas yield are 27.2 wt% and 17.9 wt% respectively.

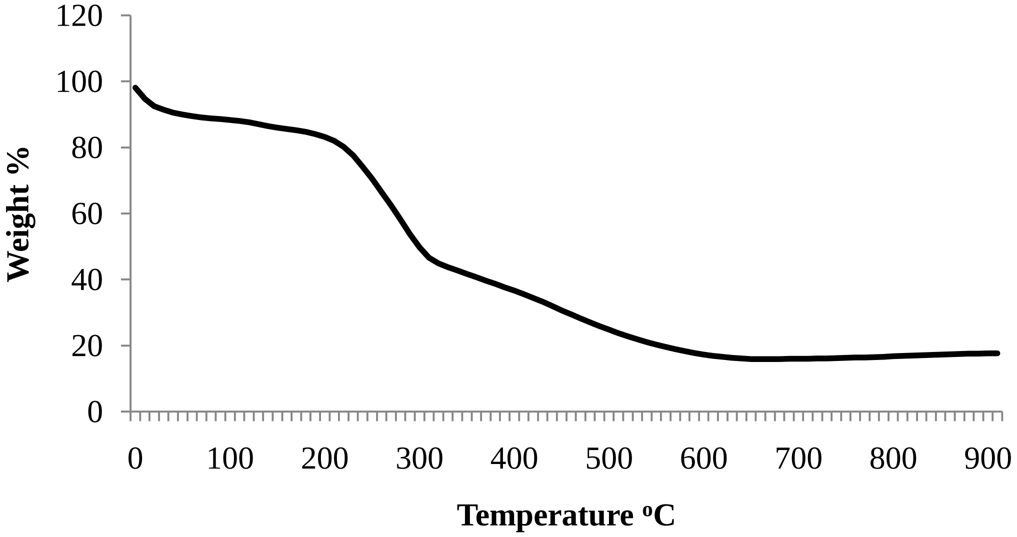

Figure 4.1: Graph of Weight % vs Temperature (°C) for POF

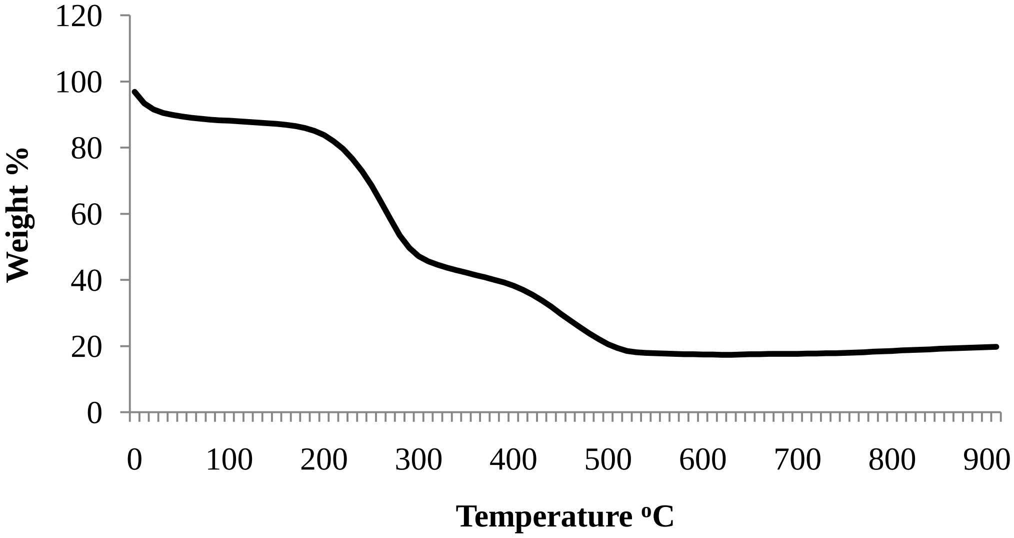

Figure 4.2: Graph of Weight % vs Temperature (°C) for EFB

4.1.2 Effect of Biomass Sample Size

The effects of biomass sample size were also analyzed by TGA. Before this, the types of biomass that have a potential to be use as a feedstock fuel have been discussed. EFB sample with the sample size of < 0.63 mm, 0.63-2 mm and 2-4 mm was used. According tu Luo et al. (2009), the hydrogen content increase with the decreasing particle size in the investigation of various sample size in the range of 0.075 mm to 1.2 mm. The Graph of Deriv.Weight % / min vs Temperature (^{o}C) is show in figure 4.3.

