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THESIS

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PRODUCTION AND CHARACTERIZATION OF BIOMASS PELLET EFFECT TOWARDS THE ENERGY APPLICATION

TENG SWEE XIM

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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Dedicated to my family and my friends

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ABSTRACT

Biomass describes as the type of renewable energy source plays an important role in the future energy balance. Biomass appears to be a promising alternative energy source to replace fossil fuels in the future as it is abundantly available. However, it presents several undesired properties that do not permit its direct exploitation. One of the biomass called oil palm trunk (OPT) which is in bulky condition and contains high moisture contents. Hence this study is to improve the properties of OPT residues toward an efficient renewable energy supply by using pelletization and torrefaction process. Pelletization is a compression process to increase the energy content. In this study, one specific ratio with 90wt% OPT fibers or powder and 10% starch as binding agent will be tested in the experiment to produce a quality OPT pellet. Torrefaction is an emerging thermochemical pre-treatment process that improves the fuel properties of OPT pellet. In this study, three temperatures: 200˚C, 250˚C, and 300˚C at a constant heating rate of 10˚C/min for 30minutes, 60minutes and 90minutes residence time are to investigate the properties of OPT pellet. The torrefied product is characterized in term of mass and energy yield of OPT pellet. The trend of the mass yield graph for torrefied fiber was decreased from 81.88% to63.51% while torrefied powder was decreased from 89.60% to 74.09% when temperature increased along the torrefaction process. This was due to the degradation of lignocellulosic components of samples during the experiment. While for the trend of the energy yield of the samples were increased as torrefaction temperature and residence time increased. The highest energy yield was 89.7% at 300°C and 30minutes while the lowest energy yield was 40.7% at 200°C at 90 minutes. From the analysis, FTIR analyzed the lignocellulosic components while SEM analyzed morphology of torrefied OPT pellet.

ABSTRAK

Biojisim adalah salah satu jenis sumber tenaga yang boleh diperbaharui dan memainkan peranan penting dalam imbangan sumber tenaga global pada masa hadapan. Biojisim dikenali sebagai sumber tenaga alternatif yang penting untuk mengganti bahan api fosil kerana penghasilannya adalah sangat banyak. Silaj batang kelapa sawit (OPT) adalah salah satu jenis daripada biojisim yang mempunyai kandungan air yang tinggi dan sangat besar dari segi penyimpanan. Namun begitu, biojisim masih mempunyai sesetengah kelemahan dari segi sifat-sifat kimia dan fizikal yang perlu ditangani untuk menjamin prestasi biomas sebagai sumber tenaga. Oleh itu, kajian ini adalah untuk meningkatkan sifat-sifat sisa OPT ke arah sumber tenaga melalui proses pelletization dan torrefacion. Proses pelletization bertujuan untuk meningkatkan kandungan tenaga OPT. Nisbah 90wt% OPT fiber dan serbuk dengan 10wt% kanji sebagai agen penyatu digunakan dalam kajian ini untuk menghasilkan kualiti pellet yang terbaik. Torrefaction adalah satu proses perawatan termal untuk meningkatkan sifat-sifat bahan api biojisim mentah ke arah bekalan tenaga yang boleh diperbaharui. Dalam kajian ini suhu torrefaction : 200˚C, 250˚C, 300˚C 10pada kadar pemanasan 10˚C/min dengan masa tinggal 30 min, 60 min serta 90 min.Produk torrefaction telah dicirikan dari segi nilai hasil berat dan hasil tenaga. graf trend untuk torrefied fiber pellet adalah menurun dari 81.88% hingga 63.51% manakala torrefied serbuk pellet adalah menurun dari 89.60% hingga 74.09% apabila suhu mengingkat sepanjang proses torrefaction. Ini adalah disebabkan kehilangkan komponent lignocelulosa pada sampel dalam eksperimen.Manakala bagi garf trend hasil tenaga untuk keseluruhan OPT sampel adalah meningkat apabila peningkatan suhu torrefaction dan masa tinggal. Hasil tenaga tertinggi adalah 89.75 pada suhu 300°C, 90 min. Hasil tenaga terendah adalah 40.7% pada suhu 200°C, 30min. Fourier Transform Infrared Spectroscopy (FTIR) menganalisis komponent lignocelulosa manakala Scanning Electron Microscopy (SEM) menganalisi morphologi struktur torrefied OPT pellet.

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LIST OF ABBREVIATIONS

GHG	Green House Gases
O/C	Oxygen-to- Carbon Ratio
EFB	Empty Fruit Bunch
OPF	Oil Palm Fibers
OPT	Oil Palm Trunk
FTIR	Fourier Transform Infrared Spectrometry
IR	Incident Ray
SEM	Scanning Electron Microscope

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Fossil fuels are the world primary energy source that provided valuable service, however, it also brought out enormous negative effects towards environment. Petroleum crude oil, coal and natural gas are class of fossil fuel which currently is the dominant energy fuel supply for transportation, heating, electricity and residential as well as industrial sites throughout the world. The extent of the greenhouse gases (GHG) released by fossil fuel is so important due to the urgent need to lower the amount of carbon footprint of the world by using the alternative energy sources that are benign to the environment (Ossai, et al., 2014) .

Utilization of alternative renewable energy source is introduced and consequently gained of interest due to excessive amount of carbon dioxide released from burning of fossil fuels. This phenomena lead to future depletion of fossil fuels and environmental issues such as emissions of greenhouse gases (GHG) which contribute to global warming. An average rate of 21% of greenhouse gases emission had increased over the years mainly due to the combustion of fossil fuels (Nyakuma, et al., 2015). Continuous emission of green house gases (GHG) certainly will effect in trapping the heat as well as carbon dioxide that will influence the temperature of the earth surface to increase. Therefore, these scenarios had urgently brought for a transition from fossil fuels to renewable energy sources such as solar, wind, tidal, wave, geothermal energy and also biomass become vital alternative ways for reducing the emission for GHG. However, these resources have their own advantages and disadvantages.

Biomass plays the important part in future energy scenario due to resources uniqueness as sustainable carbon carrier. Biomass had brought a wide attention as it able to continuously providing energy supply. Besides that, biomass becomes one of an alternative renewable fuel sources which has potential to replace coal, petroleum crude oil and natural gas. Biomass also known as natural resources that can minimize the amount of green house gases (GHG) released through combustion and also reduce the amount fossil fuels which are being burned. Furthermore, biomass exists in solid pellet form, liquid as biodiesel or gaseous form which makes it ideal for renewable energy systems since it has the potential to fully utilize in generate heat and electricity and even transport sectors (Mathiesen et al., 2012). Biomass can be converted into energy by thermo chemical conversions and biochemical conversions (Stelta, et al., 2011).Several difficulties need to be concerned for energy production such as high moisture content, non-uniform physical properties, bulky heterogeneous nature, poor heating value and conversion efficiency (Nyakuma, et al., 2015). Due to its undesirable properties, biomass treated as low grade fossil fuel .Hence many researchers (Kolokolova *et al.*, 2013; Stelte *et al.*, 2011; Singh *et al.*, 2013) tend to carried out several experimental methods such as torrefaction and pelletization process to improve the properties of biomass.

1.2 Motivation

Malaysian palm oil industry has develop to become one of the most important agriculture-based industry, where today, Malaysia is well known as one of the world’s leading producer and exporter of palm oil which come after Indonesia. According to Palm Oil Refiner Association Malaysia 2011, production of crude palm oil reaches 48.99 million metric tonnes per year globally in 2011, the main contributor is South East Asia country with Indonesia accounts 48.79%, Malaysia 36.75% followed by Thailand 2.96%. Oil palm is one of a multi-purpose plantation and main biomass producer. Production of one kg of palm oil is equal to an approximately four kg of dry biomass are produced. (Geng, 2013) Oil Palm trunk is one of the main oil palm plantations out of all the oil palm residues. Large amount of oil palm trunk (OPT) are generated from the processing of palm oil plant. OPT is also known as wood tree. Since Malaysia is the second largest producers of palm oil that comes after Indonesia, thousand tones of the annual production of OPT has brought the significant effect toward the environment due to decomposition of unused of OPT. In addition, due to its abundant availability, proper utilization of large amount of OPT needs to be concerned where it has its great potential for producing value-added product and currently not being fully utilized. Therefore, pelletization and torrefaction processes are the options to fully utilize the excessive amount of OPT and generate another product for energy generation.

1.3 Problem Statement

Biomass is known as a renewable source , however, it still be treated as a low grade fossil fuel due to its undesirable properties such as bulky and high moisture content. Hence, many researchers have been carried out in enhancing biomass properties which can improve its fossil fuel performance. Pelletization and torrefaction process has been selected as the main process of study in this research.

Pelletization is a process of drying, molding and compressing a material under high pressure into a pellet shaped products that enable to enhance the thermochemical conversion efficiency. Pelletization is a densification process carried out under high pressure to enhance thermochemical conversion efficiency. This process enhances the biomass properties and conversion efficiency for energy application used such as thermal energy application.

Torrefaction is the pretreatment process for the biomass conversion which typically operating at temperature range of 200-300˚C .It also known as mild pyrolysis where biomass undergoes thermal decomposition under atmospheric condition with the absence of oxygen (Stelta, et al., 2011). The torrefied biomass solid product will result in losing its moisture content. The main function of this process is to minimise the oxygen-to-carbon ratio (O/C) compare to original, reduce the moisture content and the hygroscopic nature of biomass for a further energy productions (Dutta & Mathias, 2014).

In addition to that, the selected material in this study is the oil palm solid waste material which is the oil palm trunk (OPT). Oil palm trunk will undergo the pelletization and torrefaction process, torrefied pellet is obtained. According to Uemura (2011) it stated that pelletization and torrefaction process had the potential to overcome the undesired properties of biomass.

1.4 Objectives

To investigate the OPT pellet performance using torrefaction process for thermal energy application

1.5 Scopes of Study

i) To examine the effect of pelletization in terms of OPT sizes (powder and fiber sizes) with 10wt% of starch ratio.

ii) To explore the torrefaction process of oil palm trunk (OPT) pellet by manipulating the operating temperature (200˚C, 250˚C, and 300˚C) and residence time (30minutes, 60minutes and 90minutes).

iii) To determine the characteristics of torrefied densified OPT pellet through FTIR and SEM

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter mainly elaborates on the general information which provides more details of understanding about this study. It explains about general knowledge, theory of its application, and concept of this study. This chapter begins with the informative description of biomass which explains the reasons biomass is used in this study and also the nature of biomass. Major constituents of biomass (cellulose, hemicelluloses and lignin) are also discussed briefly. This is then followed by the plantation area of palm oil and production of oil palm biomass in Malaysia. Moreover, it provides the explanation by using oil palm trunk (OPT) which is currently abundantly available in Malaysia. It also explains about the process and theory for each experimental method as well as the conditions set up in this study. Last but not least, it explains several operating parameters which influence the thermal treatment process

2.2 Nature of Biomass

Biomass refers to organic matter such as wood, crops, seaweed, animal wastes that have their unique regenerative resource which available for many uses toward the earth. Biomass is the fourth largest energy sources that providing at about 14 percent of the world’s total energy consumption (Anthonia et.al, 2010). For the past of thousands of years, biomass probably is the oldest form energy source after the sun. Biomass known as renewable energy since all the organic matter contains will stored energy from the Sun and convert from solar energy to chemical energy through a process called photosynthesis. Throughout the process, chlorophyll presents in plants absorb energy from sunlight as they need to convert carbon dioxide water into carbohydrates (or glucose) and oxygen that form the biomass. Radiant energy drives the photosynthesis process that is accumulated in the chemical bonds of the biomass structural components

(EUBIA, 2012).Contrary, oxygen from the surrounding atmosphere will combines with the carbon in biomass to produce water and carbon dioxide. This cyclic process is then able to reproduce new biomass.

Figure 2.1 showed the summary on the process flow of photosynthesis. Fuel and energy produced by biomass consider a complex procedure but the principle behind it corresponds directly to the process of photosynthesis. Review on the European Biomass Industry Association, biomass resources constitutes a wide array of materials in agriculture field include agricultural, and agro-industrial residues, forestry as well as municipal and industrial wastes (EUBIA, 2012). Table 2-1 showed the summary on a general classification of biomass types according to their supply sector. Forestry and agriculture sector are two main resources representing the primary sources of biomass while industry and waste residues are secondary sources of biomass derived from primary sources.

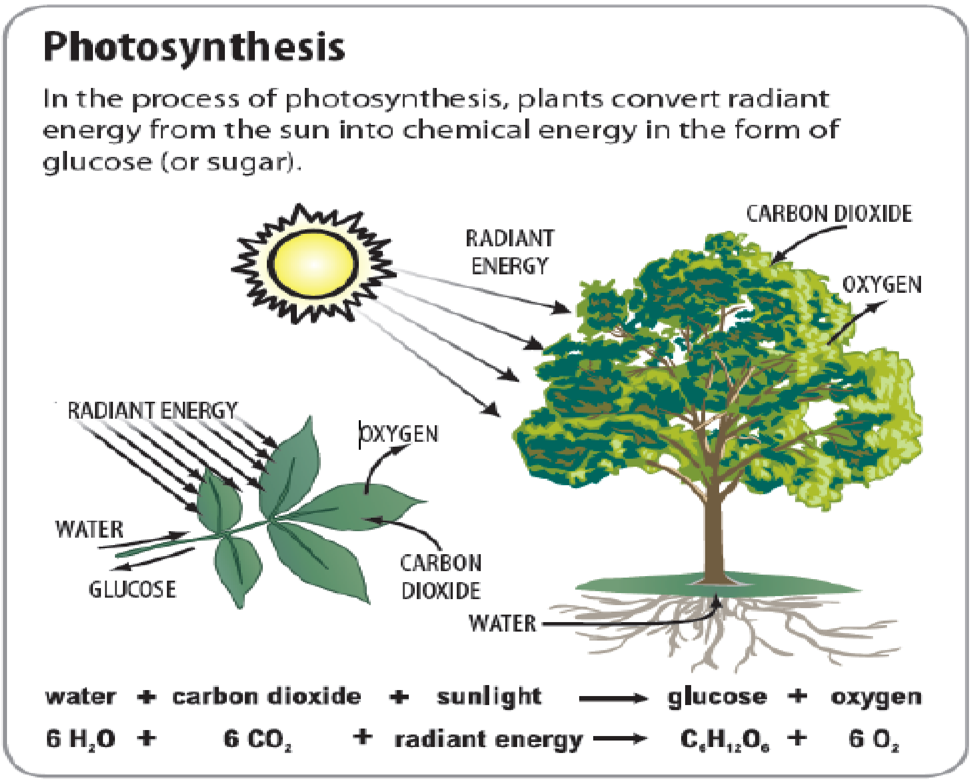
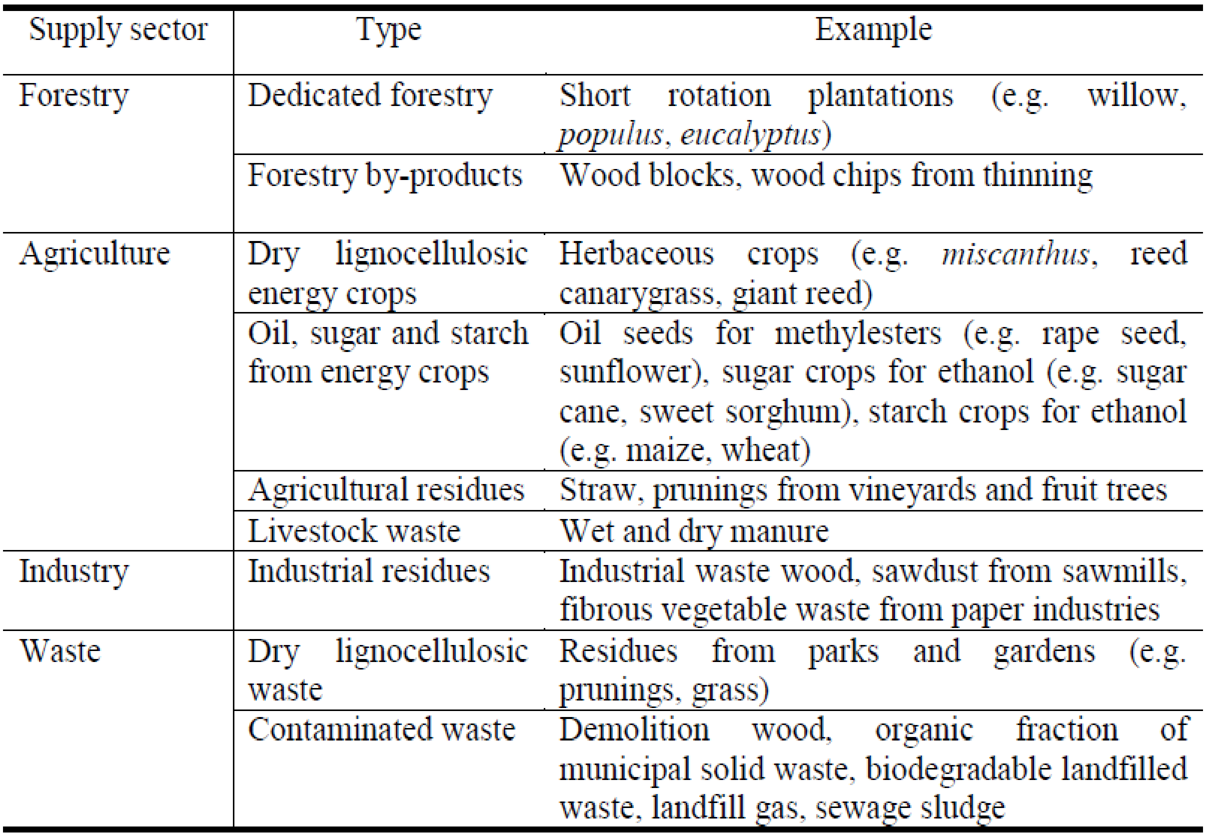


