Extraction of Cellulose Fiber from Banana Tree (stem and peduncle) Using Chemical Method

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DECLARATION

I declare that this thesis entitled "Extraction of Cellulose Fiber from Banana Tree (stem and peduncle) Using Chemical Method" 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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LIST OF ABBREVIATIONS

	REFERENCE	PAGE
RSM	Response surface methodology	4
SEM	Scanning electron microscopy	4
FTIR	Fourier transform infrared spectroscopy	4
XRD	X-ray diffraction	4
TGA	Thermogravimetric analysis	4
NaOH	Sodium hydroxide	14
H_2O_2	Hydrogen peroxide	15
HOO^-	Hydroxyl ion	15
H_2SO_4	Sulphuric acid	16
HCl	Hydrochloric acid	16
CCD	Central composite design	17
3D	Three dimensional	19
ATR	Attenuated total reflection	20
CF	Cellulose fiber	28
DOE	Design of experiment	28
ANOVA	Analysis of variance	28
CrI	Crystallinity index	31
BS	Banana stem	32
BP	Banana peduncle	32
FCC	Face centered cube	36
LOF	Lack of fit	39
CV	Coefficient of variance	39

LIST OF SYMBOLS

	REFERENCE	PAGE
%	Percentage	3
wt%	Weight percentage	12
Mm	Millimeter	20
mL	Milliliter	23
Kg	Kilogram	25
ºC	Degree celcius	25
mL/ min	Flow rate	31
ºC/ min	Heating rate	31
I_{002}	Peak intensity correspond to crystalline	31
I_{am}	Peak intensity of amorphous fraction	31
Θ	Theta	31
kV	Kilovolt	31
mA	Miliamperes	31
R^2	Correlation coefficient	37
F-value	*Fisher's* F-value	41
µm	Micrometer	49

Extraction of Cellulose Fiber from Banana Tree (stem and peduncle) Using Chemical Method

ABSTRACT

This study aims to extract the cellulose fiber from banana pseudo stem (BS) and banana peduncle (BP) by using chemical extraction method. An optimization of acid hydrolysis is conducted using Design of Experiment (DOE) through Central Composite Design (CCD) to optimize the operating parameters such as concentration of sulphuric acid (H_2SO_4), temperature and reaction time involved. The structural morphology, functional group, crystallinity and thermal stability of cellulose fiber (untreated and treated BS and BP) were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red Spectroscopy (FTIR), X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA) respectively. The optimum parameter for both BS and BP were found to be 5 mol/L of H_2SO_4 at 30 ºC for 60 minutes. Sample of characterizations indicated that the cellulose contents were improved through several chemical treatments where the hemicellulose and lignin were successfully removed. The yield of purified BS and BP cellulose fiber content after acid hydrolysis process were 88 % and 95 % respectively.

Keywords: Cellulose fiber, banana pseudo stem, banana peduncle, chemical extraction method, DOE

Pengekstrakan Selulosa Fiber dari Pokok Pisang (batang dan tandan) Menggunakan Kaedah Kimia

ABSTRAK

Tujuan penyelidikan ini adalah untuk mengekstrak selulosa fiber daripada batang pisang serta tandan pisang menggunakan kaedah pengekstrakan kimia. Pengoptimuman asid hidrolisis telah dijalankan menggunakan reka bentuk eksperimen (DOE) melalui rekabentuk komposit berpusat (CCD) untuk mengoptimakan parameter operasi seperti kepekatan sulfuric asid, suhu dan masa tindak balas yang terlibat. Struktur morfologi, kumpulan berfungsi, kehabluran dan kestabilan terma selulosa fiber (sampel batang pisang serta tandan pisang yang tidak dirawat dan dirawat) telah dicirikan menggunakan Mikroskopi Elektron Pengskanan (SEM), Spektroskopi Inframerah Transformasi (FTIR), Pembelauan Sinar-X (XRD) dan Analisis Termogravimetri (TGA). Parameter optimum untuk kedua-dua sampel batang pisang serta tandan pisang adalah 5 mol/L H_2SO_4 pada 30 ºC untuk 60 minit. Sampel pencirian menunjukkan kandungan selulosa telah diperbaiki melalui beberapa rawatan kimia di mana hemiselulosa dan lignin telah Berjaya dibuang. Hasil kandungan selulosa fiber tulen untuk BS dan BP selepas proses asid hidrolisis adalah 88 % dan 95 % kedua-duanya.

Kata kunci: Selulosa fiber, batang pisang, tandan pisang, kaedah pengekstrakan kimia, DOE

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Isolation of cellulose fiber has received tremendous attentions due to its good resistance to sunlight. Bleaching cellulose fiber have a high demand in industry that serves as chemical filter during the cleaning process at the same time protecting the cloth and act as pre coat (Patterson, 2009). While, due to similar properties of the cellulose fiber to the engineered fiber such as low density, high tensile strength and stiffness, it has potential to be another alternative for biocomposite as fiber reinforcement in composite. Cellulose is an organic compound made up from carbon, hydrogen and oxygen which act as energy sources for living things. It's a complex carbohydrate in most of a plant cell wall. Cellulose has a linear structure of polysaccharides that form long molecule chains. Cellulose is insoluble in water and serves as a primary building in plant material as well as the basis of natural cellulosic fibers.

Cellulose fiber also act as reinforce to the plant structure such as stem, leaves and roots due to its fiber content can provide strength and toughness to the plant (Rose & Bennett, 1999). There are two types of cellulose fibers which are natural cellulose fiber that originally from plant and synthetic cellulose fiber such as nylon and polyester that produced from the chemical synthesis. Natural cellulose fibers are made up from cellulose esters or ether where it can be obtained from leaves, bark and wood of plant. Cotton, ramie, flax and jute are the example of natural cellulose fiber. Among all, natural cellulose fiber that obtained from cotton stalks bark are mostly used especially in the development of composite due to its flexural and impact resistance properties (Reddy & Yang, 2009). In Malaysia, there is about 60 million tons of biomass represented by cellulose that being produced in a year. Due to this scenario, cellulose fiber is considered as unlimited sources that can be used to manufacture other products such as filter paper and thread (Kendry, 2002).

In developing country, cellulose fiber from agricultural waste such as rice husk, soy hulls and banana are left abandoned and untreated that leading to environmental pollution. Due to the abundant amount of agriculture waste, there is a need to replacing the uses of non-renewable synthetic fiber to a renewable natural fiber that is more safely and environmental friendly. Natural fiber has advantages such as lightweight, high tensile strength, high stiffness and reducing environmental pollution (Khan *et al*., 2013). Furthermore, it has gained an attention of researchers in more production of sustainable as well as environmental green component at globally. Banana tree is one of the agricultural wastes that have been left abandoned after their fruits being harvested. Different part of banana tree having different cellulose fiber content thus has raised an attention in research

study as it can be used to produce several products as well as reducing the waste produced from agricultural activities (Dungani *et al*., 2016).

1.2 Problem Statement

Synthetic cellulose fibers are mostly polymer-based that being produced through spinning process thus resulting in increment of elasticity, resistancy to acid and tensile strength. Despite all the beneficial properties, it is still having limitation such as highly flammable, costly and risk to environment. Due to this limitation, modification has been made in term of the chemical used during production. However, it still possesses some drawbacks such as consumed a lot of energy and producing undesirable effects that created during the process. Hence, natural cellulose fiber that have an excellent properties such as flexibility, biodegradability and abrasion resistance were produced. Agricultural waste has been used as the major sources due to the accumulation of waste that resulting negative side effects. Thus, the uses help in reducing excessive waste from agricultural residues as well as controlling environmental pollution.

Banana tree is one of the abundant residues that gives large contribution to the agricultural waste and has raised an attention among researcher. From their conducted study, banana pseudo stem having high cellulose fiber content up to 70 % but the other part of the banana tree were still left abandoned. Due to scanty research available on extraction of cellulose fiber from banana peduncle, this study is one of the solutions where the banana peduncle is used to extract cellulose fiber in order to determine its cellulose fiber content

for further purpose. Banana pseudo stem was used as well to compare their cellulose fiber content and structures. These will surely help in solving the environmental problem. In order to get their cellulose fiber, chemical extraction method were used as it is known having potential in producing yield up to 95 %. Thus, it is used to extract cellulose fiber from banana pseudo stem and banana peduncle in this study to enhance the yield production.

1.3 Expected Output

Expected output from this research would be the extracted cellulose fiber with high cellulose fiber content from pseudo stem and peduncle of banana tree using chemical extraction method (hydrolysis process). The processing parameters of acid hydrolysis are optimized using the experimental design of (RSM). The morphology, functional group, phase structure and thermal stability of the cellulose fiber in banana pseudo stem and banana peduncle were characterized using SEM, FTIR, XRD and TGA respectively.

1.4 Objectives

1. To extract cellulose fiber from banana pseudo stem and banana peduncle by using chemical extraction method.

2. To optimize the processing parameters of acid hydrolysis by using Response Surface Methodology (RSM)
3. To characterize the morphology, functional group, phase structure and thermal stability of the cellulose fiber.

1.5 Scope of Study

The study will be focusing on the extraction of cellulose fiber from different part of banana (banana pseudo stem and banana peduncle) through chemical extraction where the samples undergo alkali treatment, bleaching process and acid hydrolysis. The cellulose content in different part of the banana will be evaluated. The acid hydrolysis process will be optimized using RSM in order to extract cellulose fiber.

Last part involves the characterization of cellulose fibers. Four instruments are used including scanning electron microscopy (SEM), fourier transform infrared (FT-IR), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). SEM is used for the observation of surface morphology of the samples and FT-IR used to identify the unknown materials as well as the organic chemicals in the samples. Besides, XRD is also used to determine the cellulose structure and crystallinity index as well as TGA for determination of thermal stability of the fibers.

1.6 Significant of Study

This study is important in order to observe the cellulose content in banana pseudo stem and banana peduncle as well as optimizing the extraction yield. Data and detailed information of this study might be useful for the further research on the cellulose fiber from banana. This study may also contribute to the development on scientific knowledges of natural cellulose from other agricultural wastes that have potential in electronic and bio composite industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Cellulose

Cellulose is considered as natural fiber as it is produced from plants. Natural cellulose fibers having many benefits including high toughness, biodegradable, low density, low cost and having specific strength properties (Lee *et al*., 2009). Cellulose is a polymer of glucose that bounded in β – (1, 4) - D – $C_6H_{12}O_6$ (Singanusing *et al*., 2013). For the compact microfibrils formation, cellulose chains were aggregated and stabilized by intra-molecular as well as inter-molecular hydrogen bonds in between adjacent molecules for oxygen and hydroxyl groups (Abrahama *et al*., 2011). A group of more than 100 glucon chain able to form long thin crystallites which is elementary fibrils that varies according to the cellulose sources (Alemdar & Sain, 2008). Due to the partial crystalline structure and degree of polymerization, cellulose fiber cannot be dissolved easily in standard solvents. Only high concentrated acid and certain specific complexes can dissolve it (Klemm *et al*., 2005).

Cellulose fibers have been widely used in textiles industry as a main filtration which protects the cloth as well as making the cleaning process easier. In textile industry, cellulose fiber is usually extracted through retting which is the removing process of non-cellulosic substance to obtain bast fiber. Previous research showed that chemical retting is an effective method to remove hemicellulose while, enzymatic retting is effective in the lignin removal (Song & Obendorf, 2006). Cellulose fiber also gives benefits in medical industry as it is used in medical products such as bandages, dressings and absorbent pads (Patterson, 2009). While, esters and ethers derivatives of cellulose were used in pharmaceuticals industry for the formulation of dosage, stabilizer as well as enhancing compressibility for the compression tablets (Shokri & Adibkia, 2013). Cellulose serves as unlimited sources of renewable raw materials that give benefits in terms of biocompatible and eco-friendly for the production of green products (Maepa & Ramontja, 2015).

2.2 Sources of Cellulose Fiber

Sources of cellulose fiber can be divided into 2 categories which are from plants and animals. The major sources of cellulose would be the vascular plant. Other sources of cellulose fibers including soy hulls, cornstalks, mulberry bark, pineapple leaf and banana as shown in Table 2.1.

Table 2.1: Agricultural wastes and its cellulose fiber content

Agricultural Wastes	Cellulose Fiber Content (%)
Rice straw	33.0
Soybean hulls	43.7
Sugarcane leaf and stalks	40.0
Pineapple leaf	75.3
Cornstalks	87.0

Source: (Abrahama *et al*., 2011)

2.2.1 Banana

Banana is a tropical fruit crops that grown easily and commercially in the tropical climate country. Banana also known as *Musa sp.* are widely cultivated in Asia, Latin America, Caribbean countries and Africa due to its fruit that contribute to the food security as it is known to help in fighting against diabetes, kidney cancer and depression as well as socio-economical life (Wobiwo *et al*., 2017). In Asia, Philippines have become the leading exporter and second largest supplier in 2013 by supplying 2.7 million tons of bananas a year (Alemu, 2017). Banana plant is considered as perennial herb that being cultivated for their fruits and acts as the sources of vitamin B6, vitamin C, nitrogen, potassium and phosphorus that help to regenerate tissue. Banana is widely consumed in order to treat intestinal disorder as well as relieving both diarrhea and constipation (Kumar *et al*., 2012).

Banana only can be harvest once thus the banana tree are left abandoned on the soil plantation after the fruits have been fully harvest. Then, it will become an organic waste and caused to the environmental pollution as it produces bad smell and become source for human disease to be transmitted (Li *et al*., 2010). There is estimated about 1.4 million of banana parts are left abandoned to be disposed a year (Dita *et al*., 2013). Usually, the part of the banana that being left is the pseudo stem as its fruits have been taken away and its leaves are used as food wrapping and lining due to its good aroma. Apart from just being thrown away, banana stem can be served as juice in traditional recipe to control blood sugar levels as well as used as natural threads for making crafts. Meanwhile, banana peduncle is the part that holds the fruits altogether. It will be left discarded after the fruits are fully separated to be used.