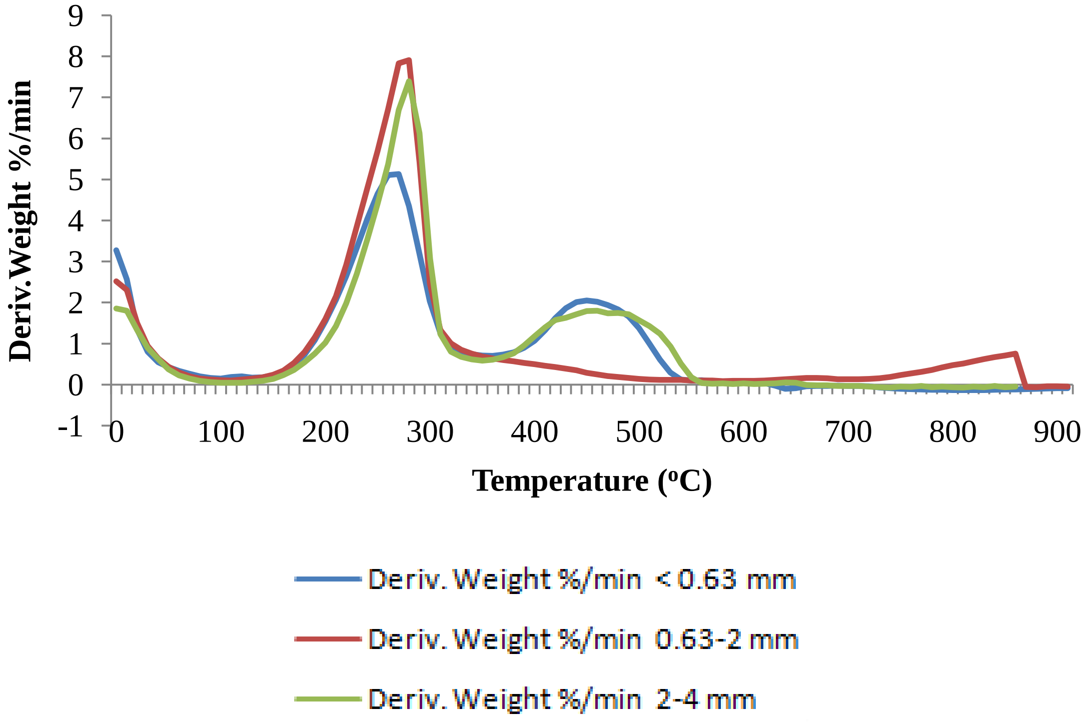

Figure 4.3: Graph of Derivative Weight % / min vs Temperature (^{o}C)

The DTG curves at different sample size indicate similar qualitative result. First, all three sample sizes start to decompose at temperature 100^{o}C. They started to release volatile at temperature 200 ^{o}C. The deviation for the sample size of < 0.63 mm is probably due to high heating rate. The small particle usually will cause high heating rate due to the surface area of the sample. This high heating rate will cause high yield of bio oil. So, this graph show that sample size of < 0.63mm was the optimum sample size to undergo pyrolysis. The deviation for sample size of 2-4 mm is not similar to sample size of < 0.63 mm and 0.63 - 2 mm maybe due to the experimental error. They are maybe some other components in the biomass such as fungal. That is maybe the reason why the graph for 0.63 - 2 mm have different peak.