Figure 2-1 : Process Photosynthesis in plant (Baumann et al., 2012)

Table 2-1 : Classification of biomass resources in different supply sector (EUBIA, 2012)



Supply sector	Type	Example
Forestry	Dedicated forestry	Short rotation plantations (e.g. willow, *populus, eucalyptus*)
	Forestry by-products	Wood blocks, wood chips from thinning
Agriculture	Dry lignocellulosic energy crops	Herbaceous crops (e.g. *miscanthus*, reed canarygrass, giant reed)
	Oil, sugar and starch from energy crops	Oil seeds for methylesters (e.g. rape seed, sunflower), sugar crops for ethanol (e.g. sugar cane, sweet sorghum), starch crops for ethanol (e.g. maize, wheat)
	Agricultural residues	Straw, prunings from vineyards and fruit trees
	Livestock waste	Wet and dry manure
Industry	Industrial residues	Industrial waste wood, sawdust from sawmills, fibrous vegetable waste from paper industries
Waste	Dry lignocellulosic waste	Residues from parks and gardens (e.g. prunings, grass)
	Contaminated waste	Demolition wood, organic fraction of municipal solid waste, biodegradable landfilled waste, landfill gas, sewage sludge

2.3 Lignocellulosic Biomass

Biomass can be classified into two classes which are lignocellulosic and non-lignocellulosic biomass. The term "lignocellulosic biomass" mainly referred to non-starch and fibrous part of the plants present in hardwood, softwood, agriculture waste as well as grass. Table 2-2 summarizes the type of lignocellulosic biomass and their chemical composition. Typical lignocellulosic biomass has a complex internal structure and strongly intermeshed which composes of three major biopolymers such as cellulose, hemicelluloses, and lignin shown in Figure 2-1. These biopolymers are not uniformly distributed to different relative composition which is chemically strong bonded within the cell walls. The composition, structure and physical interactions of the biopolymers composing the lignocellulosic matrix perform many interrelated functions for the plant such as the main function of providing structural characteristics that creating mechanical support, allowing for internal transport of water and nutrients throughout the plant (Wyman.C, 2013). Structural of the plant cell wall is depending on the species, tissues and maturity. Besides that, it includes water, small amount of proteins and other compounds, which are not significantly take part in forming the structure of the material.

Table 2-2 : Types of lignocellulosic biomass and the percentage of the chemical composition.(Isikgor & Becer, 2015)

Lignocellulosic Biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)
Main Types	Examples			
Hardwood	Poplar	50.8 – 53.3	26.2 – 28.7	15.5 – 16.3
	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Softwood	Pine	42.0 – 50.0	24.0 – 27.0	20.0
	Douglas Fir	44.0	11.0	27.0
	Spruce	45.5	22.9	27.9
Agricultural Waste	Wheat Straw	35.0 – 39.0	23.0 – 33.0	12.0-16.0
	Barley Hull	34.0	36.0	13.8 – 19.0
	Barley Straw	36.0 – 43.0	24.0 – 33.0	6.3 – 9.8
	Rice Straw	29.2 – 34.7	23.0 – 25.9	17.0 – 19.0
	Rice Husks	28.7 – 35.6	12.0 – 29.3	15.4 – 20.0
	Oat Straw	31.0 – 35.0	20.0 – 26.0	10.0 – 15.0
	Ray Straw	36.2 – 47.0	19.0 – 24.5	9.9 – 24.0
	Corn Cobs	33.7 – 41.2	31.9 – 36.0	6.1 – 15.9
	Corn Stalks	35.0 – 39.6	16.8 – 35.0	7.0 – 18.4
	Sugarcane Bagasse	25.0 – 45.0	28.0 – 32.0	15.0 – 25.0
	Sorghum Straw	32.0 – 35.0	24.0 – 27.0	15.0 – 21.0
Grasses	Grasses	25.0 – 40.0	25.0 – 55.0	10.0 – 30.0
	Switchgrass	35.0 – 40.0	25.0 – 30.0	15.0 – 20.0

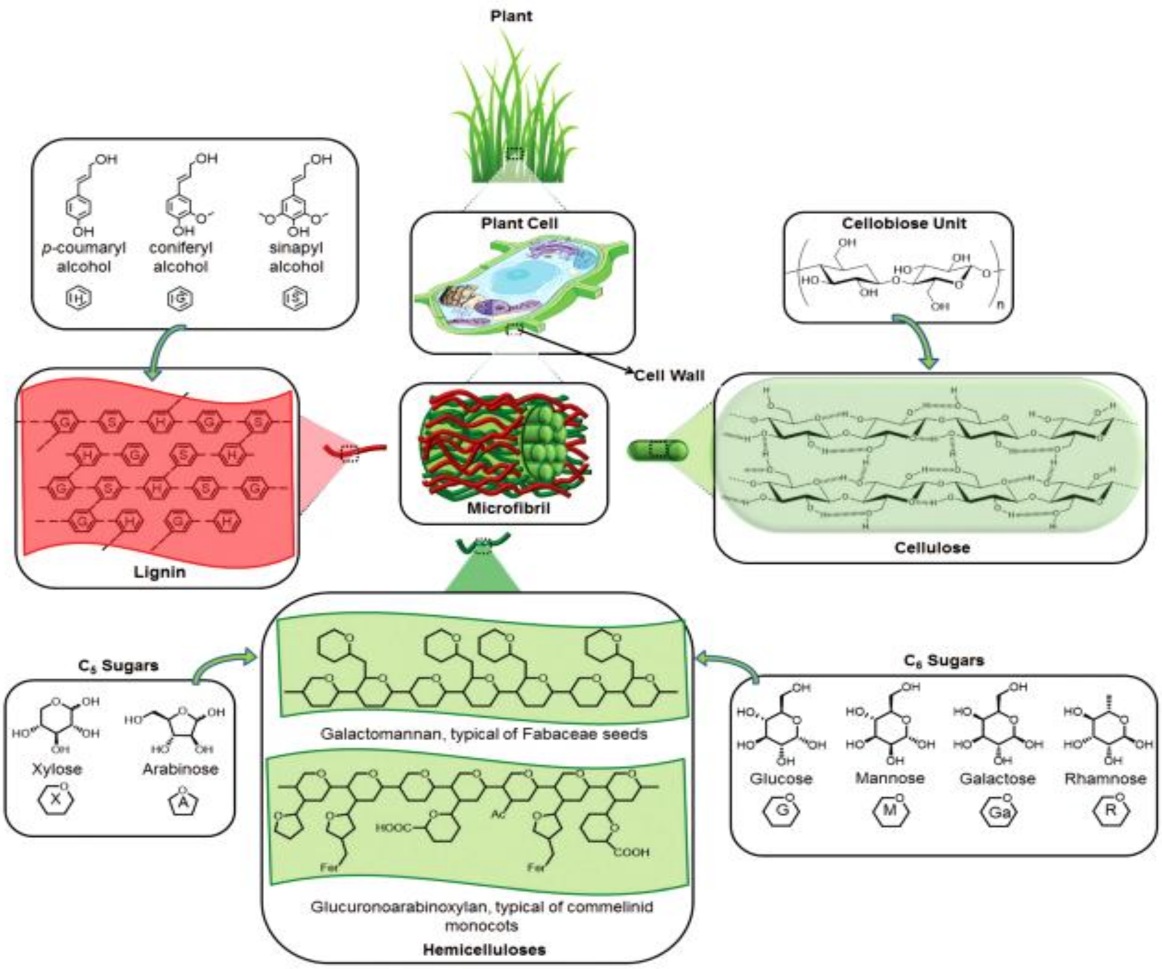


Figure 2-2 : The main components and structure of lignocellulose.(Isikgor & Becer, 2015)

2.3.1 Cellulose

Cellulose is a polymer consisting of glucose molecules. It described as an organic compound which only made up of carbon , hydrogen and oxygen that functions as energy sources for living things.(Cellulose facts, 2016) Cellulose compose of many repeating unit of glucose monomers to form long polymer chains. These chains are linear polysaccharides polymer linked by beta-(1,4) glycosidic bonds between each repeating monomer. As can be seen in Figure 2-2, each repeating monomer contains three hydroxyl groups that enable to stabilize the linkage in cellulose chain. Presence of the intermolecular (Van der Waals force) and intra-molecular hydrogen bonds which tightly bind the glucose units to form a relative stable polymer and enhance the cellulose fibrils stiffness (Isikgor & Becer, 2015). Figure2-2 illustrates the molecular structure of a cellulose unit. In addition, cellulose has low solubility, low reactivity and the thermal degradation of the cellulose starts at a temperature range of 300-400 °C. According to the Poletto (Poletto M, 2014), cellulose has a high the degree of polymerization (between 10000 and 15000) which depends on its source material.

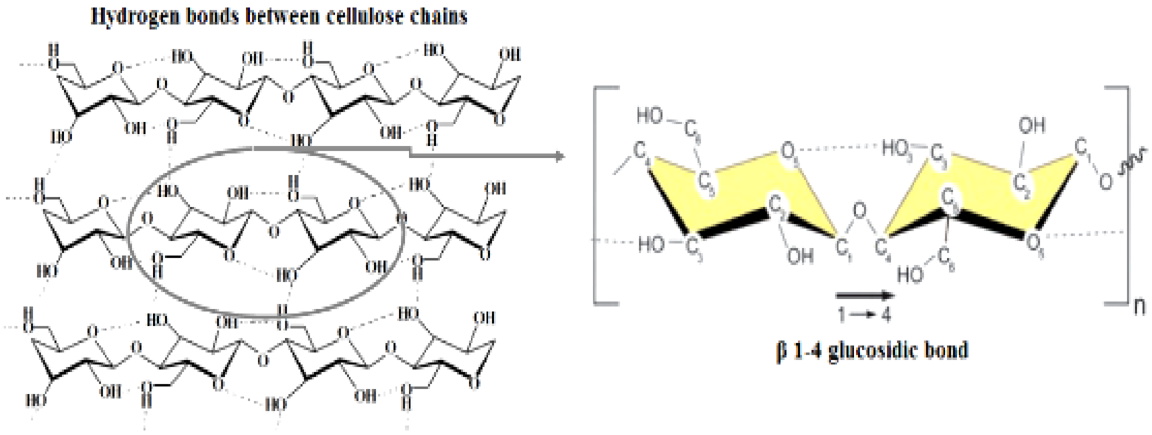


Figure 2-3 : Illustration for cellulose molecular structure (Isikgor & Becer, 2015)

2.3.2 Hemicellulose

Hemicellulose is the second most abundant polymer that comes after cellulose. Hemicellulose belongs to heterogeneous polysaccharides group that have several compositions and structures depending on the plant source. Compare with lignocellulosic biomass, hemicelluloses is the weakest constituent of biomass because of its amorphous structure. It constitutes of five different types of polymer including pentoses, hexoses, mannose, glucose, and sugar acids. Glucuronoxylan is the major component of hemicellulose in hardwood such as herbaceous grass species while galactoglucomannan is dominant in softwood (John Willey, 2015). Hemicellulose is more soluble in water, more reactive and the thermal degradation of hemicellulose starts at a temperature range of 200-300 °C (Harrept, 2014). Figure 2.4 shows the chemical structure of hemicelluloses structure for hardwood and softwood.

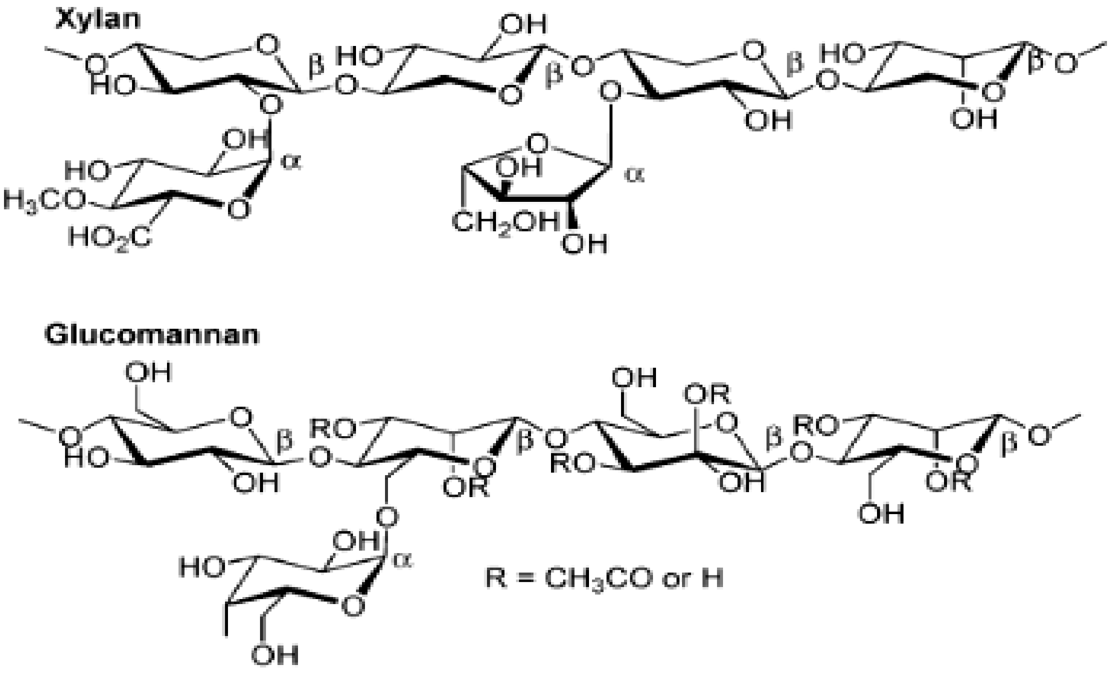


Figure 2-4 : Chemical structure of Hemicellulose a) Xylan (hardwood);
b) Glucomannan (softwood) (John Willey, 2015).

2.3.3 Lignin

Lignin described as the third most abundant organic compound after hemicelluloses followed by cellulose .It is a complex cross-linking network to form a rigid cell wall structure and amorphous organic compound polymer where it made up of different phenyl-propane groups such as p-coumaryl, coniferyl and sinapyl alcohol forming a large molecular structure as illustrated in Figure 2-5 (Harmsen. et.al, 2010). Lignin main functions as giving the structural rigidity support and allow water and nutrients transport. In addition it also acts as a key contributor to recalcitrance as lignin is chemically inert and water insoluble (Harrept, 2014). The therrmal degradation of lignin starts at 220 °C.