2.2.2 Banana Pseudo Stem

Banana pseudo stem is part of the banana plant that made from tightly packed leaf sheaths. Banana pseudo stem have contribute to the huge amounts of agriculture waste estimated about 100,296 tons of annual world production as it being felled and abandoned in the soil plantation (Khan *et al*., 2013). In Malaysia, there are about 530,000 tons per year of banana that was cultivated producing 4 tons of banana wastes that generated for every cycle of its harvested fruits (Abdullah *et al*., 2014). Banana fibers are extracted from banana pseudo stem through several methods which are physical and chemical methods that varies in term of the fiber quality effect. The extraction of fibers from banana pseudo

stem is friendly bio extraction process that leads to the production of clean fibers (Manilal & Sony, 2011).

The fibers of banana pseudo stem have water absorption capacity as well as good physical characteristics like having high tensile strength and high stiffness (Khan *et al*., 2013). Besides, banana pseudo stem also having high cellulose content (~64 %) which is show a potential to be the source of modified polysaccharide. The cellulose content of banana pseudo stem has widely used in the application of pulp and paper industry due to its high strength properties (Li *et al*., 2010). Besides that, it has great potential in pulping and papermaking industry due to high cellulose content (39.12 %) and low lignin content (8.8 %) (Li *et al*., 2010).

2.2.3 Banana Peduncle

Banana peduncle is a stalk that supports the inflorescence and attaches it to the rhizomes and the individual fruits or the part that holds the banana bunch. From the previous research, it has stated that banana peduncle is being produced approximately 2.3 million metric tons per year whether to be compost or just being left as waste. It has been considered as agricultural innovation due to its potentials in improving farming, health as well as income (Pazmiño-Hernandez *et al*., 2017). Peduncle is a part of banana plant that contain fiber as it main component. Prior research has stated that instead of being left rot in the field, fiber are extracted from the banana peduncle through retting and mechanical pressed as well as it have a longer cell length compared to other non-woods materials.

Apart from pulp and paper industry, fibers from banana peduncle are applicable in composite fiber boards manufacturing including resin – bonded and cement - bonded. This has been proven as it is being tested in term of its elasticity, endurance and absorption level to be sure that the product produce is in a good quality and meeting the demand. It is also being dried to produce banana peduncle powder that act as the frankfurters, burger and the modified ham. This is due to its high fiber content, good water retention as well as enhancing the cooking yield (Biswas *et al*., 2011). Also the banana peduncle has high specific strength and good binding properties due to its lightweight and presence of high cellulose with 72.9 wt%, low lignin with 10.01 wt% and wax with only 0.32 wt% (Manimaran *et al*., 2018).

2.3 Extraction method

Extraction is a process of separating the desired substance from mixture and serves as important step in order to discover bioactive compound from plant materials. There are three major methods for extracting cellulose fiber which are mechanical extraction method, bio extraction method and chemical extraction method. Mechanical extraction is a chemical free method involving the uses of machines in order to extract the cellulose fiber such as homogenization, microfluidisation and ultrasonication. Mechanical extraction has advantages in term of its odor control and easy removal and solid disposal but it required a regular maintenance and its initial set up is highly cost. By undergoing mechanical

extraction, cell wall is fully disrupted through shear forces thus resulting a maximum yield of cellulose fiber (Lekha *et al*., 2016).

While, biological extraction method is the method that involves the uses of living organism and its derivatives such as bacteria and enzyme in order to extract desired compound and it is considered as an alternatives method in environmentally friendly technology. This extraction method having benefits due to its high COD removal and its ability to eliminate mechanical mixing but its equipment and process are costly. Previous studies stated that the uses of bacteria and enzyme has increased the de-inking of recycled fibers such as toner released from office waste (Pe´rez *et al*., 2002). Chemical extraction method is a method of removing the extractives, lignin and hemicellulose fiber followed by the disruption of fiber into nanofibrils and microfibrils by using chemicals. Chemical extraction method only required a small space for the preparation but it process is quite complicated as well as some of the chemicals can effect to the environmental problems. Review from previous research has concluded that chemical extraction method resulting in the increasing of cellulose content due to removing some amount of lignin and hemicellulose (Xu *et al*., 2015).

2.4 Chemical Extraction Method

Chemical extraction is the method involving the alkali treatment, bleaching process and acid hydrolysis. Several factors that were known to highly affect extraction of cellulose fiber are type of solvent used, extraction time, temperature during process and pH.

2.4.1 Alkali Treatment

Alkali treatment is a chemical treatment that removes several components covering the cell wall external surface or the fibers such as the hemicellulose, lignin, oils and wax as well as one of the simplest and effectives techniques in surface modification that has been widely used in natural fiber composites. Alkali treatment also used to defibrillate the external cellulose microfibrils, depolymerizes cellulose native structure and exposes the short length crystallites (Abrahama *et al*., 2011). It can help in removing lignin that allows the rearrangement of molecule and enhance the crystallinity of cellulose. As a result, the products have better mechanical properties arised from interlocking and bonding reaction. This resulting to the increasing of fiber – matrix adhesion as the hydroxyl groups while the used of sodium hydroxide (NaOH) as a solvent will help the modification of the fiber morphology such as much rougher surface (Pickering *et al*., 2016).

The initial stage of studies stated that alkalization can improved the crystalline part of amorphous cellulose and removed the hydrogen bonds in the network structure of cellulose hydroxyl group by the removal of carbonyl group. Due to alkali treatment with sodium hydroxide (NaOH), the carboxyl groups that acts as fatty acid tracing were removed during the reaction and producing a high yield of cellulose. In addition, the tensile and the flexural properties of the composites are increased as the interfacial adhesion of the fiber is highly enhanced (Khan *et al*., 2013). Johar *et al*. (2012) shows that alkali treatment is an efficient method to remove hemicellulose as its content reduced from 33 wt% to 12 wt% after the treatment.

2.4.2 Bleaching Process

Bleaching process is process of depriving colored material by using bleaching agents. It is considered as the second step in the pretreatment of cellulose. Is it known to destruct the natural coloring matter without degrading the fiber. In bleaching process, hydrogen peroxide is the active ingredient that acts as oxidizing agent and it will oxidize the coloring matter which is then washed out in order to obtain permanent nature. Bleaching time and the concentration of solution used can affect the overall performance of the bleaching process thus it must be considered depending on the raw materials used. Bleaching process is important in order to eliminate the remaining cementing materials from the fiber completely (Abrahama *et al*., 2011).

Rayung *et al*. (2014) stated that the use of hydrogen peroxide (H_2O_2) has caused to the discoloration of the fiber. This is due to the formation of per hydroxyl ions (HOO^-) that being produced by the dissociation of the hydrogen peroxide in an alkaline medium that has attacking the light absorbing chromophoric groups of the lignin and the cellulose. During the process, it shows that the composition of fiber has changed as well as the lignin that was completely removed through the receding of the aromatic C=C bond of the lignin (Khan *et al*., 2013). Cherian *et al*. (2010) showed that the bleaching process is responsible for fibers bundles splits into individual fibers thus degrading the lignin present leading to the formation of hydroxyl, carboxyl and carbonyl groups that helps to facilitate the purification of the cellulose.

2.4.3 Acid Hydrolysis

Acid hydrolysis is a hydrolysis reaction in which using an acid as a catalyst in order to decompose and split the compounds. It is one of the fastest and easiest ways for cellulose fiber preparation. Generally, acid hydrolysis is performed in order to remove the amorphous region as well as producing nano fibrils and obtaining high crystalline particles. Usually, high concentrated acid is involves in the acid hydrolysis process as cellulose fiber cannot be easily dissolve in standard solvent due to the partial crystalline structure and the polymerization degree of the cellulose fiber itself. The most widely concentrated acid would be hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). HCl was used because it has result for the cellulose rod with minimal surface charge. Also, (H_2SO_4) has result in a high stable of aqueous suspension and the use of (H_2SO_4) in acid hydrolysis along with the constant stirring helps in reducing the length and diameter of the cellulose fiber (Sosiati *et al*., 2014).

There are four factors that affect the treatments of cellulose crystalline such as the initial concentration of the cellulose crystalline, the concentration of acid, the duration and temperature of the hydrolysis as well as the sonication (Huntley *et al*., 2015). The samples are sonicated in order to broken down into leaner fragments. The slurry obtained is often in highly viscous. Due to the shear effect and high turbulence, the size of nanocellulose is reduced (Abrahama *et al*., 2011). Studies proved that acid hydrolysis succeeded in cleaving the cellulosic microfibrils amorphous region and keeping the entire crystalline domain straight thus, increasing its crystallinity, rigidity and strength.

2.5 Factors Affecting Cellulose Fiber Extraction

Acid hydrolysis process is widely used in order to obtain cellulose fiber with better properties in fast and easier way. It is the crucial step of the chemical extraction method of cellulose fiber compared to alkali treatment and bleaching process because it has high efficiency to obtain the crystalline particles. In this process, there are some factors that affect the yield of cellulose fiber which is the temperature, reaction time and the concentration of the acid used in the process (Yalda Davoudpour *et al*., 2015). To obtain maximum extraction yield, optimal condition for the acid hydrolysis process is determined by using experimental design of RSM.

RSM is a statistical and mathematical collection technique for the building of empirical model. RSM is aiming to optimize the response which is the output variable that influenced by several dependent or independent variable. It is also aim to improve quality including the variability reduction, and process improvement as well as the performance of the product. When there is no curvature occurs in the data set, the first order models of experimental design can be used such as factorial designs. However, an experimental design for quadratic response surface is needed when the experimental data cannot be described by the linear function. There are several design involves in RSM for the quadratic response surface which are Central Composite Design (CCD), Three Level Factorial Experiments, Box-Behnken and Doehlert designs. Among these, CCD and Box-Behnken are widely used due to its high efficiency and flexibility (Dussán *et al*., 2014).

RSM is applied to design optimization in order to reduce the number of experiment run. In RSM, it consist of independent variable which can be change independently of each other as an experimental variables including pH, temperature, reagent concentration, time and flow rate. The response can be represented in graph which is either in 3-dimensional space or as contour plots and it is important for the shape of the response surface visualizing (Bezerraa *et al*., 2008). Basically, the optimization process of RSM involving 3 main steps includes performing the statistically designed experiment, estimate its coefficient in mathematical model (predicting the response) and checking the model adequacy. RSM are mostly used for industrial application in order to predict the quality and measured performance of the product and process (Sadhukhan *et al*., 2016).

2.6 Cellulose Fiber Characterization

Cellulose fiber can be characterized by many instrumental tools such as SEM, FTIR, XRD and TGA to observe surface morphology, functional group, phase structure and crystallinity and thermal properties, respectively.

2.6.1 Scanning Electron Microscopy (SEM)

SEM is function to scan focus on high energy electron beam for signals generation at the solid surface of the specimen. The signal will reveal the sample's information such as

chemical composition, morphology and crystalline structure that make up the sample. This process, SEM focuses the electron beam at sample's surface and measures the electron results with detector thus forming the pixel image. The electron beam is generated and focus at the column on top of the image. The electron beam from the column also known as primary electron will impact the surface thus, generating secondary electron, Auger electron, X-ray photons, backscattered electron and cathode luminescence.

SEM is used in order to know the effect of the pretreatment and the structural changes of the sample. Through SEM, the appearances of the sample's surfaces are observed and the presence of unwanted materials such as oils and wax can be seen. The associated fibrils in the bundles are also can be seen clearly (Cherian *et al*., 2010). The advantages of SEM are that it gives detailed 3D and topographical imaging as well as information garnered from different detectors. It only required a minimal sample preparation along with the fast working that can analyses samples in less than five minutes. In addition, the advanced technology of the modern SEM allowing the generation of data in digital form Besides, SEM also has greater resolution and larger depth of field. In previous work, SEM has shown a visual removal of the lignin, pectin, and hemicellulose that have undergone the treatment. By using SEM, the average diameters of the fibers are detected (Alemdar & Sain, 2008). More information of the surface characteristics of the samples can be determined by different magnifications of SEM uses (Manilal & Sony, 2011).

2.6.2 Fourier Transform Infrared (FTIR)

FTIR is the technique used to obtain spectrum of absorption and emission that aim to measure the amount of light absorbed by the sample at each of the wavelength. It has both application in qualitative and quantitative analysis. IR spectroscopy consists of seven components which are source, interferometer, signal sorter, sample compartments, A/D convertor, amplifier, signal detector and computer. Its mechanism starts with the source that generates radiation and passes the sample to the detector through interferometer. The signal then will amplify as well as converting to digital signal by amplifier and analog-to-digital converter respectively. Lastly, the signal is transfer to monitor of computer. There are several sampling methods for FTIR such as transmission, attenuated total reflection (ATR) and grazing angle where ATR is widely used to measure the surface properties as it can penetrates until 2 mm depth beyond the crystal surface and into the sample.

In order to study the physicochemical properties of lignocellulose materials, FTIR is a non-destructive time saving method that can detect functional groups range. Although it is sensitive changed in molecular structure, it gives benefits as it provides a precise measurement method that does not require rigorous calibration. FTIR also can enhance frequency of resolution and reanalyzed the stored data as well as less in time consuming. The data obtained through FTIR can be observed by analyzing the graph provided (Alemdar & Sain, 2008). Previous study stated that in FTIR analysis, hemicellulose, cellulose and lignin are studied in term of its infrared spectra. The peaks in the FTIR graph represent the characteristics of the component (Abrahama *et al*., 2011). The symmetry

changes in C–H groups as well as the cellulose component structure are observed through FTIR analysis (Johar *et al*., 2012).