Encinar et al. (2000) who pyrolysed cardoon (Cynara cardunculus L.) with particle size ranging from 0.43 - 2 mm hypothesized that an increase in particle size cause greater temperature gradients inside the particle. So that at any given time the core temperature is lower than that of surface which possibly gives rise to an increase in the char yields and a decrease in the yields of liquid and gases. If the particle size is sufficiently small it can be heated uniformly (Seebauer et al., 1997).

4.2 Bio oil production via micro reactor

In this investigation, the EFB sample; < 0.63 mm, was pyrolysed in the micro reactor at 500 ^{o}C for 50 minutes. Three products were produced; gas, char and bio oil. The gas product was obtained by difference mass of bio oil and char. The result of this investigation is shown in Figure 4.4 and Table 4.1. The bio oil obtained was dark brown in color. The weight of the bio oil and char remained in the reactor was measured after the pyrolysis process.

Yield of pyrolysis product	Present Study	Abdullah study, 2010
Yield of Bio oil	15.64 %	50.6 %
Yield of Char	25.4 %	27.2 %
Yield of Gas	58.96 %	17.9 %

Table 4.1: Yield of pyrolysis products and its comparison

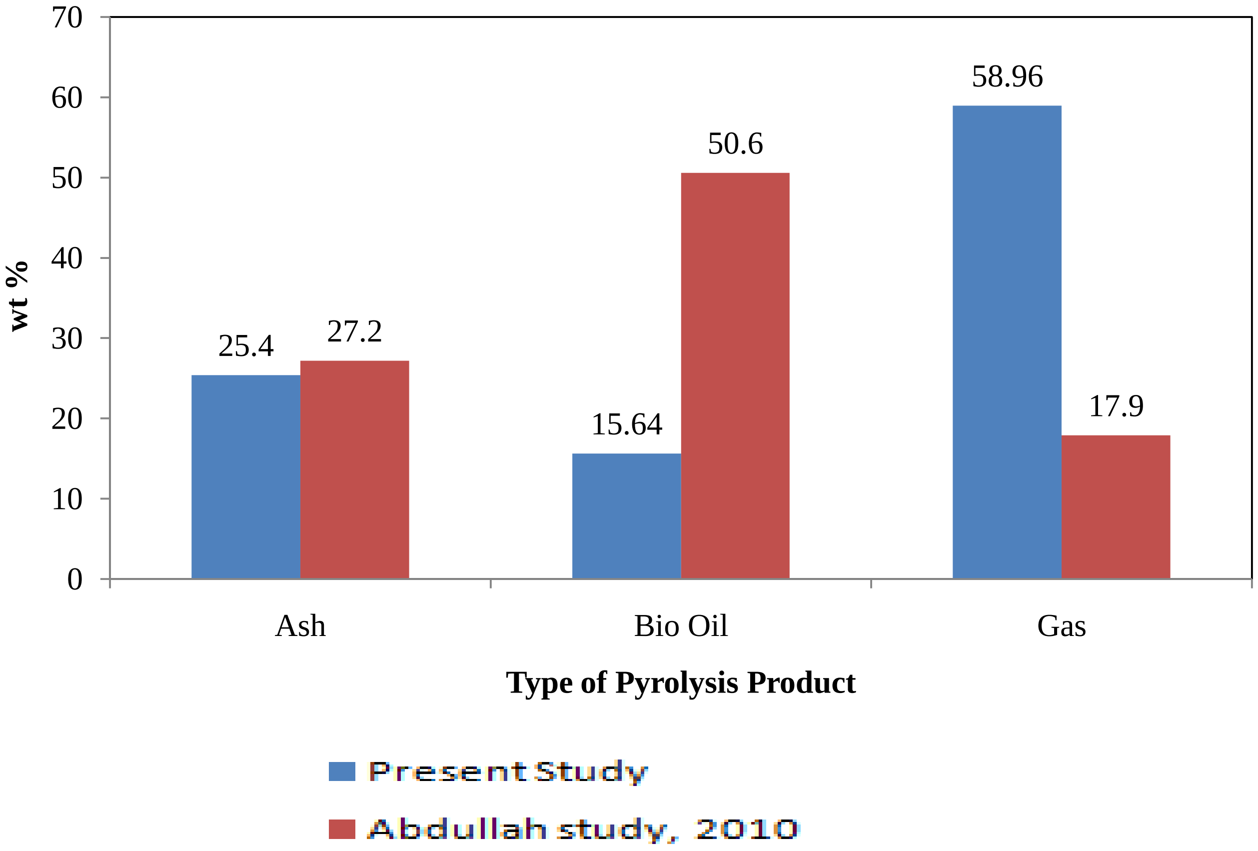

Figure 4.4: Graph of yield of pyrolysis product and its comparison