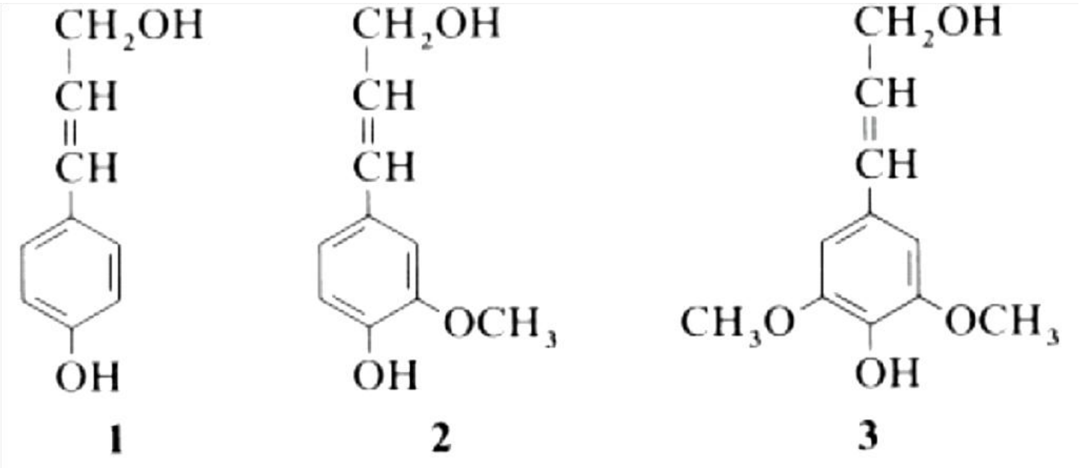
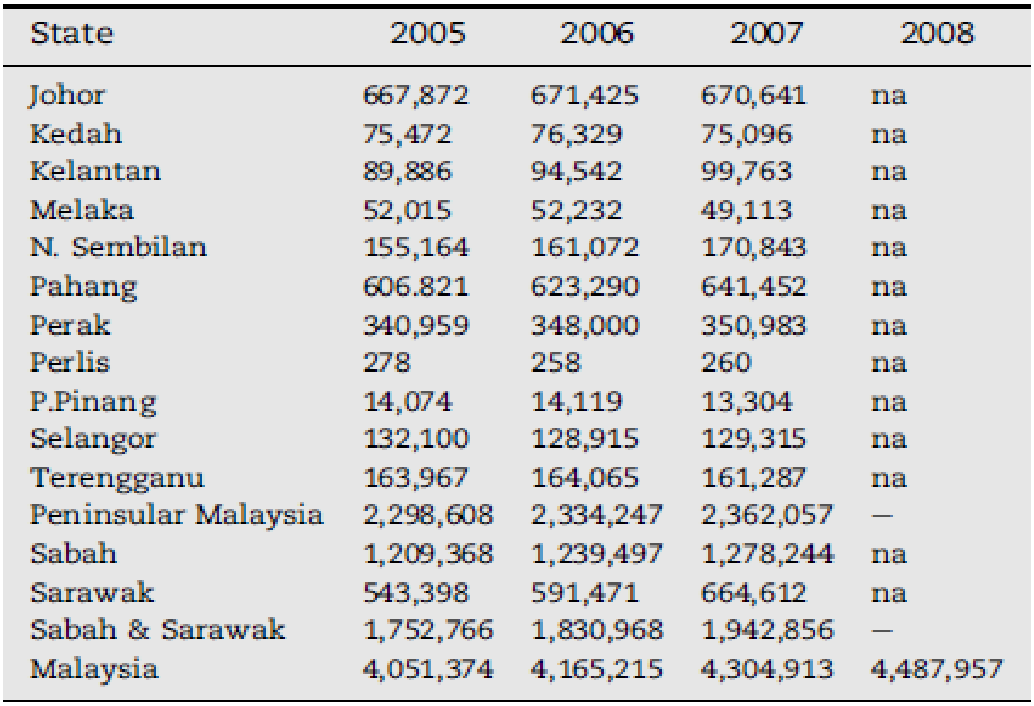


Figure 2-5 : Illustration for three-dimensional polymer lignin: P-coumaryl- , coniferyl- and sinapyl alcohol (Harmsen.P et.al ,2010)

2.4 Palm Oil and Oil Palm Biomass in Malaysia

Palm oil is one of the agriculture products which was firstly being introduced in the 19th century to South East Asia especially Malaysia and Indonesia. These two largest world producers account mostly 85% of world palm oil. Malaysia known as tropical country which experience only hot and wet climate throughout the year trigger the growth of oil palm and hence, it helps to develop the cultivation of oil palm in Malaysia. According to Abdullah & Sulaiman, 2013, the oil palm plantation area in Malaysia, it experienced an increment by 2.8% to 4.17 million hectares in the year 2006. In term of land use, the area expansion of growth with 4.5 % mainly in Sabah and Sarawak compared to 1.6% in Peninsular Malaysia. Sabah held the largest oil palm plantation area with 1.24 million hectares or 30% of the total planted area (Abdullah & Sulaiman, 2013). Oil palm plantation areas (hectares) in Malaysia from year 2005 to 2008 are summarized as shown in Table 2-3.

Table 2-3 : Oil palm planted area 2005-2008 (hectares) (Abdullah & Sulaim, 2013)



State	2005	2006	2007	2008
Johor	667,872	671,425	670,641	na
Kedah	75,472	76,329	75,096	na
Kelantan	89,886	94,542	99,763	na
Melaka	52,015	52,232	49,113	na
N. Sembilan	155,164	161,072	170,843	na
Pahang	606.821	623,290	641,452	na
Perak	340,959	348,000	350,983	na
Perlis	278	258	260	na
P.Pinang	14,074	14,119	13,304	na
Selangor	132,100	128,915	129,315	na
Terengganu	163,967	164,065	161,287	na
Peninsular Malaysia	2,298,608	2,334,247	2,362,057	–
Sabah	1,209,368	1,239,497	1,278,244	na
Sarawak	543,398	591,471	664,612	na
Sabah & Sarawak	1,752,766	1,830,968	1,942,856	–
Malaysia	4,051,374	4,165,215	4,304,913	4,487,957

Oil palm wastes are produced through the production of palm oil. Consequently, this has brought up Malaysia as worldwide oil palm biomass exporter and producer that comes after Indonesia. Every year there is an increase yield of producing oil palm biomass wastes in palm oil sectors. In 2012, those solid wastes are estimated at about 83 million tonnes of dry biomass and it is expected to increase to 100 million dry tonnes by 2020 (National Biomass Strategy 2020: New wealth creation for Malaysia's biomass industry, 2011) In term of land use, there is an increase of 13 % compare with 2008 as Malaysia had reached 5.1 million hectares of oil palm plantation in 2012 as shown in Figure 2-5. One of the major characteristic of large agriculture plantation area is the huge amount wastes production that had no economic value other than transforming into energy generation. However, Department of Environment Malaysia has strongly discourage open burning of biomass wastes due to environmental pollutions and forest burning matters (Abdullah & Sulaim, 2013).Therefore, the biomass wasters should be minimize or recycle and recover the energy for further utilization in future.

2.5 Oil Palm Trunk (OPT)

Oil palm industry in Malaysia every year generates more than 30 million tons of biomass residues especially oil palm trunk (OPT), empty fruit bunches (EFB) and oil palm fronds (OPF). There are two different ways in obtaining biomass waste residues where trunks and fronds are acquired from plantations whereas for empty fruit bunches, shells are acquired after the oil palm processing. Oil palm trunks are only available when the economic life-span reached its replanting time. The economic average life-span of an oil palm tree is approximately around 25 years due to the difficulties in harvesting and also low productivity of old trees. Several main criteria need to be concern at the replanting stage are the height of the palm trees is 7m to 13m and the diameter of the felled trunk are between 45cm to 65cm measured at the breast height (Sulaiman et al., 2012). OPT has many potential value added for particleboard, plywood, laminated board, furniture, paper and also can be used as nutrients for animal feeds as well as in plantations (Sulaiman et al., 2012).

Oil palm tree is one of the wood-based biomass material where it also rich in lignocellulosic materials. It contains of high level of carbohydrates mainly in the form of sugar-containing cellulose, starch, hemicelluloses and lignin. Table 2-4 showed the chemical composition of OPT.

Table 2-4 : Chemical composition of oil palm trunk (OPT)

Component	Ezebor et. al (2014)	Lamaming et.al (2014)	Basyaruddin et. Al (2012)
Cellulose (%)	42.29	41.18	44.40
Hemicellulose(%)	30.06	31.42	29.30
Lignin (%)	21.37	19.19	21.20
Ash (%)	1.48	2.49	1.50

2.6 Starch as Adhesive

Adhesives act as substances which apply on the surface to make two separate materials to bind or adhere together without deform the shape of the materials through a process called adhesion (Jackson Gunorubon, 2012). It plays an important fundamental role in the current technologies which able to withstand or endure their separation. Adhesives are composed of two categories which are natural and synthetic adhesive. Natural adhesives comprise animal glues, natural resins, sodium silicates and vegetables glues. Starch is one of the vegetable glues based and has its own advantages as the adhesive. Starch is a type of biodegradable, renewable, abundance with its cheapness in price and extensively used as material binders. Nevertheless, the starch bonding capacity is not applicable enough for wood sticking. Therefore, several physical and chemical modifications of starch molecules need to be done in order to overcome its drawbacks such as blending. Research studies have been done by blending process of starch/PVOH and starch/tannin to produce another new type of starch-based wood adhesive that needs to be synthesized and used under the room temperature. (Wang et.al, 2012)

2.7 Pelletization Process

Pelletization is a process of drying, molding and compressing a material under high pressure into a pellet shaped products that enable to enhance the thermochemical conversion efficiency. Oil palm trunk (OPT) fibres are normally not qualified for the pelletization process due to its originally length of approximately 200mm long. Before the process begins, OPT fibres will undergo grinding process to grind it into a shorter length of about 3mm long or shorter. The moisture contents play an important role for pelletization process due to its nature of 50-60% of moisture content. Therefore, the grinded fibres should be dried to 10-15% moisture content and maintain it at the moisture level to produce quality pellet products. The dry fibres are proceed to pelleting machine and produced a quality dense pellet form with hard shiny surface and high temperature after extruded from the machine. The hot pellet is then cooled in cooler machine. Figure 2-7 illustrated the OPT pelletization process which mainly consists of five major processes included grinding, drying, pelleting, cooling and lastly packaging.

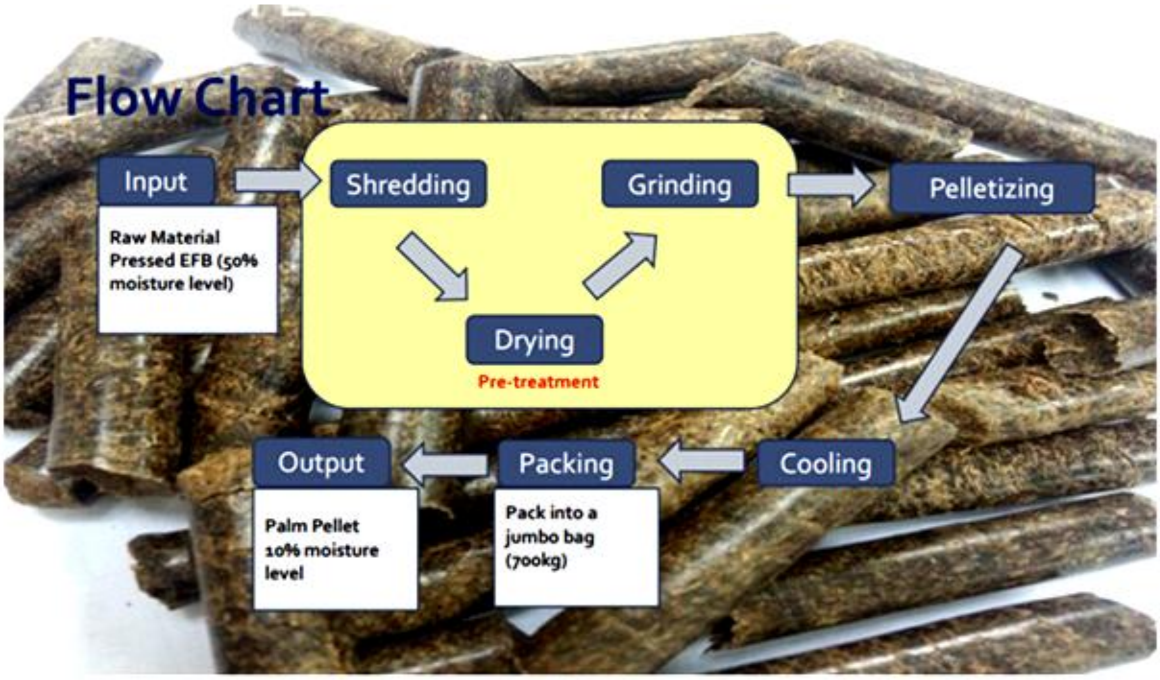


Figure 2-6 : OPT Pellet Production procedure(Huang ,2014)

There are several factors influencing the quality of pellet production. During the process, compression strength of the OPT fibers will directly affected the density and the size of the pellets. The most suitable condition for pellet production is at around 5MPa pressure and temperature of 120 C ± 2°C. In addition, the composition of the OPT fibres and the binding agent (starch) should be in an ideal range for a better holding of raw materials. Common diameters size of a quality OPT pellets are 6mm, 8mm and 10mm are mostly produced (Huang, 2012). Pelletization process is mainly to increase the energy content of the OPT fibres which can be verified through torrefaction process.

2.8 Torrefaction Process

Torrefaction is also known as mild pyrolysis carried out under the atmospheric pressure or it is a thermal pretreatment process to upgrade lignocellulosic biomass into a higher-quality energy and carbon carrier. The typical narrow temperature range throughout the biomass torrefaction is from 200°C to 300 °C in the absence of oxidizing agent (Clausen *et al.*, 2010). At this temperature, biomass will become completely dried and loose its tenacious and fibrous structure (Bergman & Kiel, 2005). This process characterized as low particles heating rate (< 50 °C/min) and the residence time not more than one hour (Chen & Kuo, 2010). The structure of biomass will becomes more brittle and hydrophobic due to the biomass decomposes during torrefaction process which results of 30% weight loss and 10% energy loss. This thermal pretreatment process results in producing three main products which are dark colour solid products, yellowish colour acidic aqueous products, and non-condensable gaseous products(CO_2, CO, CH_4) (Deng *et al.* 2009) . During the torrefaction process, the raw biomass undergoes decomposition, devolatilization and depolymerisation where this three major reactions causing the raw biomass loses its moisture content and decompose of biopolymers (cellulose,hemicelluloses and lignin)(Fauzianto, 2014). The final product remains in the dry blackened solid form namely torrefied biomass which is a homogenous solid fuel with high energy content (per volume) and has a low moisture content.

The advantages of torrefaction are to improve the physical characteristics like grindability, particle size distribution, calorific value and hydrophilic properties of biomass and the overall economics of the biomass utilization process for energy production. These improvements lead to produce a more homogenous solid fuel with high energy content (per volume) and have low moisture content where it can be more effective and compatible with coal. This process makes biomass more friable which significantly reduce 80-90% of energy required for biomass grinding .The hydrophobic characteristic of biomass which significant loss of energy due to re-adsorption moisture in biomass is saved which and negligible the biological activities such as microbial degradation and chemical oxidation for longer storage life.

However, there are still some disadvantages of torrefaction process. Despite higher calorific value can be achieved after the process, the initial energy content of the torrefied biomass is only preserved and yet not improved significantly (Van Der Stelt *et al.*, 2011). Although torrefaction process is able to enhance the quality of untreated biomass, severe mass loss is still a concern as it affects the mass and energy yields of the process. According to Sabil *et al*. (2013), it is suggested to maintain the mass loss of the torrefied materials lower than 50% to ensure the economics of the process. Other than that, there is still limited knowledge on torrefaction process such as process performance, properties of torrefied products, and composition of volatiles.

