CHEMICAL COMPOSITION ANALYSIS OF RAW AND TORREFIED EMPTY FRUIT BUNCH (EFB)

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CHEMICAL COMPOSITION ANALYSIS OF RAW AND TORREFIED EMPTY FRUIT BUNCH (EFB)

by

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DECLARATION

I declare that this thesis entitled "Chemical Composition Analysis of Raw and Torrefied Empty Fruit Bunch (EFB)"is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : 11th JANUARY 2017

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LIST OF ABBREVIATION

α	Alpha
°C	Degree Celsius
°C/min	Degree Celsius per minutes
AGU	Anhydroglucose units
EFB	Empty Fruit Bunch
G	Phydroxyphenyl
GHz	Gega Hertz
g	Gram
H	Guaiacyl
K	Kelvin
ml	Millilitre
min	Minutes
S	Syringyl
TAPPI	Technological Association of the Pulp and Paper
W	Watt

LIST OF SYMBOL

×	Multiplication
-	Substraction
=	Equal to
α	Alpha
%	Percentage

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Chemical Composition Analysis of Raw and Torrefied Empty Fruit Bunch (EFB)

ABSTRACT

From the last research, there has increasing in the research interest in value of the lignocellulosic biomass. Lignocellulosic biomass is inexpensive, most abundance and provide the large-scale. The using of the lignocellulosic material is to reduce the cost in production of ethanol. Lignocellulosic are compose into three structures which are cellulose, hemicellulose and lignin. EFB has the highest composition of cellulose, hemicellulose and lignin among the abundance fiber like coir, corn, bagasse and kenaf fiber. EFB were collected at Felda Kemahang, Tanah Merah, Kelantan. Samples then grind using grinder to breakdown the size and use siever to obtain 500 micron for torrefaction process. Torrefaction was the process pre-treatment of biomass materials in inert atmosphere (nitrogen) in temperature range 200 to 300^{o}C by using microwave. Microwave controlled all the parameter which is power level (Watt), temperature (°C), volume of nitrogen (ml/min) and mass of sample (g) during the torrefaction process. In this study, the analysis of raw and torrefied EFB was done according to TAPPI standard method, except hemicellulose, which data was collected through equation. Result acquired reveals that the highest percentage in extractive, holocellulose, α- cellulose, hemicellulose and lignin was be found in raw EFB compared to other torrefaction EFB due to the degradation of content during torrefaction process. The degradation of hemicellulose was the takes place in temperature range 200-350 °C or even lower whereas the degradation of cellulose and lignin occurs when 300°C and above. This study determined EFB as useful alternative resources in feedstock material steam in power plant application.

Analisis Komposisi Kimia di dalam Tandan Buah Kosong

ABSTRAK

Berdasarkan dari kajian yang lepas, kadar kajian dalam nilai lignosellulosik semakin meningkat. Biomas lignoselulosa adalah murah, lambakan hasil dan boleh dihasilkan didalam kuantiti yang banyak. Kegunaan bahan lignoselulosa adalah untuk mengurangkan kos penghasilan etanol. Lignosellulosa terdiri daripada tiga struktur iaitu selulosa, hemiselulosa dan lignin. Tandan buah kosong mengandungi komposis selulosa, hemiselulosa dan lignin paling tinggi di dalam kalangan lebihan serat seperti sabut kelapa, jagung, hampas tebu dan serat kenaf. Tandan buah kosong diperoleh di Felda Kemahang,Tanah Merah, Kelantan. Sampel dikisar menggunakan pengisar bertujuan untuk memisahkan menjadi saiz yang kecil dan penapis digunakan untuk mendapatkan sampel bersaiz 500 micron untuk kegunaan proses torrefaksi. Proses Torefaksi adalah salah satu dari proses pra-rawatan ke atas bahan biomas di dalam suasana gas lengai (nitrogen) di dalam suhu lingkungan 200 hingga 300^{o}C di dalam ketuhar gelombang mikro. Ketuhar gelombang mikro mengawal tiga pemboleh ubah iaitu kadar kuasa (W), suhu (˚C),isipadu nitrogen (ml/min) dan jisim sampel (g) semasa proses torrefaksi berlaku. Di dalam kajian ini, analisis tandan buah kosong mentah dan tandan buah kosong yang telah ditorefaksi dilakukan mengikut kaedah TAPPI kecuali hemiselulosa , di mana data yang terkumpul dihasilkan melalui persamaan. Hasil dari keputusan menunjukkan, sampel tandan buah kosong mentah menghasilkan kandungan ekstraktif, holoselulosa, α- selulosa, hemiselulosa dan lignin yang paling tinggi dikalangan sampel yang melalui proses torefaksi disebabkan proses degradasi kandungan. Degradasi terhadap hemiselulosa berlaku dalam kalangan suhu 200-350°C atau lebih rendah manakala degradasi bagi selulosa dan lignin berlaku apabila suhu 300°C dan ke atas. Kajian ini mendapati bahawa Tandan buah kosong sangat berguna sebagai salah satu alternatif sumber stim bahan mentah di dalam jana kuasa

CHAPTER 1

INTRODUCTION

1.1 Background

Biomass was the solar energy stored in chemical form in plant and animal materials and there are the most precious and versatile resources on earth (Demirbas, 2005). Currently, biomass come out with the fourth largest energy sources in the world and will be the new renewable sources in this world (Melkior et al., 2012). The term biomass was organic matter that is produce as a result of photosynthesis as well as municipal, industrial and animal waste material.

The increasing demand for renewable energy has given rise to biomass energy crops and the same time the depletion of conventional fossil fuel that emitted the greenhouse gas emission (Liu et al., 2014). The activities such as burning of biomass also cause increase atmospheric concentrations of CO_2 but not as the burning of the fossil fuel. When the combustion is incomplete, the CO, N_2O, CH_4 and other hydrocarbon gases (HCs) and particulate matter was emitted. Then, there are proven that the smoke from the low efficient wood fuel stoves has the risk factor in health (Demirbas, 2005).

The process biomass to liquid are usually are the conversion of lignocellulosic biomass such as the crop agriculture residue and forestry into the liquid fuel (Melkior et al., 2012). The component of biomass was cellulose, hemicellulose, lignin, extractives, lipids, protein, simple sugar, starches, water, hydrocarbon, ash, and other. The cellulose and hemicellulose are two largest carbohydrate categories that have important value. Lignin is consisting of non-sugar molecule (Demirbas, 2005).

To obtain the liquid fuel by the converting biomass into synthesis gas that are mainly consist of CO, H_2, CO_2 and H_2O (Melkior et al., 2012). The biomass material including bamboo, willow, coconut shell, wood, sugar cane bagasse, banana trunk and coconut husk.

Currently, biomass are being attention because of its renewability, carbon neutrality and low emission of pollution (Zhang et al., 2015). The converting of biomass waste into solid, liquid and gases fuel by undergoes torrefaction process are one method to solve this environmental issue. Lignocellulosic biomass is the most abundandance renewable sources and can be effeciently convert into energy by using microwave method (Huang et al., 2016). Torrefaction is pre-treatment of biomass materials in inert atmosphere in temperature range 200 to 300°C by using microwave.

During this process, biomass materials can losses moisture and a proportion of volatile content and become drier and darker (Shang et al., 2012). The microwave are used to control the torrefaction temperature, residence time and heat input in order to compare the chemical composition analysis between raw and torrefied biomass materials. In the process of torrefaction, hemicellulose was deeply decomposed whereas cellulose and lignin was partially decomposed and it has been proved that torrefaction pre-treatment not only upgrate fuel characteristic but also brittleness and hydrophobicity (Zhang et al., 2015).

To analyze chemical composition analysis between raw and torrefied biomass materials, the Technical Association of Pulp and Paper Industry (TAPPI) Standard method are use. There are to identify the percentage of cellulose, hemicellulose and lignin in the biomass material. When light torrefaction is perform, the hemicellulose was destroyed in significant way wheras the cellulose and lignin were affected only slightly. When torrefied biomass material has less than 1 hours torrefaction apllication, it was more appropriate for producing fuels with higher densities (Chen & Kuo, 2010). Biomass material such as wood, sewage, sludge, coffee hulls, oil palm biomass and sugar cane bagasse (Huang et al., 2016).

1.2 Problem Statement

Nowadays, there are many alternative new or renewable sources of energy such as wind, solar, geothermal that we can use instead of the fossil fuel and other conventional fuel (Demirbas, 2005). One of them is the biomass energy that is come out from the animal or the plant waste. To develop the energy from biomass, a variety of conversion technique such as physical, thermal, chemical and biological method have been utilized (Chen & Kuo, 2010). The lack of study in torrefaction is the factors that the fossil fuel stays the largest energy used in the world instead of biomass energy.

Torrefaction is a thermochemical process which convert biomass into solid, liquid and gases fuel that will replace the using of fossil fuel (Huang et al., 2016). There was some benefit of torrefaction of biomass materials toward the environment and economical. In torrefaction process, the carbon dioxide (CO_2) emission from biomass sample will release as neutral because CO_2 is fixed by photosynthesis in short period (Prins et al., 2006). In growth of economy, torrefaction helps to use abundant of empty fruit bunch (EFB) by converting them to functional final product. Besides that, by applying some temperature, residence time and heat into the biomass materials, the composition of cellulose, hemicelluloses and lignin will decrease due to the degradation of the component. Thus, this research is carried out to evaluate EFB by testing their chemical composition after undergo the torrefaction process.

1.3 Research Objective

The main objectives of this study are:

1. To produce the torrefied material using microwave heating.
2. To analyze the chemical properties of raw and torrefied materials.

1.4 Scope of Research Work

The scope of this research is the production of biomass material due to effect of the torrefaction parameter. Then, the chemical composition was by analyzed using Technical Association of Pulp and Paper Industry (TAPPI) Test Method. Besides that, TAPPI Standard Method was more suitable for preliminary step to determine the amount of chemical properties in biomass material. By using TAPPI Standard test for the chemical testing, the EFB sample will generate various values of cellulose, hemicellulose and lignin. The different temperature undergoes by the sample will produce different result in percentage (%).

In TAPPI test, there are some step must be undergoes for the all the EFB sample. The step was started from find the percentage of extractive by using TAPPI T264 cm-97 Method, 1997. Then followed by holocellulose that are find by using (Wise *et al.*, 1946) method. The Alpha cellulose was found by using TAPPI T203 os-74 (1997) method and hemicellulose was indicated by difference between holocellulose and alpha cellulose. Lastly, percentage of lignin was indicated by using TAPPI T222 om-88 (2002) method.

The torrefied temperature that use in this research is in the range of 200 into 300 ^{o}C. As increase the temperature, the degradation of component such as cellulose, hemicelluloses and lignin decrease step by step start from hemicelluloses. After the biomass material undergoing the torrefaction process, their expected outcome is the hemicellulose will decrease firstly and continue with the cellulose and lignin.

Their weight was decreased due the loss of the moisture and degradation of components after undergoes torrefaction process. The composition of cellulose, hemicelullose and lignin of raw was high compare to the torrefied sample because they are not undergoes the high temperature. Their cellulose, hemicelluloses and lignin are not degraded and their weights of the sample are not affected too much during the chemical testing.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Energy resource act as prime agent and act as an important role in the world's future for the next generation in economic development. Energy can be categories into the three that are fossil fuel, renewable resources and nuclear resources (Bilba et al., 2007). With large-scale industrial development, the total exploitable of fossil fuel are decline that are cause increasing of environmental pollution (Chen et al., 2011). In this study, there are more focus on the biomass energy that are one of the alternative way to reduce the air pollutant and greenhouse gasses that are due to high concentration CO_2 in the atmosphere. Other than that, higher amount of the greenhouse gasses will increase the amount of heat trapped and will cause the rising of earth's temperature. In recent year, there has been increase in concern to shift the agriculture waste to manufacturing to reduce the fossil fuel consumption (Cutz et al., 2016).

2.2 Biomass

Biomass was referring to any organic material that are derived from the animal or plant (Demirbas, 2005). The types of biomass feedstock are classified into three categories that are animal, forest and agricultural. With respect to biomass from animal origin like cattle, pigs, chickens manure and swine stock. Manure can converted into biogas through anaerobic digestion. From conversion process in biodigester, carbon monoxide (CO_2) and methane (CH_4) was produced. Biogas consists of 55-80% CH_4, 20-40% of CO_2 and traces of H_2S and other impurities (Cutz et al., 2016). Besides that, biomass includes gases and liquid from degradation of the organic material. After the organisms are died, microorganisms started to work to breakdown the biomass into the constituent part like CO_2, H_2O and potential energy (Melkior et al., 2012).

The formation of biomass by plant is through conversion of carbon dioxide (CO_2) in atmosphere into carbohydrate by sun's energy with present of chlorophyll and water. The process of photosynthesis was helped plant to breakdown water to obtain electron and proton to use them to turn CO_2 into glucose, releasing O_2 as a waste product. The chlorophyll promotes the absorption of carbon dioxide from the atmosphere and growth of the plant and converts them into hydrocarbon. Carbon was cycled in atmosphere when biomass are consume as a fuel (Chen et al., 2015). Coconut husk, sugar cane bagasse, rice husk and empty fruit bunch are the example plant that was produced biomass material from their agriculture waste.