It can be seen that the yield of bio oil from this investigation is 15.64 wt% with the char and gas yield are 25.4 wt% and 58.96 wt% respectively. Meanwhile for Abdullah study is 50.6 wt% yield of bio oil with char and gas yield were 27.2 wt% and 17.9 wt%. The less yield of bio oil compare to the others research is maybe due to drying process. The biomass drying temperature was at 100 ^{o}C. In this investigation, at this temperature, some components in the biomass might be evaporated. This is maybe the reason why only 15.64 wt% yield of bio oil was obtained.

4.3 Viscosity

The viscosity of bio oil was tested at temperature 28 ^{o}C. The value obtained was 34 cP. According to Abdullah et al. (2011) study, they found that the viscosity of bio oil obtained at temperature 25^{o}C was 46.31cP. Viscosity of bio oil may vary in range of 10 - 100 cP (Qiang et al., 2009).

4.4 Bio oil Characterization

The pH value for bio oil was 3.99 which was very acidic. The range pH of bio oil is typically at 2-4. Bio-oil is acidic due to the creation of organic acids such as formic and acetic acid when biomass degrades (Sadaka, 2008). It is corrosive to most metals except stainless steel.

FTIR is important to determine the functional groups that exist in the bio oil. The functional groups are determined based on the peak value from the graph as shown in Figure 4.5.