2.8.1 Mechanism of Torrefaction

Basically, there are two types of torrefaction mechanisms which are dry and wet torrefaction. Table 2-6 below shows the characteristics of the pre-treatment method. Dry torrefaction is classified as the thermal degradation of biomass polymeric constituents. It carried out in inert condition and comprises of four simple stages which are drying, post-drying, torrefaction, and followed by cooling process. The beginning stage is the major intensive step throughout the whole process. Drying can be sorted as a non-reacting and a reactive process. Non- reacting process in the temperature range of 50-150 °C predominantly removes the water surface which result in shrinkage of product size. It is then followed by post-drying or reactive drying process which the temperature increases from 150 to 200 °C in order to breakdown carbon-hydrogen bonds.

Torrefaction is an isothermal heating process at temperature maintain constantly above 200°C where supplied heat establishes the depolymerization, partial devolatilization, and partial carbonization reactions (Nhuchhen et.al, 2014).During the cooling process, the temperature is cooled and dropped down to ambient temperature. Figure 2-8 and Figure 2-10 illustrated the layout of the dry torrefaction process and the overall temperature and time needed for each stages of dry torrefaction process. Overall purpose of drying torrefaction process is mainly to eliminate surface bound water from the biomass materials. While for the wet torrefaction, it uses the solubility concept of different composition of biomass neither in hot nor aqueous solutions.

Wet torrefaction is define as thermo-chemical conversion process for biomass to use as fuel. This process uses hot compressed water as the reaction medium where the temperature is within the range of 180 –265 °C, pressures are above 1MPa for minimum 5 minutes to several hours. Due to the reaction medium, wet torrefaction process is suitable for low cost biomass which normally consists of very high moisture content such as forest biomass wastes, agriculture wastes as well as aquatic energy crops (Acharya et.al, 2015).

The wet torrefaction process is a non-toxic reaction as it uses a cheaper chemical media as compared to dry torrefaction. The reaction input streams consists biomass, water and an inert gas where as the output stream include water with alkali compounds traces. The layout of the process shows in Figure 2-9.

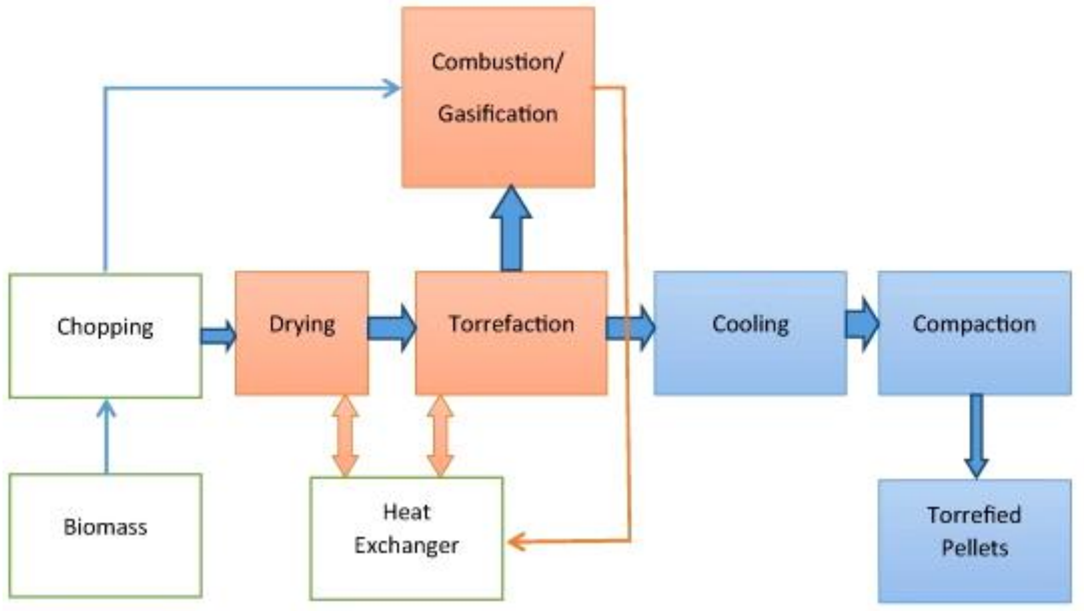


Figure 2-7: Process layout of dry torrefaction process (Acharya et.al, 2015).

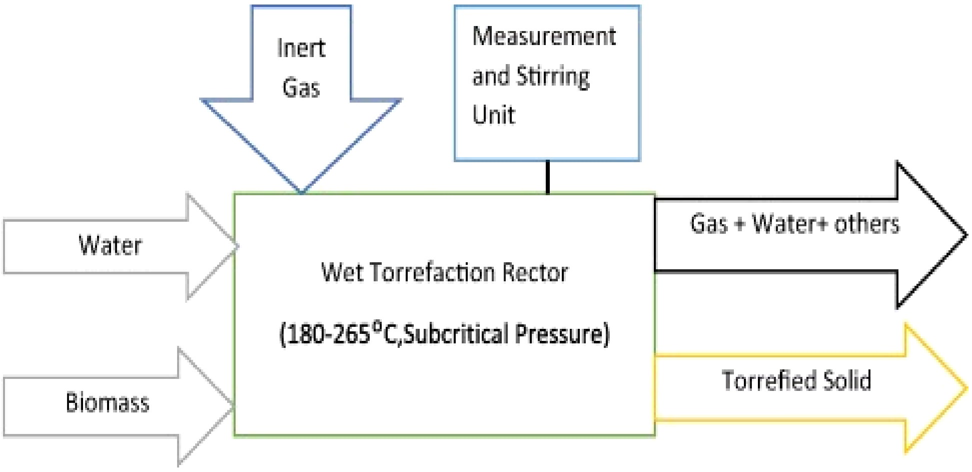
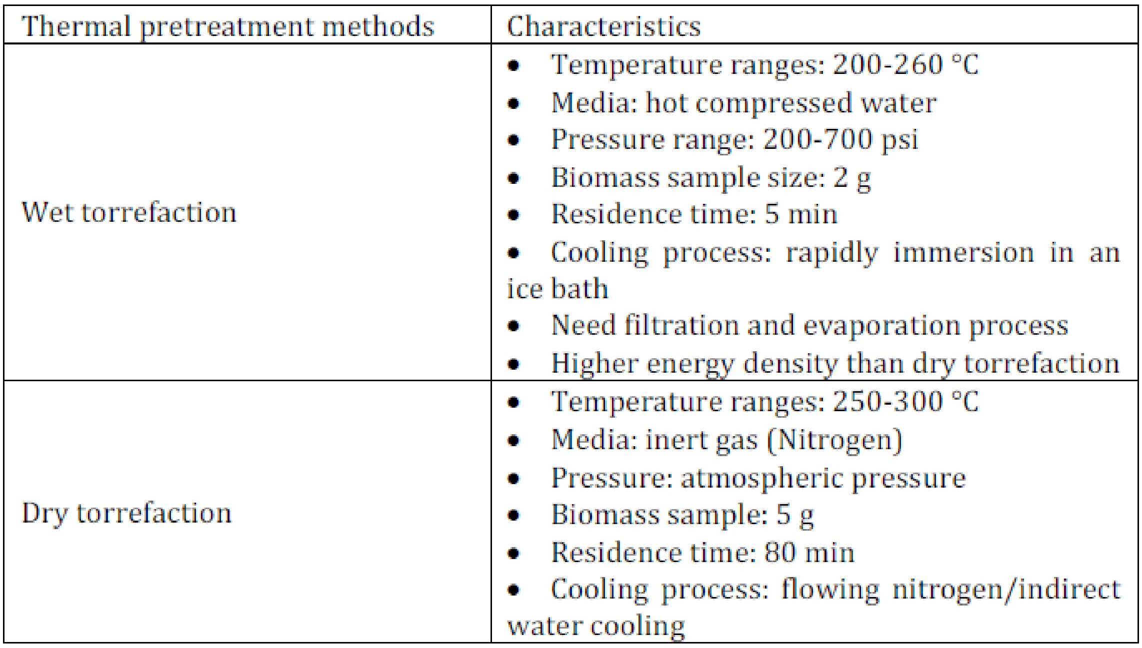


Figure 2-8 : Process layout of wet torrefaction process (Acharya et.al, 2015).

Table 2-5 : Characteristics of thermal pre-treatment methods (Nhuchhen et.al, 2014).



Thermal pretreatment methods	Characteristics
Wet torrefaction	• Temperature ranges: 200-260 °C • Media: hot compressed water • Pressure range: 200-700 psi • Biomass sample size: 2 g • Residence time: 5 min • Cooling process: rapidly immersion in an ice bath • Need filtration and evaporation process • Higher energy density than dry torrefaction
Dry torrefaction	• Temperature ranges: 250-300 °C • Media: inert gas (Nitrogen) • Pressure: atmospheric pressure • Biomass sample: 5 g • Residence time: 80 min • Cooling process: flowing nitrogen/indirect water cooling

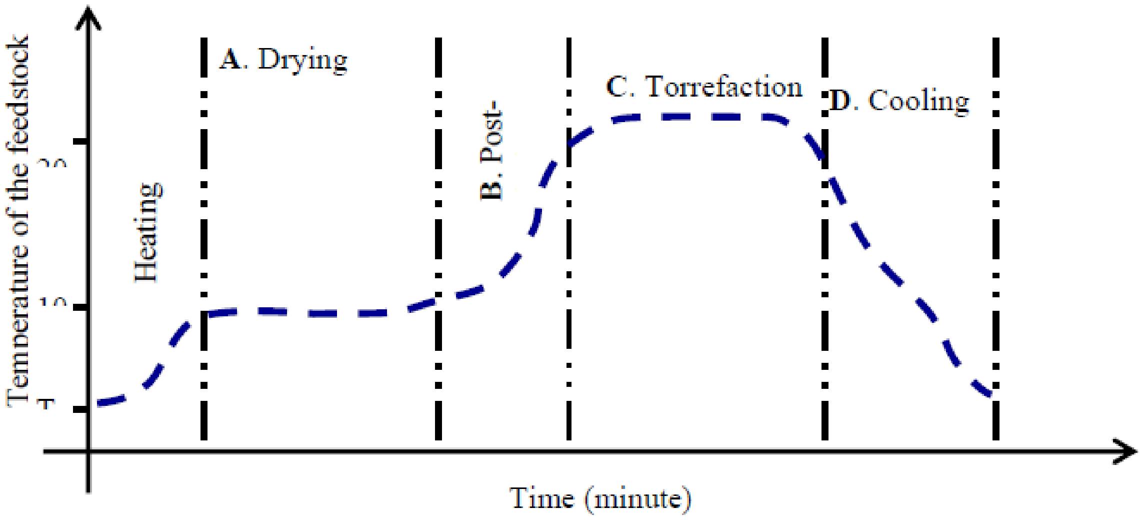


Figure 2-9 : Stages of dry torrefaction process (Nhuchhen et.al, 2014).

2.8.2 Effect of Operating Parameters

In this subchapters will discuss about the effect of operating parameters toward torrefaction process. There are four main parameters on torrefaction process which consist of temperature, residence time oxygen concentration and particle size.

2.8.2.1 Temperature

According to the researches (Chen and Kuo, 2011), there are three torrefaction temperatures of 230°C, 260°C, and 290°C respectively which were classified as the light, mild, and severe torrefaction process. Every temperature dominantly contributes the influence toward the quality of the torrified solid. Torrefied solid yield depends on the temperature, for example, a research done by Wannapera et.al (2011) reported that there was a significant dropped of torrefied solid yield from 91% to 54.5% when temperature was increased from 200°C to 275°C. Besides that, in Acharya (2013) research study of Oats torrefaction, the energy yield decreased but increased in energy density when the torrefied temperature was increased from 210°C to 300°C.

The torrefied solid yield can be explained at the different torrefaction temperatures through devolatilization and decomposition of polymeric composition of lignocellulosic biomass. Table 2-7 below showed the temperature ranges in thermal degradation of hemicellulose, cellulose and lignin during torrefaction process. From the table, lignin decomposes over a bigger range of temperature rather than cellulose and hemicellulose due to the thermal stability which contain oxygen as functional groups (Brebu & Vasile, 2010). On the other hand, hemicellulose is a highly sensitive polymer in a small temperature range while cellulose is much more stable among of them at the high torrified temperature due to its crystalline structure which consists of strong glucosidic bonds, intermolecular and intramolecular bonds. Energy retained decreases as the temperature increases .Hence, thermal degradation bring the significant mass loss percentage among the three polymeric components at different torrefied temperature shown in Table 2-8.

Table 2-6 : Temperature range for thermal degradation for hemicelluloses, cellulose and lignin(Chen & Kuo, 2011)

Degradation temperature range (°C)			**Sources**
Cellulose	Hemicellulose	Lignin	
327- 407	227-327	127- 447	Giudicianni etal. (2013)
315- 400	220- 315	160- 900	Yang et al. (2007)
275- 400	200- 400	200- 500	Sorum etal. (2001)

Table 2-7 : Mass loss in polymeric components at different temperatures (Chen & Kuo, 2011)

Torrefaction Temperature (°C)	**Hemicellulose (wt%)**	**Cellulose (wt%)**	**Lignin (wt%)**
230	2.74	1.05	1.45
260	37.98	4.43	3.12
290	58.33	44.82	6.97

2.8.2.2 Residence Time

Residence time is another operating parameter influence in torrefaction process. The effect of residence time does not perform significantly as compared to temperature in torrefaction process. However, it influences the solid torrefied product at the longer residence time. According to Chen *et.al* (2011) reported that residence time is directly proportional toward the mass loss of solid torrefied product but results in the lower solid production yield. This is because of an increase in the extend of devolatilization (Prins *et al*., 2006). Condensable products such as water and organic acids are also contribute to solid mass loss as the time increases as shown in Figure 2-9. Furthermore, the amount of carbon decreases with the increasing amount of oxygen content together with the residence time. Research done by Bates & Ghoniem ,there is 11% of carbon and 40% of oxygen lost in 15 minutes compared to 26% and 69% in the longer residence time of 40 minutes and this result a more carbon lost per a unit oxygen loss from 0.28 to 0.38. It can be conclude that the rate of deoxygenation of biomass decelerate at high residence time which the carbon content increases in the volatiles.

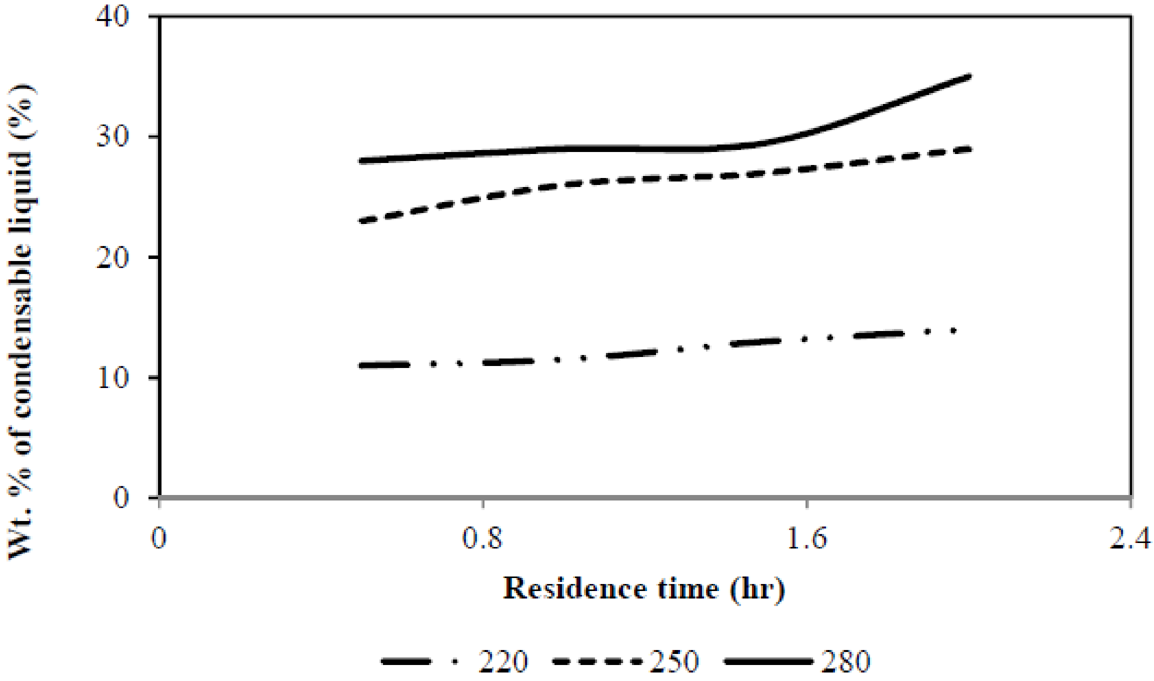


Figure 2-10 Weight loss of condensed liquid with residence time (Nhuchhen *et al.*, 2014).