The process of torrefaction generally carried out in the 200-300 ^{o}C and to be used to upgrade lignocellulosic biomass to a higher quality fuel. Torrefaction has high potential to becoming a leader of pre-treatment technology for exploitation of biomass for energy purpose. The product of torrefaction will be summarizing below (Figure 2.1) (Peduzzi et al , 2014).

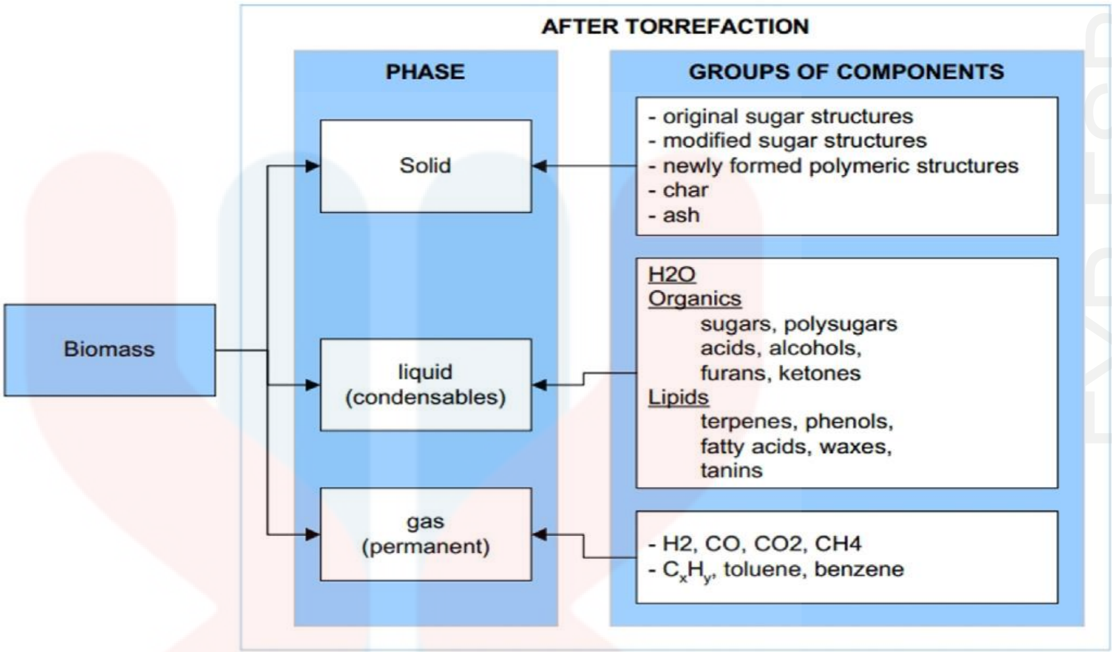


Figure 2.1: Diagrammatic illustration of product of torrefaction process (Peduzzi et al., 2014).

2.2.1 Empty Fruit Bunch

Empty fruit bunch (EFB) are widely available in Southeast Asia countries and found to have 60% (w/w) sugar components (Abdul et al., 2016). In 2010, Malaysia was the second large producer of palm oil with 17.8 million where Indonesia was the world’s largest production of palm oil that are 22.2 million tons of oil (Omar et al., 2013). In 2008, the plantation of oil palm in Malaysia covers 4.5 million hectare compare to 4.3 million hectare on 2007.

The oil palm *(Elaeis guineensis sp.)* fruit bunch and generates a lot of lignocellulosic by product, mainly empty fruit bunch (EFB), the fruit fiber and the shell (Uemura et al., 2013). The types of biomass produce by oil palm are empty fruit bunch (EFB), mesocarp fiber, kernel shells, fronds and trunk (Uemura et al., 2013). Lignocellulosic is the most abundant biomass resources on the earth and they can use as a feedstock for preparation of the fuel and chemical (Abdul et al., 2016). The EFB comprises of 17-33% of hemicellulose, 43-65% of cellulose and 13-37% lignin on the dry weight basic (Palamae et al., 2014).

2.3 **Chemical properties of Biomass Material**

Lignocellulosic agriculture biomass consists of cellulose, hemicellulose and lignin, together with smaller amount of pectic substance (Wu et al., 2016). Mostly, there are made up 10-15% of lignin, 20-30% hemicellulose and 40-50% cellulose (Gulfraz et al., 2014). Cellulose acts as a major structural component in the plant cell that is for mechanical strength whereas the hemicelluloses macromolecule that is often repeated polymers of pentose and hexoses (Anwar et al., 2014). Then, the lignin contain three aromatic alcohol that are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol that are produce by the process of biosynthetic process and form a protective seal to the both other component that are cellulose and hemicelluloses.

2.3.1 Cellulose

Cellulose was a major component of cell wall of higher plant and also produce by come bacteria,algae, amoeba and sea-animal (Matsui et al., 2009). Plant secondary wall are largely composed of cellulose, hemicelluloses and lignin and cellulose β-1, 4-linked polymer or glucose are the major unit used in biofuel production (Wang et al., 2015). Cellulose is the most abundant agriculture residue and herbaceous crop like coconut husk, bagasse, bamboo, corn and empty fruit bunch.

The chemical structure of cellulose was contained of β- anhydroglucose units with dominant hydroxyl groups which is suitable for reaction. There are mainly consisting of primary and secondary hydroxyl group in each monomer unit in polymer structure. Each anhydroglucose units (AGU) are linked together by β-1, 4-glycosidic bonds (Sahin & Arslan, 2008). There is form in cystalline microfibril, cellulose chain has a ribbon like structure and they are in the pyranose rings are in a chain formation and the glycosidic bonds connecting them in equatorial position relative to the pyranose rings (Simont et al., 1988). Due to specific chemical arrangement of cellulose, there are completely linear homopolysaccharides and has ability to make extensive and intermolecular hydrogen bond (Sahin & Arslan, 2008).

Cellulose has the distincitive structural properties and their tension resistance might be comparable to the steel (Festucci-Buselli, Otoni, & Joshi, 2007). Cellulose is water –insoluble polymer with a rigid linear structure. In nature, cellulose is the main structure of cell wall and responsible for many of its distinctive trait. The tension resistance of cellulose a comparable to steel because their controlled cellulose biosynthesis allows the arrangement of extensive linear chain that can be aligned side by side (Festucci-Buselli et al., 2007).

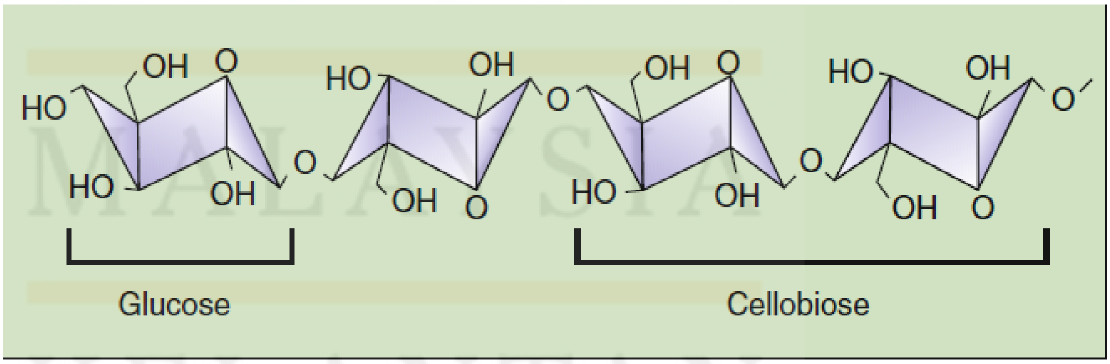


Figure 2.2: Molecular chain structure of cellulose (Chen, 2014)

2.3.2 **Hemicellulose**

Hemicelluloses was the second most abundant heterogeneous polymer (Anwar et al., 2014) and used to represent a family of polysaccharides mainly contain of arabinose-xylans, gluci-mannans, galactan and others that found in the plant. Hemicelluloses are defined by Aspinal in 1962 as derived from polysaccharides of plant and include in basic containing residue of ᴅ-xylose, ᴅ-mannose, ᴅ-glucose, ᴅ-galatose and other glycosyls as branch chain link to the basic chain (Wang et al., 2015). Hemicelluloses are also representing the largest polysaccharides fraction waste because hemicellulose is based on heterogeneous polymeric nature and their fermentability by the most common industrial (Gírio et al., 2010).

Each plant cell wall has different composition and the structures depend on the source and extraction method. The structure and composition of hemicelluloses that are lack of the crystalline structure mainly causes by highly branched structure and presence of acetyl groups connected to the polymer chain (Harmsen & Huijgen, 2010). Due to the few crystalline, hemicellulose also are easily degraded in acidic medium than cellulose (Wang et al., 2015)

Hemicelluloses are heterogeneous class of polymer that are contain 15- 35% of plant biomass and there are consists of pentose, hexoses and uronic acids. The most relevant hemicelluloses are xylans and glucomannans where xylans being the most abundance. Xylans are main hemicelluloses component in secondary cell wall (Gírio et al., 2010).

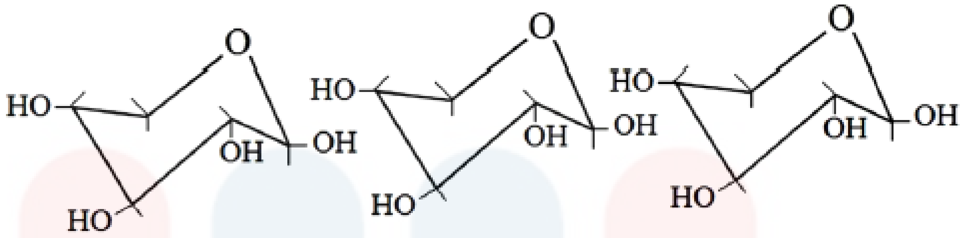


Figure 2.3: Structure of xylose unit of hemicellulose (Shahzadi et al., 2014).

2.3.3 **Lignin**

Lignin was the second abundance biopolymer after cellulose that also is an important structural component of lignocellulosic biomass. The main function lignin in plant was to provide rigidity and physical strength for plant to protect plant from microorganism and insect. It also helps plant to transport water and nutrient to all parts of body (Gordobil et al., 2016). Lignin generally was the most complex and smallest fraction represent about 10-25% of the biomass weight (Anwar et al., 2014). Lignin also was a recalcitrant amorphous aromatic compound (Mathews et al., 2016). It is made up from a long chain, three dimension polymer (Harmsen & Huijgen, 2010) composed largely of phenyl-propane (3 carbon attached with 6 carbon atom rings) unit most commonly linked by ether bonds as a building block (Anwar et al., 2014).

More specifically, lignin is complex composed of complicated phenypropane unit that are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol are the one most commonly encountered (P. Wang et al., 2015). All of these are monolignols that are give rise to different type of lignin called phydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively generating a variety of structure and linkage with polymer (Yang et al., 2016). Lignin acts as a gap between cellulose and hemicelluloses in the plant biomass and behaves as insoluble three-dimension network. It plays important rule that are to transport water, nutrient and metabolism in the plant cell (Harmsen & Huijgen, 2010). It also acts as a binder between cells creating a composite material and has the remarkable resistance to impact, compression and bending (Harmsen & Huijgen, 2010)..

Lignin are bonded together the hemicelluloses and cellulose in the microfibril. Lignin is difficult to degrade due to their complex structure that is heterogeneity. Lignin is non-toxic, inexpensive, renewable and highly available either directly from plants or as by product from lignocellulosic conversion process. Industrial lignin is use chemical, heat or pressure to seperate lignin from cellulose and hemicellulose (Mathews et al., 2016).

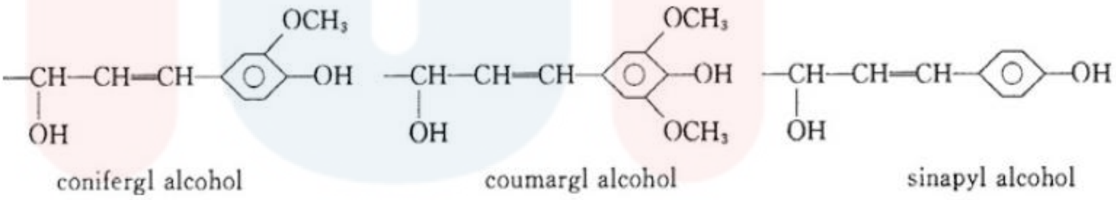


Figure 2.4: Macromolecular structures of lignin coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol (Chen, 2014).

2.4 **Microwave Irradiation for Torrefaction Process**

Microwave was a new technology that provides the many advantage over the traditional heating such as selective and controllable and cost efficient without direct contact with heated matter (Lin, 2015). There are consisting of electromagnetic wave with the frequency between 300 MHz and 300 GHz where their wavelength is between 1 m and 1 mm respectively (Huang et al., 2016). Microwave heating has two mechanism and both of them are able to heat material quickly and uniformly. The mechanism is dipole rotation and ionic conduction (Huang et al., 2016). Microwave heating is use in the pyrolysis or torrefaction of biomass material such as wood, sewage, sludge, coffee hulls, oil palm biomass and sugar cane bagasse (Huang et al., 2016).

2.4.1 Torrefaction temperature

Torrefaction was thermochemical treatment of biomass that are temperature is in the range 200-300 ^{o}C and they are carry out under atmospheric pressure in the absence of oxygen. The result shows the weight loss of the sample reduces as the torrefaction temperature are increase due to excessive devolatization (Anukam, Mamphweli, Reddy, Okoh, & Meyer, 2015).