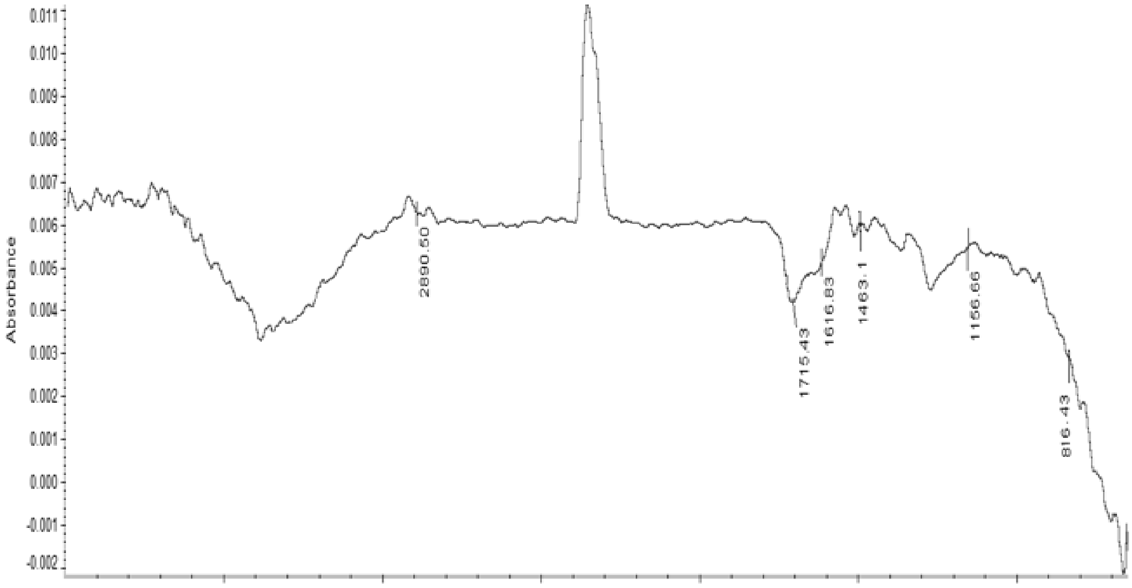

Figure 4.5: FT-IR Spectrum of bio oil obtained from EFB at 500 ^{o}C

The Fourier Transform Infrared Spectroscopic (FT-IR) spectra of the bio-oil were given in Figure 4.5 representing functional group compositional analysis of bio-oil obtained from EFB at temperature 500 ^{o}C. The O-H bending vibration between 1000 cm^{-1} and 12600 cm^{-1} of the bio-oils indicate the presence of phenols and alcohols. The C-H stretching vibrations between 2800 cm^{-1} and 2950 cm^{-1}, C-H deformation vibrations between 1450 cm^{-1} and 1500 cm^{-1} indicate the presence of alkane groups. The C=O stretching vibrations between 1700 cm^{-1} and 1730 cm^{-1} are compatible with the presence of aldehyde, ketones and carboxylic acid groups. The absorbance peak between 1610 cm^{-1} and 1640 cm^{-1} represent C=C stretching vibrations indicative of alkenes. Finally, the absorption peaks between 650 cm^{-1} and 900 cm^{-1} indicate the presence of single, polycyclic or substituted aromatic groups.

It can be seen that a significant of the carboxylic acid group was determined at 1715.43 cm^{-1}. This is an evidence to show that the bio oil obtained is an very acidic compound.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, from the thermogravimetric analysis it can be deduced that biomass that has a potential to be use as a feedstock fuel is EFB. The sample size of < 0.63 mm is the optimum size that can obtained high yield of bio oil. The pyrolysis of sample EFB with sample size < 0.63 mm is successfully performed using glass reactor with turbulent furnace. The pyrolysis at temperature 500 ^{o}C manages to produce bio oil about 15.64 wt%. The yield of production bio oil is different from the existing literature. This may happen due to high temperature of drying the samples.

The FTIR analysis shows that bio oil is low grade liquid fuels when compared with petroleum fuels. In this research, bio oil obtained has low pH values which will cause corrosive to materials. The poor fuel properties include the complex multiphase structures, high content of oxygen, water, solids and ash, low heating values, low pH values and poor ignition and combustion properties. In spite of these poor fuel properties, bio-oils also have some promising properties. They usually possess some lubricity and they are less toxic and more biodegradable fuels.

5.2 Recommendations

It is suggetested that there are several things should improve to get the better results of the research.

- Firstly, utilize the other types of biomass. The variety of biomass in Malaysia gives the opportunities for further research on other kind of biomass such as rice husk, paddy straw, sugarcane and others.
- Then, use a different temperature during the pyrolysis to look at their yield of bio oil.
- Advance analysis of bio oil such as GC-MS is also needed to know the exactly percentage of composition that exist in the bio oil.
- There are several power plants in the world using the pyrolysis process to produce energy, but its only limit for the fueling of turbine. At present, many bio oils cannot meet the fuel specification and cannot be accepted commercially. Further research is required to improve the properties of bio oil for commercialization.

REFERENCES

Abdullah.N, Sulaiman.F and Gerhauser.H. (2011). *Characterisation of Oil Palm Empty Fruit Bunches for Fuel Application*. Journal of Physical Science. Vol. 22(1). 1–24

Ahmad.S et al,. (2009).*Next Generation Biofuels: Malaysian Experience*. Pdf.

Ana-Rita F D, Ian W D (1996). *Pyrolysis of sugarcane bagasse in a wire mesh reactor*. I & EC Res 35:1263-8

Antonia V.H., Timothy E.L., Daniel M.K. *Renewable energy sources*.

Basu.P. 2010. *Biomass Gasification and Pyrolysis: Practical Design and Theory*. Academic Press.