2.6.3 X-ray Diffraction (XRD)

XRD is non-destructive analytical technique that yields the unique fingerprint of Bragg reflection associated with crystal structure. It is the common technique used to identify crystalline materials and unit cell dimension analysis. There are two types of XRD analysis that applied commonly in order to obtain specific information regarding crystalline material which are X-ray powder diffraction and single crystal XRD where X-ray powder diffraction is widely applied. XRD consist of X-ray tube, sample holder and X-ray detector where X-ray is generated in cathode ray tube by heating the filament in order to produce electrons. The electron will accelerate toward target by applying voltage as well as bombarding the targeted material with electrons. The characteristics of X-ray spectral will be produced when the electron have sufficient energy to dislodge the inner shell electrons of the target electron.

Cellulose crystalline structure is amorphous in nature and contrary to the lignin and the hemicellulose. The crystalline structure is formed caused by the Van der Waals forces between adjacent molecules as well as the hydrogen bonding interactions. Apart of measuring the size, shape and internal stress of small crystalline regions, XRD helps in evaluating the crystallinity of the samples completely as the crystallinity of the cellulose may be change due to the chemical treatment performed (Johar *et al*., 2012). The crystalline

can be observed from the XRD graph as the sharp peak of the XRD pattern represented the higher crystal content existed, associated to amorphous dissolution zones and removal efficiency of non – cellulosic polysaccharides (Samir *et al*., 2004). By using XRD, the phase structure and the composition of the crystalline compound can be measured.

2.6.4 Thermogravimetric Analysis (TGA)

TGA is a technique in which changes in physical and chemical properties of materials are measured as function of increasing temperature (with constant heating rate) and as function of time (with constant temperature and mass loss). TGA can provide information about physical phenomena such as vaporization, sublimation and absorption. It also can provide chemical phenomena including dehydration, decomposition and oxidation reduction reaction.

Based on the previous study, chemicals modification such as alkalization has caused decreasing in the thermal stability of the natural fibers (Abrahama *et al*., 2011). During the decomposition of the lignin, the temperature observed are in wider range that caused by the different in activities of the chemical bonds that present in the structure. By this, α–cellulose is protected by the lignin-cellulose complex. The thermal stability of the natural fibers and the thermal properties are determined as it is important for its further potential used (Johar *et al*., 2012). TGA have a wide range of application such as oxidative stability of materials, decomposition kinetics of materials, moisture and volatiles contents of materials as well as estimated lifetime of product.

CHAPTER 3

METHODOLOGY

3.1 Apparatus and Materials

The materials used were banana pseudo stem, banana peduncle, sodium hydroxide (4 wt% NaOH), acetic acid, sodium chlorite, sulphuric acid, oven, blender, miller, soxhlet extractor, thimble, heating mantle, round bottom flask (500 mL), beaker (100, 500 and 1000 mL), erlenmayer flask, measuring cylinder (5 and 50 mL), zipper bag, Buchner funnel, vacuum pump, and water bath, stirrer, hot plate and pH meter.

3.2 Sample Preparation

Sample of banana pseudo stem and banana peduncle was collected at Agropark in Universiti Malaysia Kelantan (UMK). 5 kg of banana pseudo stem and banana peduncle were used respectively. Banana pseudo stem and banana peduncle were rinsed with

distilled water and dried in an oven for 24 hours at 80 ºC. Then, they were ground to form fine powder and stored in zipper bag for further used.

3.3 Chemical Extraction

The powder samples of banana pseudo stem and banana peduncle undergo three continuous process of chemical extraction which are alkali treatment, bleaching process and acid hydrolysis.

3.3.1 Alkali Treatment

Approximately 320 g of banana pseudo stem and banana peduncle powder samples were treated with 300 ml of an alkali solution of 4 wt% NaOH as solvent through soxhlet extractor for 6 hours continuously as shown in Figure 3.1. The samples were then filtered using vacuum pump and washed with distilled water for several times to remove the alkali-soluble components.

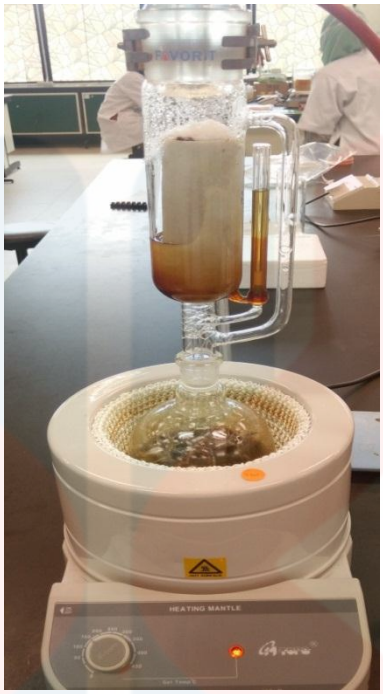

Figure 3.1: Extraction process of BS and BP samples

3.3.2 Bleaching Process

Banana pseudo stem and banana peduncle samples from the alkali treatment undergo bleaching process by mixed up with a solution that consist of 25 ml acetic acid, 6 g sodium chlorite and 200 ml distilled water for every 40 g samples. The bleaching treatment was performed by heating using double boiled method using magnetic hot plate stirrer at temperature ranged from 80 ºC to 100 ºC for 90 minutes and allowed to cool in ice for another 60 minutes. Then, it was filtered, washed with distilled water until no acid left and dried in an oven for overnight at 60 ºC. The amount of sample after bleaching was recorded.

3.3.3 Design of Experiment for Acid Hydrolysis

The samples of banana pseudo stem and banana peduncle that have undergone alkali treatment and bleaching process are continued with acid hydrolysis process. Acid hydrolysis process were conducted to purified the cellulose fiber content and obtaining high crystalline particles using RSM for optimization designed in minimal number of experimental run. 3 g of samples and aqueous sulphuric acid solution with ratio of 1:8 solid to liquid were loaded in a beaker and heated in the water bath. After that, the cellulose fiber hydrolysates were filtered, washed thoroughly with distilled water and oven dried at 60 ºC for overnight. The dried cellulose fiber hydrolysates were weighed and the yields were calculated by using Eq (3.1).

$$\text{Yield } (\%) = \left(\frac{m_{\text{CF}}}{\text{m}_{initial}}\right) \times 100\% \qquad \text{Eq. (3.1)}$$

Where m_{CF} is the mass of dried cellulose fiber hydrolysate (g), $\text{m}_{initial}$ is the initial mass of the cellulose fiber used. The results represent the average values of three sample's replication in order to increase the accuracy.

For optimization of cellulose fiber yield, the acid hydrolysis process was done using a Central Composite Design (CCD) of RSM. In this process, a full 2^3 factorial designs of experiment (DOE) from RSM was performed with 3 variables which are the

concentration of sulphuric acid, temperature and the reaction time, respectively as show in Table 3.1. All the variables values were selected based on the previous study. The response variable was the yield of the cellulose fiber hydrolysates (%). Central Composite Designs (CCD) experiment was utilized to determine the optimal combination factors for maximum yield.

The data obtained were then fitted into the mathematical models equation. Three tests which are test for significance of regression, test for significance individual model coefficients via R^2 and analysis of variance (ANOVA) were performed in order to ensure good models of the response. A three-dimensional (3D) response surfaces generated from the equation model were used to identify the interaction between the variables factor towards the response. The statistical results were conducted by the software Design-Expert version 6.0.10.

Table 3.1: Factors and levels used in experimental three level factorial designs.

Variable	**Factor**	**Unit**	**Minimum value**	**Center point**	**Maximum value**
			-1	**0**	**+1**
A	Concentration of sulphuric acid	mol/L	5.00	10.00	15.00
B	Temperature	ºC	30	50	70
C	Reaction time	min	20	40	60

3.4 Characterization of Cellulose Fiber

A cellulose fiber sample of both banana pseudo stem and banana peduncle that obtained a maximum yield undergo testing characterized by SEM, FTIR, XRD and TGA measurements in order to analyze their physical and chemical properties.

3.4.1 Scanning Electron Microscopy (SEM)

The morphology of cellulose fiber for both banana pseudo stem and banana peduncle was observed using SEM, brand JEOL JSM-IT 100. SEM is used as it provides a high resolution of sample's images by focusing on the electron beam across the surface and detects the secondary electron signal. The samples were oven dried to remove all the moisture content before analyzed.

3.4.2 Fourier Transforms Infrared (FTIR) Spectroscopy

FTIR spectroscope was used in order to identify the functional group of the cellulose fiber structure changes after the treatments. Cellulose fiber samples of both banana pseudo stem and banana peduncle were milled and characterized using Thermo Scientific Nicolet iZ10 FT-IR Spectrometer.

3.4.3 X-ray Diffraction (XRD)

X-ray diffraction was used to determine the crystallinity structure of the cellulose fiber in both banana pseudo stem and banana peduncle samples after being fully treated. The crystallinity of the cellulose fibers was determined using X-ray diffractometer, Bruker D2 Phaser model system with Cu Kα radiation at the operating voltage and current of 30 kV and 10 mA respectively. The diffraction intensity was recorded in 2θ range between 10º and 90º. In order to characterize the crystallinity, the crystallinity index value, CrI are calculated according to amorphous subtraction method of Segal et al. (1959) as following Eq (3.2):

$$\mathrm{CrI}\ (\%) = \frac{(\mathrm{I}_{002} - \mathrm{I}_{\mathrm{am}})}{\mathrm{I}_{002}} \times 100 \qquad \text{Eq. (3.2)}$$

Where, I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the samples. The diffraction peak for plane (002) is located at diffraction angle around 2θ = 22º and the intensity scattered by the amorphous part is located at a diffraction angle around 2θ = 18º.

3.4.4 Thermogravimetric Analysis (TGA)

TGA was used to determine the thermal stability of the cellulose fiber samples of both banana pseudo stem and banana peduncle. The measurements was performed by using Mettler Toledo TGA/DSC 2-thermogravimetric analyzer under nitrogen atmosphere over a room temperature until 900 ºC with gas flow of 10 mL/ minute and heating rate of 10 ºC/ minute.

Research Method flowchart

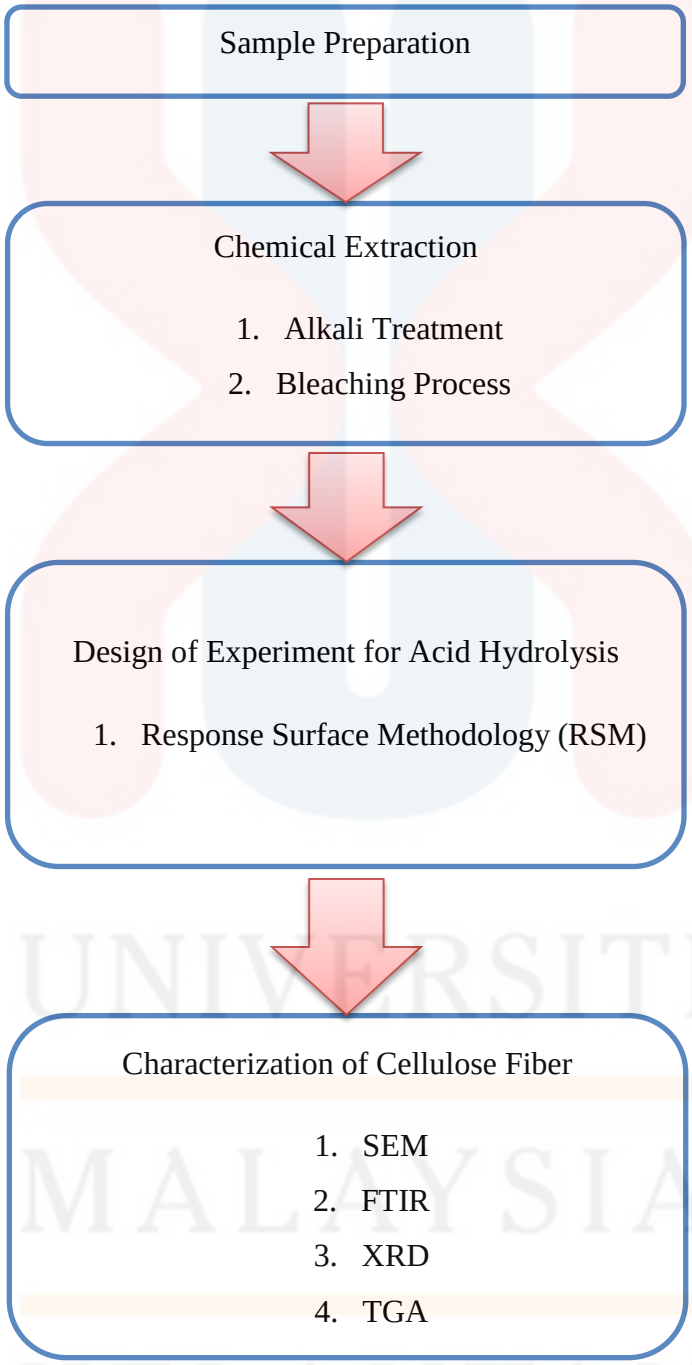

Figure 3.2: Overall research method

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect on Alkali Treatment and Bleaching Process

Banana pseudo-stem (BS) and banana peduncle (BP) were treated with an alkali solution to remove hemicellulose, oils and wax. The yield product usually decreased after the treatment process. In this study, the amount of BS, 320 g before being treated has decreased to 239 g while, 320 g of BP has reduced to 247 g after the alkali treatment. There are 81 g reductions of BS were recorded while, only 73 g of BP is recorded. The physical appearance of the alkali treated BS and BP is rough surface and dark brown. It can be observed that the color changes may be due to the removal of impurities and non-cellulosic material such as hemicellulose, lignin and wax (Alemdar & Sain, 2008). Figure 4.1 shows the changes in color appearance of untreated, bleached and acid treated BS and BP samples.