When the torrefaction temperature was increasing, they had reduction on the moisture and volatile content in the sample (Anukam et al., 2015). Hemicellulose was started to decompose for the chemical composition at the 200-250 ^{o}C and were totally degraded when torrefied temperature at 300 ^{o}C for 2 hour (Shang et al., 2012). Whereas, the cellulose and lignin began to decompose at about 270-300 ^{o}C (Shang et al., 2012).The tensile failure strength and strain energy are clear reduce due to the increasing temperature (Shang et al., 2012). TAPPI Standard test was use to analyze the chemical properties of the sample which is the percentage of cellulose, hemicellulose and lignin whereas each property has their calculation due to TAPPI Standard.

2.4.2 Residence Time

The sample was undergoes the different of temperature that are 200 ^{o}C and 300 ^{o}C for 20, 40, 60 min to study effect of the different of residence time in sample. Due to its ability to consider the cumulated effect of both temperature level and residence time into consideration, the mass loss is good indicator of the extent of treatment (Oak, 2011). Since the temperature increase during the experiment, volatile in the biomass are not completely release to the atmosphere (Zhang et al., 2015). When the residence time increases, it will influence moisture, heat and mass of the sample due to the degradation of hemicelluloses, cellulose and lignin. When the residence time is longer, there are more mass and moistures content are loss from the sample (Zhang et al., 2015).

2.4.3 Heat Input

Heat input defined as the measurement the energy transfer in the material per unit length. Heat input can be calculate in the form of ratio of power to the velocity of the source like microwave (Funderburk, 1999). In this experiment, heat input is test by the sample was 100,200,385,540 and 700 W. The impact of microwave power is given more significant to the moisture content. For torrefied sample, there will give impact on increase the energy density biomass material but the moisture content will substantially reduced and the component has low weight compare to the raw (Chen & Kuo, 2010). In contrast, the raw sample has high content of moisture and lead to higher content of ash (Lin, 2015).

CHAPTER 3

MATERIAL AND METHOD

This experiment was used to compare chemical composition between raw and torrefied empty fruit bunch (EFB) in term of hemicelluloses, cellulose and lignin. All the sample for the torrefied empty fruit bunch was undergoes three parameters that are temperature, heat input and residence time. These parameters will influence the percentage of cellulose, hemicelluloses and lignin and lastly analyzed by using TAPPI Standard Method.

3.1 Material

The biomass material used in this study is EFB that showed in Figure 3.1. This sample was obtained from oil palm *(Elaeis guineensis sp.)* fruit bunch at Felda Kemahang at Tanah Merah, Kelantan. The study was done in the material technology laboratory at Material Science Laboratory and Wood laboratory in Agro Park at Universiti Malaysia Kelantan Kampus Jeli.

Figure 3.1: Sample of empty fruit bunch from palm oil

3.2 Methods

3.2.1 Preparation of samples

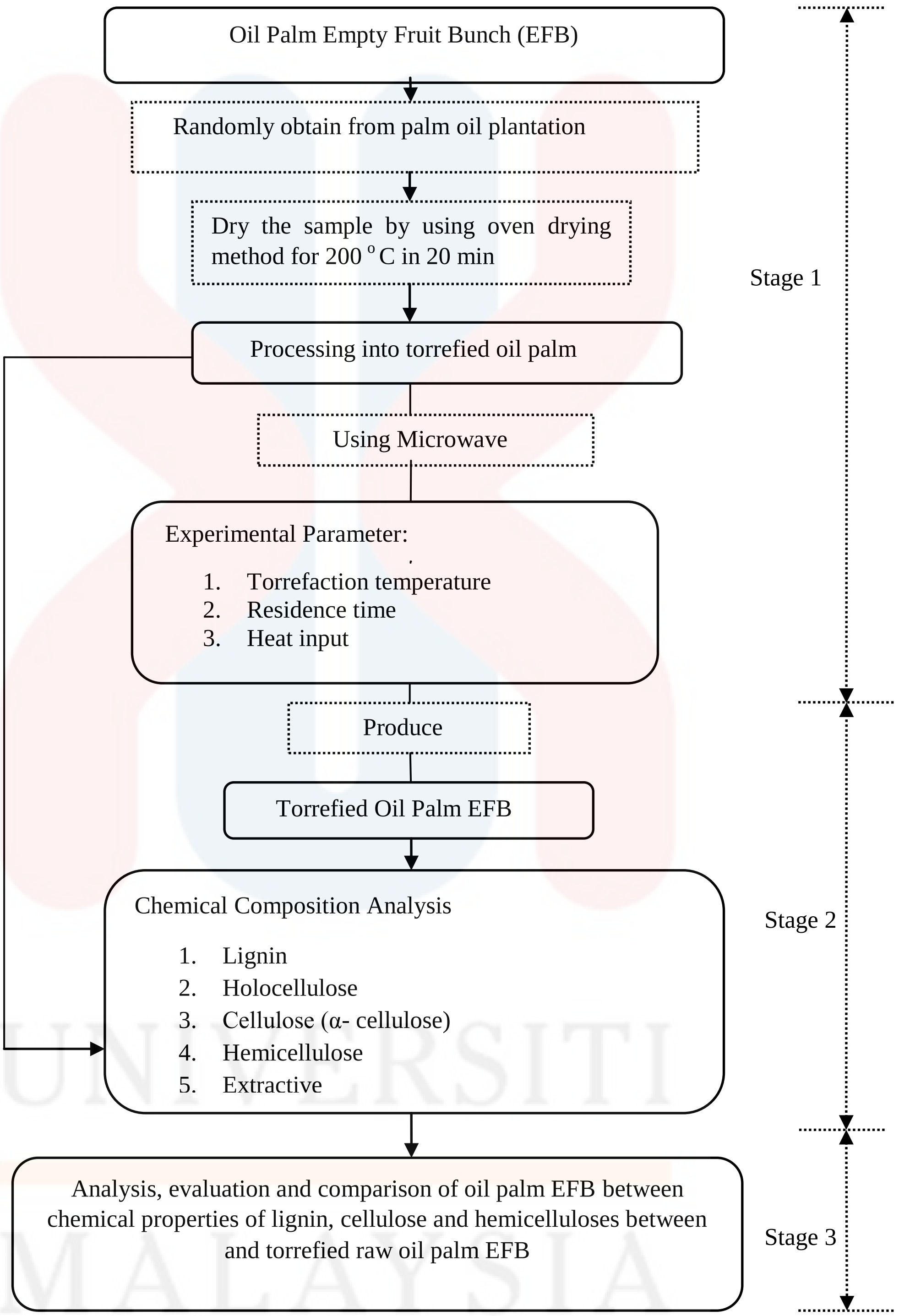
The objective of this study was produced the torrefied material by used microwave heating and to analyze the chemical properties of raw and torrefied materials and finally made a comparison between both of them. Process of torrefaction was started with the drying of sample to remove the moisture content using the oven drying method for 200 ^{o}C in 20 minutes. The sample was grinded by using grinder to reduce their size of particles. After that, the sample of raw EFB was divided into two parts. One part are the raw sample and the others are undergoes the torrefaction process.

Then, the biomass material undergoes the thermochemical process that temperature in the range 200 to 300 ^{o}C by using the microwave that are set up in Figure 3.2. The gas cooling system in the microwave has a function as to collect all the gases and liquid formed during the torrefaction process. The peristaltic pump has the function to pump out all the gases and liquid out from the microwave and the temperature controller function as to control the desired temperature that want to use during the heating process. Last but not least, the function of nitrogen gas tank is to provide the nitrogen gas into the microwave during torrefaction process. Three parameters that was controlled by the microwave which is heat input (100,200, 385, 540 and 700 W), temperature (200 and 300 ^{o}C) and residence time (20, 40, 60 min).

Figure 3.2: Set up of microwave

(a) Gas cooling system (b) Peristaltic pump (c) Temperature Controller (d) N_2 gas tank.

3.2.2 Flow Chart of Research Activities



Note:

Stage 1: Sample preparation (process include collecting, drying followed by experimental set up for microwave reactor) and processing oil palm EFB with variable parameter such as torrefaction temperature, residence time and heat input.

Stage 2: Testing of EFB based on the chemical composition.

Stage 3: Analysis, evaluation and comparison of the obtained experimental data

3.2.3 Preparation of Chemical Composition Analysis

The torrefied powder of empty fruit bunch (EFB) was analyzed the chemical composition. This chemical composition analysis was analyzed the composition extractive, holocellulose, cellulose, hemicelluloses and lignin by using the TAPPI standard method.

a. Determination of extractive

The experiment carried out by using extraction method solubility in Alcohol-Benzene extractive following TAPPI Test Method T264cm- 97 (1997) (Hemmasi, 2012). This experiment was started with approximately of 15 g sample of empty fruit bunch was weighted. Then, free thimble and free round bottom flask was weighted. The 5 g sample was placed on thimble and the thimble was placed at the soxhlet extraction.

After that, the 300 ml of Ethanol - Benzene with the ratio (2:1) was placed in the round bottom flask. The extraction was run for 6 until 8 hours in chemical fume hood. The extractive solution evaporated by using rotary evaporator in order to have only extractive. Then, the extractive will be obtained and put in the glass petri dish and the sample dried at 105 ^{o}C for 24 hours to get extractive. The soxhlet apparatus was set up as Figure 3.3 and the calculations of extractive in the sample like below.

$$\%\text{extractive}= \frac{Weight\ of\ extractive}{Weight\ of\ dry\ sample(g)}\text{x}100 \qquad (3.1)$$

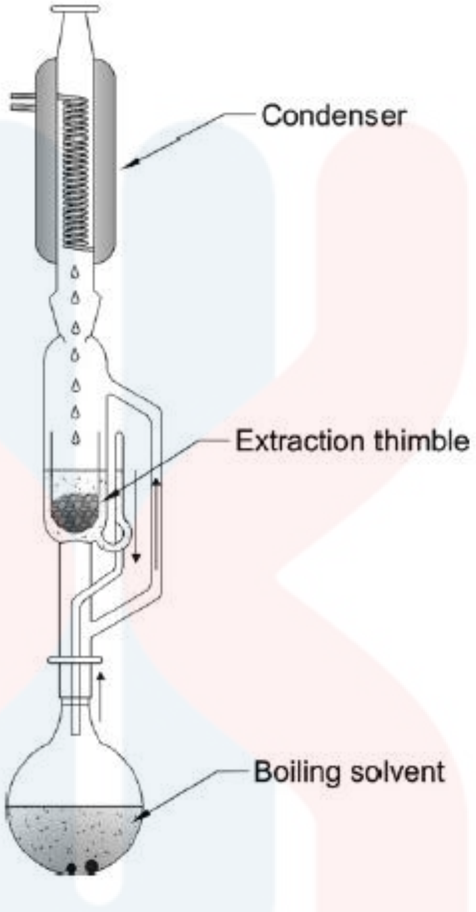


Figure 3.3: Set up of Soxhlet apparatus for extraction process (Zygler et al., 2012).

b. Determination of holocellulose

Holocellulose content was determined by using Wise *et al.*, 1946 method (X. Wang et al., 2012). In this experiment, 3g of sample was put into 250 ml conical flask and 100 ml of distilled water, 1.5 g Sodium Chloride crystals and 5 ml 10% acetic acid also was added. Then, the flask was put into 70˚C water bath.

The experiment conducted in fume cupboard. After 30 minutes, 5 ml 10% acetic acid was added and after 30 more minutes, 1.5g Sodium Chloride (NaCl) also was added. For every 30 minutes, 1.5g NaCl added, which sums to 6g, 4 hours duration. The sample was heated for 30 minutes more. After that, the sample was filtered with filter paper number four. Then the sample washed with cold distilled water 500 ml, acetone 15ml and left to dry in oven 60˚C for 24 hours. The equation was used to determine the holocellulose is show below.

$$\text{Holocellulose Content (\%)} = \frac{Weight\ of\ holocellulose\ (g)}{Weight\ of\ oven\ dries\ (g)} \text{ x } 100 \tag{3.2}$$

c. Determination of α-cellulose

The content of α-cellulose then was determined and compared. The content determined by using the Equation 3.3 below. In this experiment, TAPPI T203 os-74 (1997) method was carried out and handle in ice water bath (Hemmasi, 2012) . Firstly, 1g holocellulose was mixed with 15ml 17.5% NaOH in 250ml beaker. Then, the solution stirred slowly for 1 minute, 10ml 17.5%, and after 45 seconds, the mixture added 10ml more of 17.5% NaOH. The mixture then left for 3 minutes and after 2.5 minutes, the mixture was added 10ml more of 17.5% NaOH, and at minute 5 and 7.5 added the same amount which sums to 65ml of 17.5% used.