Bridgewater.A.V. (1999). *Principles and practice of biomass fast pyrolysis processes for liquids*. J. Anal Apply Pyrolysis. 24:615-25

Dermibas A (2007). *Combustion of biomass.*

Encinar.J.M., Gonzalez.J.F., Gonzales.J (2000). *Fixed bed pyrolysis of Cynara cardunculus L. Product yields and compositions*. J. Fuel Processing Technology. 68: 209-222

Haiping.Y., Rong.Y., Terence.C., David.T.L., Hanping.C, Chuguang.Z. (2004). *Thermogravimetric Analysis-Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis*. Energy & Fuels. 18:1814-1821

Isha.R and Williams.P.T (2011). *Pyrolysis-gasification of agriculture biomass wastes for hydrogen production.*Journal of the Energy Institute. p.80-87

Jenkins BM, Baxter LI, Miles Jr TR, Miles TR (1998). *Combustion properties of biomass.*

Joseph.J.B. (1999). *Renewable feed-stocks for the production of chemicals.* In: Proceedings of the 217th ACS national melting, vol.44. Division of fuel chemistry. p.204-9

Jun.S, Xiao.S.W., Perez.M.G, Mourant.D, Rhodes.M.J, Chun.Z.L. (2009). *Effects of particle size on the fast pyrolysis of oil malee woody biomass*. Fuel. 88: 1810-1817

Kawser.M.D and Nash.F. (2010). *Oil palm shell as a source of phenol*. Journal of oil palm research, vol 12, p. 86-94

Luo, S.Y., B.Xiao, X.J.Guo, Z.Q.Hu, S.M.Liu and M.Y.He (2009). *Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor:Influence of particle size on gasification performance*. International Journal of Hydrogen Energy. 34(3):p. 1260-1264

McKendry P (2002). Energy *production from biomass (part 1): overview of biomass*. Bio resource Technology 83: 37-46

McKendry P (2002). *Energy production from biomass (part 2): overview technologies*. Bio resource Technology 83: 47-54

Mohan.D., Pittman.C.U., Jr., Steele.P.H. (2006). Pyrolysis *of Wood/Biomass for Bio-oil: A Critical Review*. Energy & Fuels. 20:848-889

Othmer.K. *Encylopedia of chemical technology*, voll.11. 3rd ed.p.347-60

Putun.AE., Ozcan.A., Gercel.HF., Putun.E. (2001). *Production of biocrudes fro biomass in a fixed bed tubular reactor; product yields and compositions*. Fuel. 80:1371-8

Qiang.L,Wen-Zhi.L., Xi-Feng.Z. (2009). *Overview of fuel properties of biomass fasr pyrolysis oils*. Energy Conversion and Management. 50:1376-1383

Quaak P, Knoef H, Stassen H (1999). *Energy from biomass, a review of combustion and gasification technologies.*

Saxena.R.C., Adhikari.D.K., Goyal.H.B. (2009). *Biomass-based energy fuel through biochemical routes: A review*. Renewable & Sustainable Energy Reviews. 13:167-178

Seebaur.V., Petek.J., Staudinger.G (1997). *Effects of particle size, heating rate and pressure on measurement of pyrolysis kinetics by thermogravimetric analysis.* J. Fuel. 76(13): 1277-1282

Sukiran.M.A., Bakar.N.K.A., Chow.M.C. (2009). *Optimization of Pyrolysis of Oil Palm Empty Fruit Bunches*. Journal of oil palm research vol. 21.p. 653-658

Sukiran.M.A, Chow.M.C, Bakar.N.K.A. (2009). *Bio-oils from pyrolysis of oil palm empty fruit bunches.*

Wikepedia. 2012. *Biofuel* (online). http://en.wikipedia.org/wiki/Biofuel. (10 Jun 2012)

Williams.P.T. and Besler.S. (1996). *The influence of Temperature and heating rate on the slow pyrolysis of biomass*. Renewable Energy, vol 3, p.233-250.

Wind Power. 2008. *Biomass* (online). http://windturbine.me/biomass.html. (3 Jun 2012)

Xu.R., Ferrante.L., Hall.K., Berruti.F. (2011). *Thermal Self-sustainability of biochar production by pyrolysis*. Journal of Analytical and Applied Pyrolysis.

Zheng J.L. (2008). *Pyrolysis oil from fast pyrolysis of maize stalk*. Journal of Analytical and Applied Pyrolysis. 83: 205-212

APPENDICES

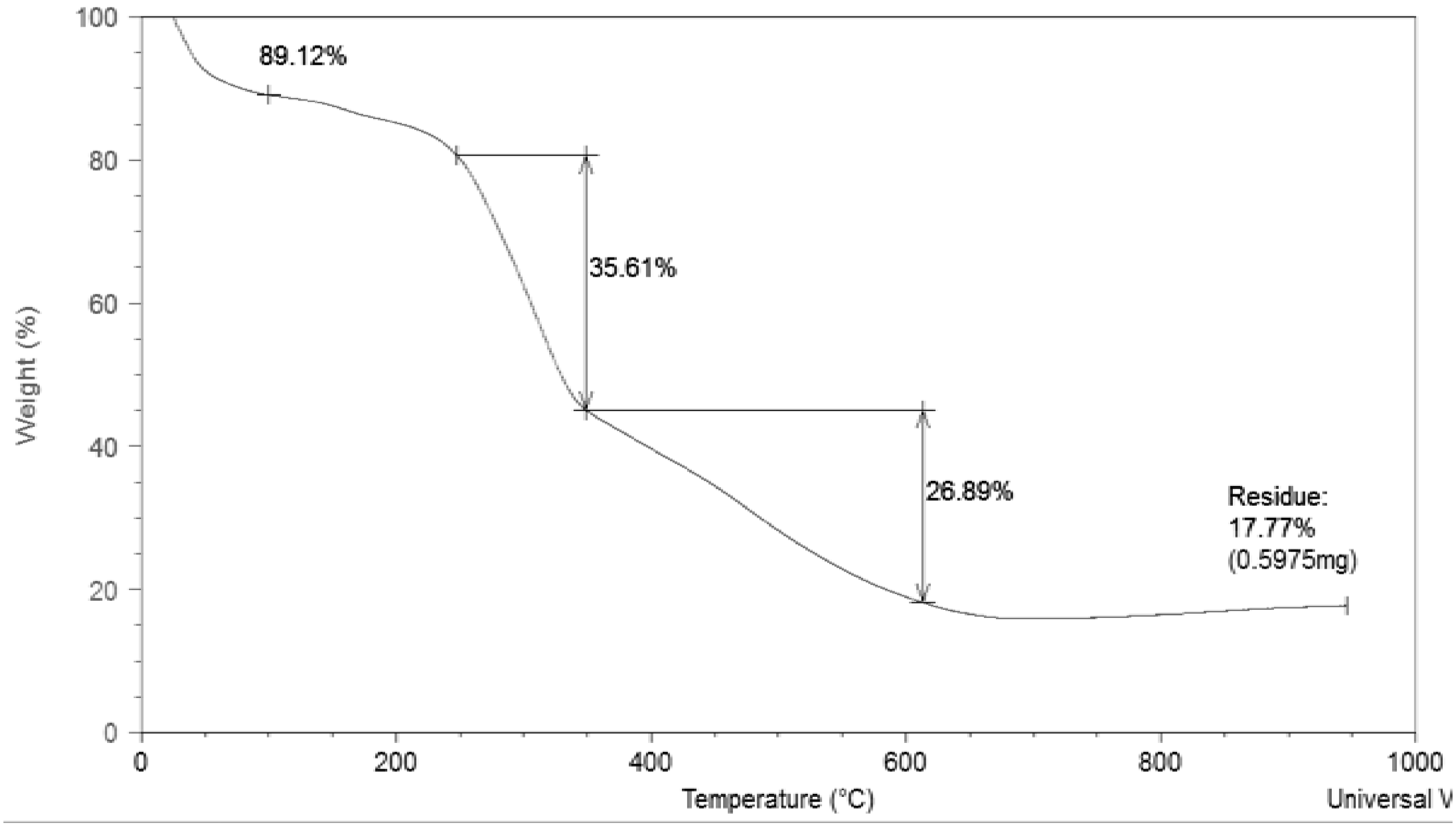

Figure 1: Graph of Weight% vs Temperature (^oC) for POF in TGA

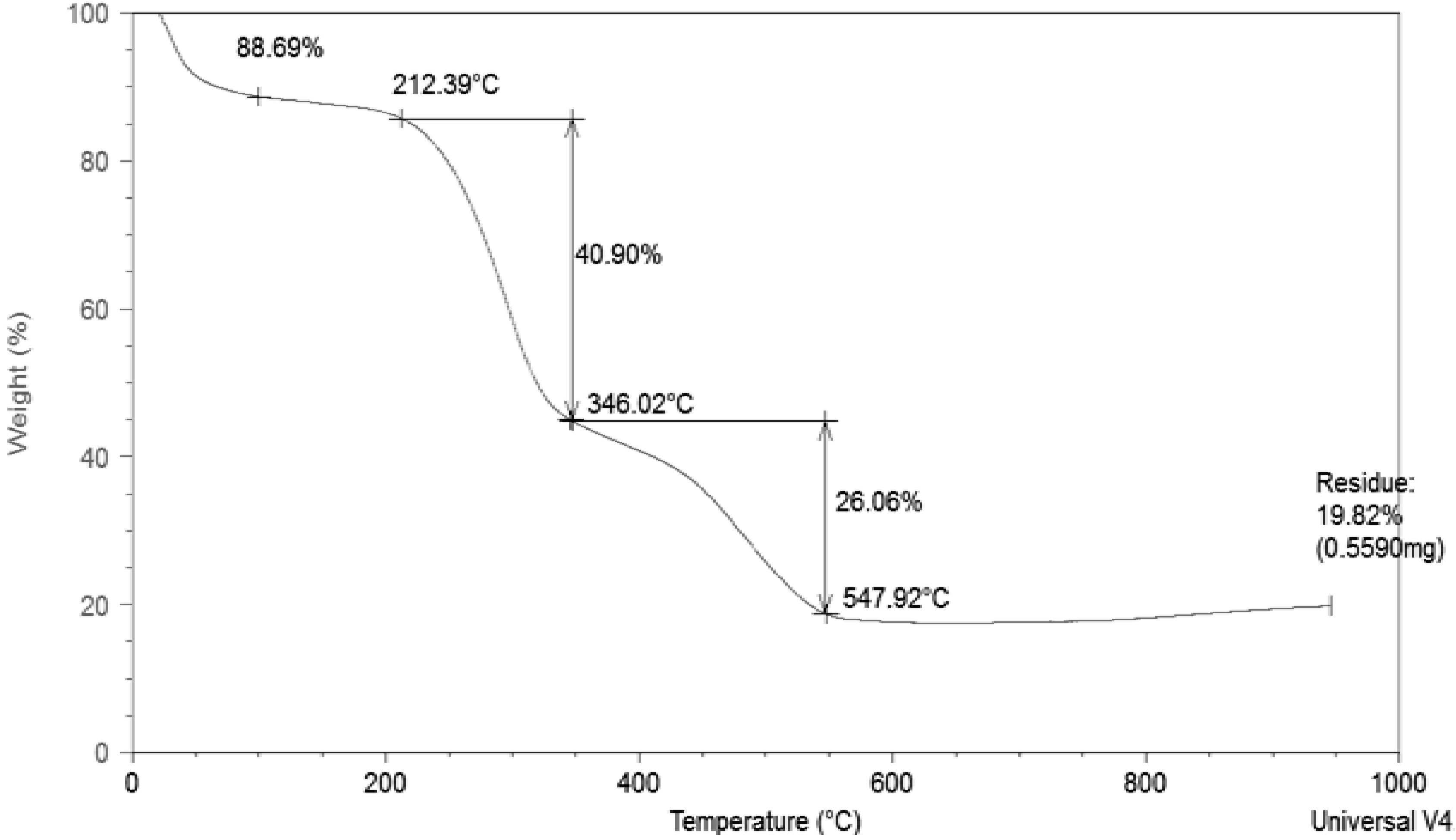

Figure 2: Graph of Weight% vs Temperature (^oC) for EFB in TGA