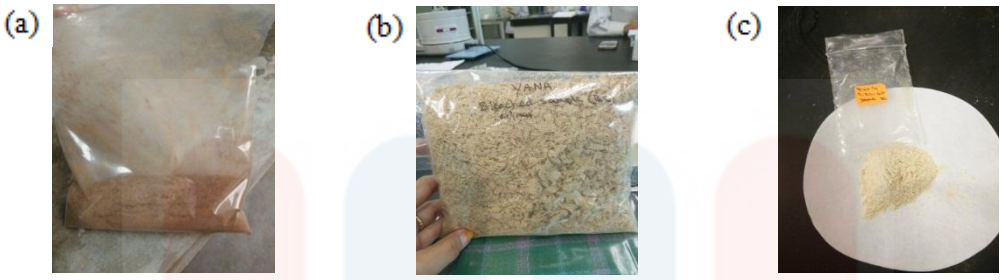

Figure 4.1: Samples of BS and BP for (a) untreated, (b) bleached and (c) acid hydrolysis

Bleaching is known for the removal of major residual lignin. The decreasing amount of BS from 239 g to 171 g and 247 g to 155g for BP after bleached indicate that the lignin content were removed during the treatment. The color of both BS and BP also change from dark brown to pale yellow. This implies the theory and other previous works that bleaching agent such as sodium chlorite used has caused to discoloration of the cellulose fiber which indicates that the samples is almost pure cellulosic materials (Johar *et al*., 2012).

Table 4.1: Percentage removal for hemicellulose and lignin of BS and BP after chemical treatment

Samples	**Banana Pseudo Stem (BS) (%)**	**Banana Peduncle (BP) (%)**
Hemicellulose	25.3	22.8
Lignin	28.5	37.2
Cellulose	46.2	40.0

Table 4.1 describes the percentage removal of hemicellulose and lignin for BS and BP after being chemically treated. The hemicellulose was found to have higher removal in BS by 25.3 % compared to BP by only 22.8 %. However, BP has higher removal of lignin than BS as it removed 37.2 % compared to BS which only 28.5 %. This shows that BS has low lignin content compared to BP. As expected, the removal of hemicellulose and lignin in both BS and BP samples indicate that the alkali treatment and bleaching process were efficiently removed the hemicellulose and lignin and produce pure cellulose (Johar *et al*., 2012).

While, the cellulose content was observed to be higher in BS (46.2 %) than BP (40.0 %). The cellulose content in both BS and BP samples proved that agricultural waste from banana crop having potential to become the source of cellulose fiber together with other agricultural wastes such as rice straws, soybean hulls and sugarcane (leaf and stalk) which having the cellulose fiber content of 33 %, 43.7 % and 40 % respectively (Abrahama *et al*., 2011).

4.2 Optimization of Acid Hydrolysis using RSM

Optimization of acid hydrolysis process was designed by using Design Expert of Response Surface Methodology (RSM) to obtained maximum cellulose fiber yield of BS and BP. After acid hydrolysis process, cellulose fiber content for both BS and BP was calculated to be 88 % and 95 % respectively.

4.2.1 Model Adequacy Checking

The complete design layout of cellulose fiber yield for banana pseudo stem and banana peduncle for 20 runs with the output response is given in Table 4.2.

Table 4.2: Process data layout using Face Centered Cube (FCC) and test results.

Run	Factor A Concentration of sulphuric acid (H_2SO_4) (mol/L)	Factor B Temperature (°C)	Factor C Reaction time (min)	Yields (%) For Banana pseudo-stem	Yields (%) For Banana peduncle
1	10	50	40	81.17	85.83
2	10	50	40	82.67	84.67
3	15	30	20	85.17	85.17
4	15	70	20	69.33	69.00
5	10	70	40	70.33	71.00
6	10	50	60	78.33	84.00
7	10	50	40	81.67	85.67
8	10	50	40	80.67	83.00
9	10	30	40	84.84	88.67
10	15	30	60	84.17	85.84
11	10	50	20	83.17	84.67
12	15	50	40	77.67	81.00
13	10	50	40	82.67	84.00
14	5	30	60	88.00	95.33
15	5	50	40	86.33	88.00
16	15	70	60	64.67	65.00
17	5	70	60	73.00	74.00
18	5	30	20	86.00	87.00
19	5	70	20	77.00	83.00
20	10	50	40	81.00	85.33

Face centered cube (FCC) were utilized in order to ensure that the selected variables values are within its specified range. 20 tests were performed in the experiment to optimize the 3 variables involved and to investigate the relationship between all the variables toward the response. By applying multiple regression analysis, the data obtained in Table 4.2 were fitted with second order polynomial equation:

$$\text{Yield}_{\text{BS}} = 81.44 - 2.93\text{A} - 7.39\text{B} - 1.25\text{C} + 0.85\text{A}^2 - 3.56\text{B}^2 - 0.40\text{C}^2 - 1.42\text{A} - 0.46\text{AC} - 1.21\text{BC}$$

$$\text{Yield}_{\text{BP}} = 84.55 - 4.13\text{A} - 8.00\text{B} - 0.47\text{C} + 0.25\text{A}^2 - 4.42\text{B}^2 + 0.084\text{C}^2 - 1.46\text{AB} - 0.33\text{AC} - 2.75\text{BC}$$

The regression analysis of the experimental data suggested that the relationship between response of yield and the factors (A, B and C) was best fitted with the quadratic model. The positive sign in front of the terms indicate that the factor is independent to the response and the negative sign indicate that the factor is dependent to the response. The dependent of a single factor relatively has no effect to the other factor while the dependent of interactive factor has affecting other factors as it is the interaction between 2 factors.

While, for the result of R^2 test was shown in the Table 4.3. R^2 and adjusted R^2 are the main indicator for the model to be significant. R^2 should not be less than 0.80 in order to have a good fit model as when it is below 0.80, the relationship between the variables cannot be explained (Hidayah *et al.,* 2017). R^2 that approach 1 illustrate that calculated and

observed result having good agreement within the experiment ranged. However, larger R^2 does not always point out that the model is adequate, hence adjusted R^2 is referred to provide proper evaluation for the model adequacy. The adequate precision would measure the signal to noise ration where it is desirable if the ratio is greater than 4.

Table 4.3: Result for R^2 test

Response	**Yield of Cellulose Fiber**	
	(BS)	**(BP)**
Std. Dev	1.16	1.72
Mean	79.89	82.51
C.V	1.46	2.09
R^2	0.98	0.97
Adjusted R^2	0.97	0.94
Predicted R^2	0.88	0.50
Adequate Precision	29.12	25.01

Table 4.3 shows that values of R^2 of BS and BP are 0.98 and 0.97 respectively. The values that approach to 1 indicate that 98 % and 97 % of variability in response can be explained by the models of BS and BP. The adjusted R^2 for BS and BP are 0.97 and 0.94 respectively. While, predicted R^2 of BS is 0.88 and only small difference with it adjusted R^2 considering the value have a reasonable agreement. There a quite larger difference between adjusted R^2 and predicted R^2 of BP as its predicted R^2 only 0.50. This was

normally expected as it may indicate a large block effect or possible problem with the model and data.

This may indicate that a large block effect or possible problems including the model reduction and response transformation with the model. The coefficient of variance (C.V) obtained were 1.46 % and 2.09 % respectively where low C.V predicts the reliability and precision satisfactory of this experiment. The larger values of adequate precision of both BS by 29.12 and BP by 25.01 indicate an adequate signal as well as the model can be used to navigate the design space.

4.2.2 Analysis of Variance (ANOVA)

Analysis of variance (ANOVA) is based on positioning variation in data into component. In ANOVA, F-value is used to evaluate the statistical significance of the model equation. Several sources such model, lack of fit (LOF) and interaction between factors were involved in the ANOVA in order to measure the suggested model quality as well as whether it fit the experiment or not. In statistic, larger F-value and smaller P-value considered the model to be significant. Furthermore, lack of fit (LOF) is observed as an indication of the model failure as it comparing the residual error to pure error from the experiment design. LOF must be not significance as its significance shows that the response predictor of the model is not valid (Davoudpour *et al*., 2015). Table 4.4 shows ANOVA for response yield of cellulose fiber for BS and BP.

Table 4.4: ANOVA for response surface quadratic models for yield of BS and BP

Source	Sum of squares		DF		Mean square		F value		Prob > F		
	(BS)	(BP)	(BS)	(BP)	(BS)	(BP)	(BS)	(BP)	(BS)	(BP)	
Model	732.34	980.66	9	9	81.37	108.96	60.08	36.79	< 0.0001	< 0.0001	Significant
A	85.97	170.73	1	1	85.97	170.73	63.48	57.65	< 0.0001	< 0.0001	Significant
B	545.38	640.16	1	1	545.38	640.16	402.70	216.14	< 0.0001	< 0.0001	Significant
C	15.62	2.18	1	1	15.62	2.18	11.54	0.74	0.0068	0.4109	
A^2	2.01	0.17	1	1	2.01	0.17	1.48	0.058	0.2511	0.8152	
B^2	34.85	53.63	1	1	34.85	53.63	25.73	18.11	0.0005	0.0017	Significant
C^2	0.43	0.019	1	1	0.43	0.019	0.32	6.566E-003	0.5859	0.9370	
AB	16.07	17.05	1	1	16.07	17.05	11.87	5.76	0.0063	0.0373	Significant
AC	1.67	0.88	1	1	1.67	0.88	1.24	0.30	0.2922	0.5967	
BC	11.66	60.50	1	1	11.66	60.50	8.61	20.43	0.0149	0.0011	Significant
Residual	13.54	29.62	10	10	1.35	2.96	-	-	-	-	
Lack of Fit	9.85	23.64	5	5	1.97	4.73	2.67	3.95	0.1528	0.0789	Not significant
Pure Error	3.69	5.98	5	5	0.74	1.20	-	-	-	-	
Cor Total	745.88	1010.28	19	19	-	-	-	-	-	-	

From Table 4.4 for the BS cellulose fiber, has F-value of 60.08 implies the model is significant and there is only 0.01 % chance the model F-value this large could occur due to noise. For the Prob > F values, it must be less than 0.05 to indicate that the model terms are significant and values that greater than 0.1 indicate the model terms are not significant. In this case, A, B, C,B^2, AB, BC are significant model terms. For the first order effect, all 3 parameters which are concentration of sulphuric acid (A), temperature (B) and reaction time (C) are significant but it is found that A and B influent the most yield of BS as it values are very minimal (< 0.0001) compare to C. In the second order effect, only B^2 that influent the BS yields. While for the interactive effect, AB and BC are significance where AB influent more to the BS yield. Besides, the lack of fit F-value of 2.67 implies the lack of fit is not significant relative to the pure error and it is good fit to the model. There is a 15.28 % chance that lack of fit F-value this large could occur to noise.

For BP cellulose fiber, the model F-value of 36.79 implies the model also significant and only 0.01% chance the model F-values this large could occur due to noise. The model terms are significant when the Prob > F values are less than 0.05 and not significant if it is greater than 0.1. For this case, only A, B, B^2, AB, BC are significant model terms. It is observed that the first order effect of A and B to be the most influential parameter on BP yield due to its minimum value of < 0.0001. Similarly to BS yield, only B^2 of the second order effect has influent the yield of BP as the other 2 parameters are not significant. In term of interactive effect, AB and BC are significance where BC is more influencing the BP yield due to its 0.0011 Prob > F values. However,

the lack of fit of 3.95 implies that there is only 7.89 % chance that lack of fit F-value this large could occur due to noise but it is still not significant and fit the model.

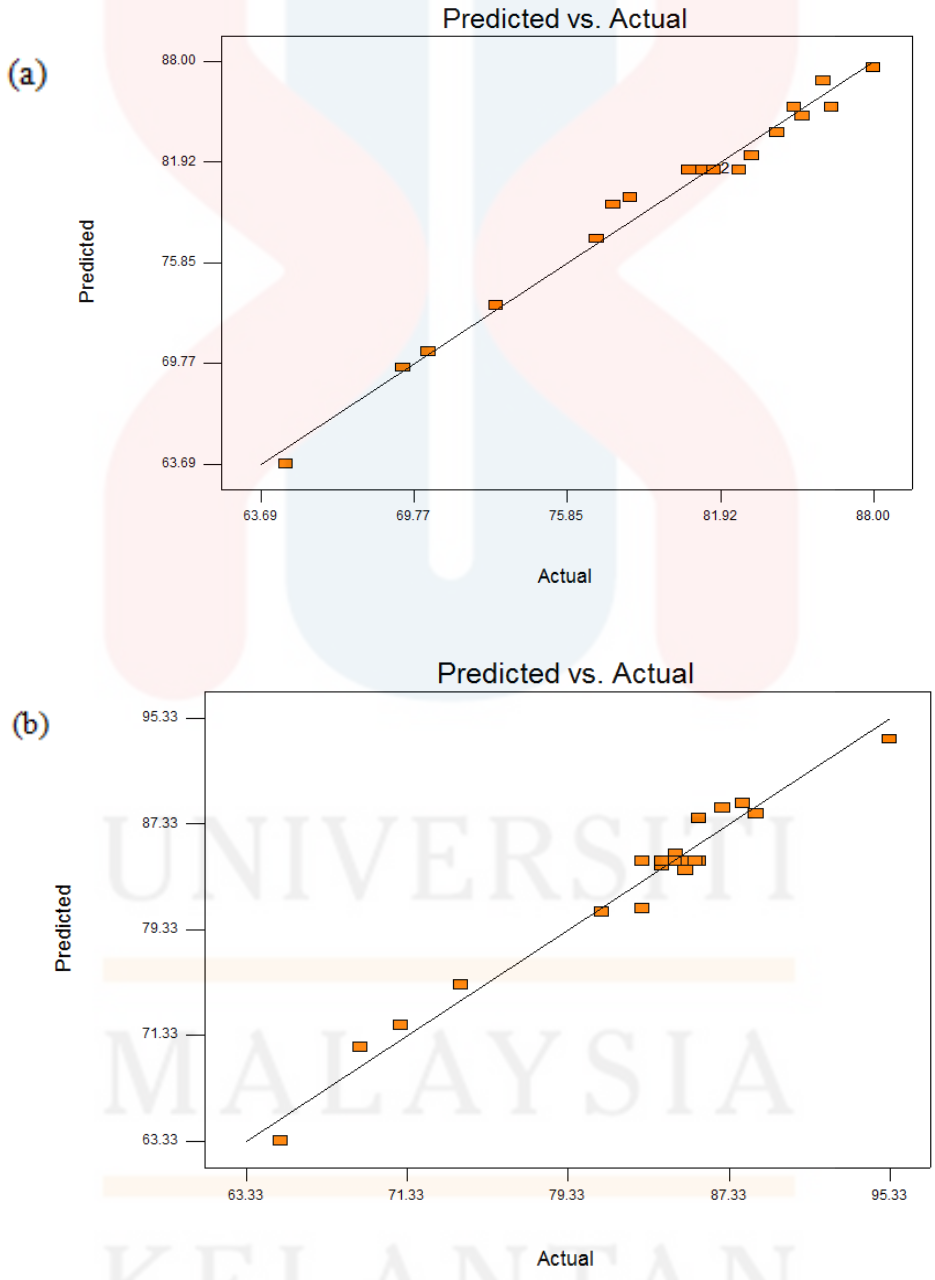

Figure 4.2: Predicted response versus actual response of (a) BS cellulose fiber yield and (b) BP cellulose fiber yield