2.8.2.3 Oxygen Concentration

Torrefaction with the presence of oxygen content is lead to combustion reaction which will release carbon and turn into flue gas instead of remaining as solid product. Moreover, oxygen is not suitable in torrefaction process because of the product temperature increase due to combustion (Nhuchhen *et al*., 2014). Therefore, torrefaction process need to carried out either by indirect heating or continuous supply of inert gas. Presence of oxygen in torrefaction process increases the devolatilization reactions resulting in lower solid and energy yield.

2.8.2.4 Particle Size

Nhuchhen *et al*. (2014) noted that heat source is desired in torrefaction process to preheat, dry and devolatilize the raw biomass materials while the amount of heat source depends on the properties, size and shape of the biomass. These parameters take into account as they alter both conductive and convective heat transfer rate neither from the reactor to biomass nor within the biomass. For instance, larger piece of biomass has a smaller surface area will results in weakening the convective heat transfer rate. This is because of the heterogeneous properties of biomass, larger particle encounter a non-uniform heat distribution within the biomass. Moreover, larger biomass pieces may decelerate the volatile diffusion through particles as well as the mass transfer resistance. Pang et.al (2012) found that throughout the experiment, mass loss during the torrefaction of small particles are greater than larger particles due to the lower resistance volatile diffusion and higher heat transfer rate presence in small particles. In addition, as the particles size increases, the mass and energy yield decreases in torrefaction process at the different temperatures as well as residence times. Hence, the efficiency of torrefaction process depends on the particle size of the biomass.

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CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter will discuss on the materials and methodology applied for this study. A general description on the raw material and chemical used for the experimental study is presented.

Pelletization experiment is conducted by only 90wt% of OPT (powder or fibres) together with 10wt% starch in order to get the optimum and firm pellet fibers. The sample preparation methods, experimental setup for pelletization and torrefaction process, measurements of mass and energy yield were implemented in this experiemnt. The torrefied pellets were then proceed to Fourier Transform Infrared Spectrometry (FTIR) and Scanning Electronic Microscope (SEM) analysis method.

3.2 Raw Materials

The raw biomass materials used in this study included oil palm trunk (OPT). Fresh oil palm trunks were collected at LCSB Lepar Oil Palm Mill near Gambang, Pahang .The raw material obtained was first be shredded and further proceed to pelletization and then continue undergo torrefaction process. The long fibrous length OPT is not suitable for pelletization process.

3.3 Pre- treatment process of Oil Palm Trunk (OPT)

The oil palm trunk (OPT) is in oily and bulky condition and contain of impurities. Sorting process of the OPT starts from wash and clean need to be done so that there are no any impurities or contaminants presence inside the raw materials. The washed OPT need to dry in an open air area or sun dried within a week in order to remove its moisture content. According to research from Joseph (2013), it is difficult to produce a good quality pellet when the raw material of the oil palm trunk contain too high or too low of its moisture content. After that, the washed OPTs are grind and cut into small pieces with the length of 3mm or shorter for convenient of blending purposes. The final steps are some of the grinded OPTs are blended or pulverized into powder form. These procedures are taken as to enhance the quality of the OPT pellets. (Abdul Rahman et al., 2013)

Figure 3-1 : Sun-dry of OPT fiber

Figure 3-2: Illustration for Grinder machine

Figure 3-3 : OPT fine powder and fiber as raw material

3.4 Pelletization

Two types of pellets are produced in this study with varying the weight composition of OPT and starch. In the pelletization process, 90wt % OPT (fibrous and powder) will mix together with 10 wt% of starch is selected for the experiment. The starch functions as the binding agent.

The blended mixture will compressed manually into mould at the temperature of 120˚C ± 2°C and pressure of 5Mpa by using hot press machine.

Figure 3-4 : Illustration of Hot Press Machine

Leave it for about 10 minutes time. After the process is completed, the OPT pellets produced are removed from the mould manually and then cooled it to the room temperature. The pelletized OPT will proceed to torrefaction process to further improve and enhance its quality as bio-fuel product for energy generation (Rahman *et. al*, 2013). The torrified OPT pellets will continue for the characterization analysis.

3.5 Torrefaction

Torrefaction of the densified OPT is carried out using a simple furnace reactor which made of stainless steel. The ceramic crucible is filled with pellet and placed inside the furnace reactor. After that, the temperature is set at 200 °C. The heating rate of the reactor is estimated as 10°C/min. After 30minutes of torrefaction, the heater is turned off and the reactor is left to cool down to room temperature. Then, the condition of torrefied material is recorded, weighed and (Uemura et. al, 2011). Each experiment will be repeated 2 times by manipulating temperature to 250°C and 300°C as well as residence time of 60 minutes and 90 minutes in order to obtain the optimal torrefaction results.

3.6 Calorific Value

The calorific value of torrefied Oil Palm trunk (OPT) is obtained from the researches studies and tabulated in Table 4-1.

Table 4-1 Calorific Value for torrefied OPT

Temperature (°C)	Residence Time (Min)	Calorific value (MJ/kg)	Reference
200	30	18.3	Yuliansyah & Hirajima, 2012)
	90	18.08	Nipattummakul *et al.*, 2012)
250	30	17.59	(MPOB, 2011)
	90	17.47	(MPOB, 2011)
300	30	17.38	(Guangul *et al.*, 2012)
	90	17.27	(UNEP, 2012)

3.7 Mass and Energy yield measurement

Mass yield and Energy yield from the torrefaction process varies with temperature, time and also heating rate. To measure the percentage of mass yield, equation below is used (Wang et.,2012)

$$Mass\ Yield = \frac{Mass\ of\ sample\ after\ torrefaction}{MAss\ of\ untreated\ sample} \tag{3.1}$$

$$CV\ Ratio = \frac{CV\ of\ sample\ after\ torrefaction}{CV\ of\ untreated\ sample} \tag{3.2}$$

$$Energy\ yield = Mass\ yield\ \times CV\ Ratio \tag{3.3}$$

3.8 Characterization of Torrefied OPT Pellet

The further characterizations of Fourier Transform Infrared (FTIR) Spectrometry and Scanning Electron Microscope (SEM) of the torrefied OPT pellet are presented in the following subtopics.

3.8.1 Fourier Transform Infrared (FTIR) Spectrometry

Infrared (IR) spectroscopy is one of the preferred methods used in Fourier Transform Infrared (FTIR) Spectrometry. The technique used in this method is based on the molecular vibrations. An infrared spectrum is obtained when infrared radiation transmitted through a sample and determining the incident radiation fraction which absorbed at a particular energy. FTIR can identify the unknown components present inside the sample and determine the quality or consistency of the sample as well as the amount of the components in the mixtures (Stuart, 2004).

The energy at any peak of the absorption spectrum which correspond to the vibration frequencies between the atomic bonds of the sample molecule. This is because every material is made up of different combination of atoms where FTIR can be identified. Besides that, there are no two compounds which will produce the identical infrared spectrum (Stuart, 2004).

The process flow of FTIR begins from the source where the infrared (IR) energy emitted from a glowing black body source. The energy contents presented to the sample are controlled when the beam is transmitted through the aperture. After that, the beam enters the interferometer where the spectral encoding takes place and thus the resulting interferogram signal is then leave the interferometer. Then, the beam at the sample compartment is passed through or reflected off of the sample's surface which it depends on the analysis type being achieved. The specific energy frequency which represents the sample absorbed characteristics. The beam is then transmitted to the detector where it designed for special interferogram signal measurement. The signal for final measurement is then sent to computer for further manipulation and interpretation (Thermo Nicolet Director, 2001).

In this research, FTIR was employed to inspect the lignocellulosic component of OPT pellet after torrefaction. To have a clear view on the effect of torrefaction, raw materials and its respective torrefieds were subjected to the FTIR testing. From the typical peaks of the FTIR absorption spectra, estimation on the decomposition of hemicelluloses, cellulose and lignin were indicated. The characterization with FTIR was done in the Faculty of Industries Science lab of University Malaysia Pahang (UMP).

3.8.2 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is a type of microscope that uses focused beam with high-energy electrons to generate high resolution surface images. Signals produced by the focus beam display information including the morphology, crystalline structure, chemical compositions and the materials orientation of the specimen. SEM gives a much higher magnification images and greater depth which up to 100 times than a light microscope.

The process flow of generating a SEM image begins with generates a ray of incident electrons in an electron column on top of the sample chamber. The electrons are generated by thermal emission source such as tungsten filaments. The energy range of the incident electrons are in between 150 eVto 30k eV. After that, the electrons will be focused by electromagnetic lenses inside the SEM column. Scanning coil at the end of the column will direct the position of the incident electrons to the focused beam onto the specimen surface. Scanning of the electron beam will be in raster order across the surface of the specimen. Electron detector will detect every single of the emitted electrons in the scanned area. The magnitude of the emitted electron signal is reveal in a digital image or display monitor. The texture surface area of the sample image is created when scanning and collecting the secondary electrons that are released by electron detector. Basically, scintillator type detector such as backscattered electrons is one of the types of detector used for secondary electron imaging. It is charge with a positive voltage to pull the electrons toward the detector in order to improve the signal to noise ratio. ("Scanning Electron Microscopy | SEM Failure Analysis | SEM Material Analysis", 2014)

In this research, SEM was employed to inspect the morphology structure of the torrefied OPT pellet and raw pellet materials. The characterization with SEM was done in the CARRIF of University Malaysia Pahang (UMP).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results and discussions for all the research experiments work. Preliminary experiment works such as pelletization of oil palm trunk (OPT) powder and fiber need to be done before torrefaction of OPT pellet with three different temperatures with three different time intervals. The results on FTIR analysis and SEM analysis were presented and discussed in this chapter.

4.2 Preliminary Result for OPT Pelletization

The pelletization process is to densified the oil palm trunk (OPT) for easy transportation. Before pelletization process, the grinded OPT is sieved and the length of each fibre should be less than 3mm. The size of 2cm x 2cm hole of the mould shown in Figure 4-1 is chosen with the density of the OPT pellet is fixed at 650 kg/m^3 (Rahman *et. al*, 2013). Then, the mass of OPT used is 0.018852kg for the mold which its volume is $2.5136\times10^{-5}m^3$. For both set of the experiment which contains 10% starch and 90% OPT which corresponds to both of the mass of OPT fibre and powder are 4.2417g and the starch used is 0.4713g. According to the result from precious researchers' work, the starch content are set as 5% ,15% do not showed any optimum compact result as the fibers are easily break and the starch is overload on the surface of the mould. Therefore, the most suitable ratio of starch content for OPT pellet is 10% as the pellet is strongly rigid in cylindrical shape and not easily fall off. As a conclusion, the optimum starch content for OPT pellet is 10%. Figure 4-2 and Figure 4-3 show the pictures of pellet fiber and powder OPT with 10% of starch content.

Figure 4-1 : Molding for OPT Pelletization Process

Figure 4-2 : OPT powder pellet with10% of starch content

Figure 4-3 : OPT fiber pellet with 10% of starch content

4.3 Effect of Temperature and Residence Time on OPT Pellet

After the pelletization process had completed, the pellets will undergo torrefaction process. This torrefaction process is run in an inert atmosphere with the heating rate of $10℃/min$. There are two sets of experiments conducted in this process for both powder and fiber pellet. First set of the experiment was manipulating three different residence time (30 minutes, 60 minutes and 90 minutes) at 200℃ . Second set of the experiment was manipulated two temperatures which are 250℃ and 300℃ with two residence time which are 30 minutes and 90 minutes. This is because after torrefaction at 250℃ and 300℃, there are not much difference in term of the pellet colour appearance however the weight of the pellet was decreased at high temperature and long residence time. The colour change for powder and fiber torrefied pellet is observed. Figure 4-4 shows the colour change of OPT powder pellet toward three different torreaction temperature at 30 minutes while Figure 4-5 show the colour change of OPT fiber pellet towards three different torrefaction temperatures at 30 minutes.

Figure 4-4 : Colour change of OPT powder pellet towards three different torrefaction temperatures at 30 minutes

Figure 4-5: Colour change of OPT fiber pellet towards three different torrefaction temperatures at 30 minutes

The weight of the pellet is weighed before and after the torrefaction process. Figure 4-6 shows the graph trend for the torrefied pellet mass along the time for set 1 experiment while Figure 4-7 showed the graph trend for set 2experiment. The result of the pellet weight is tabulated in appendix and the sample torrefied pellets were illustrated in Figure 4-6.

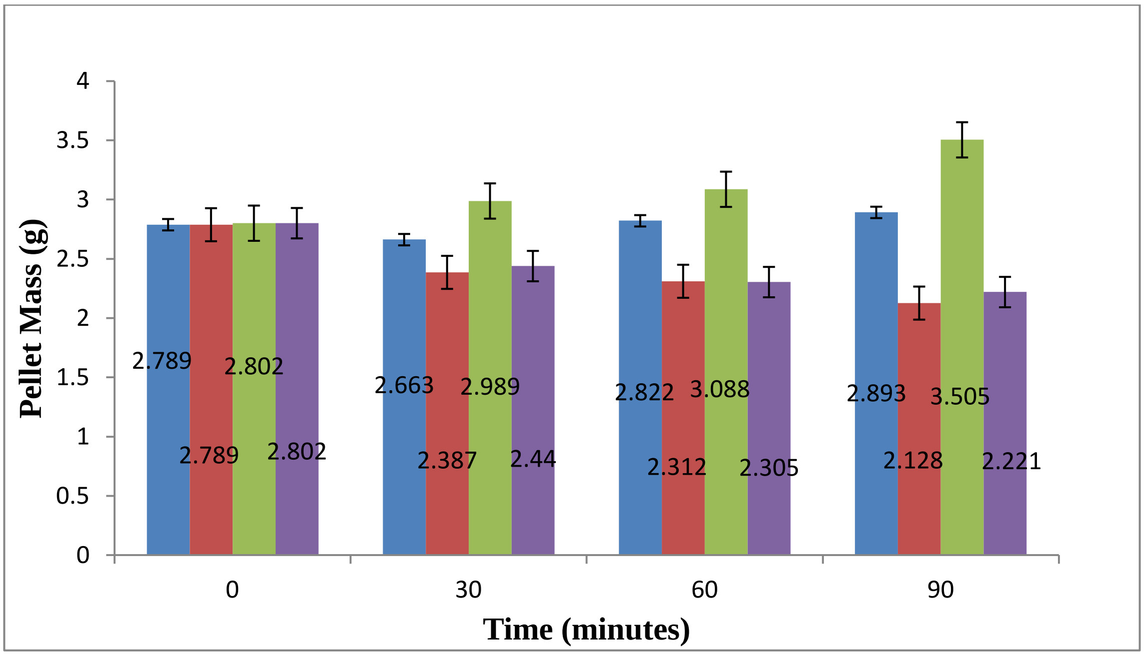

Figure 4-6 : Effect on residence time on powder and fiber pellet OPT mass at 200°C