Then, 100 ml of cold distilled water was added and stir quickly for 30 minutes. Next, the cellulose was filtered with filter paper number 4. Beaker and leftover was washed by using 25ml 8.3 % NaOH. After that, the sample washed by using 250ml of distilled water and then soaked with 15ml of 10% acetic acid for 5 minutes. Samples then dried in 50˚C oven for 24 hours and finally weighted and recorded.

$$\alpha\text{- cellulose (\%)} = \frac{Weight\ of\ \alpha-cellulose(g)}{Weight\ of\ oven\ dry\ holocellulose(g)} \times 100 \tag{3.3}$$

d. Determination of hemicellulose content

Hemicellulose determined by using the following equation 3.4.

$$\text{Hemicellulose} = \text{Holocellulose} - \alpha\text{-cellulose} \qquad (3.4)$$

e. Determination of lignin content

Lignin determination was carried out based on TAPPI T222 om-88 (2002) method (Saad & Ibrahim, 2014). Firstly, 1g sample was put into 150 ml beaker and placed in iced water bath. The 25ml of 72% Sulphuric acid (H_2SO_4) was added and stirred with glass rod for every 10 minutes for 2 hours. Then, mixture was transformed into 1L conical flask that already contains 400 ml distilled water, and heated in hot plate at 170˚C with reflux for 4 hours. The sample cooled overnight and filtered and wash with hot 500 ml distilled water until pH level neutralized. Lastly, the sample dried until the weight is constant. The lignin content was determined by using equation 3.5.

$$\text{Lignin (\%)} = \frac{Weight\ of\ Lignin\ (g)}{Weight\ of\ oven\ dry\ extractive{-}free\ (g)} \times 100 \qquad (3.5)$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result overview

Microwave was defined as high-frequency electromagnetic wave placed between radio frequency and the infrared light region of the electromagnetic spectrum that are consist frequency range from 0.3 to 300GHz corresponding to the wavelength of 1m to 1 cm (Lopez, Clara, & Mae, 2014). In this study, the microwave assisted to undergoes the torrefaction process for the empty fruit bunch fiber (EFB). This microwave has to control all the parameter which is power level (Watt), temperature (°C), volume of nitrogen (ml/min) and mass of sample (g) during the torrefaction process. The biomass material used in this study is empty fruit bunch (EFB). EFB was obtained from oil palm *(Elaeis guineensis sp.)* fruit bunch. The main reason EFB was chosen as research material because the factor of abundant material. In Malaysia, the total crop of fresh fruit bunch is more than 30 million tons per year, which generated more than 10 million ton of EFB. Only 10% of the EFB was used and the rest are abundant (Ngadi & Lani, 2014). Besides that, EFB fiber contain about 40% to 60% cellulose, 15 to 25% of hemicellulose and 12% to 20% of lignin and it has the highest composition of cellulose compare to coir, corn, bagasse and kenaf fiber (Ching & Ng, 2014).

4.2 Effect of heating rate towards the power selection.

Based on study by Mertke & Aneziris (2014), the alumina crucible able to retain their strength when thermal shock at 14.51 MPa, maximum temperature 500°C and the maximum thermal expansion of alumina crucible was 7.2 x $10^{-6}K^{-1}$ (Kuscer et al., 2016). Based on observation in Table 4.1, the increase the heating rate will increase the value of thermal expansion. The cracking of alumina crucible was happen due the factor of alumina crucible not able to withstand thermal expansion more 7.2x $10^{-6}K^{-1}$ and the crack was happened in this study when the power used more than 385 W. At 540 W, the thermal expansion produce was $27.8 \times 10^{-6}K^{-1}$ whereas at 700 W, there was produce $37.7 \times 10^{-6}K^{-1}$ that is exceeds the maximum value used during heating process and cause the cracking happened.

Table 4.1: Heating rate and thermal expansion of alumina crucible on power selection.

Power (watt)	Heating rate (°C/min)	Thermal Expansion (K^{-1})	Condition
100	2.86	6.94×10^{-6}	Not crack
230	4.54	7.34×10^{-6}	Not crack
385	20.90	7.74×10^{-6}	Not crack
540	29.00	27.8×10^{-6}	*Crack
700	41.60	37.7×10^{-6}	*Crack

*Notes: $7.0-8.0\times 10^{-6}$ K^{-1} was the maximum value of thermal expansion alumina to retain the cracking issue (Kuscer et al., 2016).

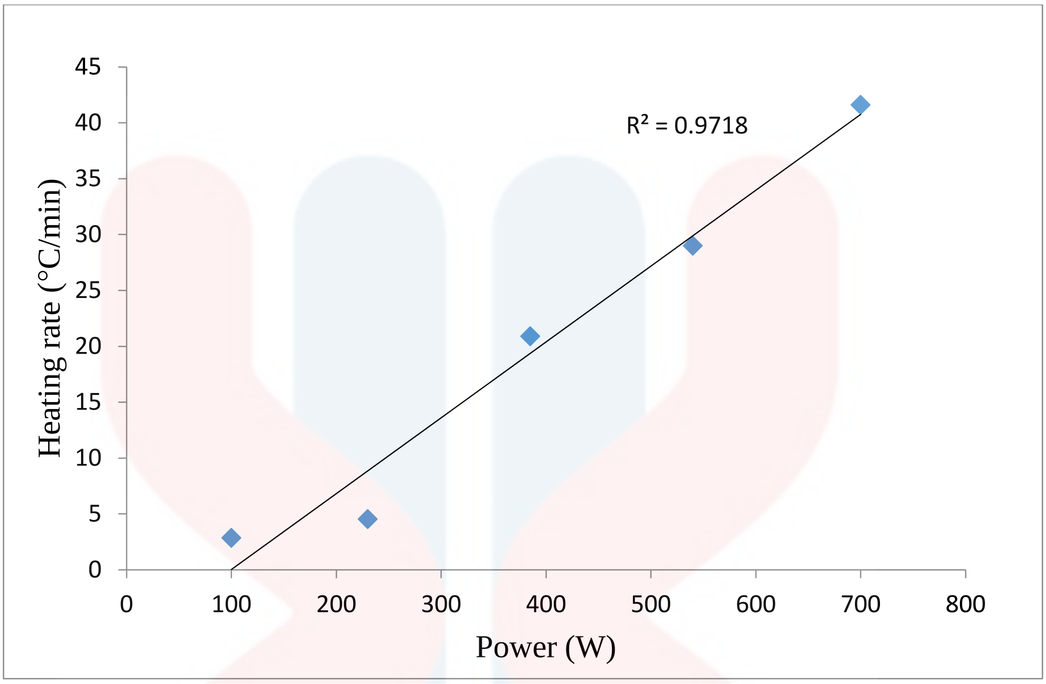


Figure 4.1: Heating rate effect on power selection.

Figure 4.1 shows the result heating rate of EFB that handle on the different power on 500 micron. Heating rate can be defines as the ability of the sample to increasing temperature per minutes while conducting sample. Huang, Chiueh, Kuan, & Lo (2016) stated that the heating rate increase with the increasing microwave power level. The finding close to the result yield that is the trend of heating rate increase drastically when the power increase. At 100 W, the heating rate produced was 2.86°C/min whereas at 700 W the heating rate was 41.60 °C/min.

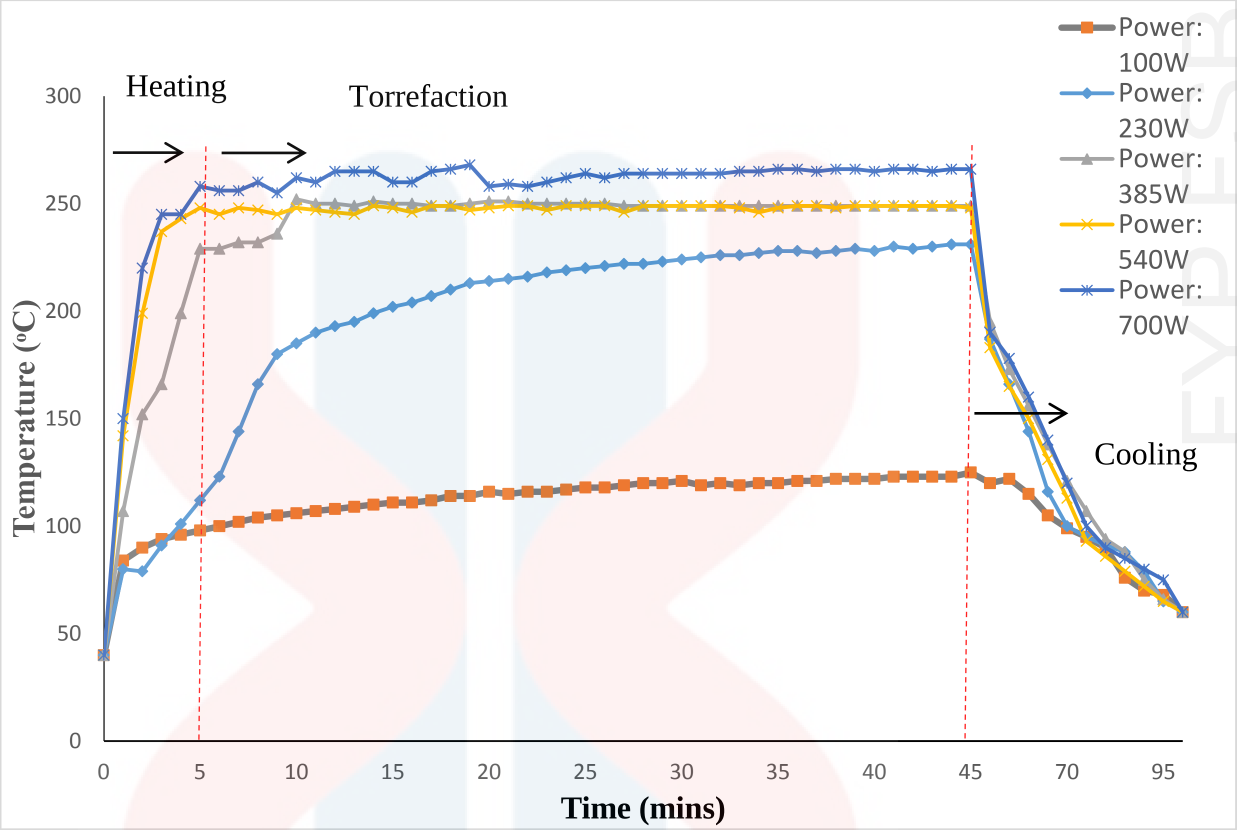


Figure 4.2: Temperature profile in torrefaction power.

In this study, 500 micron of EFB were heated at microwave power level for 100 W, 230 W, 385 W, 540 W and 700 W. 15 ml/ min of nitrogen was purged inside the microwave to maintain their inert atmosphere and the heating process was run in 45 minutes. The different power used will affect the temperature reading of the samples. From the pattern in the Figure 4.2, one of the best powers will be selected among all the power level.

Based on the previous research by Liu (2016), at 400-700 W, there are experienced three stages including slow temperature-rising, a rapid temperature-rising stage and a slow temperature-reduction stage. In this study, at higher power such as 385W, 540 W and 700 W, the trend shows the slow temperature rising at minutes 1 until 10, followed by rapid temperature rising and lastly reduction state or cooling state. This trend matched with the previous research trend. When the power used at low rate like 100 W and 230 W, the trend of the temperature only experience two steps that are slow temperature rising then followed with temperature-reduction state. The low power, 100 and 200W was insufficient to used as torrefaction power for heating process due to lower heating value (Huang et al., 2016). The heating rate for 100 W and 238 W was 2.86 and 4.54 °C/min.

As a conclusion, the most suitable power to be selected in this study was 385 W because they were achieve all the criteria need in this study like achieve the optimum temperature within three stage of heating rate. After that, the sample produce after torrefaction heating process are not include the ashes phenomena that will affect the final result of chemical composition analysis. Ash phenomenon occurs as residue powder left after the heating process in white colour. This phenomenon occurs due the overload heating rate use in this study (Bach, Chen, Lin, Sheen, & Chang, 2016). Lastly, heating rate of 385 W was able to withstand with thermal shock and thermal expansion that is 7.74×10^{-6} K^{-1} in range $7.0 - 8.0 \times 10^{-6}$ K^{-1} that are safe from cracking issues.

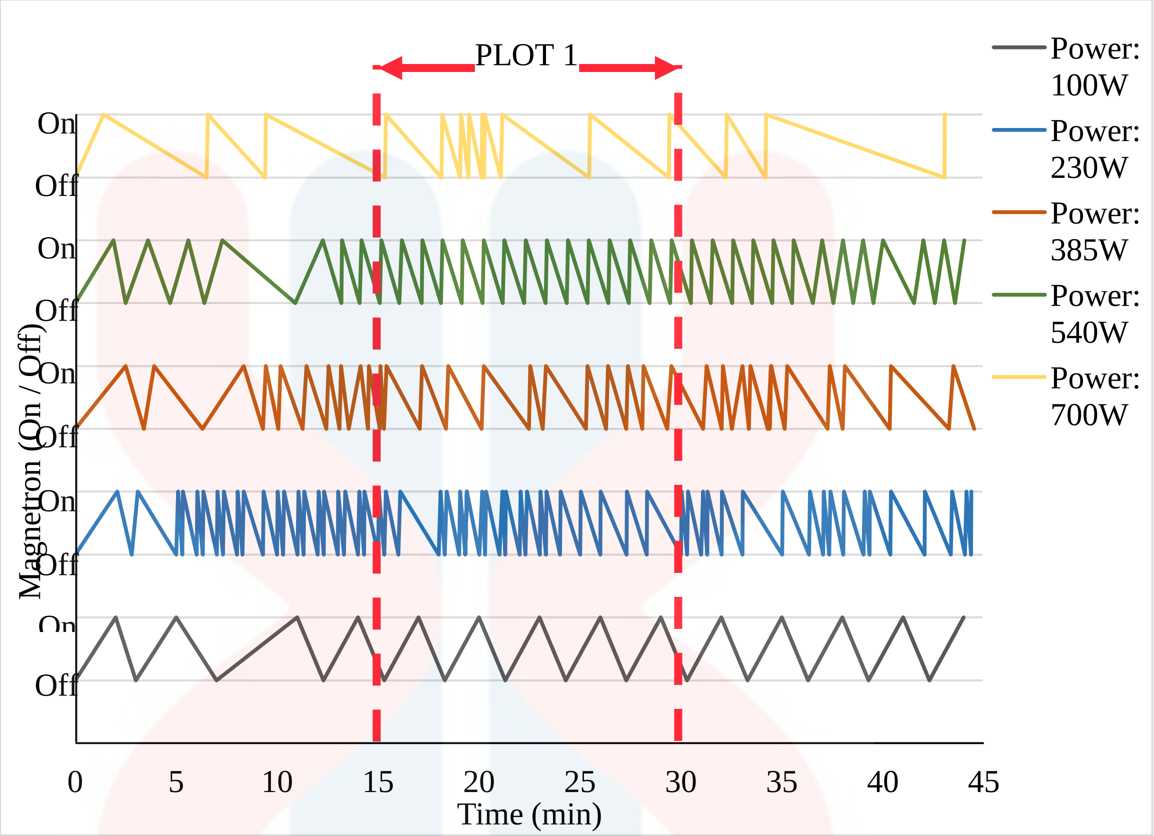


Figure 4.3: Magnetron effect on power selection.