The relationship between actual which is the experimental and predicted values of both response were illustrate in Figure 4.2. By applying these diagnostic plots, the adequacy of the model can be observed. The residual for the prediction of both responses were minimum as they relatively distributed and lied close to the linear straight line. The values of adjusted R^2 for both BS and BP yield that approaching 1 has supported these plots as it indicate the good agreement between observed and predicted results. It is also shows that the experimental data is correspond with the model as well as demonstrating that the CCD model are fitted and can be effectively applied for optimization.

4.2.3 Interaction of Design Factors and its Effects toward Cellulose Fiber Yield

Response surface plot is a three-dimensional graph that helps to identify the type of interactions between two test variables on the response, while other variable held in at constant level. The 3-D graph used to determine the interaction between factors towards the response as show in Figure 4.3 and 4.4.

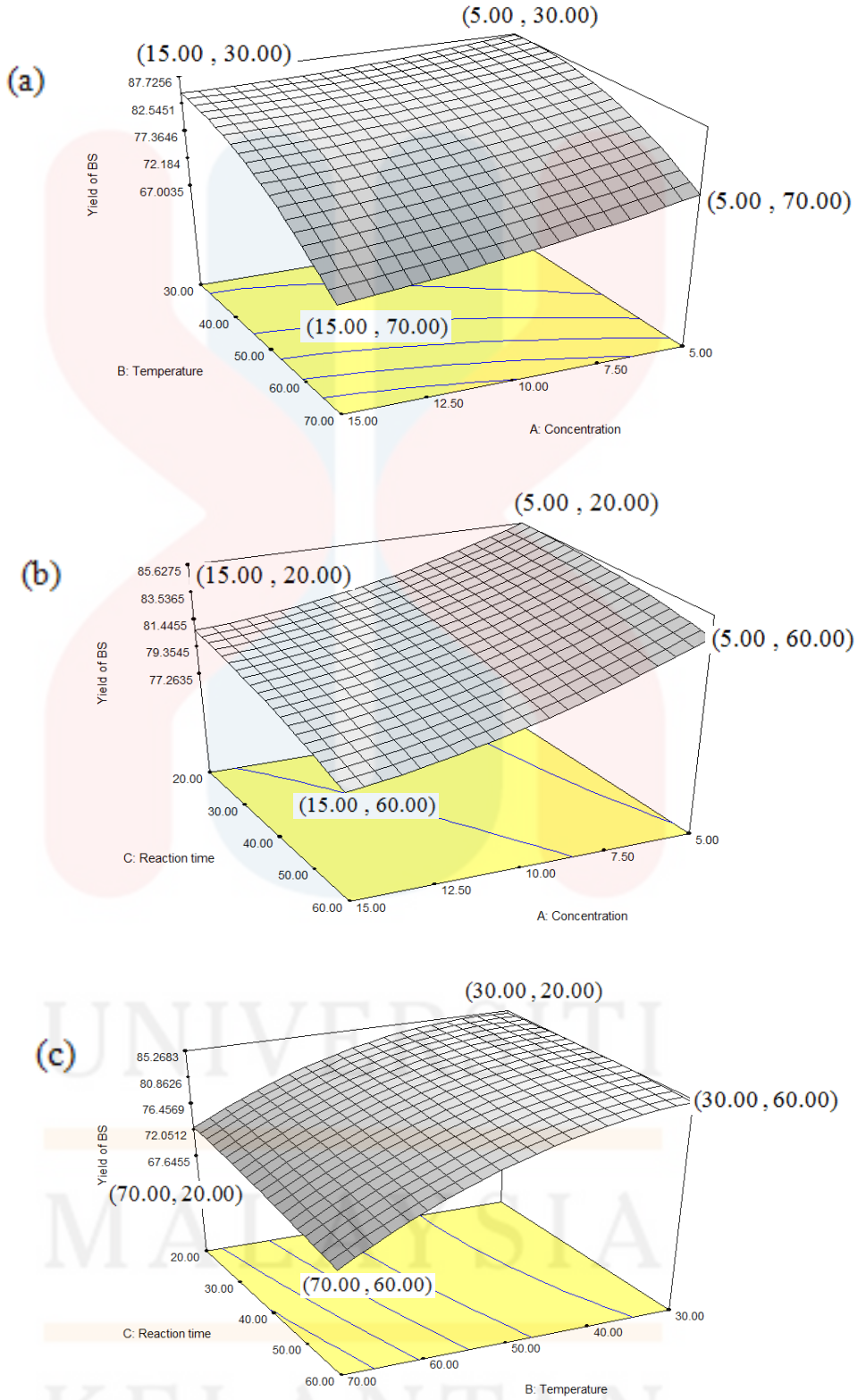

Figure 4.3: 3D surface response plots of interactions between (a) concentration and temperature, (b) concentration and reaction time and (c) temperature and reaction time towards BS yield.

Figure 4.3 shows three-dimensional (3D) illustration for the relationship between factors and yield BS cellulose fiber. Figure 4.3 (a) represent the interaction between concentration of sulphuric acid and the temperature towards the BS yield. It show the low concentration by 5 mol/L at low temperature of 30 ºC resulting the highest BS yield by 88 % as well as the high concentration and temperature contribute to the lowest yield by 64.67 %. This is because the cellulose fiber cannot withstand in high temperature as it can degrade the cellulose fiber content. While, the interaction between concentration and the reaction time in Figure 4.3 (b) resulting to the highest yield when both factors are in low value by 5 mol/L and 20 minutes respectively. This is because a longer reaction time will caused the cellulose fiber to degrade due to strong acid used even though in lower concentration. As concentration increased to 15 mol/L for longer time reaction by 60 minutes, the BS yield produced is only 64.67 %.

In Figure 4.3 (c), the interaction between temperature and reaction time resulting to two highest point of BS yields. One observed at low temperature in a shorter reaction time while, another one would be still at low temperature but in longer reaction time that contribute the both yield ranged from 84 % to 88 %. The lowest yield contribution in this interaction was in between 64 % and 73 % at temperature of 70 ºC in 60 minutes of reaction time. Among these 3 interaction factors, interaction between concentration and temperature was found to be the optimum and can highly contribute to the highest yield. This were correspond with the p-values in ANOVA table that show the values for AB interactions was 0.0063.

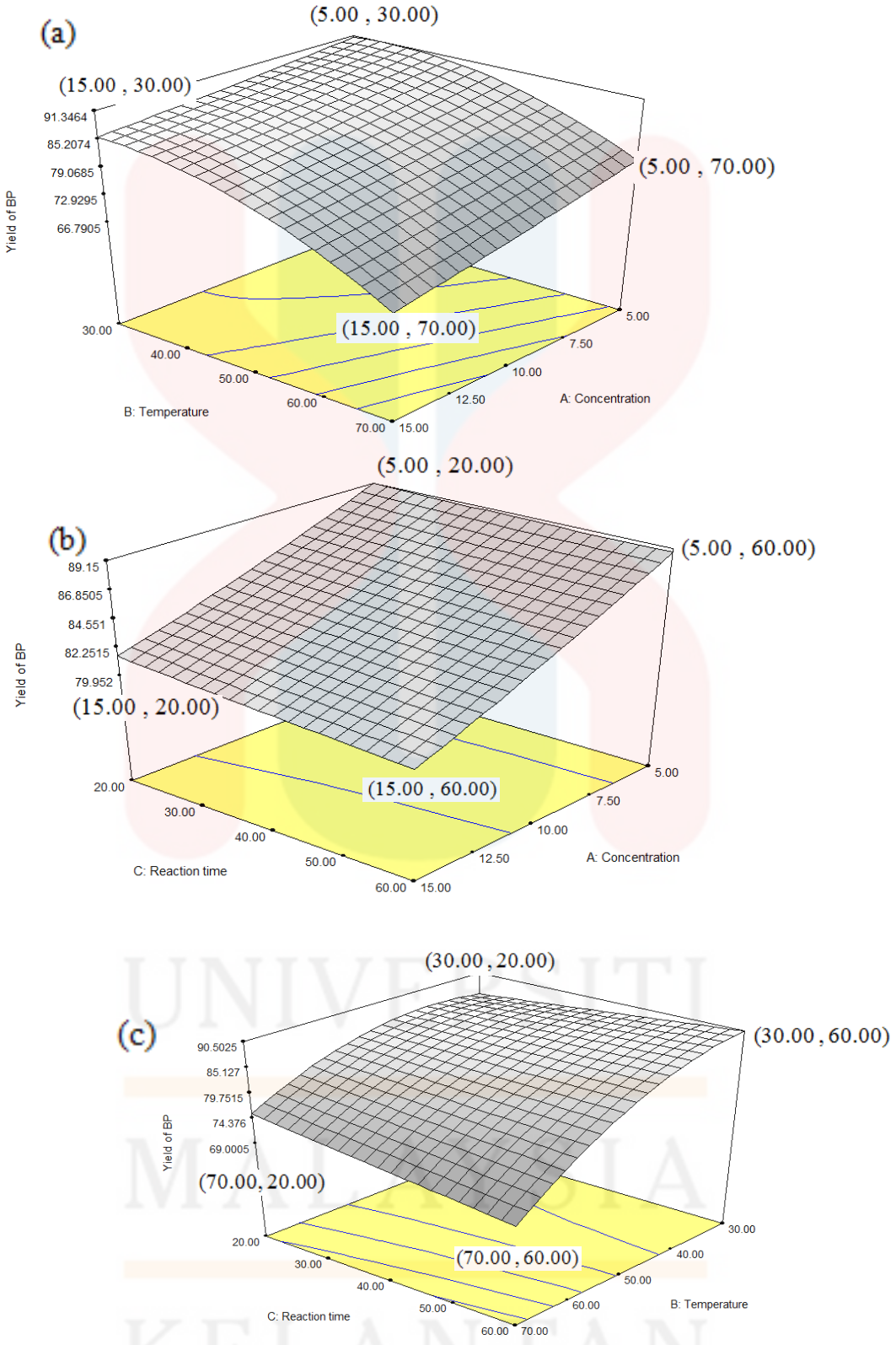

Figure 4.4: 3D surface response plots of interactions between (a) concentration and temperature, (b) concentration and reaction time and (c) temperature and reaction time towards BP yield.

The interactions of 3 factors towards BP yield were illustrated by 3D model in figure 4.4. For Figure 4.4 (a), the model show the highest BP yield ranged from 87 % to 95 % was contributed by 5 mol/L sulphuric acid at 30 ºC. It shows that low concentration and temperature produce highest yield and the lowest yield would be at 70 ºC of 15 mol/L. Figure 4.4 (b) illustrated the interaction between concentration and reaction time. Similarly to the AB interaction, the highest yield ranged from 83 % to 87 % was produced at concentration of 5 mol/L in 20 minutes. The lowest yield would come from high concentration in longer reaction time.

While, interaction between temperature and reaction time in Figure 4.4 (c) having the highest BP yield at 30 ºC for reaction time of 60 minutes. This can be related to the physical of the BP as its surface is much rougher than BS thus, a longer time reaction will resulting the BP to become more fine and smooth. The yield was in between 85 % and 95 %. As when the temperature increased to 70 ºC in constant reaction time (60 minutes), the yield was decreased to 65 - 74 %. For those interactions, it is found that interaction AB and BC were significant and BC has the most effect on the BP yield due to its highest cellulose fiber content (95 %) and this was corresponding to the p-values of 0.0011 in ANOVA table.

4.3 Characterization of Cellulose Fiber

A cellulose fiber sample of both banana pseudo stem and banana peduncle that obtained a maximum yield were characterized by using SEM, FTIR, XRD and TGA in order to analyze their structures and components.

4.3.1 Morphology Study of Cellulose Fiber using Scanning Electron Microscopy (SEM)

SEM is used to investigate the structure of the BS and BP samples before and after the treatment. These visually suggest the removal of hemicellulose, lignin, wax and other materials after being chemically treated. The results were show in Figure 4.5 (a) and (b).