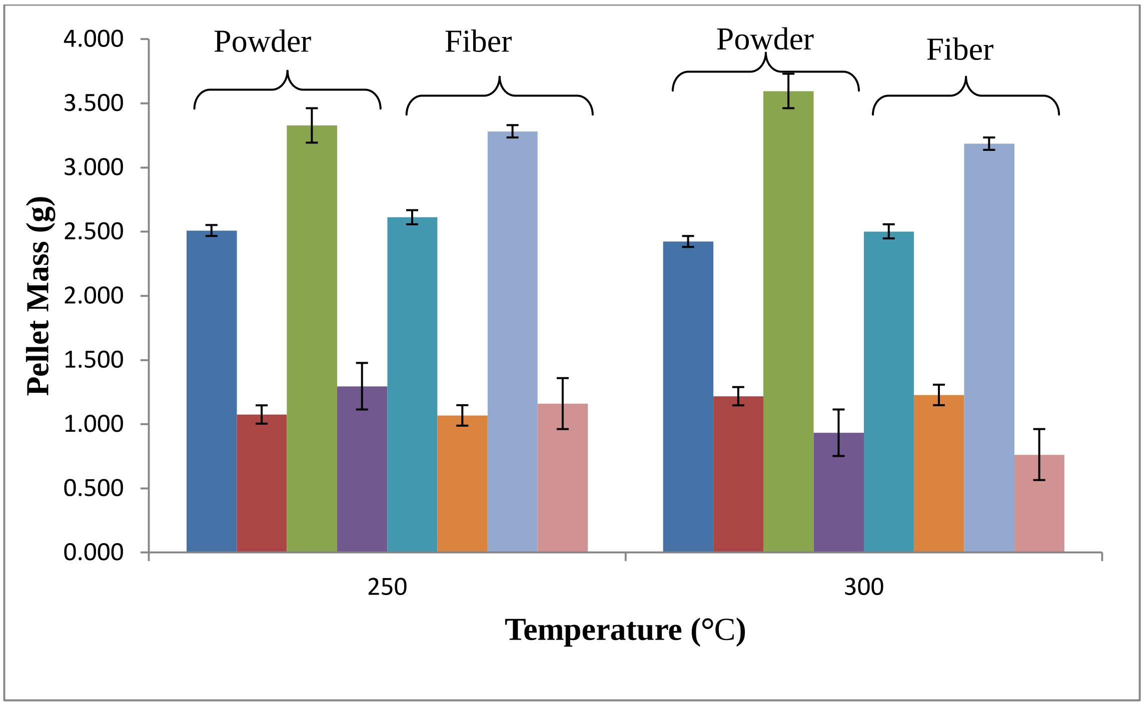

Figure 4-7 : Temperature effect on powder and fiber pellet OPT mass

Figure 4-6 and Figure 4-7 shown above that the residence time and temperature are a significant variable in the torrefaction OPT. For biomass pellet types, increasing the severity of the residence time and torrefaction temperatures caused an increment on the mass reduction. From of the graphs shown above, they having the same trend where the different mass of the torrefied pellet are increasing as the residence time and temperature are increasing.

4.4 Mass yield

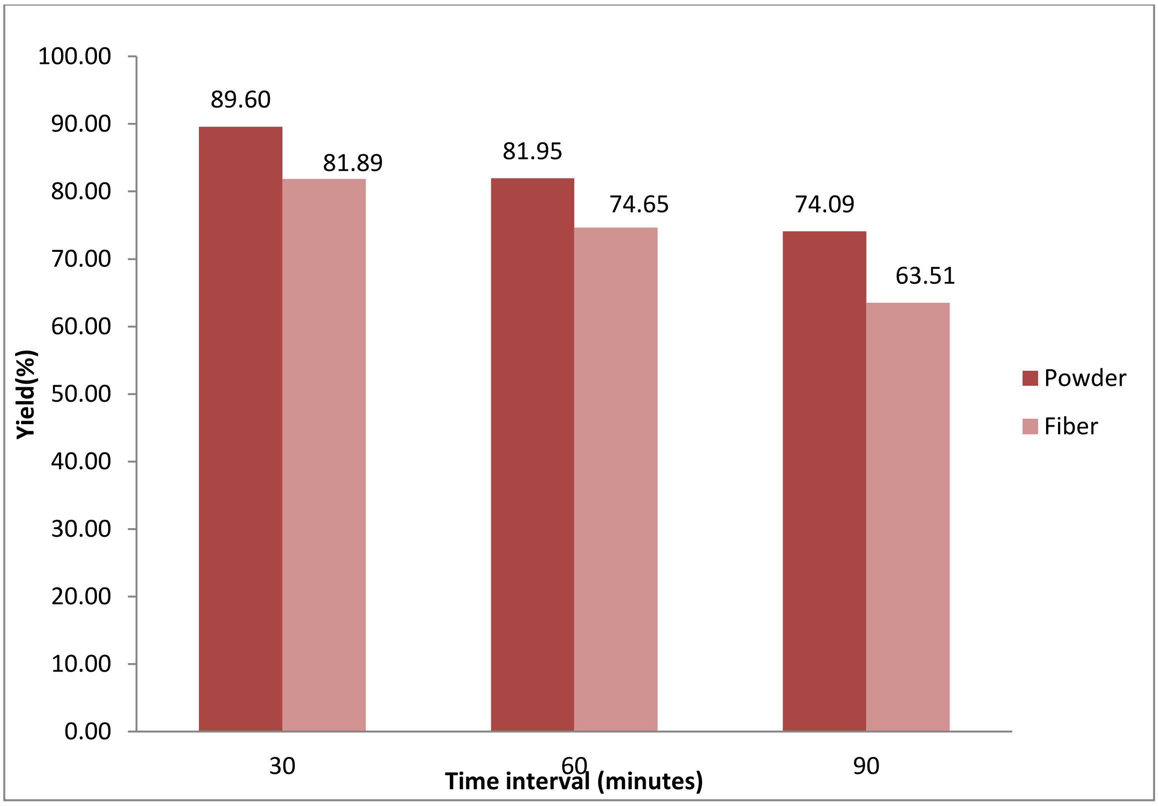

Figure 4-8 Graph of mass yield versus time interval at 200℃ (average)

The Figure 4-8 shows the graph of mass yield versus time interval in OPT pellet. The results of OPT torrefied mass yield shown in Appendice A-1. The mass yield of both powder and fiber torrefied OPT pellet were significantly decreased with the increment of torrefaction residence time at 200℃. However, among the two raw materials, fiber torrefied OPT pellets appeared to degrading at a faster rate during torrefaction contributing a lower mass yield at three different respective residence time of 30 minutes, 60 minutes and 90 minutes. Mass loss during torrefaction was due to the loss of moisture content, volatile organic compounds and also degradation of lignocellulosic component such as hemicellulose, cellulose as well as some part of lignin (Ciolkosz & Wallace,2011). Thus the mass yield was expected dwindled by the increase of residence time due to the decomposition of hemicelluloses and cellulose at long residence time and temperature (Wang et al., 2012).

4.5 Energy Yield

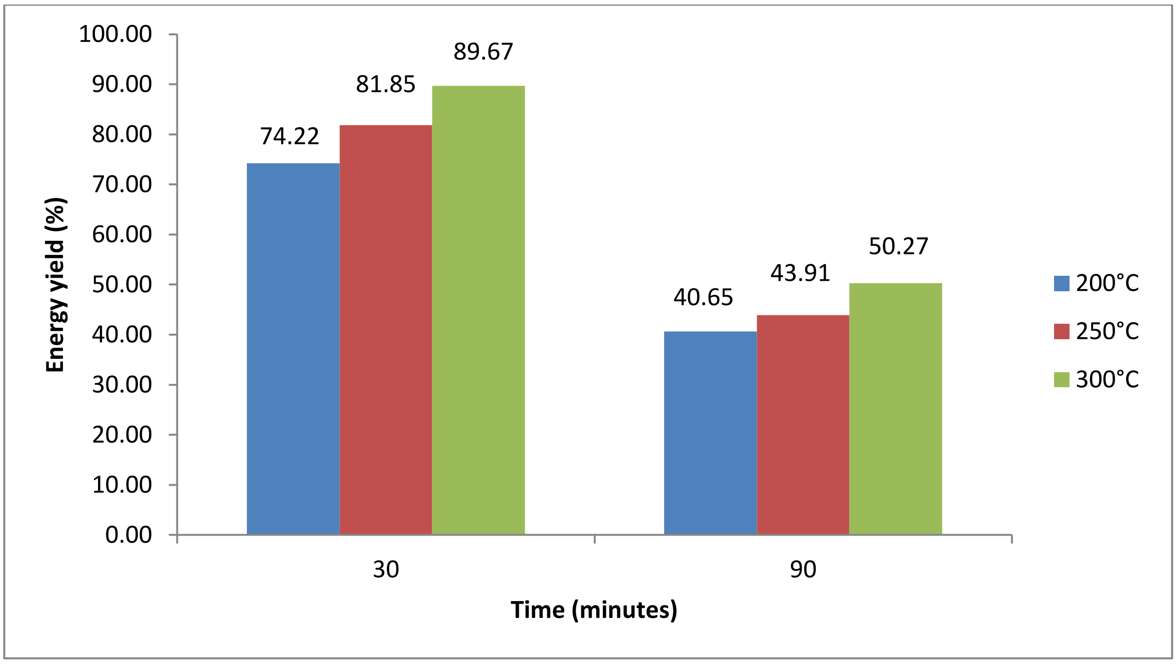

Figure 4-9: Energy yield of torrefied OPT pellet (average)

The Figure 4-7 shows the graph of energy yield of OPT torrefied pellet versus residence time with the elevated torrefaction temperature. The result of the energy yield is tabulated in Appendice A-1. The energy yield of the torrefied OPT pellet was decreased at elevated torrefaction temperature due to the thermal degradation of polymeric composition of lignocellulosic biomass and combustible element contents in pellet samples were mostly combusted. Thus, low energy yield is obtained. The energy yield of torrefied OPT pellet is remarkably peak at temperature of 300°C and at residence time of 30 minutes which is 89.67%. This shows that shorter residence time and larger torrefaction temperature gave a more significant effect in retaining its energy yield. The gap between mass and energy yield from Figure 4-6 and Figure 4-7 implied that the torrefied pellet mass loss is balanced by the increasing calorific value with elevated torrefaction temperature. Therefore, from this study, the temperature of 300°C gives the best torrefaction result for OPT to acquire high energy yield.

4.6 Fourier Transform Infrared (FTIR) Analysis

The torrefied OPT pellets were inspected by using JASCO Model FTIR-60 at CARRIF center. Fourier transform infrared spectroscopy was used to identify changes in functional groups of solid torrefied products. Figure 4-8 and Figure 4-9 show the FTIR spectra result of powder and fiber torrefied OPT pellet at 200°C with three different residence time while Figure 4-10 and Figure 4-11 show the FTIR spectra result of powder and fiber torrefied OPT pellet at 30 minutes with three different operating temperatures. All the results were recorded in the transmittance mode as a function of wave number in the range of 4000 to 500 cm^{-1}. Peaks are assigned based on literature data (Kobayashi *et al.*, 2009; Yang *et al.*, 2006; Yuliansyah & Hirajima, 2012) as in Appendix A.2