Yeon, Jo, & Min (2017) stated that the magnetron in the microwave generate 2.45 GHz wave discharge operated at power level of 50-1000 while in this study used similar frequencies. Movement of magnetron was calculated by on/off the light produce during the heating process. The higher the power level used, the higher the electron will be produce in the microwave. The on/off light in the microwave during heating process are shows about the formation of electron inside the microwave. Based on observation in Plot 1, at power level 100W, the on/off peak inside the microwave quit stable. In this power, the peak ‘on’ are delay for 1 mins. The electron will be produce more at 100 W but this power cannot be selected as a best power to use in this study due the low heating rate. At 200 W, their peak was too sharp and the peak ‘on’ only delay for a few second. In this situation, the electron produce was too low and not suitable to be select as a power used in this study. At high power such as

540 and 700 W, the peak ‘on’ delay for a long time especially for 700 W that are delay for 5 minutes. The higher electron could be produce during the delay time but this power cannot be as selected power due to thermal shock, thermal expansion and ashes phenomena. The best power that be selected to used in this study was 385 W where the peak ‘on’ delayed for 1-2 minutes. The electron produced not high as at 700W but in this power level, the problem such as thermal shock, thermal expansion and ashes phenomena will be avoided.

4.3 Effect of power on fractional biomass.

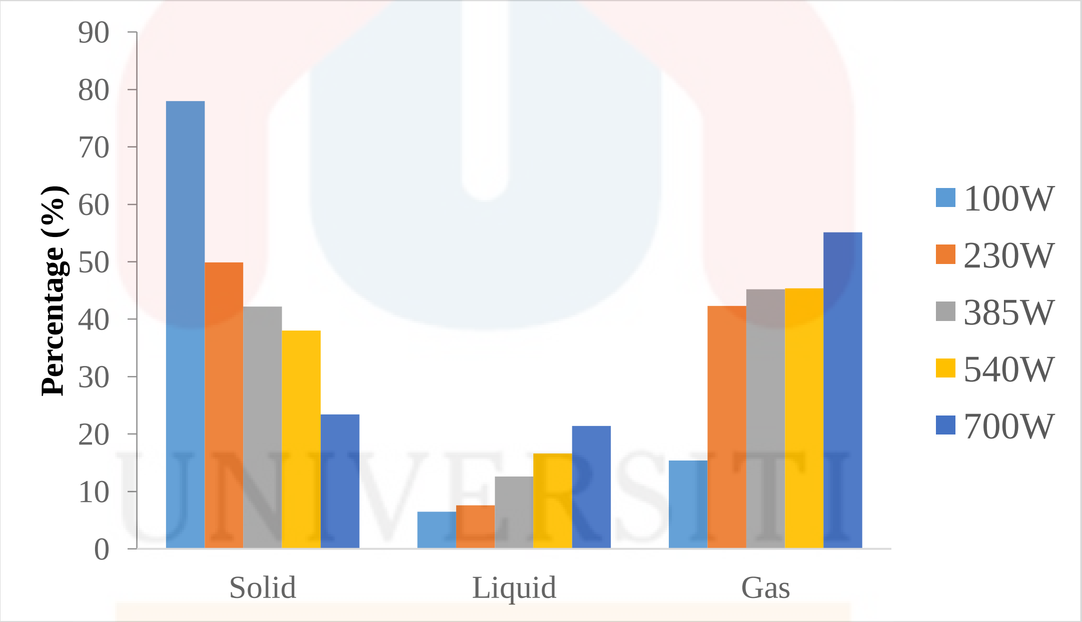


Figure 4.4: Effect rate of power on fractional biomass.

Figure 4.4 shows the comparison yield of solid, liquid and gas after the heating process in the different microwave power. The power use was influenced the final percentage of the solid, liquid and gas. Solid and liquid fraction was determined from weight changes before and after the cooling process while gas fraction was taken from by-product of liquid fraction from 15 g of the EFB (Jamaluddin et al., 2013). The minimum and maximum power was used for this study was 100 W and 700 W. From the observation from trend of percentage of solid above, the increase the power used will reduced the percentage of remaining solid due to the evaporation of moisture content and slight decomposition of cellulose, hemicellulose and lignin inside the sample (Chen & Kuo, 2011). The highest percentage of remaining solid produce after the heating process was at 100 W with 78 % of solid whereas the lowest solid percentage produces at 700 W that is 22%. Lin (2015) stated that the microwave power at 450W used within 30 minutes formed only 23-33% of solid yield. Based on the graph above, sample EFB was applied by power 540 W for 45 minutes finally comes out with 20% of remaining solid that was near with the previous research.

Contrast from the trend percentage of solid, the trend for remaining liquid percentage was increase due to power increase. When 100 W applied towards EFB sample, the percentage of remaining liquid was 7% whereas at 700 W, there are slightly increase to 20%. This situation was explained by previous study by Wright, Boardman, & Hess (2011) proved that water was release as major condensable product. Water was released when the degradation of acetoxy- and methoxy- group in xylose unit present hemicellulose fraction. The increase the power and torrefaction temperature used towards the sample, the increase the condensable product after the torrefaction process. Same situation happened to liquid, the trend for of percentage remaining of gas also increases due to power used from 100 W until 700 W. The highest percentage of remaining gas obtained from this study was 50% at 700 W where the lowest percentage was 10% that used 100 W of power. In torrefaction process, the major gasses formed were carbon dioxide (CO2) and carbon monoxide (CO). The ratio of CO to CO2 increased with temperature and power used because the factors of the degradation of cellulose and lignin at high temperature and power (Wright et al., 2011). Hydrogen and methane also detected in non-condensable product.

4.4 Effect temperature on mass loss of biomass.

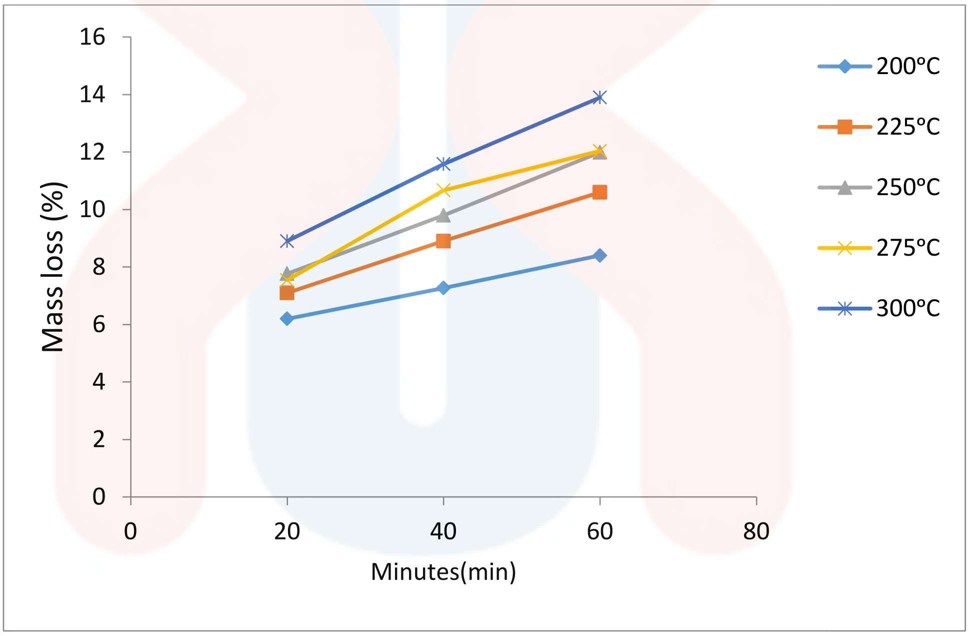


Figure 4.5: Effect of temperature on mass loss of biomass.

Based on the observation in Figure 4.5, the maximum of the weight loss observed for EFB was about 13.90% at 300°C in minutes 60 and the lowest mass loss was at 200 °C in minutes 20 that are 6.2%. This was expected because as time goes by, more water in EFB is evaporated leaving behind the solid and lead to the mass loss. In addition, the trend for 300°C increase drastically compared to other temperatures. Referring to the Harun, Afzal, & Azizan (2010),the mass loss also occurs when higher temperature and residence time that promotes the higher evaporation and changes the solid to gases form. This is because more cracking occur at high temperature resulting the higher gas yield and lower solid yield. This previous trends also was proved by this study in effect rate of power on yield of solid, liquid and gas above in Figure 4.4.

After finished all the study about effect of heating rate on different power, effect temperature on power selection, effect magnetron on power selection, effect power on fractional biomass and effect temperature on mass loss, there are some conclusion that come out from this study. Firstly, the best power that comes out with the high amount of torrefaction product was 385 W. This power had been selected in this study because of the factor formation ashes phenomena, thermal shock and thermal expansion inside the alumina when the higher power used. After that, the amount of nitrogen selected was 15ml/min and actually does not give huge effect to the mass yield instead for to ensure an inert atmosphere inside the microwave during heating process (Bach et al., 2016).Lastly, the mass had been selected in this study was 15 g. This mass was already proved as suitable mass because the process selection will come out with maximum yield among the other mass.

4.5 Chemical Properties of Empty Fruit Bunch (EFB)

Chemical properties study was looking at several chemical compositions that were analyzed consist of extractives, holocellulose, α-cellulose, hemicellulose and lignin in raw and torrefied sample. For free extractive the data collected was used only for extractive percentage calculation. These free extractives were used for other chemical compositions holocellulose, α-cellulose, hemicellulose and lignin analyses. The result was comprised and discuss between raw and torrefied of EFB. The temperature used only two that are 200 and 300 °C and each temperature consist of 3 residence time that was 20,40 and 60 minutes.

Chemical properties of EFB were determine with the respective TAPPI standards for different component namely T-9m-54 for holocellulose,T-222 for lignin, T-203 OS-61 for hot water soluble, T-212 FOR 1% NaOH soluble and T-204 for ethanol-benzene extractive (Industry & Formic, 2011). Based on the data collected in this experiment, the most abundant properties in EFB is holocellulose. From the previous research by Ferrer (2011), holocellulose consists of the highest chemical content in EFB which is 66.97%. The second highest chemical content in the EFB is α-cellulose that are consist 47.91% and lastly lignin that are consist 24.45%.

4.5.1 Extractives

Extractive present in plants may be extracted using alcohol-organic solvent. After the drying and torrefaction process into the sample, the sample was subjected into the soxhlet extraction by using (2:1) ethanol: benzene to avoid present of lignin and polyphenolic compound in extractive-free. This extractive- free was needed into the next step that was to find holocellulose (Pelaez-samaniego et al., 2014).

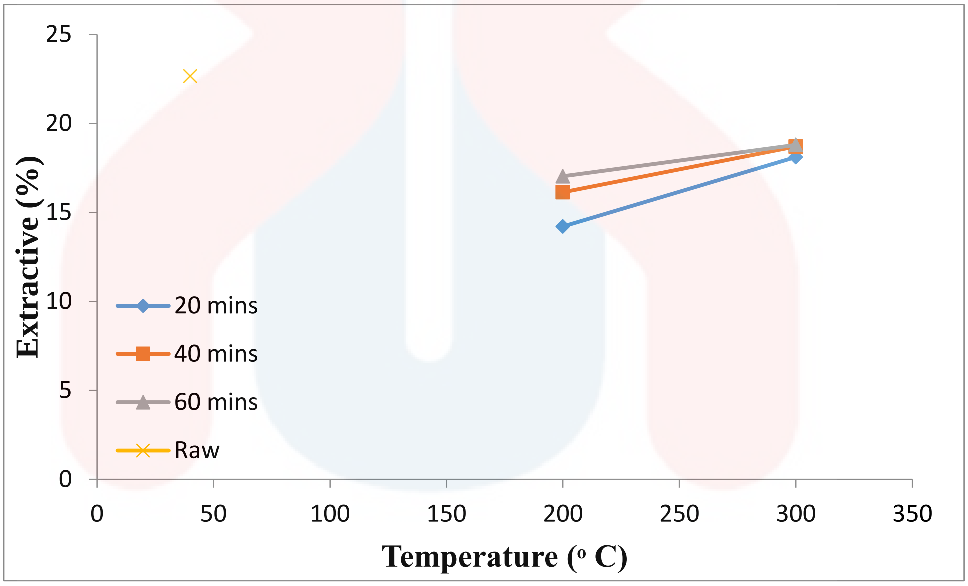


Figure 4.6: Effect temperature on percentage of extractive.