Bleaching treatment was known can destruct the natural coloring matter without degrading the fiber as well as eliminating the remaining cementing materials from the fiber. Figure 4.5 (a) shows bleached cellulose fiber analyzed using SEM under 100 x magnification. It is clearly show the structure of both BS and BP after alkali treatment and bleaching exhibits rougher surface due to the removal of oils and wax during the alkali treatment. The structure as labeled in Figure 4.5 (a) also shown that fibrillation were took place in several parts of the cellulose fiber due to the partial removal of

cementing materials such as lignin and hemicellulose around the fiber bundles after the bleaching process (Arifuzzaman *et al*., 2012).

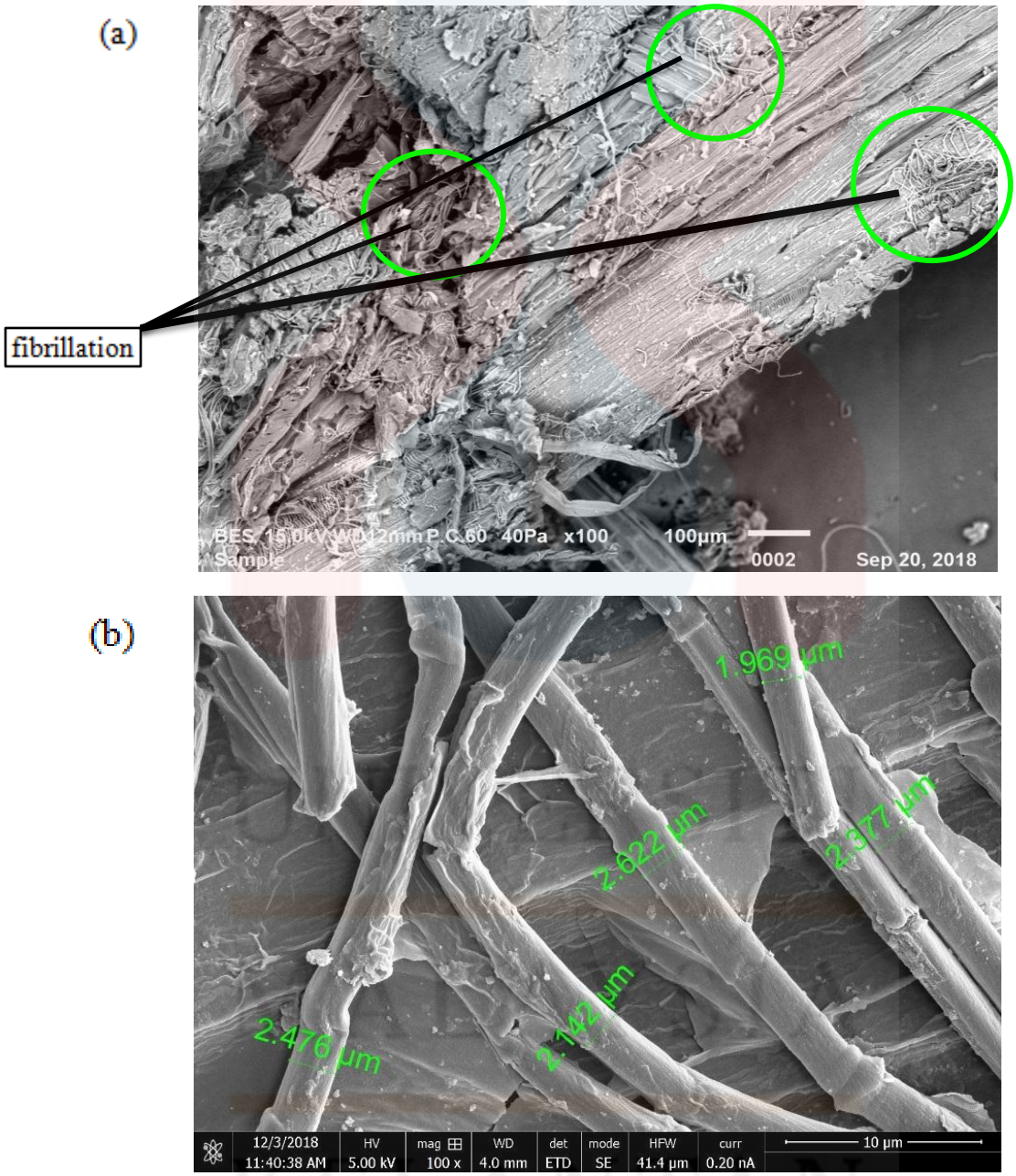

Figure 4.5: SEM under 100 x magnifications for both BS and BP (a) bleached and (b) acid treated.

While, Figure 4.5 (b) show cellulose fiber after being treated with acid hydrolysis process and was analyzed under 100 x magnification of SEM. The picture clearly show the presence of fibers which are not clearly seen in Figure 4.5 (a). It is also observed that the diameter and size of acid treated cellulose fiber was decreased to around ~2 µm. The reduction indicates that the cellulose fiber was further fibrillated due to the removal of lignin during acid treatment thus, enabling the fiber to separate into an individual form (Hanieh *et al*., 2012). Previous study from Johar *et al*. (2012) was observed that acid treatment should eventually reduce the fiber size from micron to nanometer scale range from 10-20 nm. This is because acid hydrolysis was expected to cleave the amorphous region of cellulosic nanofibrils transversely thus keeping the crystalline domains intact. However, this study shows that the cellulose fiber size was not reaching the nano scale level and this may be due to the partial cleavage of the amorphous region.

4.3.2 Identification of Functional Group of Cellulose Fiber using Fourier Transforms Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a non-destructive method in order to study the physico-chemical properties of cellulose fiber. The infrared spectra of the cellulose, hemicellulose and lignin of both BS and BP were observed before treatment as well as after being chemically treated. The FTIR spectra of BS and BP were shown in Figure 4.6 and 4.7 respectively.

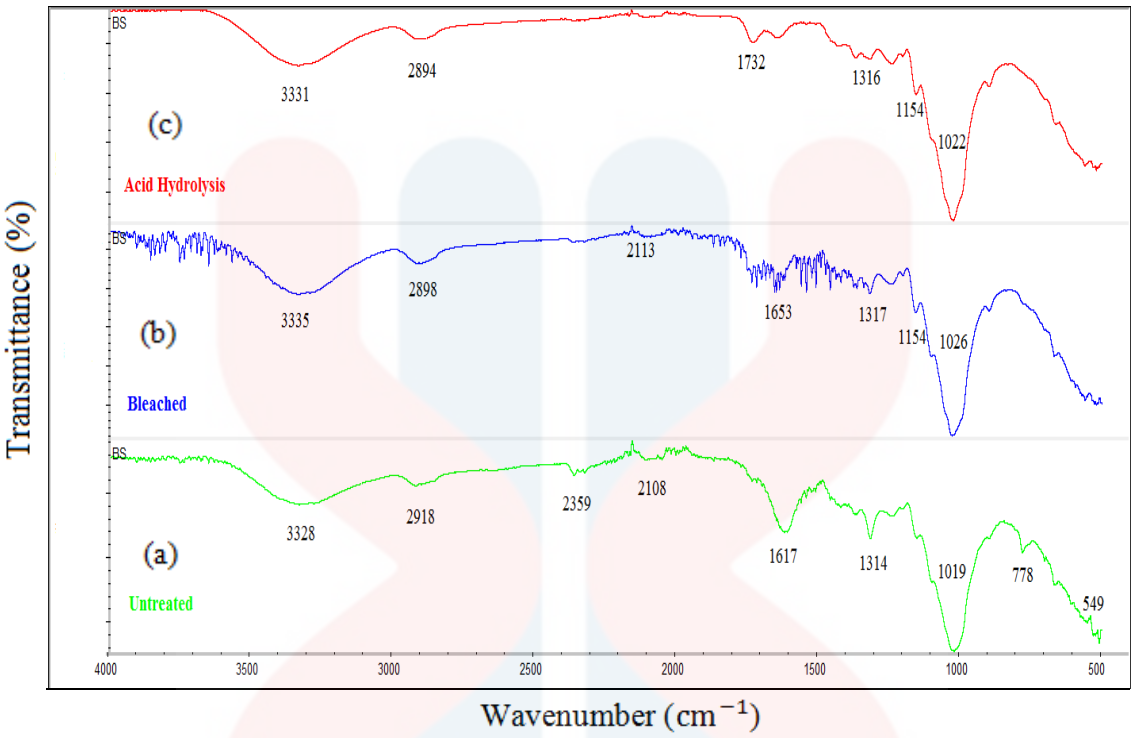

Figure 4.6: FTIR spectra of (a) untreated BS, (b) bleached BS and (c) acid hydrolysis BS cellulose fiber

Figure 4.6 shows FTIR spectra of untreated, bleached and acid treated of BS cellulose fiber. The peaks around 3300 - 3400 cm^{-1} were observed in all spectra that representing N-H stretching. The region between 3500 - 4000 cm^{-1} was known to be the dominant peaks caused by the stretching vibration of O-H and C-H. The O-H group was found in both untreated and treated BS as it was bound to the cellulose structure indicating the presence of cellulose component in the BS (Johar *et al*, 2012).

While, there were same vibration occur in both untreated and bleached BS at peaks 2108 cm^{-1} and 2113 cm^{-1} respectively. The peaks were representing C=C stretch of lignin aromatic ring. It was also observed at peak 1617 cm^{-1} of untreated BS. The decreasing in peak intensity of the aromatic C=C stretch in acid treated shows that the

lignin was partially removed (Alemdar & Sain, 2008). At peaks around 1300 - 1400 cm^{-1} shows the O-H bending of adsorb water. Although BS cellulose fiber were dried before being analyzed, the water adsorb in the cellulose molecule were not completely removed (Abrahama *et al*., 2011).

However, peak 1733 cm^{-1} was observed in acid treated BS cellulose fiber that indicate the presence of C=O linkage. Alemdar & Sain (2008) reported that the linkage attribute to whether uronic ester groups of hemicellulose or the ester linkage of carboxylic acid of ferulic and *p*-coumeric lignin acid thus implying that the hemicellulose and lignin were not completely removed during the acid treatment of BS cellulose fiber.

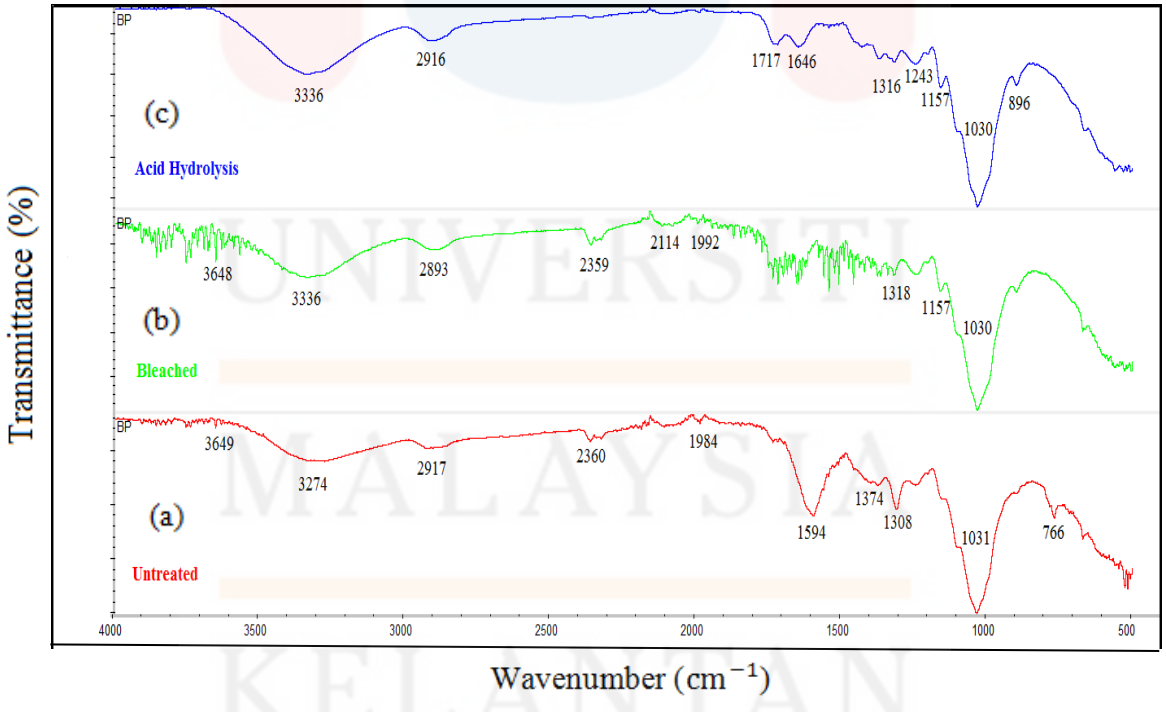

Figure 4.7: FTIR spectra of (a) untreated BP, (b) bleached BP and (c) acid hydrolysis BP cellulose fiber

From Figure 4.7, the FTIR patterns were similar to each other, but there is a small changes as no vibration peak observed on acid treated BP cellulose fiber. At the early stages of untreated, bleached and acid treated BP, there were O-H stretching vibrations around peak 3200 - 3650 cm^{-1} showing that the cellulose component were not removed through the chemical treatment (Johar *et al*., 2012). In untreated BP, C-H stretching and its bending were found at peaks 2917 cm^{-1} and 1984 cm^{-1} respectively. As for the bleached BP, both N-H and C-H stretching were found at peak 2893 cm^{-1} as well as C-H bending at peak 1992 cm^{-1}.