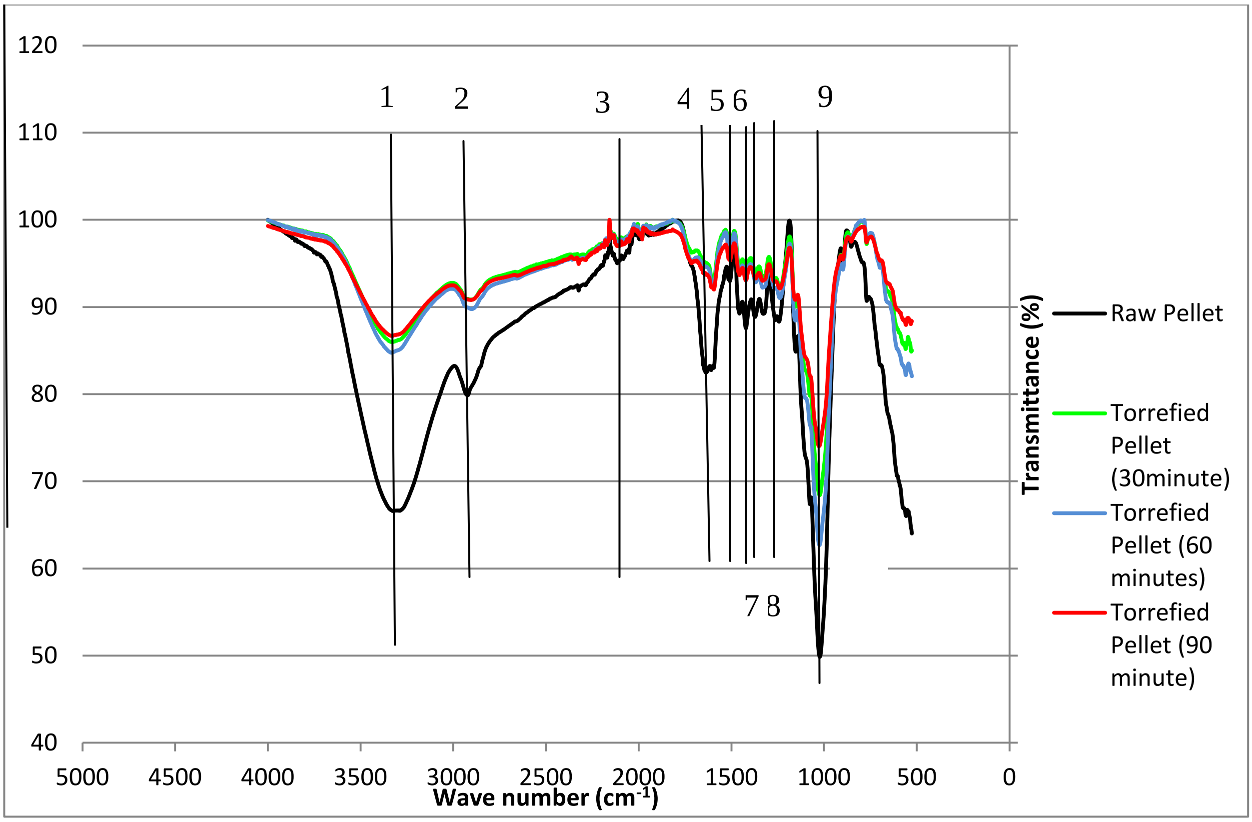

Figure 4-10 : FTIR spectra of raw and torrefied powder OPT pellet at 200°C

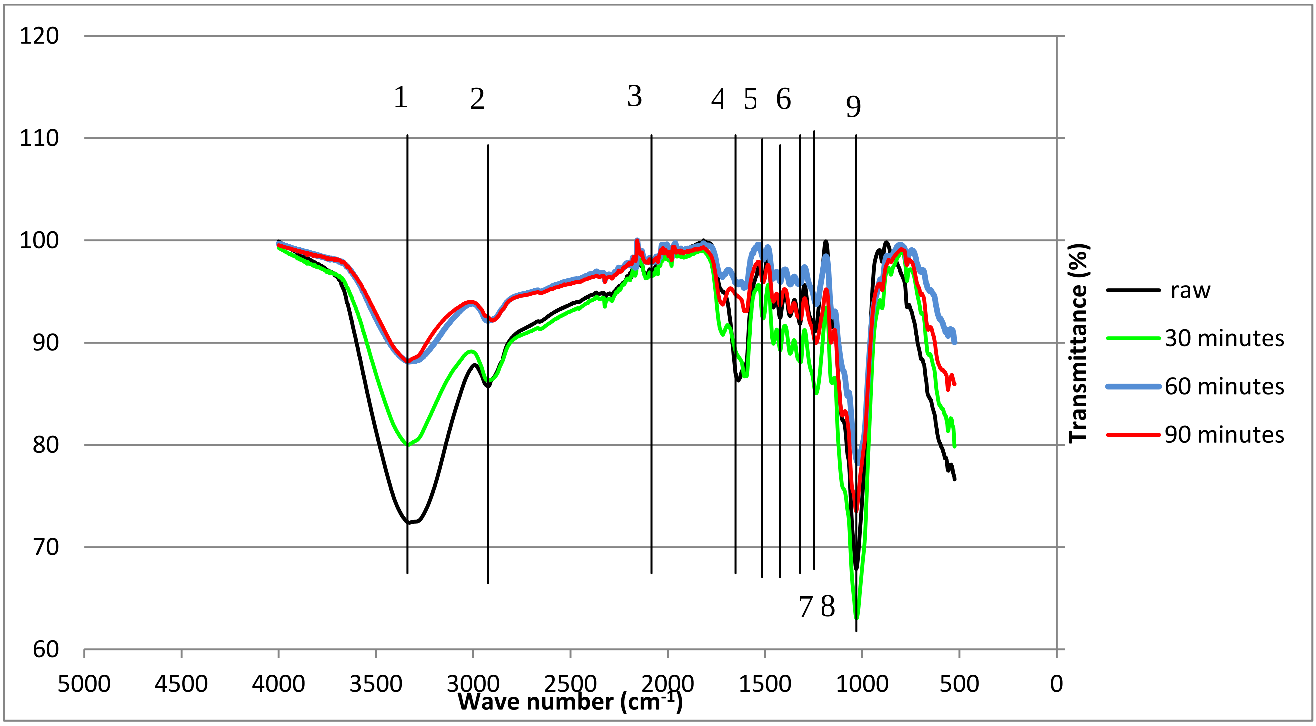

Figure 4-11 : FTIR spectra of raw and torrefied fiber OPT pellet at 200°C

The Figure 4-10 and Figure 4-11 show the comparison of the FTIR analysis of the samples .The first peaks in the graph lie on the line 1 which indicates the N-H bond from amide and amine group stretching. For the peaks lie on line 2 is identified as the vibration from C-H from alkanes group stretch and O-H from carboxylic acid group stretch. The strength of the peak marked as the O-H group decreases at longer residence time which indicate lignocellulosic dehydration occurs. It also showed that presence of the water molecules contain in the pellets were slowly removed. The loss of O-H group also explains the improved hydrophobicity of torrefied OPT (Lai & Idris, 2013). The peak on the line 3 is analyzed as vibration from the stretching of C=O from esters group which is also proven the present of hemicelluloses and cellulose as the C=O present in their structures. More distinctive peaks are observed in the region below 2000 cm^{-1}.

The peak at ~1500-1250 cm^{-1} indicate the presence of –NO_2 from nitro groups, the C-H in-plane from alkenes group bend, and C-F from alkyl halides stretch. At the peak lies at line 7 represents aromatic skeletal while line 8 represents C-O-C aryl-alkyl ether linkages where lignin stats to decompose. (Ibrahim *et al*., 2013). At the peak lies at line 9 ascribed to glycosidic bonds. The presence of cellulose is slowly degraded at the longer residence time for both powder and fiber torrefied OPT pellet.

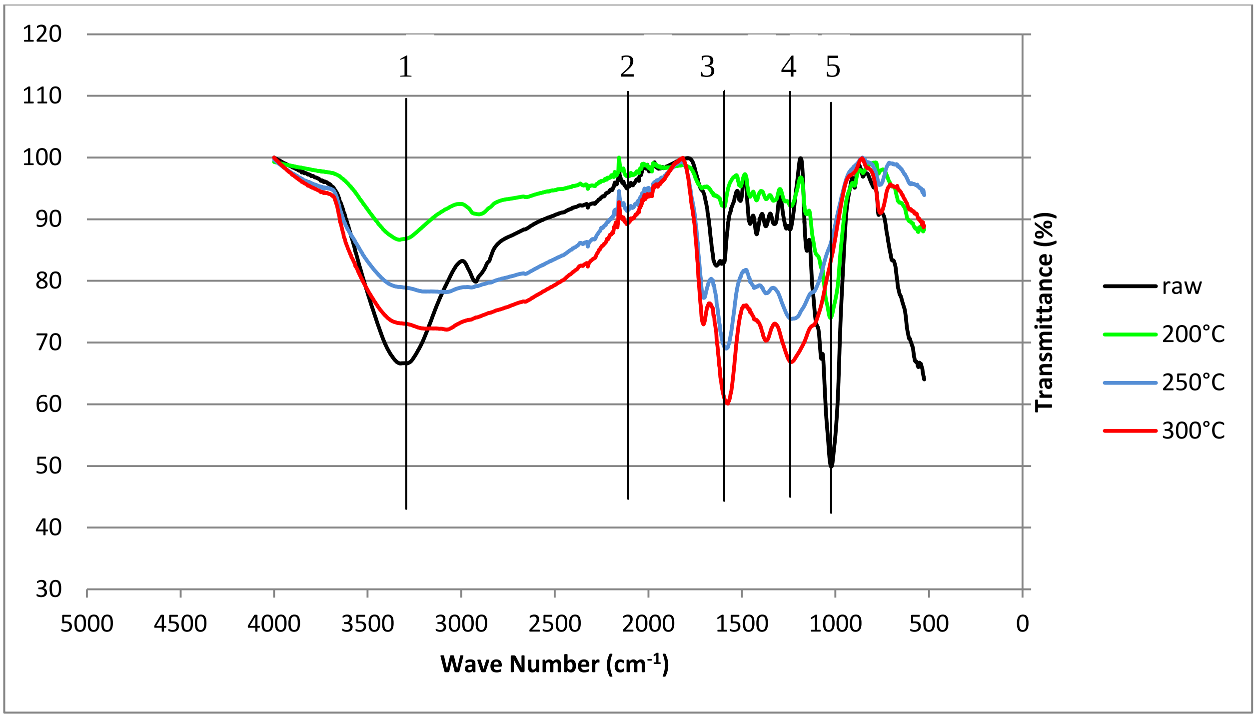

Figure 4- 12 :FTIR spectra of raw and OPT torrefied powder pellet at 30 minutes

The first peak in the graph lies on the line 1 is identified as the vibration from C-H from alkanes group stretch and O-H from carboxylic acid group stretch. The strength of the peak marked as the O-H group decreases at longer residence time which indicate lignocellulosic dehydration occurs. It also showed that presence of the water molecules contain in the pellets are slowly removed. The peak on the line 2 is analyzed as vibration from the stretching of C=O from esters group which is also proven the present of hemicelluloses and cellulose as the C=O present in their structures. At the peak of line 3 indicate the decrease in strength for aromatic skeletal vibrations. The peak at line 4 and 5 (~1250- 1020 cm^{-1}) represent that the presence of C—N stretch in aliphatic amines groups are slightly degraded.

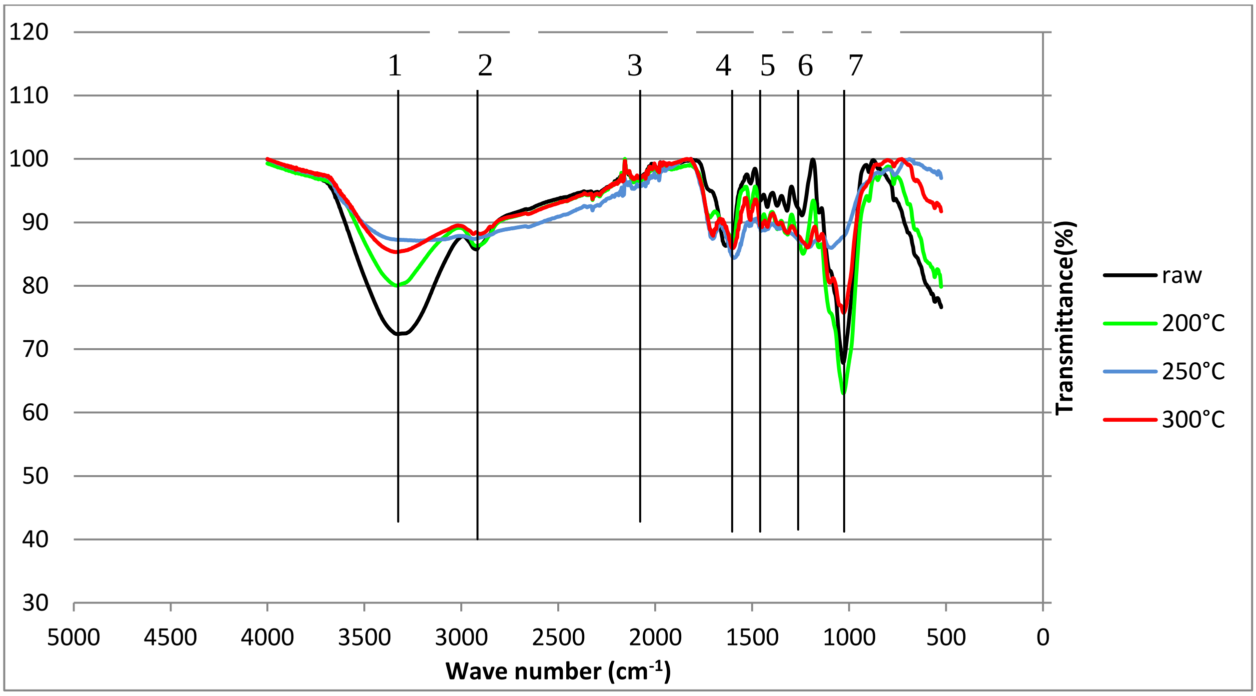

Figure 4-13 : FTIR spectra of raw and OPT torrefied fiber pellet at 30 minutes

The first peak in the graph lies on the line 1 is identified as the vibration from C-H from alkanes group stretch and O-H from carboxylic acid group stretch. The strength of the peak marked as the O-H group decreases at higher temperature which indicate lignocellulosic starts to dehydrate. In other words, it also showed that water molecules in the pellets are slowly removed. The peak on the line 2 is analyzed as vibration from the stretching of C=O from esters group which is also proven the present of hemicelluloses and cellulose as the C=O present in their structures. At the peak of line 3 indicate the decrease in strength for aromatic skeletal vibrations. The peak in line 4 and 5 indicate the presence of $–NO_2$ from nitro groups, the C-H in-plane from alkenes group bend, and C-F from alkyl halides stretch. The peak at ~1250- 1020 cm^{-1} represent that the presence of C—N stretch in aliphatic amines groups are slightly degraded. Those components are the compounds in the hemicelluloses and cellulose. At the peak lies at line 7 ascribed to glycosidic bonds. The presence of cellulose is slowly degraded as temperature increases for both powder and fiber torrefied OPT pellet.

By analysing the FTIR spectra of the torrefied samples, it can be concluded that there is no significant structural changes for both OPT powder and fiber at 200°C and 250°C torrefaction conditions. These low temperature effects however contributed to degradation and depolymerisation of hemicellulose in both OPT powder and fiber. At

300°C torrefaction condition, hemicellulose is mostly disappeared and slight degradation of cellulose and lignin is significant at this temperature.

4.7 Scanning Electron Microscope (SEM) Analysis

The torrefied OPT pellets were inspected using EVO50 Scanning Electron Microscopy (SEM) equipped with computer image analysis at CARRIF center. There are four samples were inspected which are two torrefied OPT pellets and two non-torrefied OPT pellets.

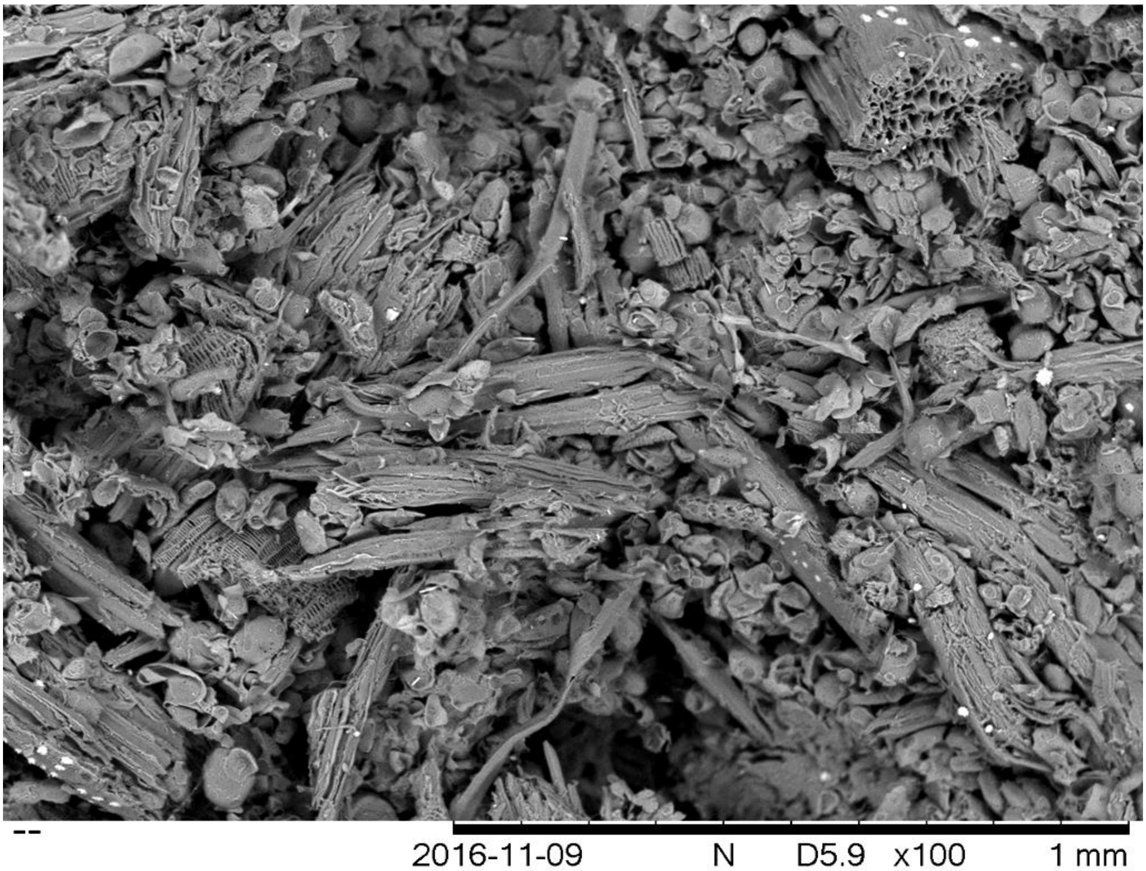

Figure 4-14 : SEM morphology structure of non-torrefied OPT powder pellet

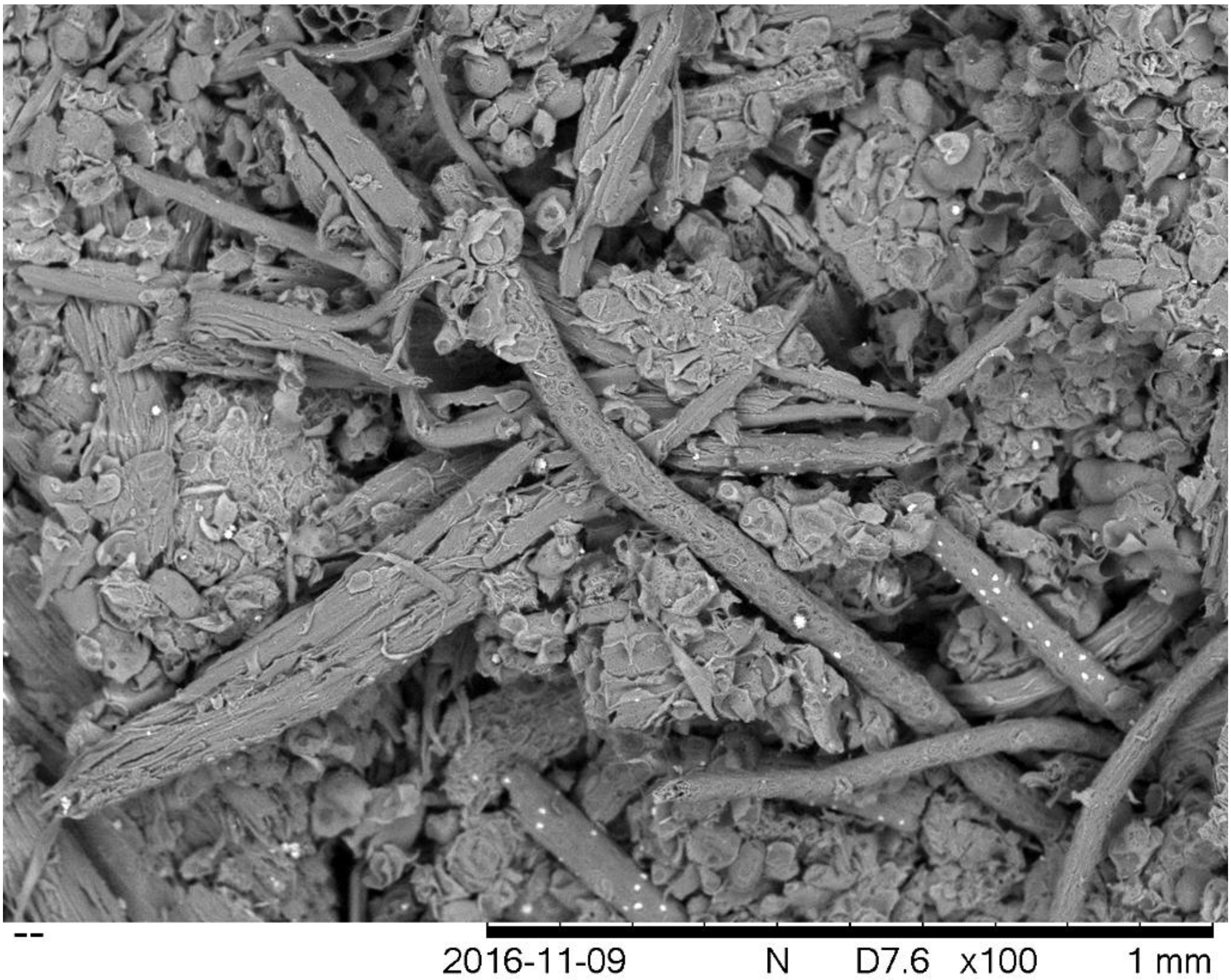

Figure 4-15: SEM morphology structure of torrefied OPT powder pellet at 200℃ at 90minutes