Based on Figure 4.6 above, extractive content is highest at raw EFB that are 22.65% compared to other torrefied sample. The lowest extractive percentage was sample (200°C, 20 min) that are 14.20%.The trend of the graph above slightly increase from 200 to 300°C, means that the extractive content produce after extraction process are high in 300°C compare to 200°C. The trend for minutes 20 was increased gradually when temperature increase compared to other 40 and 60 minutes. Observation recorded includes, the colour of the extractives obtained after the Soxhlet extraction process made during the study. There are showed darker colour for sample (300°C, 20 minutes) which is more concentrated, compared to the other samples. Extractive content in sample (300°C, 20 minutes) are relatively second higher after raw EFB. As a conclusion the darker the colour of sample after extraction process, the higher the concentrated of extractive product.

4.5.2 Holocellulose

Chemically, holocellulose is the mixture of cellulose and hemicellulose in EFB fiber, the fibrous residue that remain after the extractive, the lignin, and the ash forming element have been removed (Yaman & Kucukbayrak, 2010). Holocellulose consist of the highest percentage of chemical content among the others composition in EFB which is 66.97% (Sudiayani et al., 2011).

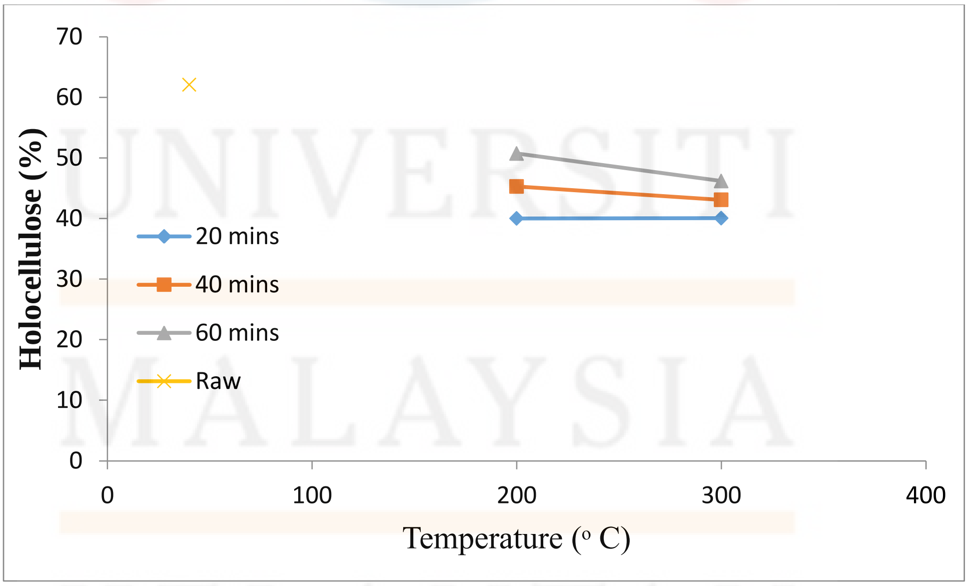


Figure 4.7: Effect temperature and time on percentage of holocellulose.

In this study, holocellulose in raw sample recorded the highest percentage content that is 62.08%. The holocellulose from raw EFB consist of 36.30 % of α-cellulose and 25.78 % of hemicellulose. The percentage of holocellulose obtain by this study are close with previous study by Sudiayani (2011) that come out with EFB consist of 56.49% as the total biomass. There are consist 33.25% of α-cellulose and 22.24 % of hemicellulose. Perkebunan (2011) also prove that the holocellulose of raw EFB was 66.97% that also strongly supports the result obtain in this study.

The lowest percentage of holocellulose was sample (200°C, 20 min) that consists of 24.01% which comprise 20% of α-cellulose and 20.01% of hemicellulose. This degradation of holocellulose happen because the degradation of hemicellulose and the increase the percentage of cellulose obtained due to the rise of temperature in the raw and torrefied sample.

The temperature and the times of torrefaction play a main role for final percentage of the holocellulose. The percentage of holocellulose starts to decrease when temperature increases and degradation decrease sharply for the minutes 60 compared to others 20 and 40 minutes. It was proved that the temperature and time of torrefaction process influenced the final percentage of holocellulose. Chen (2014) stated that the heating period 10 to 30 mins caused difficult to determine precise torrefaction time to perform torrefied sample. The samples not reach fully the torrefaction temperature in this period. Esmeraldo (2010) also reported that the holding time will affect the amount of holocellulose to support the result obtain in this study.

4.5.3 α-cellulose

α-cellulose is the major component of wood and paper pulp. It was separated from the other components by soaking the pulp in a 17.5% solution of sodium hydroxide. One of three classes of cellulose, alpha cellulose has the highest degree of polymerization and is the most stable. The other two class, known as beta cellulose and gamma cellulose (Rawangkul, Khedari, Hirunlabh, & Zeghmati, 2010).

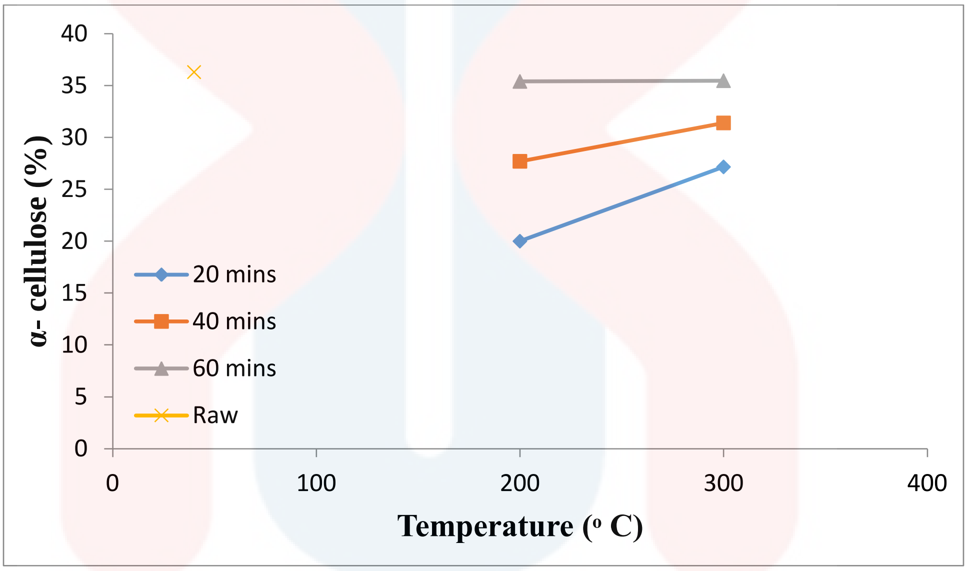


Figure 4.8: Effect temperature and time on percentage of α-cellulose.

Based on Figure 4.8 shows the highest percentage of α-cellulose that are raw EFB with 36.30% whereas sample (200°C, 20 min) shows the lowest percentage that are 20%. Chen & Kuo, (2010) stated that cellulose was depleted at light torrefaction from 200-235°C and mildly affected at severe torrefaction (275-300°C). The increasing temperature lead to more cellulose consumed. This phenomena happen because of the disruption inside cell wall matrix including the connection between carbohydrate and lignin as well as depolymerization and solubilizing the hemicellulose leaving the α-cellulose content (Ramli, Junadi, Beg, & Yunus, 2015).

These finding are close to result yielded in this study that are state that the percentage of cellulose at temperature 200°C show the lowest reading. After 200°C, the percentage of cellulose started to increase until degradation temperature and the main decomposition of cellulose occur at 315- 400°C (Yaman & Kucukbayrak, 2010). The percentage of cellulose shows the highest at 300°C. When the sample has longer treated by torrefaction, the percentage of the cellulose was also increase but the percentage of torrefied sample not high as raw EFB. The percentage of cellulose relatively highest at minutes 60 compared to other 20 and 40minutes. This was proved that, temperature and times influenced the final percentage of cellulose.

4.5.4 Hemicellulose

In previous study by Silva (2017), xylan or hemicellulose prepared by alkaline extraction was acidic polysaccharides containing arabinose (50.0%), xylose (38.5%), and uronic acid (9.0%) by using sodium hydroxide (NaOH) and followed by the alkaline filtrate. Hemicellulose plays a fundamental role in linking the fibers of cellulose to each other (Chen et al., 2014).

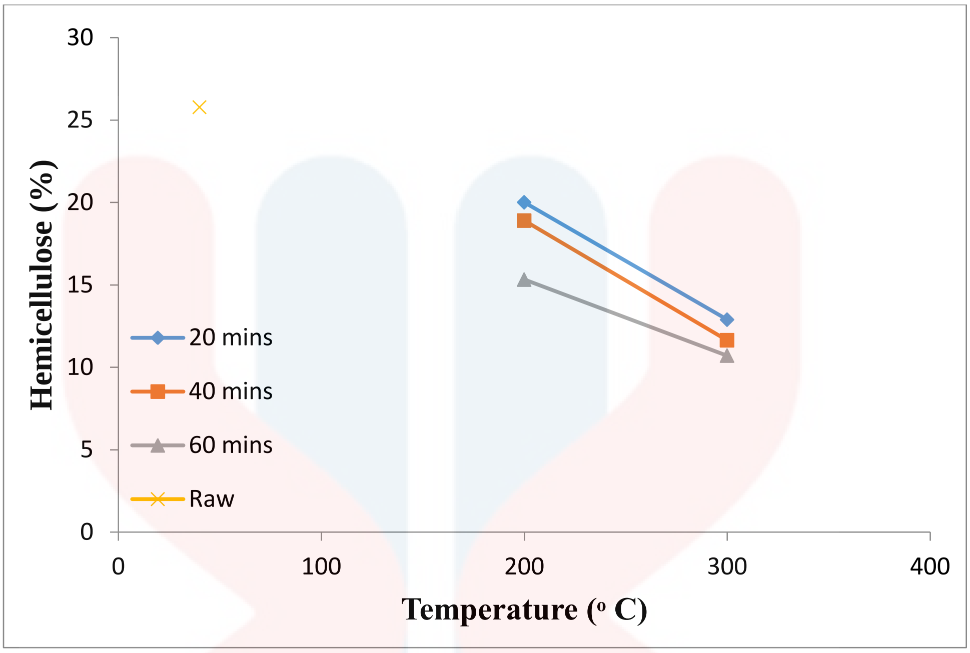


Figure 4.9: Effect temperature and time on percentage of hemicellulose.

Based on observation on Figure 4.9 above, the hemicellulose in raw EFB shows the highest percentage that are 25.78% where sample (300°C, 60 min) shows the lowest reading that was 10.71%. Shen (2015) proved that the degradation of hemicellulose takes place in temperature range 200-350 °C or even lower. These finding was close to the result obtained in this study. From the figure above, the percentage of hemicellulose was slightly dropped starting from 200°C. When the trend reached 300°C, the hemicellulose content was totally low especially for minutes 60 that are from 15.32% at 200°C to 10.71% at 300°C.

The degree of hemicellulose degradation due the increase of time occur because of the factor of the damage hydroxyl group in hemicellulose (Chen et al., 2014).The percentage of hemicellulose was nearly lost especially for minutes 60 at 300°C due to degradation compared to minutes 20 and 40. This case happen because, the sample was precisely reaches the torrefaction temperature. As a conclusion, minutes 60 were the best residence time to hemicellulose to fully reaches the torrefaction temperature and starts the rapidly degradation.

4.5.5 Lignin

Lignin was particularly important in the formation cell wall and gives strength to the fibrils and polysaccharides, especially cellulose and hemicellulose (Ramli et al., 2015). The lignin was different between the types of wood. The content in EFB was 25.83% where the lignin content in the hard wood is 18-25% that are low compared to the non-woody plant (Sudiayani et al, 2010). The high lignin content was the main reason of alkaline-pre-treatment which was applied to EFB. By this pre-treatment, the lignin will be removed and composition of lignin decreased.

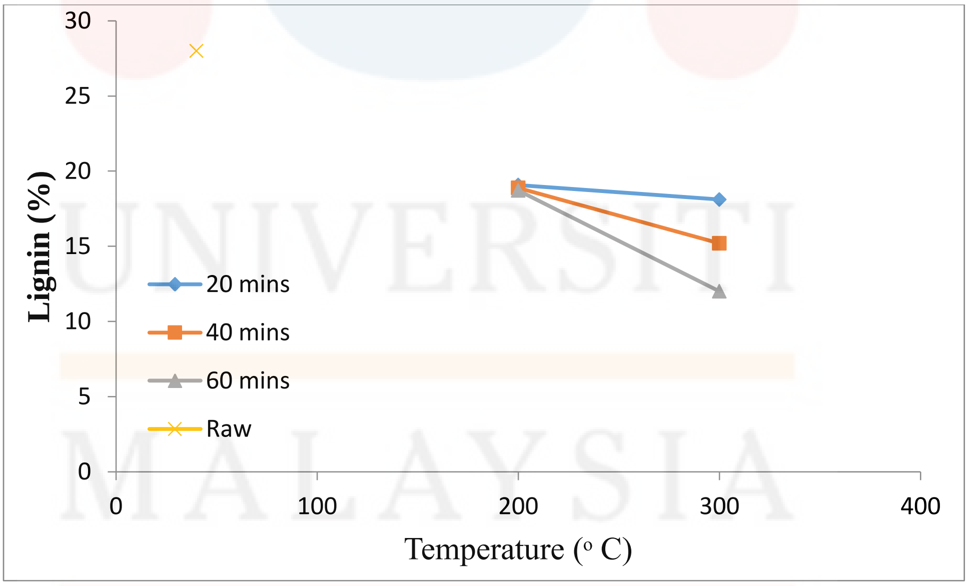


Figure 4.10: Effect temperature and time on percentage of lignin.

Chen, Peng, & Bi, 2015 stated that when biomass is torrefied, the pre-treatment been categorize into light, mild and severe torrefaction, corresponding to the temperatures approximately 200-235°C, 235-275 °C and 275-300°C, respectively. Lignin was most difficult to be thermally degraded because their decomposes was in much wider temperature range compared to the cellulose or hemicellulose (Dieguez-alonso, Anca-couce, Zobel, & Behrendt, 2015).

Based on the Figure 4.10, the highest percentage of lignin was in raw EFB that consist of 28% where the lowest value of lignin was for the sample (300°C, 60 min) with 12.01%. The percentage of lignin has a nearly value for minutes 20, 40 and 60 at 200°C and there were show that there are only small degradation happen at this temperature. The trend rapidly decrease when there are achieve the temperature 300°C.Similar trend observable, there was proven that the degradation of lignin was started at 275°C. Trend percentage of degradation of lignin can see clearly at temperature 300°C in minutes 60 compare to other minutes. These finding are close to the previous research that prove that holding times more than 30minutes are the better compare to the less than 30 minutes. From the observation, minutes 60 were the best for the lignin degradation.

Lignin is difficult to degrade due to their complex structure that is heterogeneity. More specifically, lignin is complex composed of complicated phenypropane unit that are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol are the one most commonly encountered (Popova et al., 2016). When the degradation of the lignin occurs, these chemical properties will breakdown into sugar breakdown product like furfural and 5-hydroxylfurfural.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The data acquired from this study on comparison chemical properties in raw and torrefied Empty Fruit Bunch (EFB) is useful for the future research. The finding in this study determined that the torrefied EFB was a very useful resource for manufacturing the carbon product use as feedstock material in steam power plant application. Both of objectives in this study was successfully achieved in this study that were able to produce the torrefied material using microwave heating. Microwave was success to control all the parameter during the torrefaction process that is 200 and 300°C, residence time (20,40 and 60 min) and power level (100,200,385,540 and 700W).

The chemical properties which are extractives, holocellulose, α-cellulose, hemicellulose and lignin of raw and torrefied EFB was successful analyzed by using TAPPI standard and equation. During torrefaction, the degradation of hemicellulose occurs in light torrefaction when the temperature reaches 200°C and degradation of cellulose and lignin occurs in severe torrefaction at 300°C. This chemical properties induced by torrefaction thoroughly studied in this study. The best torrefaction sample that suitable to use to as feedstock material in steam power plant application was (300 °C, 60 min) due to the lowest lignin content, and highest holocellulose content. Lignin act as a binder between cellulose and hemicellulose and when the lignin was degrade, the structure of sample was brittle and will improve their grindibility. Besides that, the sample (300 °C, 60 min) contain the high mass loss and easy for transportation compared on raw EFB.

5.2 Recommendation

In the future, if this study is to be continued, there are several recommendations that can be considered which is firstly to further studies in chemical properties to be compared with other part in EFB like biomass from oil palm residue include the oil palm trunks (OPT) and fronds (OPF), kernel shell, EFB, presses fruit fiber (PFF) and palm oil mill effluent (POME) (Ngadi & Lani, 2014) due to it is widespread abundant in Malaysia besides Empty Fruit Bunch (EFB) itself. Besides that, the further study must look a new type of crucible material that has ability to retain with high temperature, thermal expansion and high thermal shock such as boron nitride or quartz. Lastly, the further study must be more exploration in heating rate by design a heating rate controller. In this study, it only able to control temperature because use temperature controller, but not able to control the overload heating rate due to lack of heating controller that cause the thermal shock and ashes phenomenon.

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APPENDIX A - RAW DATA AND CALCULATION

A.1 DATA CALCULATION

A.1.1Heating rate

Heating rate = $\frac{Temperature}{minutes}$

$= \frac{250°\mathrm{C}}{15\ min}$

= 16.67 $°\mathrm{C/min}$

A.1.2 Thermal Expansion

$$\frac{\Delta L}{L_o} = \alpha\Delta T$$

$\frac{8.437-8.4}{8.4} = \alpha\ (600)$

$$\alpha = \frac{0.0044}{600}$$

$\alpha = 7.74\times10^{-6}\ \mathrm{K}^{-1}$

A.1.3 Mass loss (200 °C, 20 min)

Mass loss (%) = $\frac{Mass\ before\ (g) - mass\ after(g)}{mass\ before} \times 100$

$= \frac{15g - 14.07g}{15g} \times 100$

$= 6.2\%$

A.1.4 Extractives

% extractive = $\frac{Weight\ of\ extractive}{Weight\ of\ dry\ sample(g)}$ x100

$$= \quad \frac{1.11}{4.9} \times 100$$

$$= 22.65\%$$

A.1.5 Holocellulose

$$\text{Holocellulose Content (\%)} = \frac{Weight\ of\ holocellulose\ (g)}{Weight\ of\ oven\ dries\ (g)}\ \text{x}\ 100$$

$$= \frac{3.0419}{4.} \times 100$$

$$= 62.08\%$$

A.1.6 α-cellulose

$$\alpha\text{- cellulose (\%)} \quad = \frac{Weight\ of\ \alpha{-}cellulose(g)}{Weight\ of\ oven\ dry\ holocellulose(g)} \times 100$$

$$= \quad \frac{0.3957}{1.090} \quad \times 100$$

$$= 36.30\ \%$$

A.1.7 Hemicellulose

Hemicellulose (%) = Holocellulose – α-cellulose

= 62.08– 36.30

= 25.78%

A.1.8 Lignin

$$\text{Lignin (\%)} = \frac{Weight\ of\ Lignin\ (g)}{Weight\ of\ oven\ dry\ extractive{-}free\ (g)} \times 100$$

$$= \quad \frac{1.372}{4.9} \quad \times 100$$

$$= \quad 28\%$$

A.2 RAW DATA

A.2.1 Extractives

Temperature (°C)	Times (min)	Sample Weight (g)	Dried Extractive weight (g)	Extractives Content (%)
Raw	-	5.0193	1.1100	22.65
200	20	5.0094	0.6910	14.20
200	40	5.0034	0.7464	16.13
200	60	5.0120	0.7240	17.02
300	20	5.0013	0.9750	19.98
300	40	5.0076	0.8950	19.05
300	60	5.0106	0.8240	18.79

A.2.2 Holocellulose

Temperature (°C)	Times (min)	Free Extractives Weight (g)	Holocellulose weight (g)	Holocellulose Content (%)
Raw	-	1.0800	3.0419	62.08
200	20	1.0050	1.9465	40.01
200	40	1.0030	2.0956	45.28
200	60	1.0120	2.1576	50.72
300	20	1.0900	1.9548	40.05
300	40	1.0070	2.0255	43.08
300	60	1.0100	2.0255	46.18

A.2.3 α-cellulose

Temperature (°C)	Times (min)	Holocellulose weight (g)	α-cellulose weight (g)	α-cellulose Content (%)
Raw	-	1.0900	0.3957	36.30
200	20	1.0040	0.2008	20.00
200	40	1.0730	0.2886	27.70
200	60	1.0120	0.3533	35.40
300	20	1.0780	0.2914	27.16
300	40	0.9980	0.3357	31.40
300	60	1.0380	0.3682	35.47

A.2.4 Hemicellulose

Temperature (°C)	Times (min)	α-cellulose Content (%)	Holocellulose Content (%)	Hemicellulose Content (%)
Raw	-	36.30	62.08	25.78
200	20	20.00	40.01	20.01
200	40	27.70	45.28	18.90
200	60	35.40	50.72	15.32
300	20	27.16	40.05	12.89
300	40	31.40	43.08	11.64
300	60	35.47	46.18	10.71

A.2.5 Lignin

Temperature (°C)	Times (min)	Free Extractives Weight (g)	Lignin weight (g)	Lignin Content (%)
Raw	-	1.030	1.3720	28.00
200	20	1.010	0.9282	19.08
200	40	1.008	0.8742	18.89
200	60	1.009	0.8036	18.72
300	20	1.012	0.8839	18.11
300	40	1.091	0.7141	15.2
300	60	1.034	0.5267	12.01

APPENDIX B- GALLERIES

C.1 SAMPLE PREPARATION

EFB was grinded to reduce the size by using grinder at Agro Park.

After grinding, the sample was sieve by using a auto sieve shake to get the 500 micron.

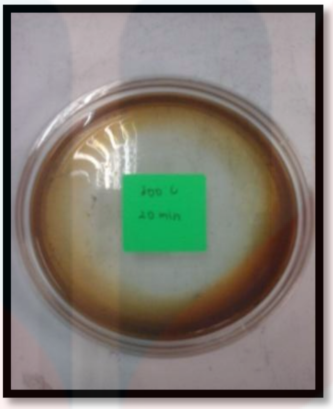
The sample was handling by microwave

to undergoes the torrefaction process.

The sample was ready for chemical test.

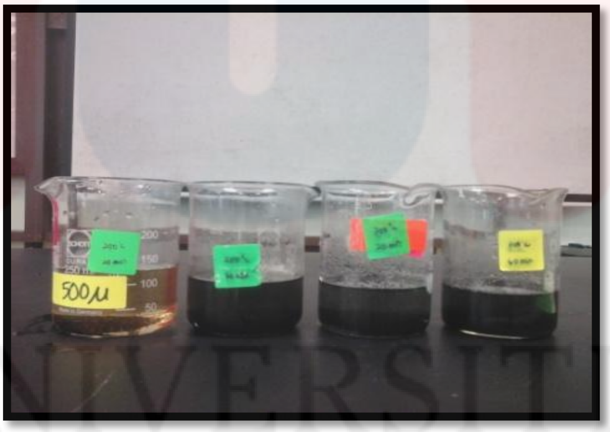
C.2 EXTRACTIVE

The process of extraction that used 300ml ethanol: benzene (2:1) place



The process evaporation of extractive by using rotary evaporator.

The crude will form after dried in fume cupboard in two days.



Comparison of extractive colour for Sample (200°C, 20 min), sample (300°C, 20 min, sample (200°C, 60 min) and sample (300°C, 60 min)

C.3 HOLOCELLULOSE

Sample is filter by using buncher funnel.

Oven-dried holocellulose of torrefaction sample placed in oven at 70°C for 24hours.

Oven-dried holocellulose of raw sample placed in oven at 70°C for 24hours.

C.4 α-CELLULOSE

Process to determined α-cellulose by mixing 17.5% NaOH with stirring iced environment due to exothermic nature of reaction

Sample is filter by using buncher funnel and vacuum pump with 250ml cold dH20, 25ml of 8.3% NaOH and 50 ml acetone

Oven-dried α-cellulose after placed in oven at 60°C for 24hours.

C.5LIGNIN

Sample was transfer in conical flask and heated with reflux at 170^{o}C for 4 hours

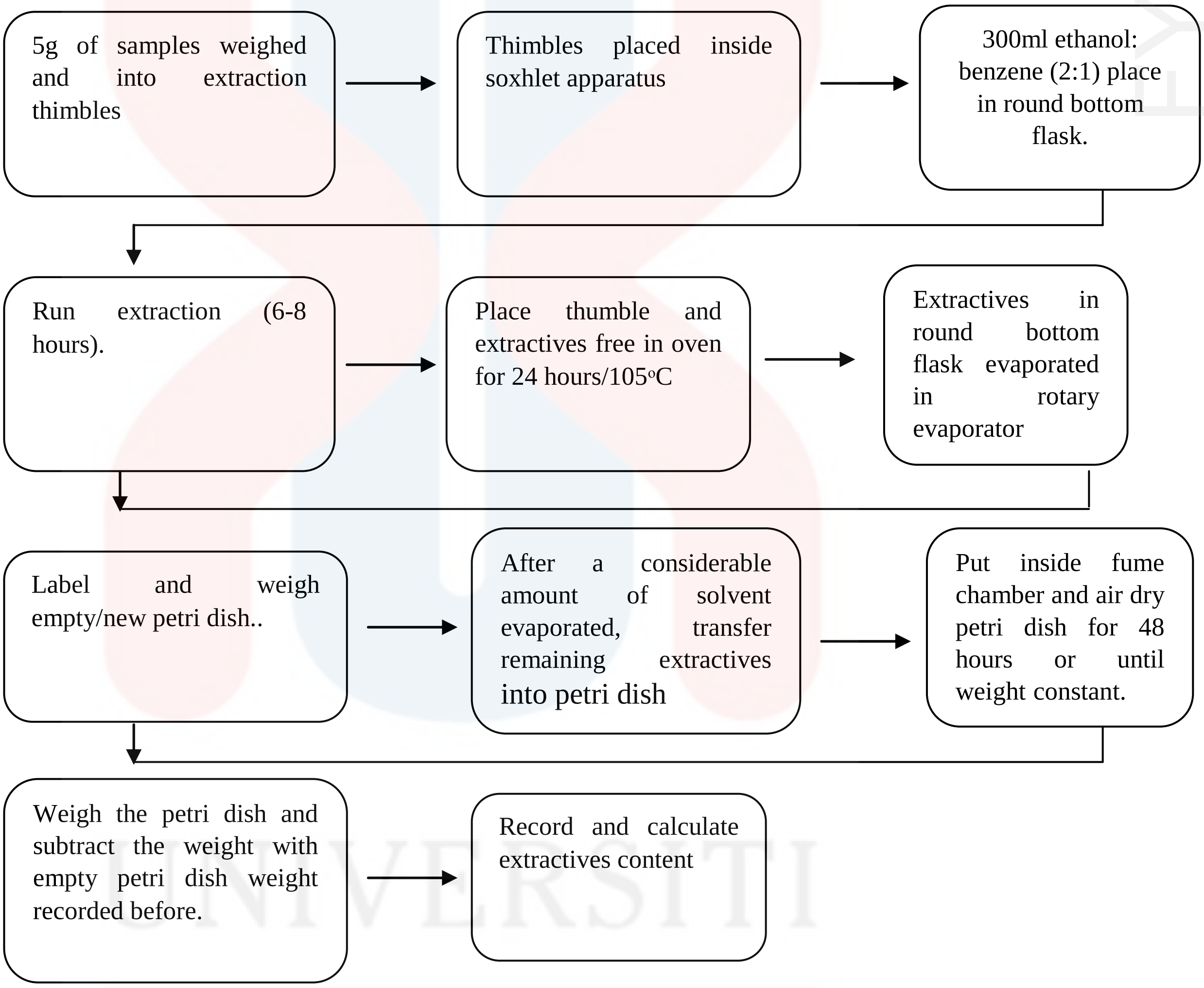
Sample was filtered with buncher funnel after heated.

The oven dried lignin for 105^{o}C for 24hours.

APPENDIX C- STANDART OF PROCEDURE

D.1 Chemical Properties

D.1.1 Extractive Content



5g of samples weighed and into extraction thimbles

Thimbles placed inside soxhlet apparatus

300ml ethanol: benzene (2:1) place in round bottom flask.

Run extraction (6-8 hours).

Place thumble and extractives free in oven for 24 hours/105^{o}C

Extractives in round bottom flask evaporated in rotary evaporator

Label and weigh empty/new petri dish..

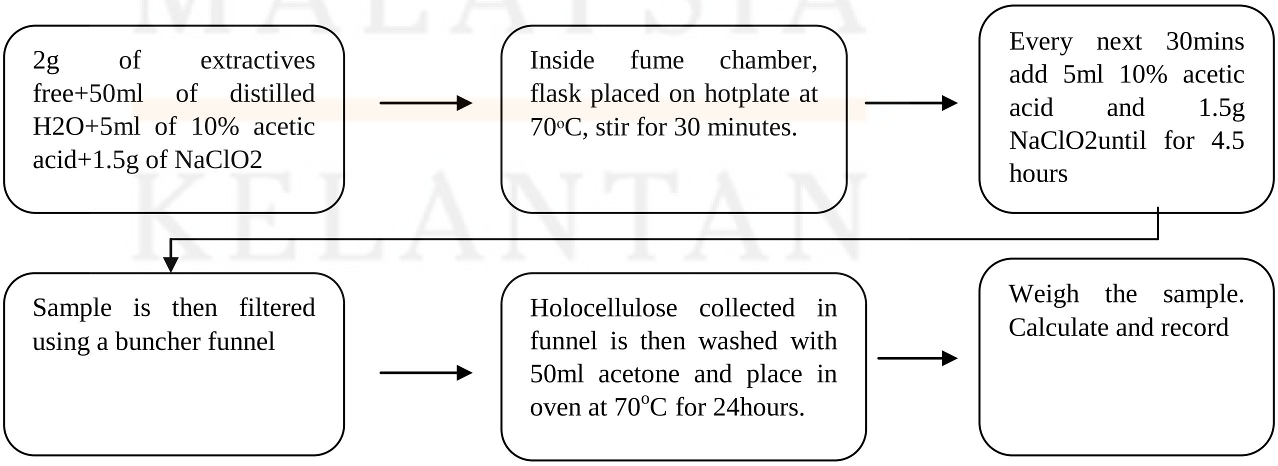
After a considerable amount of solvent evaporated, transfer remaining extractives into petri dish

Put inside fume chamber and air dry petri dish for 48 hours or until weight constant.

Weigh the petri dish and subtract the weight with empty petri dish weight recorded before.

Record and calculate extractives content

D.1.2 Holocellulose



2g of extractives free+50ml of distilled H2O+5ml of 10% acetic acid+1.5g of NaClO2

Inside fume chamber, flask placed on hotplate at 70^{o}C, stir for 30 minutes.

Every next 30mins add 5ml 10% acetic acid and 1.5g NaClO2until for 4.5 hours

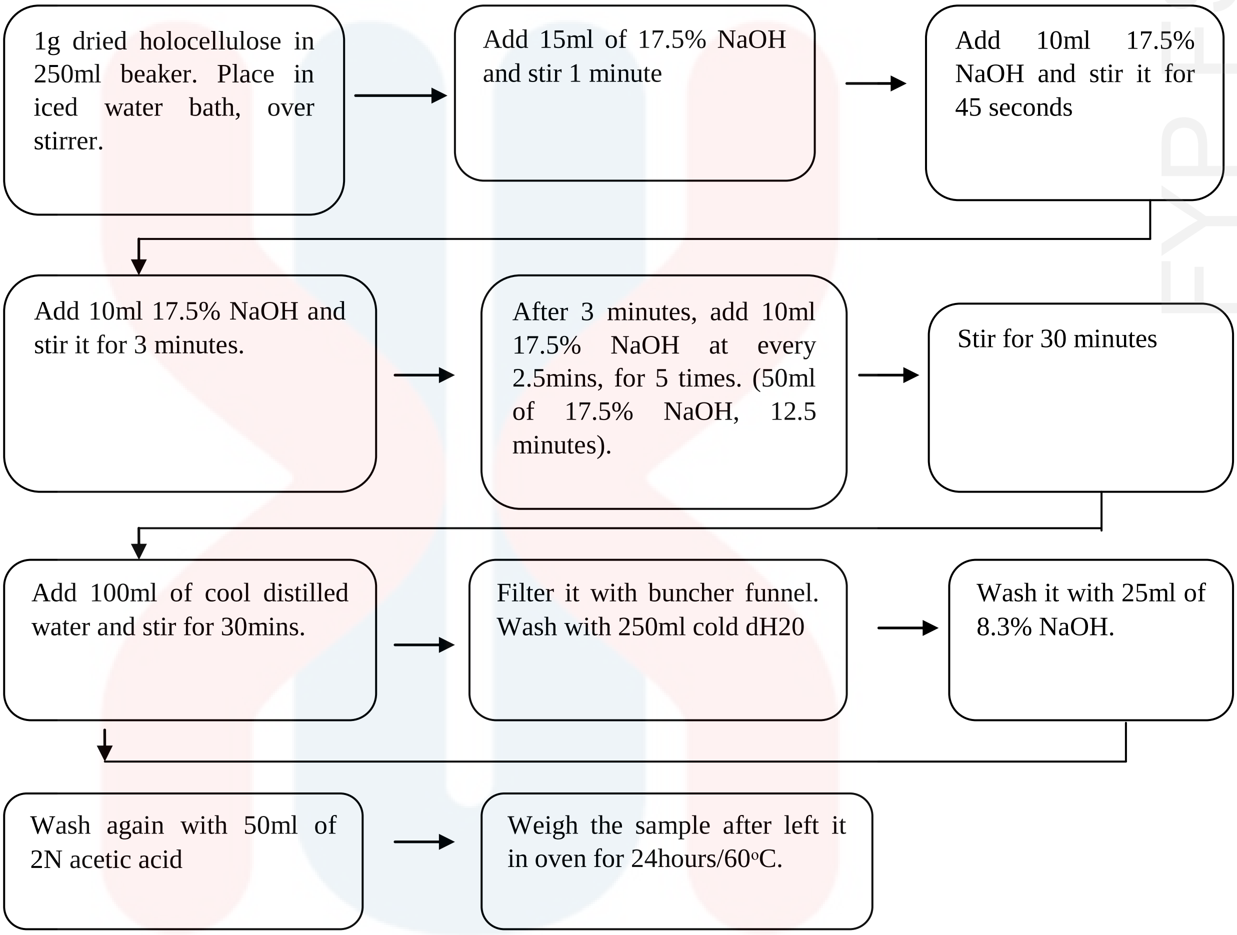
Sample is then filtered using a buncher funnel

Holocellulose collected in funnel is then washed with 50ml acetone and place in oven at 70^{o}C for 24hours.

Weigh the sample. Calculate and record

D.1.3 α-cellulose

D.1.3 α-cellulose



1g dried holocellulose in 250ml beaker. Place in iced water bath, over stirrer.

Add 15ml of 17.5% NaOH and stir 1 minute

Add 10ml 17.5% NaOH and stir it for 45 seconds

Add 10ml 17.5% NaOH and stir it for 3 minutes.

After 3 minutes, add 10ml 17.5% NaOH at every 2.5mins, for 5 times. (50ml of 17.5% NaOH, 12.5 minutes).

Stir for 30 minutes

Add 100ml of cool distilled water and stir for 30mins.

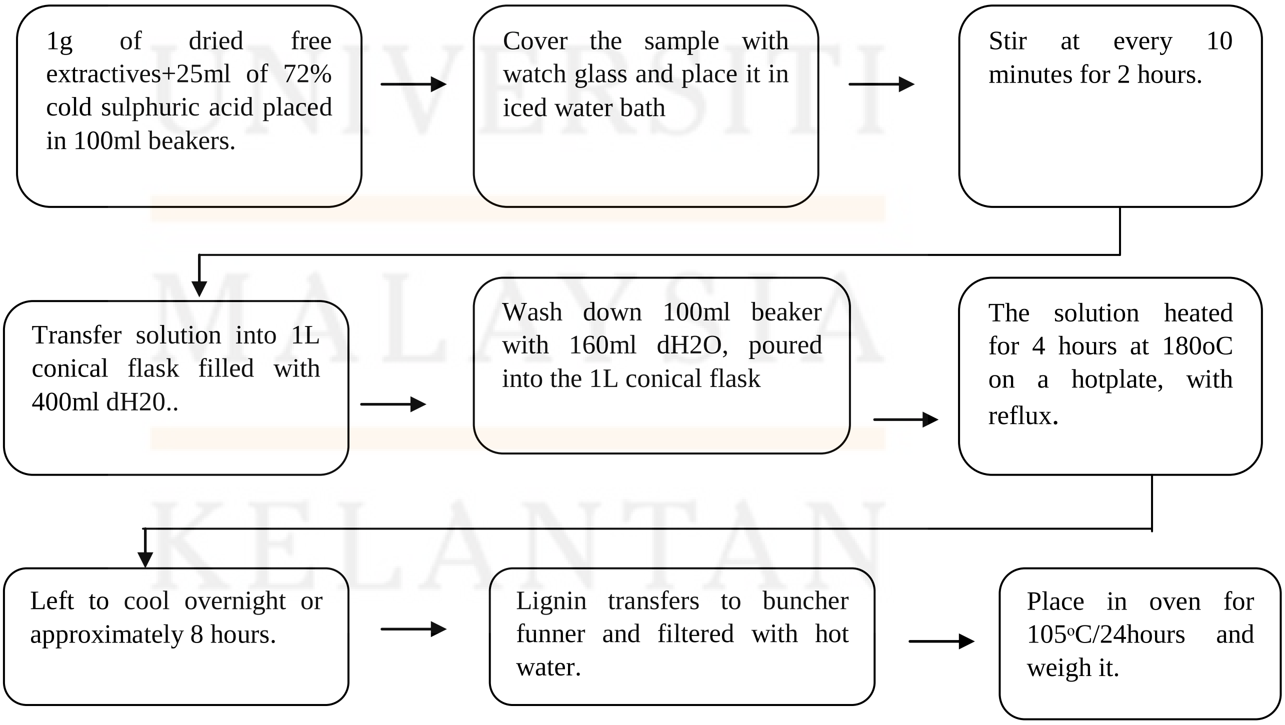
Filter it with buncher funnel. Wash with 250ml cold dH20

Wash it with 25ml of 8.3% NaOH.

Wash again with 50ml of 2N acetic acid

Weigh the sample after left it in oven for 24hours/60^{o}C.

D.1.4 Lignin



1g of dried free extractives+25ml of 72% cold sulphuric acid placed in 100ml beakers.

Cover the sample with watch glass and place it in iced water bath

Stir at every 10 minutes for 2 hours.

Transfer solution into 1L conical flask filled with 400ml dH20..

Wash down 100ml beaker with 160ml dH2O, poured into the 1L conical flask

The solution heated for 4 hours at 180oC on a hotplate, with reflux.

Left to cool overnight or approximately 8 hours.

Lignin transfers to buncher funner and filtered with hot water.

Place in oven for 105^{o}C/24hours and weigh it.