An aromatic C=C stretch of lignin was detect at peak 2114 cm^{-1} indicate that there is still a lignin present in bleached BP but it was partially removed after being treated with acid due to the decreasing in peak intensity of acid hydrolysis BP (Alemdar & Sain, 2008). While, an O-H bending were observed in untreated, bleached and acid treated BP at peaks 1374 cm^{-1}, 1318 cm^{-1} and 1316 cm^{-1} respectively. This is because of the difficulties of water adsorption in the cellulose molecule due to cellulose-water interaction (Abrahama *et al*., 2011). Besides, for the acid treated BP, C=O stretching and aromatic C=C stretch were observed at peaks 1717 cm^{-1} and 1646 cm^{-1} respectively. Both C=O and aromatic C=C stretch were indicating the presence of hemicellulose and lignin in BP cellulose fiber thus, implies theory that the hemicellulose and lignin were not completely removed during the whole chemical treatment of BP cellulose fiber.

4.3.3 Determination of Crystallinity Structure of Cellulose Fiber using X-ray Diffraction (XRD)

Cellulose is known having crystalline structure that contrary to hemicellulose and lignin which are amorphous in nature due to the interaction of hydrogen bonds as well as Van der Waals forces between the adjacent molecules. XRD analysis was conducted in order to analyze the crystallinity of cellulose fiber extracted from both BS and BP. The diffraction patterns that obtained for untreated, bleached and acid treated of BS and BP were shown as in Figure 4.8 and 4.9.

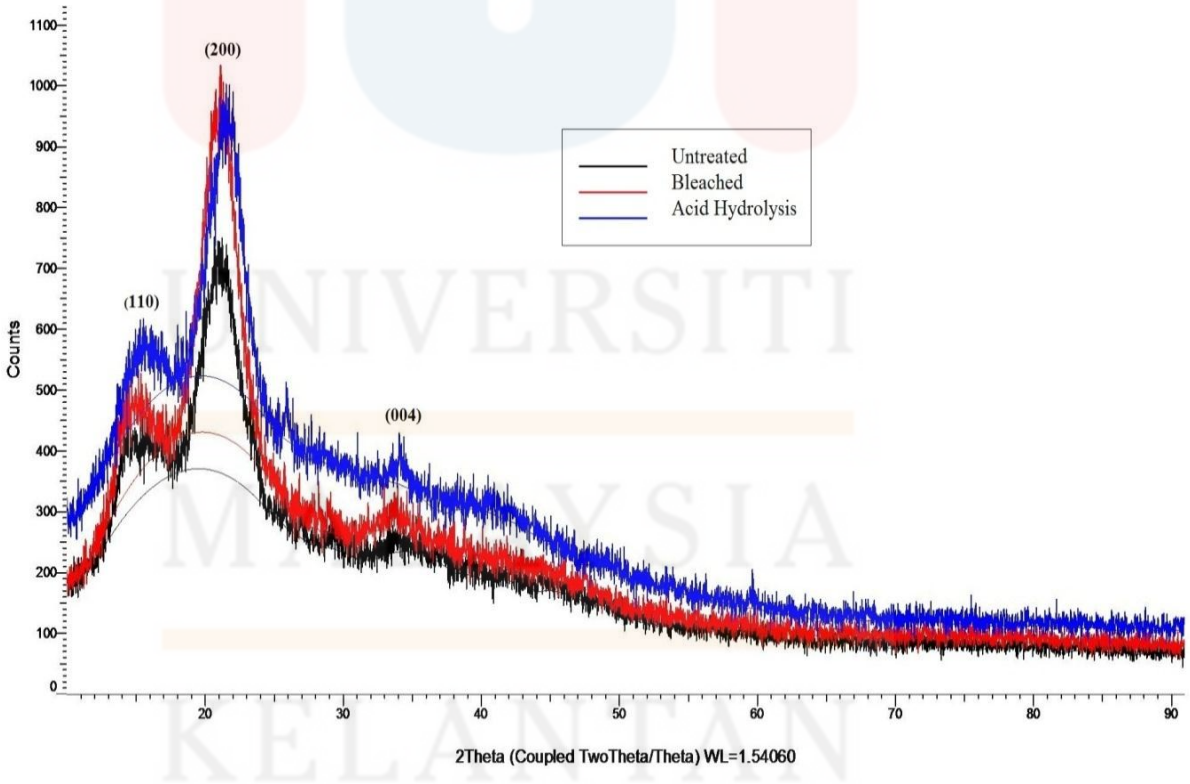

Figure 4.8: XRD analysis for (a) untreated BS, (b) bleached BS and (c) acid hydrolysis BS cellulose fiber

From Figure 4.8, the pattern XRD for untreated, bleached and acid treated BS samples shows a quite similar to each other. All the BS samples were assumed as semi crystalline as it consist of broad peak of amorphous region as well as the crystalline peak. They are typical of cellulose-I structure with well-defined amorphous XRD bump that were present around 2θ = 15º, 21º and 34º which correspond to the (110), (200) and (004) crystallographic planes respectively. The entire untreated, bleached and acid treated BS shows the highest and sharpest peak at 2θ = 21º that will correspond to the high crystalline content. Besides, the pattern shows that there is an only small difference between all the peaks of untreated, bleached and acid treated BS. As expected, the crystalline peaks were increased upon the purification of the cellulose fiber before and after treatment.

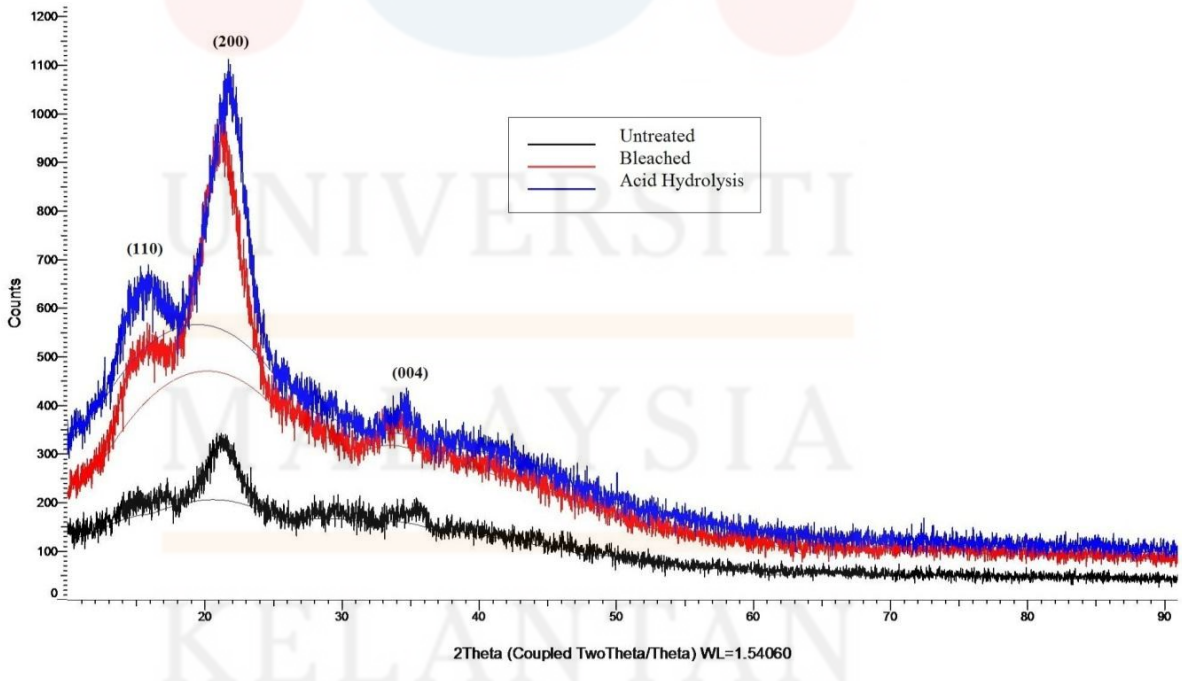

Figure 4.9: XRD analysis for (a) untreated BP, (b) bleached BP and (c) acid hydrolysis BP cellulose fiber

As for the BP samples, untreated, bleached and acid treated XRD analysis was shown in Figure 4.9. The combination of broad and crystalline peak in this sample indicates that this sample have both amorphous and crystal thus, it is considered as semi crystalline peak. The pattern also quite similar with each other for bleached and acid treated BP but not for the untreated BP as it only having amorphous XRD bump around $2\theta = 21^{\circ}$ as it is much blunt and broaden. While, there are three well defined amorphous XRD bump around $2\theta = 15^{\circ}$, 21° and 35° correspond to the planes (110), (200) and (004) for both bleached and acid treated BP. Among the peaks, $2\theta = 21^{\circ}$ would have the highest intensity. The entire crystalline peaks (intensity) of untreated, bleached and acid treated BP have increased accordingly upon the treatments which indicate that acid treated have the highest crystallinity value. The crystallinity index determined for the various samples were summarized in Table 4.5.

Table 4.5: Crystallinity index of BS and BP at different stages treatment.

Samples	**Crystallinity index (%)**	
	BS	**BP**
Untreated	30.88	28.18
Bleached	49.02	38.56
Acid Hydrolysis	41.01	41.15

Table 4.5 shows the crystallinity index for both BS and BP samples of untreated, bleached and acid treated. The crystallinity indexes were estimated as 30.88 %, 49.02 % and 41.01 % for untreated, bleached and acid treated BS respectively. In most cases, the cellulose fiber crystalline portion would be higher for treated compare to the untreated one. The increasing crystallinity index in bleached BS was correspond to the partial removal of hemicellulose and lignin during the treatment (Alemdar & Sain, 2008). However, the crystallinity index for acid treated BS were found to be decreasing to only 41.01 % from 49.02 % opposing the expected result as it supposed to increase as well as having higher value than the bleached BS. This result may be caused by the chemical solvent that has dissolved partly the crystalline part thus decreasing the crystallinity index.

As for the BP sample, a continuous increased of the crystallinity index was observed upon the successive treatment from untreated, bleached and acid treated which are 28.18 %, 38.56 % and 41.15 % respectively. The highest value would be 41.15 % correspond to the acid treated BP which is also display the highest peak at $2\theta = 22^{\circ}$ for BP sample. The increasing crystallinity pattern was following their treatment stages which can be related to the progressive removal of amorphous non- cellulosic materials. Furthermore, the highest value upon acid hydrolysis treatment was due to the penetration of hydronium ions in the cellulose amorphous regions allowing the hydrolytic cleavage of glycosidic bonds thus, releasing the individual crystallite as well as improving the crystallinity of the cellulose fiber. In addition, the increases in cellulose fiber crystallinity were associated with the higher tensile strength as well as their stiffness and rigidity (Johar *et al*., 2012).

4.3.4 Thermal Stability Study of Cellulose Fiber using Thermogravimetric Analysis (TGA)

TGA was measured in order to acquire the thermal stability of both BS and BP cellulose fibers before and after treated by several treatments. Figure 4.10 and 4.11 shows the TG curves for BS and BP cellulose fiber after being chemically treated, respectively.

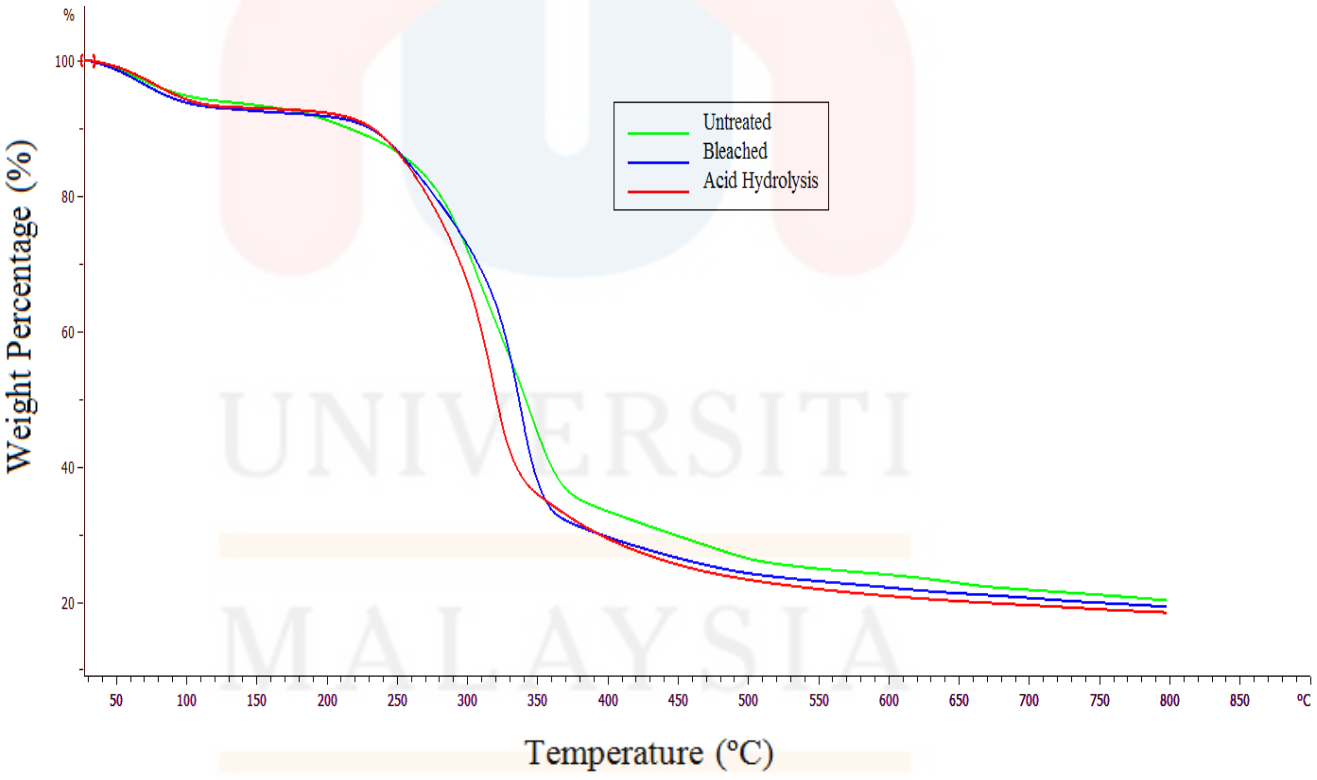

Figure 4.10: TG analysis for (a) untreated BS, (b) bleached BS and (c) acid hydrolysis BS cellulose fiber

Figure 4.10 show TG curve for BS cellulose fiber. It illustrates that initial weight loss start occurring at temperature range from 50 – 100 ºC but only in small amount. Temperature 200 – 350 ºC was observed to be the degradation temperature as there were huge amount of weight loss by 60 % was appear during this temperature. The weight loss of entire BS were decreased slightly at temperature 340 ºC until it maximum temperature of 900 ºC. It was found that acid treated has the lowest residues left after 550 ºC followed by bleached and untreated was having the highest residues.

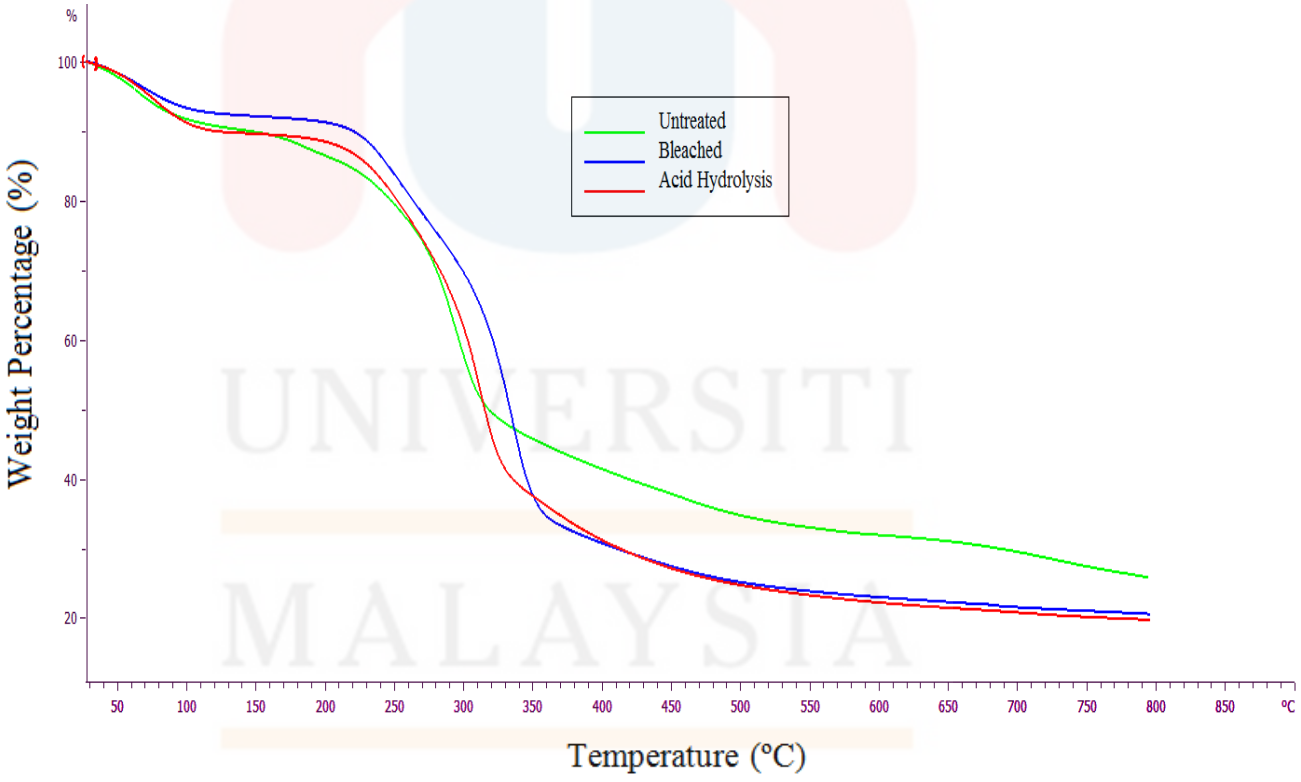

Figure 4.11: TGA analysis for (a) untreated BP, (b) bleached BP and (c) acid hydrolysis BP cellulose fiber

There were quite similar results obtained for BP cellulose fiber in the Figure 4.11. All the untreated, bleached and acid treated cellulose fiber starts reducing weight at temperature from 50 – 120 ºC. Then, the acid treated start decomposing before the temperature reach 200 ºC while, untreated and bleached cellulose fiber decomposed after reaching 200 ºC. In term of the residues, untreated cellulose fiber has the highest amount of residues left about 30 – 40 %. Meanwhile, the residues of the bleached and acid treated cellulose fiber were less compared to the untreated by only 20 %.

Both BS and BP cellulose fiber shows sharp weight loss at higher temperature. Among all the untreated, bleached and acid treated of both BS and BP cellulose fiber, acid treated was observed to have highest thermal stability of materials. This is because of the absence of component that being reported to have low decomposition temperature compare to cellulose fiber which are hemicellulose and lignin as it have been removed during the chemical treatment. These have proved that the removal of hemicellulose and lignin through the several chemical treatments has improved the thermal stability of the BS and BP cellulose fiber (Johar *et al*., 2012). Besides, from the observation, there were still remaining residues after all the BS and BP samples (untreated, bleached and acid hydrolysis) are burnt at maximum temperature indicating the presence of carbonaceous materials in BS and BP cellulose fiber in nitrogen atmosphere. While, acid treated of both BS and BP cellulose fiber was found to have lesser residual left due to the removal of hemicellulose and lignin as well as related to the high crystallinity of the cellulose fiber (Alemdar & Sain, 2008).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this present work, cellulose fibers were successfully extracted from banana pseudo stem (BS) and banana peduncle (BP) through chemical extraction. The composition of the BS and BP cellulose fibers were determined as well as the cellulose fiber content of BS and BP after acid hydrolysis was found to be 88 % and 95 % respectively. Besides, the processing parameters of acid hydrolysis were successfully optimized using RSM where the optimum parameters for both BS and BP were 5 mol/ L of H_2SO_4 at 30 ºC in 60 minutes. In this study, untreated and chemically treated BS and BP cellulose fiber were being compared.

The characterization of structural morphology, functional group, phase structure and thermal stability of the cellulose fiber were successfully performed using SEM, FTIR, XRD and TGA. SEM visualized clear pictures of BS and BP after chemical treatment. It was found that component that bind the fibrils structure in BS was

completely removed but not in BP as the fiber bundles were not completely separate into individual fibers.

While, FTIR analysis show quite similar pattern for the untreated, bleached and acid treated of both BS and BP cellulose fiber. The decreasing in peak intensity of aromatic C=C stretch in acid treated for both BS and BP indicate that hemicellulose and lignin were only removed partially. This is because the C=O stretching and aromatic C=C stretch peaks that present the hemicellulose and lignin were still found in acid treated BS and BP cellulose fiber.

Besides, results from XRD analysis performed that the crystallinity index in BP sample were increasing upon the treatment stages where acid treated BP having highest crystallinity index. As for the BS sample, the crystallinity index were increased after bleaching treatment but the acid treated BS sample having lower crystallinity index than the bleached BS. Overall for both BS and BP samples, bleached BS has the highest crystallinity value by 49.02 % followed by acid treated BP with 41.15 %.

While, TGA analysis displayed that acid treated of both BS and BP cellulose fibers were having good thermal stability compared to untreated and bleached. It implies that the thermal stability of BS and BP cellulose fibers were improved through the chemical treatment. The residual left for acid treated BS and BP also observed to be lesser compared to others indicate the removal of hemicellulose and lignin as well as can be relate to high crystallinity of cellulose fiber.

5.2 Future Recommendation

Cellulose fibers were obtained through several chemical treatments. However, this research was only manages to removed partly of the non-cellulosic compounds. Highly purified cellulose fiber can be obtained by combining microwave liquefaction and chemical treatment together with ultrasonication. This is because microwave liquefaction could eliminate almost all lignin resulting high cellulose fiber content in an efficient time as well as economically viability.

Further with chemical treatment will help to purify the enriched cellulose fiber. Thus, these combinations were significantly efficient in completely removing non-cellulosic compounds. While, ultrasonication will separate the nanofibrils in order to extract cellulose nanofibers. In addition, the characterization of structural morphology can be supported by using Transmission Electron Microscopy (TEM) as it has the smaller electrons wavelength that might be useful to observe internal structure of the cellulose fiber especially for crystal structure.

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APPENDIX A

CALCULATIONS

A1 Concentration of Sulphuric Acid

M of sulphuiric acid = 98.07 g/mol

Sample volume = 24 mL / 0.024 L

a) **5.00 mol/L**

$M_1V_1 = M_2V_2$

$98.07\frac{g}{mol}(V_1) = 5\frac{mol}{L}(0.024\ L)$

$V_1 = \frac{0.12}{98.07}$

$V_1 = 1.22 \times 10^{-3}\ L$

$= 1.22\ mL$

b) **10.00 mol/L**

$M_1V_1 = M_2V_2$

$98.07\frac{g}{mol}(V_1) = 10\frac{mol}{L}(0.024\ L)$

$V_1 = \frac{0.24}{98.07}$

$V_1 = 2.45 \times 10^{-3}\ L$

$= 2.45\ mL$

c) **15.00 mol/L**

$M_1V_1 = M_2V_2$

$98.07\frac{g}{mol}(V_1) = 15\frac{mol}{L}(0.024\ L)$

$V_1 = \frac{0.36}{98.07}$

$V_1 = 3.67 \times 10^{-3}\ L$

$= 3.67\ mL$

A2 Percentage Removal of Hemicellulose and Lignin

a) BS sample

Untreated = 320 g

After alkali treatment = 239 g

After bleached = 171 g

Removal amount of hemicellulose

320 g – 239 g = 81 g

$$\text{Removal (\%)} = \frac{81\ \text{g}}{320\ \text{g}} \times 100\ \%$$

$$= 25.3\ \%$$

Removal amount of lignin

239 g – 171 g = 68 g

$$\text{Removal (\%)} = \frac{68\ \text{g}}{239\ \text{g}} \times 100\ \%$$

$$= 28.5\ \%$$

Amount of cellulose

% = 100 – 25.3 – 28.5

= 46.2 %

b) BP sample

Untreated = 320 g

After alkali treatment = 247 g

After bleached = 155 g

Removal amount of hemicellulose

320 g – 247 g = 73 g

$$\text{Removal (\%)} = \frac{73\ \text{g}}{320\ \text{g}} \times 100\ \%$$

$$= 22.8\ \%$$

Removal amount of lignin

247 g – 155 g = 92 g

$$\text{Removal (\%)} = \frac{92\ \text{g}}{247\ \text{g}} \times 100\ \%$$

$$= 37.2\ \%$$

Amount of cellulose

% = 100 – 22.8 – 37.2

= 40.0 %

A3 Yield of Cellulose Fiber

$$\text{Yield (\%)} = \left(\frac{m_{\text{CF}}}{m_{\text{initial}}}\right) \times 100\%$$

a) BS cellulose fiber run 14

$\text{m}_{\text{CF}} = 2.64\ \text{g}$

$\text{m}_{\text{initial}} = 3\ \text{g}$

$$\text{Yield (\%)} = \left(\frac{2.64\ \text{g}}{3\ \text{g}}\right) \times 100\%$$

$$= 88\ \%$$

b) BP cellulose fiber run 14

$\text{m}_{\text{CF}} = 2.86\ \text{g}$

$\text{m}_{\text{initial}} = 3\ \text{g}$

$$\text{Yield (\%)} = \left(\frac{2.86\ \text{g}}{3\ \text{g}}\right) \times 100\%$$

$$= 95.33\ \%$$

A4 Crystallinity Index

$$\text{CrI (\%)} = \frac{(\text{I}_{002} - \text{I}_{\text{am}})}{\text{I}_{002}} \times 100$$

Where, I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the samples. The diffraction peak for plane (002) is located at diffraction angle around 2θ = 22º and the intensity scattered by the amorphous part is located at a diffraction angle around 2θ = 18º.

	a) BS sample	b) BP sample
Untreated	I_{002} = 625 I_{am} = 432 $\text{CrI}\ (\%) = \frac{(625 - 432)}{625} \times 100$ $= \frac{193}{625} \times 100$ = 30.88 %	I_{002} = 291 I_{am} = 209 $\text{CrI}\ (\%) = \frac{(291 - 209)}{291} \times 100$ $= \frac{82}{291} \times 100$ = 28.18 %
Bleached	I_{002} = 865 I_{am} = 441 $\text{CrI}\ (\%) = \frac{(865 - 441)}{865} \times 100$ $= \frac{424}{865} \times 100$ = 49.02 %	I_{002} = 848 I_{am} = 521 $\text{CrI}\ (\%) = \frac{(848 - 521)}{848} \times 100$ $= \frac{327}{848} \times 100$ = 38.56 %
Acid Hydrolysis	I_{002} = 929 I_{am} = 548 $\text{CrI}\ (\%) = \frac{(929 - 548)}{929} \times 100$ $= \frac{381}{929} \times 100$ = 41.01 %	I_{002} = 1023 I_{am} = 602 $\text{CrI}\ (\%) = \frac{(1023 - 602)}{1023} \times 100$ $= \frac{421}{1023} \times 100$ = 41.15 %

APPENDIX B

FIGURES

B1: Banana pseudo stem before dried

B2: Banana pseudo stem after oven dried

B3: Bleached and alkali treated samples after oven dried

B4: Bleaching process of cellulose fiber