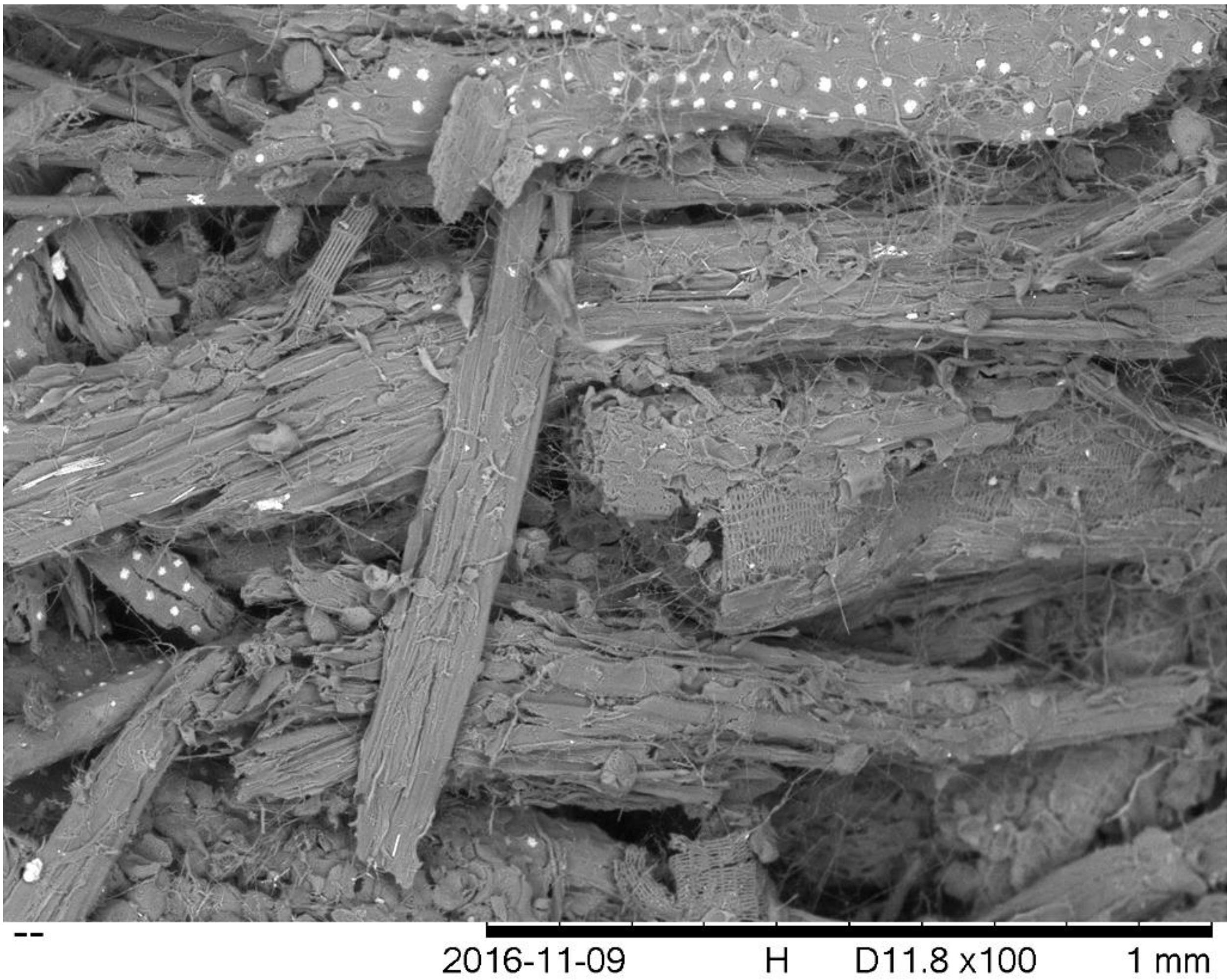

Figure 4-16: SEM morphology structure of non-torrefied OPT fiber pellet

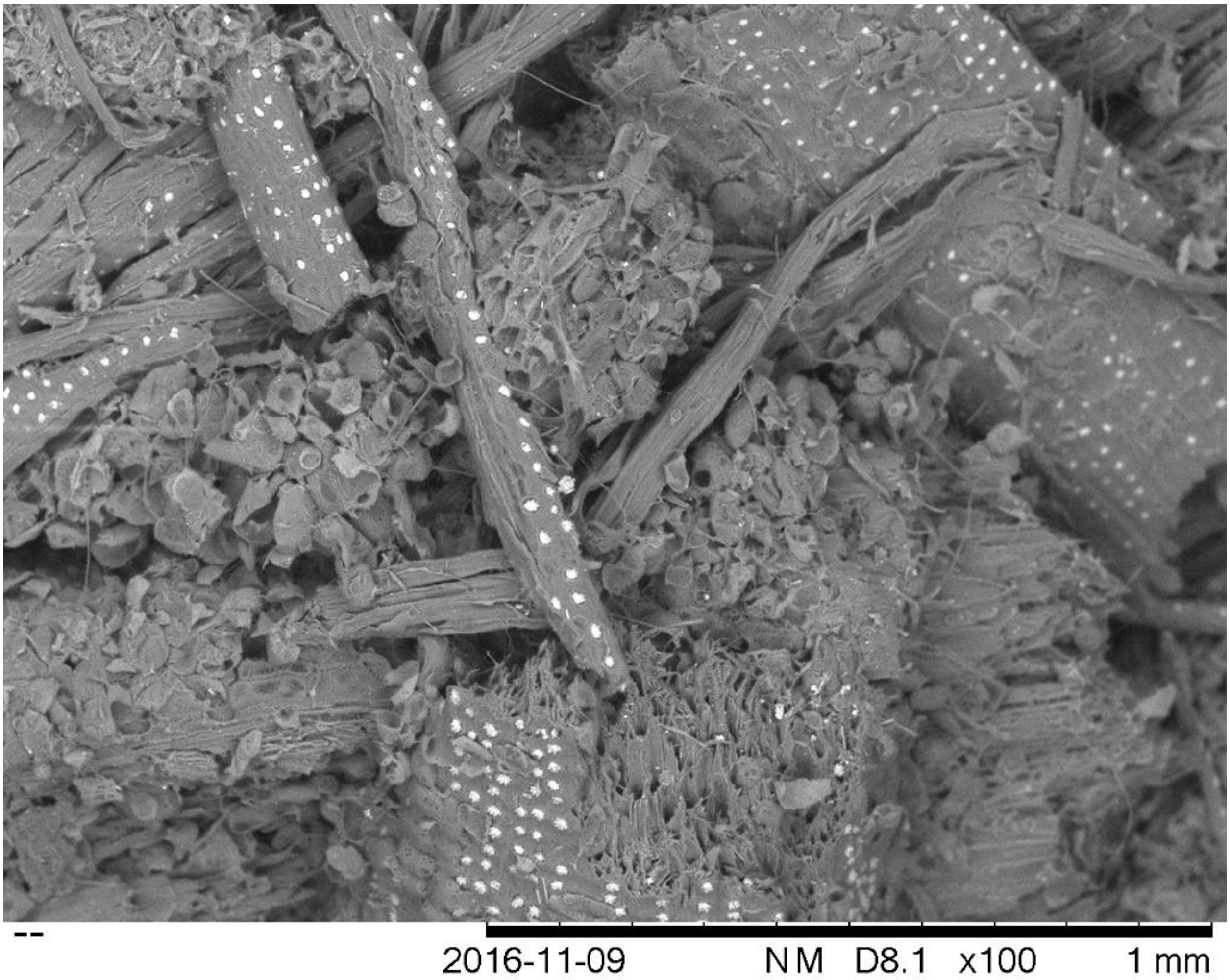

Figure 4-17: SEM morphology structure of torrefied OPT fiber pellet at 200℃ at 90minutes

From Figure 4-12 to Figure 4-15 shows that there are no any significant different in morphology structure. Thus, temperature and residence time do not have any effect toward pellet morphology structure .

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This research was conducted to study the torrefaction effect on physical and chemical properties of oil palm trunks (OPT) at different temperature levels and residence time intervals. Furthermore, mass yields of both sample materials (powder and fiber) were found to reduce with increasing torrefaction temperature. Reduction of mass yield can be implied that degradation of lignocellulosic components such as hemicellulose, cellulose, and lignin occurs. At a torrefaction temperature of 200°C at 90 minutes, the energy yield of the torrefied OPT pellet is the highest with 89.67% of the energy retained in the OPT pellet. Moreover, the lignocellulosic structures of OPF for both powder and fiber form were qualitatively identified via Fourier Transform Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM) analysis.

From the analysis, torrefaction process was proven to enhance the physical properties of OPT such as homogeneity, hydrophobic and negligible biological activities which favours the storage and transport applications. Therefore, the oil palm plantation residues, OPT represents a good source for torrefaction purpose. Also, this process is an attractive method to produce a renewable fuel with favourable properties for gasification and/or co-/combustion applications.

5.2 Recommendation

The following recommendations should be considered throughout this research works. First of all, proper pre-treatment of freshly obtained OPT should be done accordingly. After collected from LKPP Palm Oil industry, they should be immediately processed into fibre form as well as powder form after properly dried for preservation to prevent biodegradation such as mould and rotting. Improper pre-treatment and preservation methods might influence the analysis result such as FTIR and SEM due to early degradation of lignocellulosic composition.

Furthermore, during the torrefaction process, it is compulsory to ensure that the process is fully carried out in the absence of oxygen. The time taken for the cooling process after torrefaction can be shortened by direct blowing with portable fan which effectively reduces the progress delay.

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APPENDIX

Appendice A-1

Mass yield

POWDER						
Temperature (°C)	Time (min)	Sample	Mass (g)			Mass yield
			Mb	Ma	Difference	
200	30	1	2.6787	2.4685	0.2102	92.1529
		2	2.6474	2.3047	0.3427	87.0552
	Average					89.6041
	60	1	2.8034	2.3716	0.4318	84.5973
		2	2.8404	2.2527	0.5877	79.3093
	Average					81.9533
	90	1	2.5976	2.064	0.5336	79.4580
		2	3.1892	2.1915	0.9977	68.7163
	Average					74.0871
250	30	1	2.2176	1.1397	1.0779	51.3934
		2	2.7989	1.0097	1.7892	36.0749
	Average					43.7341
	90	1	2.4317	1.4313	1.0004	58.8601
		2	2.4138	1.003	1.4108	41.5527
	Average					50.2064
300	30	1	2.3816	0.8898	1.4918	37.3614
		2	2.8417	1.245	1.5967	43.8118
	Average					40.5866
	90	1	2.4617	1.7101	0.7516	69.4683
		2	2.5413	0.7439	1.7974	29.2724
	Average					49.3703

FIBER						
Temperature (°C)	Time (min)	Sample	Mass (g)			Mass yield (%)
			Mb	Ma	Difference	
200	30	1	3.1283	2.397	0.7313	76.6231
		2	2.8499	2.4838	0.3661	87.1539
	Average					81.8885
	60	1	3.182	2.3401	0.8419	73.5418
		2	2.9948	2.2689	0.7259	75.7613
	Average					74.6516
	90	1	3.3926	2.3002	1.0924	67.8005
		2	3.6172	2.1424	1.4748	59.2281
	Average					63.5143
250	30	1	3.3818	1.2589	2.1229	37.2257
		2	3.272	1.3312	1.9408	40.6846
	Average					38.9552
	90	1	3.3468	0.8552	2.4916	25.5528
		2	3.844	1.0096	2.8344	26.2643
	Average					25.9085
300	30	1	3.261	1.0056	2.2554	30.8372
		2	3.3013	1.3136	1.9877	39.7904
	Average					35.3138
	90	1	3.0979	0.7289	2.369	23.5288
		2	3.2718	0.7959	2.4759	24.3261
	Average					23.9275

Energy yield

Temperature (°C)	Time (min)	Sample	CV	CV ratio	Energy yield (%)
200	30	1	20.1068	1.0256	81.4930
		2	19.1026	0.9744	66.9564
	Average		19.6047	2.0000	74.2247
	60	1	25.1373	0.9932	68.9948
		2	25.4823	1.0068	29.4719
	Average		25.3098	2.0000	49.2334
	90	1	25.1489	0.9803	36.6246
		2	26.1608	1.0197	44.6758
	Average		25.6549	2.0000	40.6502
250	30	1	20.1049	0.9602	81.2307
		2	21.7714	1.0398	82.4654
	Average		20.9382	2.0000	81.8480
	90	1	22.1209	1.0234	52.5963
		2	21.1091	0.9766	35.2306
	Average		21.6150	2.0000	43.9134
300	30	1	20.1068	1.0256	94.5131
		2	19.1026	0.9744	84.8256
	Average		19.6047	2.0000	89.6693
	90	1	22.1229	1.0077	59.3140
		2	21.7843	0.9923	41.2323
	Average		21.9536	2.0000	50.2731

Appendice A-2

Identification of functional groups at various wave number range

Wave number , cm^{-1}	Bond	Functional group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1˚, 2˚ amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	Aromatics
3100–3000 (m)	=C–H stretch	Alkenes
3000–2850 (m)	C–H stretch	Alkanes
2830–2695 (m)	H–C=O: C–H stretch	Aldehydes
2260–2210 (v)	C≡N stretch	Nitriles
2260–2100 (w)	–C≡C– stretch	Alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	Alkenes
1650–1580 (m)	N–H bend	1˚ amines
1600–1585 (m)	C–C stretch (in–ring)	Aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	Aromatics
1470–1450 (m)	C–H bend	Alkanes
1370–1350 (m)	C–H rock	Alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds

1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	Alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1˚, 2˚ amines
900–675 (s)	C–H “oop”	Aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	Alkanes
700–610 (b, s)	–C≡C–H: C–H bend	Alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp