PRODUCTION OF MICROCRYSTALLINE CELLULOSE FROM PALM CELLULOSE PULP

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Thesis submitted in partial fulfilment of the requirements
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Name of main supervisor	: TN HAJI MOHD NOOR BIN NAWI
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ABSTRACT

Malaysia currently accounts for 39 % of world palm oil production and 44% of world exports. Being one of the biggest producers and exporters of palm oil and palm oil products, the palm oil production in Malaysia contributes 85.5% of the total biomass production in Malaysia. From the 85.5%, empty fruit bunches (EFB) are the most that contribute to biomass waste produced. Biomass is made up of cellulose, hemicellulose, and lignin. Thus, it has great potential for use as a cellulose source for the production of microcrystalline cellulose (MCC). Just like that, we can produce very valuable product from waste that are free. The study on the operable condition in synthetizing the microcrystalline cellulose (MCC) take place by understanding the effect of consistency and sodium hydroxide (NaOH) concentration in the alkaline pretreatment for the production of microcrystalline cellulose (MCC) from empty fruit bunch (EFB). The empty fruit bunch are pretreated using hot water that proceeded by with alkaline pretreatment using sodium hydroxide (NaOH) and lastly, the microcrystalline cellulose (MCC) were produced by using hydrolysis process using hydrochloric acid (HCL). The alkaline pretreatment was optimized by using different concentration of sodium hydroxide (NaOH) solution and the operable condition for the synthesis of microcrystalline cellulose (MCC) was determined by the consistency of the slurry solution. The total weight loss during the alkaline pretreatment produced was determined using a formula and the lignin content was determined by using TAPPI standard T-222 method. The properties of original fiber, treated fiber, alpha cellulose and microcrystalline cellulose (MCC) were determined by Fourier Transform Infrared (FTIR) Spectroscopy. Scanning Electron Microscope (SEM) analysis has shown clearly visible alteration before and after hydrolysis. The operable condition of for the synthesis of microcrystalline cellulose (MCC) is with the consistency of 5% and the optimal concentration for the alkaline pretreatment using sodium hydroxide (NaOH) solution is 20%. These optimization factors allowed the production microcrystalline cellulose (MCC) from the empty fruit bunch (EFB). Thus providing plenty of opportunities for its many applications.

ABSTRAK

Malaysia pada masa ini mencakupi 39% daripada pengeluaran minyak sawit dunia dan 44% daripada eksport dunia. Sebagai salah satu pengeluar dan pengeksport terbesar produk minyak sawit dan minyak kelapa sawit, pengeluaran minyak sawit di Malaysia menyumbang 85.5% daripada jumlah pengeluaran biomas di Malaysia. Daripada 85.5% yang, tandan buah kosong (EFB) adalah yang slah satu penyumbang kepada sisa biomas yang dihasilkan. Biomas terdiri daripada selulosa, hemiselulosa dan lignin. Oleh itu, ia mempunyai potensi besar untuk digunakan sebagai sumber selulosa untuk pengeluaran microcrystalline selulosa (MCC). Dengan mudah saja, kita dapat menghasilkan produk yang sangat bernilai daripada sisa biomas yang percuma. Kajian tentang kondisi beroperasi untuk menghasilkan selulosa microcrystalline yang (MCC) dilakukan dengan memahami kesan konsistenci dan kepekatan natrium hidroksida (NaOH) dalam rawatan alkali untuk pengeluaran microcrystalline selulosa (MCC) daripada tandan buah kosong (EFB). Tandan buah kosong di rawat dengan menggunakan air panas yang diteruskan dengan dengan rawatan alkali menggunakan natrium hidroksida (NaOH) dan akhir sekali, selulosa microcrystalline (MCC) telah dihasilkan dengan menggunakan proses hidrolisis menggunakan asid hidroklorik (HCL). Rawatan alkali telah dioptimumkan dengan menggunakan kepekatan larutan natrium hidroksida (NaOH) yang berbeza dan keadaan beroperasi untuk sintesis microcrystalline selulosa (MCC) telah ditentukan oleh consistency larutan. Berat yang hilang semasa rawatan alkali dapat ditentukan dengan menggunakan formula dan kandungan lignin yang telah ditentukan dengan menggunakan TAPPI standard kaedah T-222. Ciri-ciri fiber, fiber yang dirawat, alpha selulosa dan microcrystalline selulosa (MCC) telah ditentukan oleh Fourier Transform Infrared (FTIR) Spektroskopi. Mikroskop Imbasan Elektron (SEM) analisis telah menunjukkan perubahan sebelum dan selepas hidrolisis dapat dilihat dengan jelas. Keadaan beroperasi daripada untuk sintesis microcrystalline selulosa (MCC) adalah dengan konsistensi 5% dan kepekatan yang optimum untuk rawatan alkali menggunakan larutan natrium hidroksida (NaOH) adalah 20%. Faktor-faktor ini pengoptimuman membolehkan penghasilan selulosa microcrystalline (MCC) daripada tandan buah kosong (EFB). Sekali gus menyediakan banyak peluang untuk untuk aplikasinya.

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LIST OF SYMBOLS

W_1	Dry weight before alkaline pre-treatment
W_2	Dry weight after alkaline pre-treatment

LIST OF ABBREVIATIONS

AGU	Anhydro glucopyranose unit
CPO	Crude palm oil
EFB	Empty fruit bunch
FTIR	Fourier transform infrared
HCL	Hydrochloric acid
H_2SO_4	Sulphuric acid
MCC	Microcrystalline cellulose
NaOH	Sodium hydroxide
NaOCL	Sodium hypochloride
OPF	Oil palm frond
OH	Hydroxyl group
POMS	Palm oil mill sludge
PKC	Palm kernel cake
POMW	Palm Oil Mill Wastes
XRD	X-ray powder diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Malaysia is the world's second largest palm oil producer with 38% of the global market, and is the largest palm oil exporter, consisting of about 88% of the market's palm oil in 2011 (Aghamohammadi et al., 2016). Oil palm plantations have turned into the most important economic contributor in Malaysia. But at the same time, palm oil mills produce a large amount of solid waste. Right now, the largest solid biomass generated in Malaysia originated from oil palm plantations (Farhana Harun et al., 2013).

Annually, a minimum of 168 million tonnes of biomass waste is generated in Malaysia. In general, palm oil waste accounts for 94% of biomass feedstock while the remaining contributors are agricultural and forestry by-products, such as wood residues (4%), rice (1%), and sugarcane industry wastes (1%) ("Malaysia's biomass potential," 2012). If this biomass is used properly, it will not only solve the waste problem but also can create value added product. Lignocellulosic biomass which is produced from the oil palm industries include oil palm trunks, oil palm fronds, empty fruit bunch and palm pressed fibres, palm shells and palm oil mill effluent palm (Abdullah & Sulaiman, 2013).

Typically, most of the agricultural lignocellulosic biomass is comprised of about 10-25% lignin, 20-30% hemicellulose, and 40-50% cellulose. Cellulose is a highly stable polymer consisting of glucose and attached with linear chains up to 12,000 residues. It is majorly composed of (1,4)-D-glucopyranose units, which are attached by b-1,4 linkages with an average molecular weight of around 100,000 (Anwar, Gulfraz, & Irshad, 2014). Cellulose is aligned parallel to each other in fibrils, which are surrounded

by a matrix of lignin and hemicellulose. In addition, cellulose has properties such as low density, good mechanical properties as well as bio degradability (Tasaso, 2015).

Cellulose is commonly converted into useful derivatives by etherification. Among these microcrystalline cellulose (MCC) that has generated much attention and interest during these few last decades in both academic and industrial fields. Microcrystalline cellulose (MCC) gained major interest in various applications, such as stabilizer, fat replacer and texturing agent in food industry (Singh, Kanawjia, Giri, & Khetra, 2015), binder and water retainer in pharmaceutical industry (Johansson & Alderborn, 2001), and reinforcing agent in plastic industry (Wittaya, 2009).

1.2 Motivation

The global microcrystalline cellulose (MCC) market in terms of revenue, the global microcrystalline cellulose (MCC) market was valued at US$ 632.9 Mn in 2013 and is projected to reach US$ 936.3 Mn by 2020, expanding at a CAGR of 5.8% from 2014 to 2020. Pharmaceutical was the largest segment of the global microcrystalline cellulose (MCC) market, accounting for more than 35% share in 2013 ("Microcrystalline Cellulose (MCC) Market- Global Industry Analysis, Size, Growth and Forecast 2014-2020," 2016). The increased acceptance of microcrystalline cellulose as an excipient in food industry coupled with the growth of the global pharmaceutical industry is expected to drive the demand of global microcrystalline cellulose (MCC) market during the forecast period. Moreover, increasing demand for low fat food and processed food is also expected to fuel the growth of microcrystalline cellulose market over the forecast period. Rising demand for microcrystalline cellulose (MCC) in rapidly growing end-user segments such as pharmaceutical and food and beverage is likely to drive the global microcrystalline cellulose (MCC) market in the next few years. Production of microcrystalline cellulose (MCC) from eco-friendly raw materials is predicted to act as an opportunity for the MCC market in the next six years.

In addition, in Malaysia there is no company that produces microcrystalline cellulose (MCC). If we can develop more company in Malaysia, we can turn the value-

less biomass waste from the oil palm can be turned into a valuable product. At the same time, there will be no problem in getting the raw material to produce microcrystalline cellulose (MCC) because of the free abundance of oil palm biomass resource. Cheap and easy availability of raw material, regulatory support, and increasing huge demand for pharmaceutical products in the region is expected to be the driving factor for microcrystalline cellulose (MCC) production in Malaysia. We can meet the increasing demand microcrystalline cellulose (MCC) in the near future and improve the downfall economic performance of Malaysia

1.3 Problem Statement

Currently the main raw material of cellulose derivative is cellulose from wood and cotton linter. However, deforestation and acceleration of greenhouse affects gradually grown interest on agriculture products and by-products as alternative cellulose resources (Bono et al., 2009). Thus, we need to change our raw material for cellulose derivative such as oil palm biomass. The oil palm empty fruit bunch (EFB) is one the oil palm biomass product. The empty fruit bunch (EFB) traditionally are being burnt in simple incinerators, as a means of disposal and the ash recycled onto the plantation as fertilizers. But, this process causes air pollution and has now been banned in Malaysia. Furthermore, under this route of disposal, no energy is recovered. Alternatively the empty fruit bunch (EFB) has been composted and returned to the plantation. But disposing of empty fruit bunch (EFB) back to oil palm plantation without recovering remnant oil in the EFB contributes to oil spills. Empty fruit bunch (EFB) is a resource which has huge potential to be used for cellulose production, currently not being utilized (Abdullah & Sulaim, 2013).

In Malaysia there is no company that produces microcrystalline cellulose (MCC). Therefore, consumer in Malaysia had to import microcrystalline cellulose (MCC) from outside Malaysia such as China. The demand of microcrystalline cellulose (MCC) had increased from years to years.

1.4 Objectives

The following are the objectives of this research:

1) To study the effect of consistency in synthetizing the microcrystalline cellulose (MCC).
2) To study the effect of sodium hydroxide (NaOH) concentration on the alkaline pretreatment.
3) To produce microcrystalline cellulose (MCC) from empty fruit bunch (EFB).

1.5 Scopes of Study

The following are the scopes of this research:

1) The optimum consistency on the synthesized of the microcrystalline cellulose (MCC).
2) The effect of varied concentration of sodium hydroxide (NaOH) (10%, 20%, 40%) during the alkaline pretreatment for the synthesized of the microcrystalline cellulose (MCC).
3) To evaluate the pretreated fiber by using a formula to calculate the total weight loss, TAPPI standard T-222 method to calculate the percentage of lignin and fourier transform infrared (FTIR). The produced microcrystalline cellulose (MCC) was characterized by using fourier transform infrared (FTIR) and surface morphology (SEM) analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction and history

The oil palm tree (Elaeis guineensis) is originally an ancient tropical plant in the West Africa tropical rainforest where it grows wild. Palm oil has been utilized as food and medicine throughout the ages. The evidence for the statement that the oil palm had been used for ages was the discovery of earthenware jar containing residue of palm oil in a 5000 years old Egyptian Tomb. The oil palm tree then was developed into an agricultural crop due to the increasing demand in the early 19th century during The Industrial Revolution where the palm oil were being used as lubricant in steam engines and other machinery and soap. In 1848, the first African oil palm seedlings were planted at the botanical garden of Bogor, Java as a decoration plants. . The oil palm was planted commercially in South East Asia in the early 20th century. This is because of the suitable soil conditions and constant rainfall and sunshine made the region one of the most suitable places to grow oil palm.

In 1917, the first commercial planting in Malaysia took place in Tennamaran Estate in Selangor, laying the foundations for the vast oil palm plantations and the palm oil industry in Malaysia. Most of the early oil palm plantation s were developed and run by the British planters. Guthrie & CO. was the first who plant the oil palm actively in Kluang, Johor under a new company known as Elaeis. In 1926, two of Harrisons & Crosfield's estates in Sumatra (Rambong Sialang and Hoenong Malajoe) began planting oil palm, while in Malaya one of their agency estates planted them in Sungai Samak estate because its land was unsuitable for rubber.

Figure 2.1: Malaysian 1st oil palm mill. (Sawit Industry: History: First Palm Oil Mill in Malaysia, n.d.)

The cultivation of oil palm increased at a fast pace in early 1960s under the government's agricultural diversification programme, which was introduced to reduce the country's economic dependence on rubber and tin. Later in the 1960s, the government introduced land settlement schemes for planting oil palm as a means to eradicate poverty for the landless farmers and smallholders. Malaysia is now one of the big names in Palm Oil thanks to the seeds, trees and previous government initiatives. We have to respect the Palm Tree in Malaysia and those who were responsible for the initiatives because it has provided employment for over half a million people and the profits from this industry sustain many others. Oil palm is a crop that has also shown itself to be the most efficient producer of edible oil.

2.2 Oil palm tree

Oil palm tree is a monoecious crop as it has both male and female flowers on the same tree. The oil palm trees grow the best within 5º north and south of the equator, where rainfall is evenly spread throughout the year, sufficient sunshine and temperatures of 25-33ºC (Gunstone, 2011). The average productive life span of oil palm tree is around 25 years and then it need to be replanted (Lin, 2011). The oil palm tree will start to produce fruit as it reach three years and the peak is between 9 to 12 years (Hasnah Fleming & Coelli, 2004).

Figure 2.2: Palm oil tree

One oil palm tree can grows compact bunch weighing between 10 to 25 kilograms, and each bunch can contain many fruitlet from 1000 up to 3000 fruitlets. The fruitlet is almost spherical or elongated in shape or oval in shape. Each fruitlet can weigh up to 30g. Usually, the fruitlet is dark purple, almost black and the color turns to orange red when ripe. Often the indication to measure the ripeness of a bunch by the number of lose fruitlet that fallen from the ripe bunch. These lose fruitlets are the ripest in the bunch, and therefore they contain the highest amount of oil.

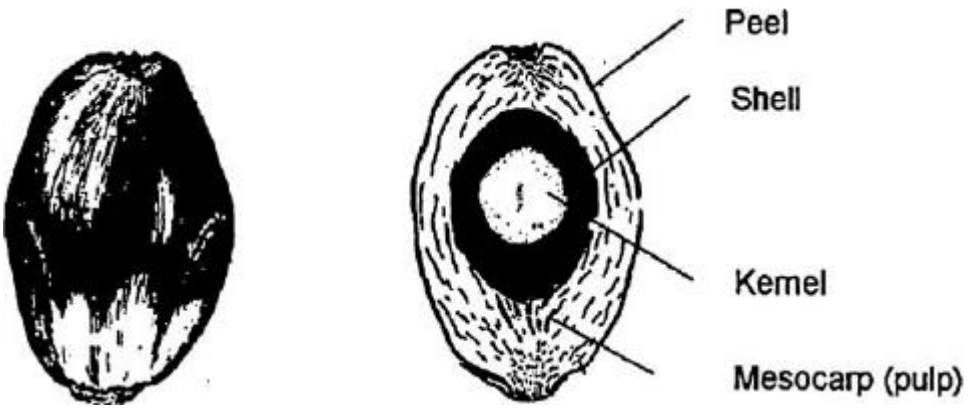


Figure 2.3: Fresh oil palm fruit and its longitudinal section

Each fruitlet consists of a hard kernel (seed) enclosed in a shell (endocarp) which is surrounded by a fleshy mesocarp. From the outer flesh, mesocarp, palm oil can be extracted and this part consists of around 20% of the fruits total weight. The palm kernel oil, which is extracted from the nut, consists of 5% of the weight of the fruit (Henderson and Osborne, 2000). Palm trees may grow up to sixty feet and more in height. The trunks of young and mature trees are wrapped in fronds which give them a rather rough appearance. The older trees have smoother trunks apart from the scars left by the fronds which have withered and fallen off.

In Malaysia, the oil palm trees planted are mainly the tenera variety, a hybrid between the dura and pisifera. The tenera variety yields about 4 to 5 tonnes of crude palm oil (CPO) per hectare per year and about 1 tonne of palm kernels. The oil palm is the most efficient oil-bearing crop in the world, requiring only 0.26 hectares of land to produce one tonne of oil while soybean, sunflower and rapeseed require 2.22, 2 and 1.52 hectares, respectively, to produce the same ("Oil Palm Tree," n.d.).

2.3 Palm oil plantation, processing and waste

Since the government has introduced the agricultural diversification programme in the early 1960, the cultivation of oil palm increased at a fast pace since then. Statistics show that the cultivation of oil palm in year 1960s, Malaysia has had only 54000 hectares of oil palm plantations. The cultivation of oil palm had increased rapidly since then. In the new millennium, oil palm plantations have occupied 3.38 million

hectares of Malaysian soils. By 2014, Malaysia has recorded a staggering 5.39 million hectares of oil palm plantations, an increase of 11.0% from the previous 4.85 million hectares in 2010 (Awalludin, Sulaiman, Hashim, & A. W. Nadhari, 2015). Malaysia's total landmass is 32.98 million hectares, meaning that oil palm plantation alone covers more than 16% of the available land. Strong worldwide demand for edible vegetable oil, palm oil-based products and palm oil biodiesel each year has made this expansion become more significant.

A number of stages is needed to produce the palm oil, the stages are from the sterilization of the fresh fruit bunch to the digestion, threshing and clarification of the oil. At each stages of the process different type of biomass waste will be produced. In general all wastes from the palm industry are termed as Palm Oil Mill Wastes (POMW). The milling process and plantation activities generate a large amount of solid waste consisting of trunks, fronds, leaves from the plantation and empty fruit bunch (EFB), palm oil mill sludge (POMS), palm kernel cake (PKC), decanter cake, fiber and shells from processing (Embrandiri, Ibrahim & Singh, 2013).

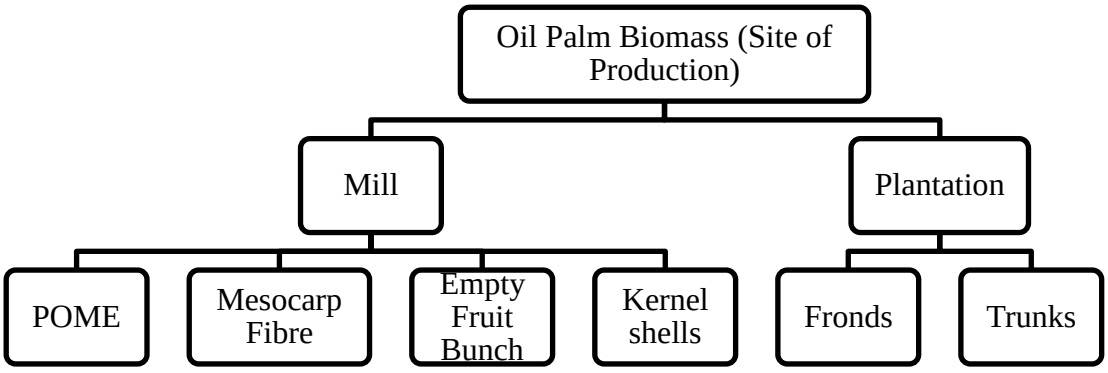


Figure 2.4: Oil Palm Biomass (Site of Production)

Biomass can generally be described as all organic matters or compounds either produced from crops, forestry or marine life. Other wastes such as sewage and municipal solid waste are also categorized as biomass. Biomass is a type of hydrocarbon material consists of carbon, hydrogen, oxygen and nitrogen (Yaman, 2004). However,

some of the biomass may contain sulphur and other inorganic substances, but present in a small proportion. A plant biomass is produced through the photosynthesis process during its lifetime.

The palm oil industry contributes 85.5% of the total biomass production in Malaysia (Umar, Jennings, & Urmee, 2013). In the palm oil mill, palm oil consists only 10% of the total biomass. The rest, 90% biomass are discarded as wastes (Abdullah & Sulaiman, 2013). At present, Malaysia has at least 417 productive palm oil extraction mills nationwide (Umar, Jennings, & Urmee, 2013). In combined, these mills can generate more than 12.4 million tonnes of empty fruit bunch as solid waste at yearly basis. . During oil palm fruit harvesting, the pruning of oil palm fronds produces approximately 44 million tonnes dry weight of oil palm fronds annually. During the replanting season, oil palm fronds and oil palm trunk can mountain up to 4 and 18 million tonnes (dry weight) respectively (Kong, Loh, Bachman, Rahim, & Salimon, 2014). Biomass is made up of cellulose, hemicellulose, lignin, extractives and inorganics with different physical and chemical properties due to its diverse origin and species.

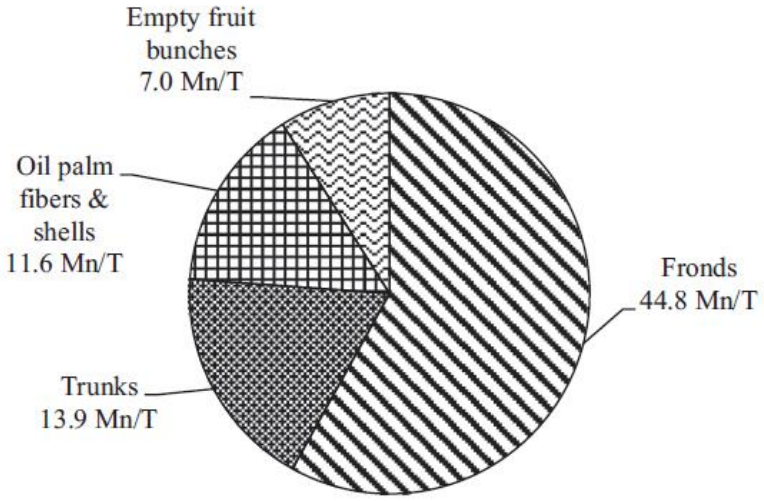


Figure 2.5: Availability of dry weight oil palm biomass in Malaysia in 2009 (Awalludin, Sulaiman, Hashim, & A. W. Nadhari, 2015).

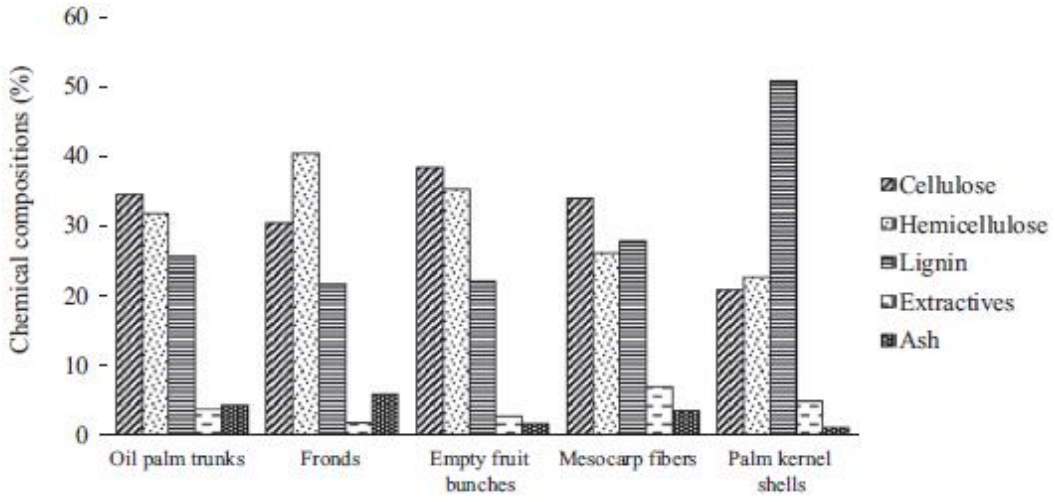


Figure 2.6: Chemical compositions of oil palm biomass (Awalludin, Sulaiman, Hashim, & A. W. Nadhari, 2015).

2.4 Empty fruit bunch (EFB)

The empty fruit bunch (EFB) constitutes about 20% to 22% of the weight of fresh fruit bunch and contains 30.5% dry matter, 2.5% oil and 67% water. An approach towards adding value to empty fruit bunch (EFB) is by chemical modification. Empty fruit bunch (EFB), like other woody products is made up of cellulose, lignin and hemicelluloses. The empty fruit bunch (EFB) has the highest fibres yield is the only material commercially utilized for fibre extraction compared to other oil palm residues. Empty fruit bunch (EFB) typically comprises of cellulose about 24–65%, hemicellulose about 21–34% and finally lignin about 14–31% (Chang, 2014).

Empty fruit bunch (EFB) are free of chemical and mineral additives. It is saturated with water due to the biological growth and steam sterilization at the mill. The empty fruit bunch (EFB) have traditionally been burnt in simple incinerators, as a means of disposal and the ash recycled onto the plantation as fertilizer. However, this process causes air pollution and has now been banned in Malaysia, furthermore, under this route of disposal, no energy is recovered. Alternatively empty fruit bunch (EFB) can be composted and returned to the plantation, or returned directly as mulch. Thus converting these residues into a useful biomass will provide a new alternative resource of cellulose rather than depending on wood source alone (Abdullah & Sulaim, 2013).

Element	Composition
H	6.3
C	48.8
S	0.2
N	0.2
O	36.7
Ash	7.3

Table 2.1: Chemical composition on dry basis of empty fruit bunch (EFB) waste (Mahlia, 2001).

Parameters	Empty fruit bunch (EFB)
Moisture content, %	60
pH	6.7±0.2
Total nitrogen (TN)	58.9 (%)
Phosphorus (P_2O_5)	0.6±0.1 (%)
Potassium	2.4±0.4 (%)

Table 2.2: Physicochemical analysis of empty fruit bunch (EFB)(Baharuddin et al., 2009).

Figure 2.7: Empty fruit bunch (EFB)

2.5 Cellulose and Microcrystalline cellulose (MCC)

Cellulose is a naturally occurring polysaccharide and it is one of the most abundant renewable resources available on planet earth. It is a glucose polymer photosynthesized by solar energy in various plants and act as the structural basis of the plant cell wall. Cellulose has a molecular weight of about 100,000. Cellulose is a simple linear macromolecule polymer consisting of anhydroglucopyranose unit (AGU) linked together with β-(1,4) -glycosidic bonds formed between carbon 1 and carbon 4 of adjacent glucose. The second major constituent with lower molecular weight, hemicellulose, is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, methyl glucuronic acid and galacturonic acid residue (A. Mohammed et al., 2011). Lignin, a highly branched polymer attached with polysaccharides, is composed of phenyl propane based monomeric units linked together by several types of ether linkages and also various kinds of carbon-carbon bonds (Kong, S. H., Loh, S. K., Bachman, R. T., Rahim, S. A., & Salimon, J, 2014).

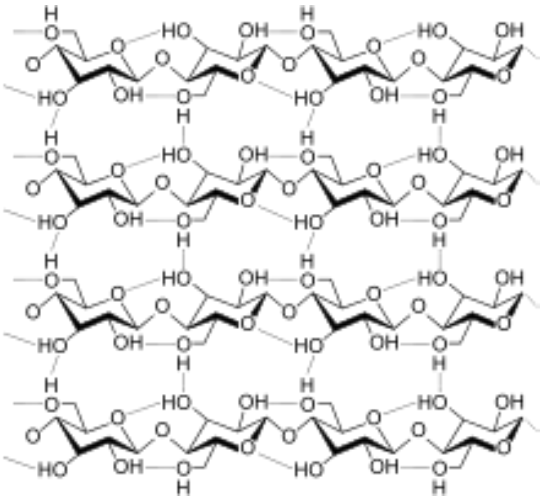


Figure 2.8: Cellulose strand ("Cellulose - Wikipedia,").

The chemical character of the cellulose is determined by the sensitivity of the β-glucosidic linkages to hydrolytic attack and by the presence of three reactive hydroxyl group groups: the primary OH on C(6) and the two secondary OHs on C(2) and C(3) in the AGUs (Ambjörnsson, Schenzel, & Germgård, 2013). Each of the AGU units consists of three hydroxyl groups at carbon 2, 3 and 6 positions. Cellulose is aligned parallel to each other in fibrils, which are surrounded by a matrix of lignin and hemicellulose. In addition, cellulose has properties such as low density, good

mechanical properties as well as bio degradability. Cellulose is aligned parallel to each other in fibrils, which are surrounded by a matrix of lignin and hemicellulose. In addition, cellulose has properties such as low density, good mechanical properties as well as bio degradability. The chemical formula of cellulose is $(C_6H_{10}O_5)_n$ (Anwar, Gulfraz, & Irshad, 2014).

Microcrystalline cellulose (MCC) is a fine powder, odourless, purified and partially depolymerised (hydrolysed) cellulose, containing both crystalline and non-crystalline (amorphous) domains. The isolation of microcrystalline celluloseparticles can be done via mechanical treatments, biological treatments and chemical treatments. By using a chemical treatment microcrystalline cellulose (MCC) can be prepared by treating alpha-cellulose from fibrous plant material with mineral acids (Thoorens, Krier, Leclercq, Carlin, & Evrard, 2014). Microcrystalline cellulose (MCC) are rich with hydroxyl groups and relatively large surface to volume ratio making it naturally hygroscopic. Microcrystalline cellulose (MCC) characterised with high degree of crystallinity, which values are typically in the range from 55% to 80% (Chuayjuljit, Su-uthai, & Charuchinda, 2010).

Microcrystalline cellulose (MCC) has been found useful as a common filler for the extrusion/spheronization process and as reinforcement in a transparent polymeric matrix (Haafiz et al., 2013, p. xx). Due to its excellent properties, microcrystalline cellulose (MCC) has generated much attention and interest during these few last decades in both academic and industrial fields. Microcrystalline cellulose (MCC) gained major interest in various applications, such as stabilizer, fat replacer and texturing agent in food industry (Singh, Kanawjia, Giri, & Khetra, 2015), binder and water retainer in pharmaceutical industry (Johansson & Alderborn, 2001), and reinforcing agent in plastic industry (Wittaya, 2009).

Molecular Formula	$C_{14}H_{26}O_{11}$
Molecular Weight	370.351 g/mol

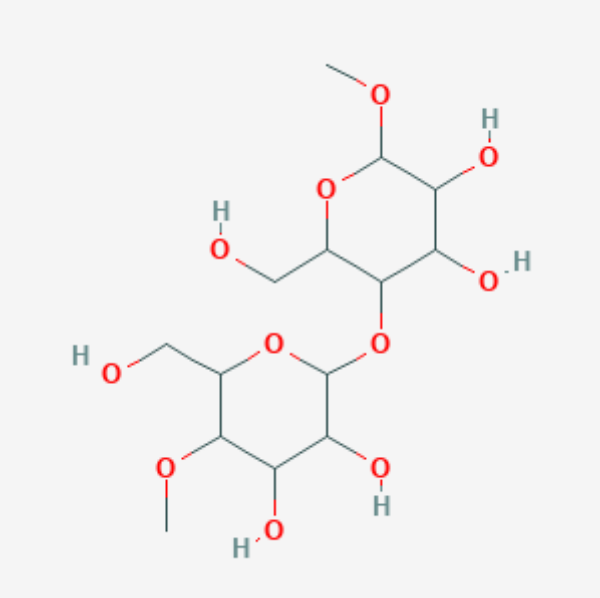
2D Structure	
IUPAC Name	2-[4,5-dihydroxy-2-(hydroxymethyl)-6-methoxyoxan-3-yl]oxy-6-(hydroxymethyl)-5-methoxyoxane-3,4-diol
MeSH Synonyms	1. Abicel 2. beta-Amylose 3. Cellulose crystalline 4. Crystalline cellulose 5. Cupricellulose 6. Dispersible cellulose 7. Microcrystalline cellulose
Physical Description	Fine, white or almost white, odourless, free flowing crystalline powde
Properties	Microcrystalline cellulose (MCC) is a free-flowing crystalline powder (a non-fibrous microparticle). It is insoluble in water, dilute acids and most organic solvents, but slightly soluble in the alkali solution of 20%. It has an extensive variety of uses in the pharmaceutical excipients and can be directly used for tabletting of dry powder. It is widely used as pharmaceutical excipients, flow aids, fillers, disintegrating agents, anti-sticking agents, adsorbents, and capsule diluents.

Table 2.2: Information on microcrystalline cellulose (MCC)

Industries	Applications
Food productions	• Hot and cold stabilizer: in ice cream, frozen food, canned meat and condiments to improve the stability. • Anti-caking agent: in baking goods to improve water retention and reduce food calories. • Fat substitute and emulsifier: in ice cream, low-fat meat products and condiments to increase the viscosity and reduce fat.
Beverage productions	• Gelling agent, stabilizer, anti-caking agents and suspending agents: in instant beverage to improve the stability of liquid.
Pharmaceutical productions	• Binders: in tablet manufacturing to increase tablet hardness. • Adsorbents, flowability: in tablet manufacturing to waterproof and improve mobility.
Cosmetics productions	• Fat substitude and thickener: in cosmetic and personal care product to keep stable quality and fresh.
Clay productions	• Binder: in Clay craft to increase the intensity of clay

Table 2.3: Microcrystalline cellulose (MCC) applications in industries.

Figure 2.9: Microcrystalline cellulose (MCC)

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CHAPTER 3

METHODOLOGY

3.1 Introduction

The purpose of this study is to produce microcrystalline cellulose (MCC). The aim of this chapter are to outline the research methodology of this study, explains the selection of the raw materials, describing the tool and methods use and the selection of parameters in order to achieve objectives of this study..

3.2 Materials

i. Empty fruit bunch (EFB) from LCSB palm oil mill
ii. Sodium hypochloride (NaOCL) 15% from Sigma Aldrich
iii. Sodium hydroxide (NaOH) pallet 98% from Sigma Aldrich
iv. Hydrochloric acid (HCL) 37% from Sigma Aldrich
v. Sulphuric acid (H_2SO_4) 98% from Sigma Aldrich

3.3 Apparatus and equipments

i. Filter funnel
ii. Filter paper
iii. Measuring cylinder
iv. Beaker
v. Hot plate with stirrer

vi. Oven

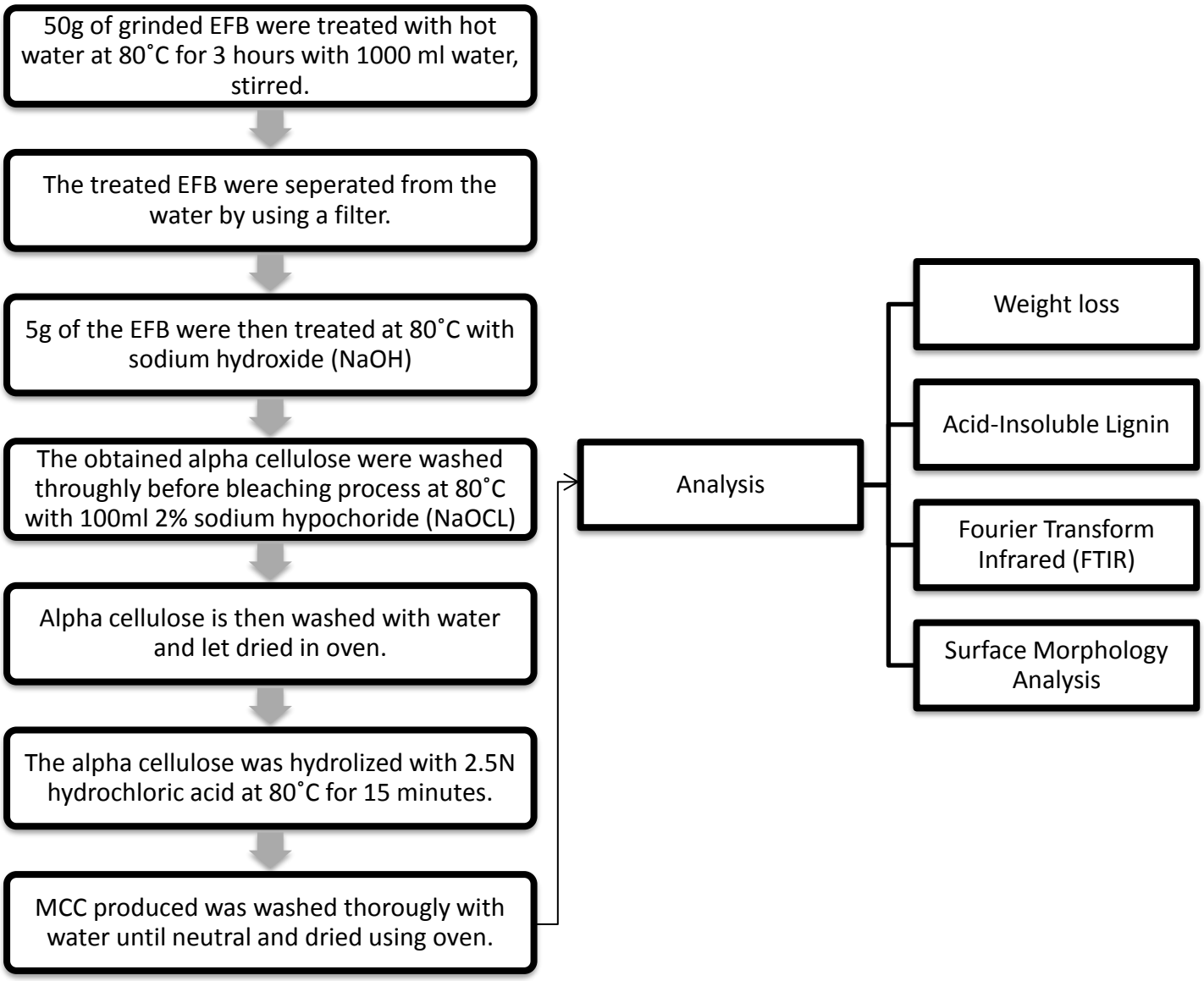
vii. Electronic balance

viii. Electron microscope

ix. Fourier Transform Infrared (FTIR)

3.4 Overview of overall experiment

Figure 3.1: Flowchart of the overall experiment



3.5 Synthesizing of microcrystalline cellulose (MCC)

Empty fruit bunch (10g, 20g, 50g, 75g, 100g) was pretreated with 1000ml hot water at 80˚C for 3 hours and stirred. 5g of treated empty fruit bunch then treated with 100 ml of (10%, 20%, 40%) sodium hydroxide at 80˚C for 60 minute and stirred. The produced alpha cellulose was washed thoroughly with water. Then the bleaching of the alpha cellulose at 80˚C with 100ml 2% sodium hypochoride (NaOCL). Then, the bleached alpha cellulose was washed thoroughly with water before the hydrolysis process. The alpha cellulose was hydrolyzed with 2.5N hydrochloric acid at 80˚C for 15 minutes. The produced microcrystalline cellulose (MCC) produced was washed thoroughly with water until neutral and dried using oven.

3.6 Analysis

i. Consistency of fiber.

Fiber was dried in oven at 105 ˚C for 2 hours before being weight using analytical balance Formula is used to calculate the consistency of fibre for the synthesis using equation 1.

$$\frac{oven\ dry\ weight\ of\ fiber}{weight\ of\ fiber + water} \times 100\% \qquad Equation\ (1)$$

ii. Weight loss after alkaline pretreatment.

Formula is used to calculate the weight loss after alkaline pretreatment using equation 2.

$$\frac{W_1 - W_2}{W_1} \times 100\% \qquad Equation\ (2)$$

Where W_1 is the dry weight before alkaline pretreatment and W_2 is the dry weight after alkaline pretreatment.

iii. Fourier Transform Infrared (FTIR).

Infrared spectroscopy of pretreated cellulose, alpha cellulose and microcrystalline cellulose (MCC) were carried out. Bands were recorded in the region from 4000 to 500cm-1

iv. Acid-Insoluble Lignin

Acid-insoluble lignin content was measured in accordance with TAPPI standard T 222 om-98 “Acid-insoluble Lignin in Wood and Pulp.” The moisture content of the sample is determined for air-dried wood/pulp and was used to weigh a known weight of wood/pulp. Concentrated sulfuric acid was utilized to hydrolyze and solubilize the carbohydrates in wood and pulp samples. The acid-insoluble lignin was filtered, dried, and weighed.

v. Surface Morphology Analysis

The scanning electron microscope (SEM) was used to analyse the morphology of alpha cellulose and microcrystalline cellulose (MCC). The morphology of sample was performed using scanning electron microscope.

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 Introduction

This chapter present all the experimental result and discussion of this study. Firstly, the effect of consistency for the operability of the synthesis of microcrystalline cellulose (MCC). Secondly, the alkaline pretreatment on the effect of sodium hydroxide (NaOH) concentration and the lignin content. Lastly, the characteristic of synthesized microcrystalline cellulose by using scanning electron microscopy (SEM) and fourier transform infrared (FTIR).

4.2 Effect of consistency on the synthesis.

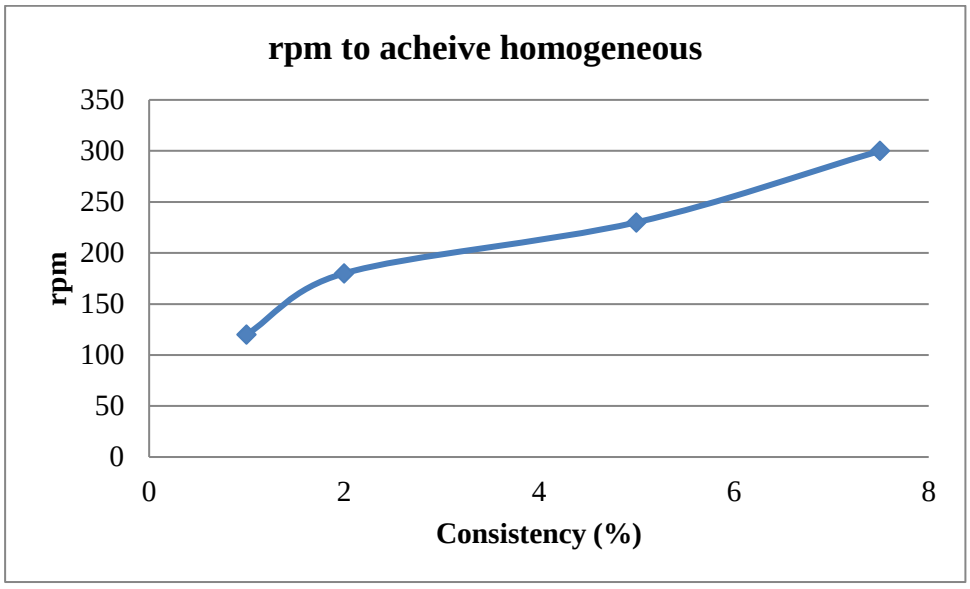


Figure 4.1: Effect of consistency (%) on the rpm needed to achieve homogeneous slurry

Consistency is defined as the percentage of weight of bone dry fibrous material in any combination of pulp and water. Figure 4.1 shows the graph between consistency and the rpm needed to achieve homogeneous slurry solution. The consistency has been

varied from (1%, 2%, 5%, 7.5%, and 10%). This process was done at a lab scale using a magnetic stirrer. From the figure it can be seen that as the rpm needed to achieve homogeneous proportional to the consistency. But when the consistency of the fiber reaches 10%, the solution cannot achieve a homogeneous solution. It also can be conclude that when the rpm increases the amount of power needed also increases. From the result we conclude that most feasible and applicable consistency is 5%. This is because this value is at the low consistency which is below 6% (Lindsay & Gullichsen, 1994). It is also applicable because it uses a medium range of rpm and medium range of power for the slurry solution to achieve homogeneous. Thus this may reduce the energy cost.

4.3 Alkaline pretreatment.

4.3.1 Effect of sodium hydroxide (NaOH) concentration.

Alkaline pretreatment has been identified as one of the best chemical pretreatment methods for delignification of lignocellulosic biomass (Iberahim, Jahim, Harun, Nor, & Hassan, 2013). Pretreatment of the empty fruit bunch (EFB) with sodium hydroxide (NaOH) allowed the removal of hemicellulose and lignin. Lignin is the most difficult component of biomass to be degraded due to its complex structure, high molecular weight and high insolubility. Empty fruit buches (EFB) fiber is governed by the lignocellulosic components, especially the lignin that gives strengths to the fibrils and the polysaccharides, especially the cellulose and hemicellulose (Ramli, Junaidi, H. Beg, & Yunus, 2015). The sodium hydroxide (NaOH) mechanism during the alkaline pretreatment is by saponification of intermolecular ester bonds crosslinking xylan hemicellulose and other polymeric materials, such as lignin or other hemicellulose. Sun and Cheng stated that the saponification of the uronic ester linkages in 4-O-methyl-D-glucuronic acids pendant along the xylan chain readily occurred in presence of alkali. Dilute sodium hydroxide (NaOH) solution during the alkaline pretreatment lead to the swelling of lignocellulosic compound, increasing a surface area and decreasing the polymerization degree of empty fruit bunch (EFB), then resulting to lignin and hemicellulose removal (S. Amin et al., 2012).

Figure 4.2 shows the effect of sodium hydroxide (NaOH) concentration used in the alkaline pretreatment expressed by percent of loss in weight. It is notable that the non-cellulosic material like hemicellulose and lignin are present in a form of network binding the fiber bundles in a composite-like structure. Treatment with alkaline solutions such as sodium hydroxide (NaOH) is possible to improve delignification process (Ibrahim, Badri, & Hassan, 2012). The removal of hemicellulose during the alkali treatment weakens this network and some lignins become loose and removed due to this damaged network. Alkaline pretreatment could cause cellulose fibers to swell rather than directly degrading it. They concluded that this pretreatment is the best method to avoid further fragmentation of hemicelluloses polymers as well as break up the ester bonds between lignin, hemicelluloses and cellulose (Iberahim, Jahim, Harun, Nor, & Hassan, 2013). When the lignocellulose crosslinks has been removed, it will cause the fibre to increase its porosity. It also will lead to decrease in crystallinity and degree of polymerization of the fibre, but the internal surface area of the lignocellulose increased. Separation of cellulose hydrogen bonds had caused cellulose depolymerisation.

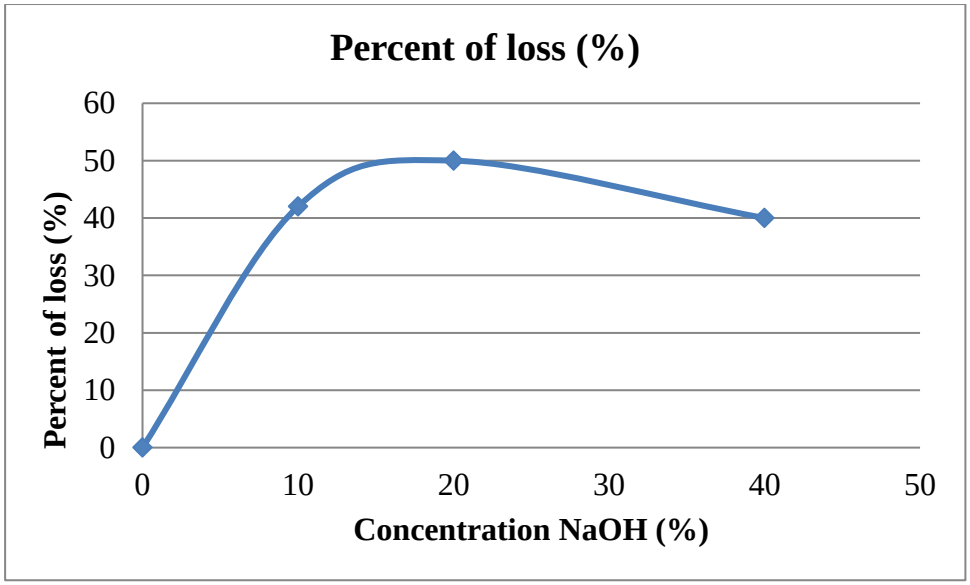


Figure 4.2: Effect of sodium hydroxide concentration on percent loss in weight

From Figure 4.2 shows that significant weight loss at 10% of sodium hydroxide (NaOH). This indicates that the amount of hemicellulose and lignin removed increases gradually with increasing the strength of the sodium hydroxide (NaOH) solution. The extent of hemicellulose and lignin removal reaches the highest value at 20% with 50%

loss in weight at sodium hydroxide concentration (NaOH) of 20%. From the literature review, Chang stated that empty fruit bunch (EFB) typically comprises of cellulose about 24–65%, hemicellulose about 21–34% and finally lignin about 14–31% respectively. It can be seen that when the sodium hydroxide (NaOH) solution concentration is 20% the weight loss is 50% and the typical empty fruit bunch hemicellulose and lignin are 35-65%, it can be concluded that almost all of the hemicellulose and lignin are removed in that condition. At 40% of concentration of sodium hydroxide (NaOH), the weight loss shows the decrease. It has been reported that cooking at 20% NaOH for three hours at 170°C will produced pulp without shives (Rushdan, Latifah, Hoi, & M. Nor, 2007).

4.3.2 Fourier Transform Infrared (FTIR).

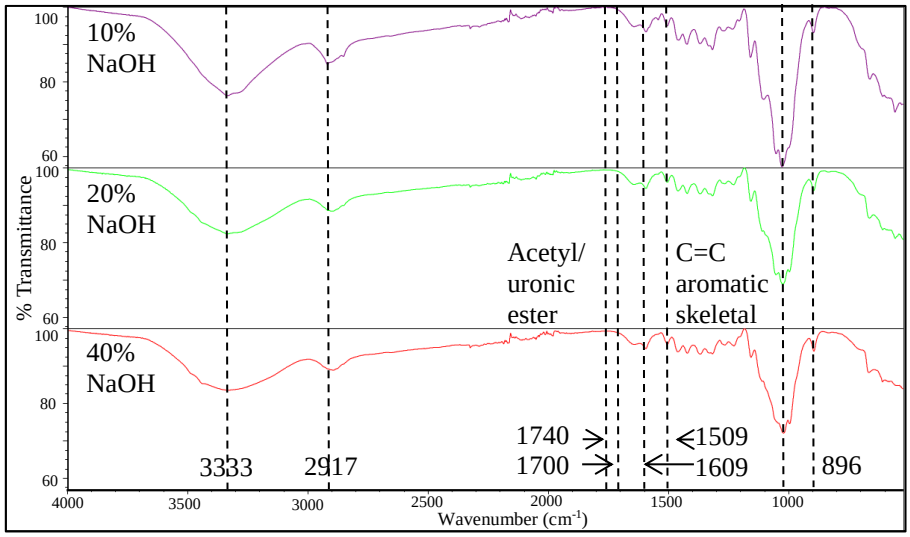


Figure 4.3: Fourier Transform Infrared (FTIR) spectra of the 10%, 20% and 40% sodium hydroxide (NaOH) concentration

Based on figure 4.2, the Fourier Transform Infrared (FTIR) for lignocellulose was divided into two part namely –OH and –CH stretching vibration part (4000-2700cm^{-1}) and finger print part (1800-800cm^{-1})(Barlianti, Dahnum, Hendarsyah, & Abimanyu, 2015). The stretching vibration of -OH group (3333 cm^{-1}), CH group (2917 cm^{-1}), O-H bending (1592 cm^{-1}), C–O-C stretching (1027 cm^{-1}), CH2 symmetric bonding (1422cm^{-1}) and the β-glycosidic linkage (896 cm^{-1}) (Khalil, Ismail, Rozman, & Ahmad, 2001; Barlianti, Dahnum, Hendarsyah, & Abimanyu, 2015; Nacos et al., 2006).

The figure shows the transmission band of –OH group (3333cm^{-1}) shows that as the concentration of the sodium hydroxide (NaOH) increase the transmission of the –OH group decreased. It was caused by the ruptured hydrogen bond (Rahnama et al., 2013). The transmission peak for the C-H group (2917 cm^{-1}) and C-O-C stretching 1027 cm^{-1}) were lower when the concentration of sodium hydroxide (NaOH) increases. This indicates mainly the methyl or methylene cellulose were destroyed (Barlianti, Dahnum, Hendarsyah, & Abimanyu, 2015). The transmission at the crystalline band that is the CH_2 symmetric bonding (1422cm^{-1}) band decrease as the concentration of sodium hydroxide (NaOH) increase but the amorphous (896cm^{-1}) remains stable. The peaks located in the range 1509–1609 cm^{-1} is correspond to C=C aromatic skeletal vibrations and indicate removal of lignin. The band in the region 1700–1740 cm^{-1} corresponds to either the acetyl or uronic ester groups of hemicelluloses normally appears , this band is absent, indicating the removal of hemicelluloses (Mohamad Haafiz, Eichhorn, Hassan, & Jawaid, 2013).

4.3.3 Lignin content

The acid-insoluble lignin content of fibre treated with 20% sodium hydroxide (NaOH) solution was measured using TAPPI standard T 222 om-98 "Acid-insoluble Lignin in Wood and Pulp." The result of the method is it can be found that the lignin content in the treated fiber using 20% sodium hydroxide (NaOH) solution is only 6.5%. The typical lignin content in an empty fruit bunch (EFB) is between 14–31%. From the typical lignin content, we can conclude that around 24.5% of the lignin has been removed during the alkaline treatment using 20% sodium hydroxide (NaOH) solution.

From the result it can be concluded 20% of sodium hydroxide (NaOH) concentration is the best condition of the alkaline pretreatment have the maximum amount of hemicellulose and lignin removal. At the same time to reduce the cost treatment and the impact of the treatment to the environment due to solvent usage.

4.4 Characterization of synthesized microcrystalline cellulose (MCC)

4.4.1 Scanning Electron Microscopy (SEM)

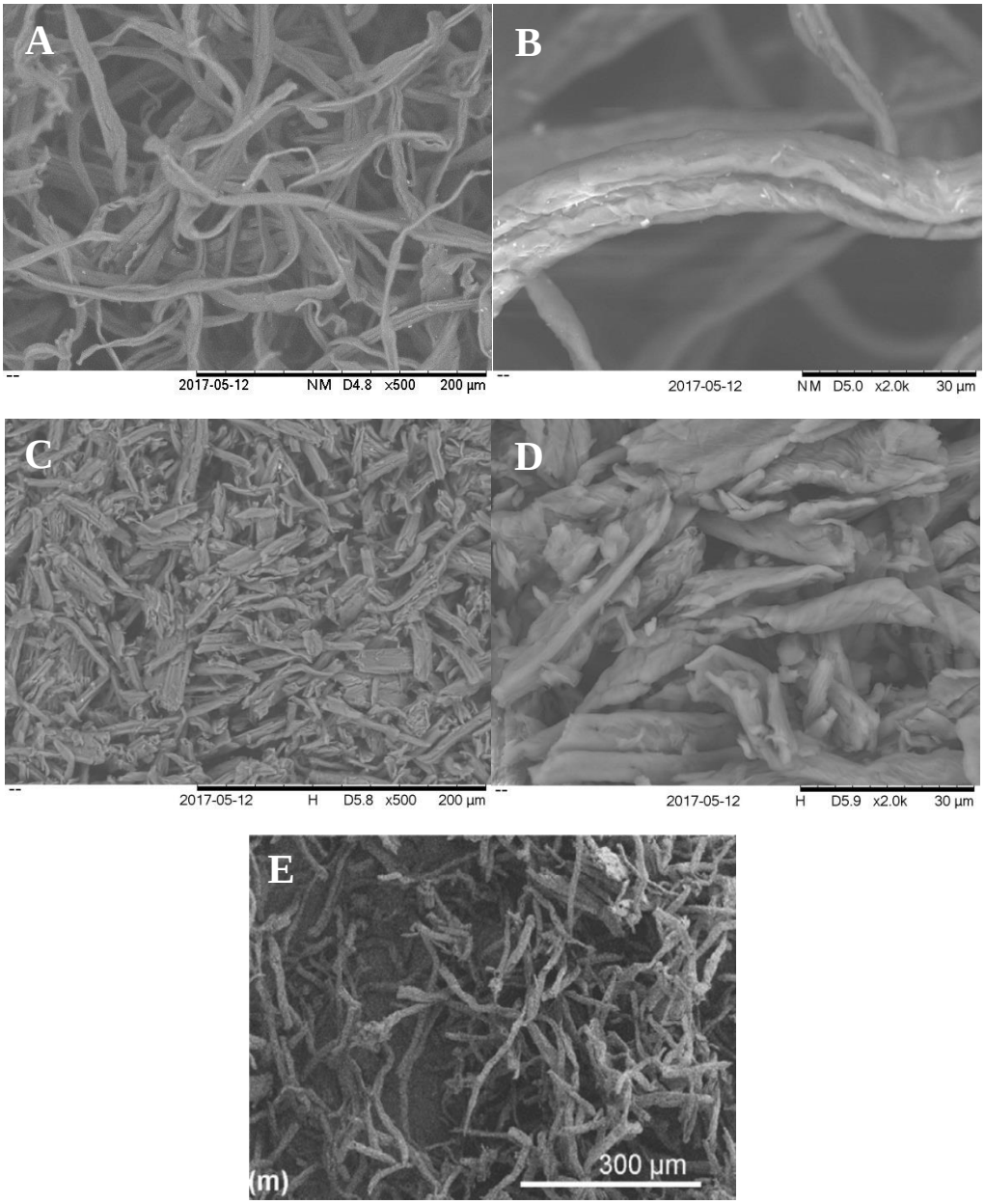


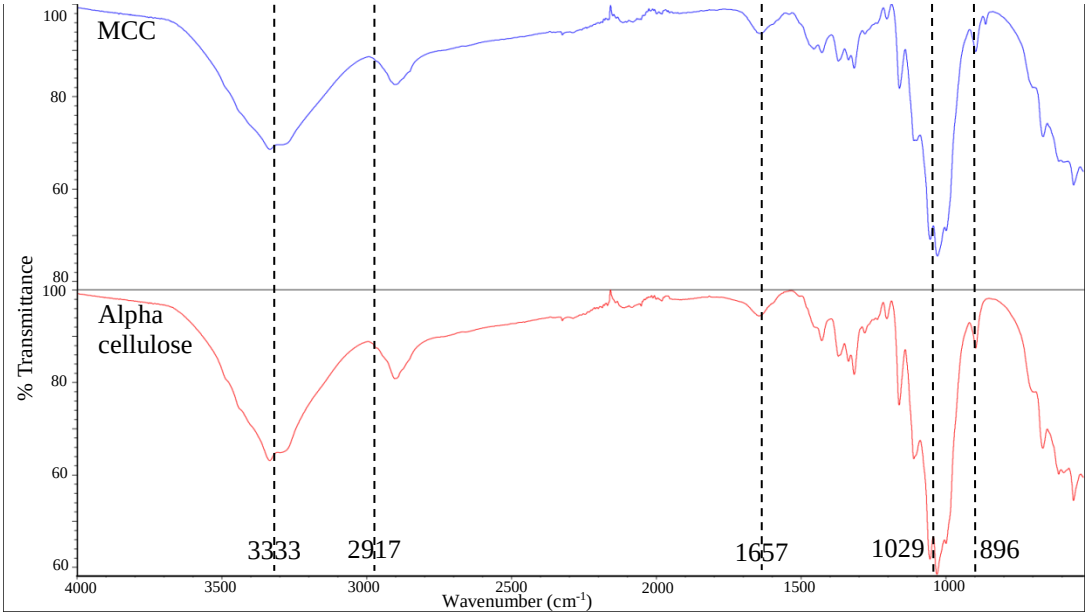
Figure 4.4: SEM micrographs of (A) alpha cellulose and (C) microcrystalline cellulose (MCC) at magnification of 500X; (B) alpha cellulose and (D) microcrystalline cellulose (MMC) at magnification 2000X and (E) commercial microcrystalline cellulose (MMC) at magnification 500x (Xiang, P. Mohammed, & Samsu Baharuddin, 2016)

Figure 4.3 shows scanning electron microscopy (SEM) images of alpha cellulose and microcrystalline cellulose (MMC) derived from empty fruit bunch (EFB) under 500X and 2000X magnification. The SEM micrographs for the alpha cellulose (Figure 4.3, A and B), showed a long smooth fibrils. On the other hand, the microcrystalline cellulose (MCC) image shows a fibrous structure and individualized (Figure 4.3, C and D). The fibrillar structure of alpha cellulose was destroyed and changed into small irregular particles during acid hydrolysis. Acid hydrolysis led to changes in morphological structure. The microcrystalline cellulose (MCC) obtained showing fibers strands which appear like rod-shaped. The microcrystalline cellulose (MCC) appeared to be irregular fiber fragments and also show a network-structure (Nasution, Yurnaliza, Veronicha, Irmadani, & Sitompul, 2017). According to Elanthikkal, Gopalakrishnapanicker, Varghese, & Guthrie (2010), hydrolysis process penetrates the amorphous regions of alpha cellulose, and cleave the β-1,4-linkage between the cellulose repeating units, where the alpha cellulose fibers were broken into shorter cellulose microcrystalline cellulose (MCC).

For comparison purpose, Figure 4.3 (E) shows the microstructure of commercial microcrystalline cellulose (MMC). The Figure 4.3 shows the morphology of commercial microcrystalline cellulose (MMC) are long narrow fibrils strand which are different from the synthesized microcrystalline cellulose (MMC). The morphology of the synthesized microcrystalline cellulose (MCC) was shorter and less fibril than the commercial microcrystalline cellulose (MCC). This indicated that the characteristics of the extracted microcrystalline cellulose (MCC) such as particle sizes and aggregation were influenced by the raw materials and the conditions used during the hydrolysis process (Das et al., 2009) This clearly shows that the different shape of the microcrystalline cellulose (MCC) particles can be influenced by the different raw materials.

4.4.2 Fourier Transform Infrared (FTIR).

Figure 4.5: Fourier Transform Infrared (FTIR) spectra of the obtained alpha cellulose (A) and microcrystalline cellulose (MCC) (B)



Fourier transform infrared (FTIR) spectra of the different samples of cellulose were recorded in the range of 4000–500 cm^{-1}. Figure 4.4 shows the stretching vibration of OH group (3200 to 3400 cm^{-1}), C–H group (2886 cm^{-1}), O-H bending (1657 cm^{-1}), C–O-C stretching (1029 cm^{-1}) and β-glycosidic linkage (896 cm^{-1}) (Khalil, Ismail, Rozman, & Ahmad, 2001; Nacos et al., 2006).There are difference between the transmittance for OH group of microcrystalline cellulose (MCC) (3328 cm^{-1}) as compared to alpha cellulose (3342 cm^{-1}). The crystalline of the microcrystalline cellulose (MCC) was more that the alpha cellulose and the difference of the band prove it. Moreover, microcrystalline cellulose (MCC) have the characteristic intermolecular and intermolecular -OH stretching vibration band in the broader than alpha cellulose. The broadening was prominent and attributed to the presence of amorphous fraction of the cellulose. This was due to the degradation of the hydrogen bond between the cellulosic chains during the hydrolysis process (Nasution, Yurnaliza, Veronicha, Irmadani, & Sitompul, 2017) and indicating that the hydrolysis process weakened the hydrogen bonding of cellulose (Zhang, Ren, & Li, 2013). The infrared spectroscopy show that the acid hydrolysis reaction performed to obtain microcrystalline cellulose (MCC) does not affect the chemical structure of the cellulosic fragments. It mean that acid hydrolysis of alpha cellulose did not affect the cellulosic component

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion.

Microcrystalline cellulose (MCC) has been successfully synthesized from empty fruit bunch (EFB), which is one of the most abundant sources of biomass planted in Malaysia. The most suitable fibre pulp consistency for the synthesis of microcrystalline cellulose was 5%. Microcrystalline cellulose (MCC) was obtained from alpha cellulose which was isolated from cellulose derived from empty fruit bunch (EFB) by using alkaline pre-treatment. Alkaline pre-treatment of empty fruit bunch by sodium hydroxide has been able to reduce hemicellulose and lignin. This study showed that pre-treatment at 20% of sodium hydroxide (NaOH) concentration at temperature 80°C gave the best result.

Microcrystalline cellulose (MCC) was prepared by hydrolysis acid using hydrochloric acid (2.5N). The results obtained from Fourier transform infrared (FTIR) analysis confirmed that chemical structure of the cellulosic fragments is not influenced by the acid hydrolysis. scanning electron microscopy (SEM) shows that the microcrystalline cellulose (MCC) has a rough and compact structure, similar to the commercial microcrystalline cellulose (MCC), although it exhibits much smaller fragments.

5.2 Recommendations

Based on the results obtained in this research study, the following recommendations were proposed:

i. In the extraction of hemicellulose and lignin using the alkaline pre-treatment, the temperature and time should be considered to find the most optimum condition for the hemicellulose and lignin removal.

ii. In the acid hydrolysis of the microcrystalline cellulose, the type of acid should be considered to study the effect of different type of acid on the synthesized microcrystalline cellulose (MCC).

iii. In the characterization of the microcrystalline cellulose (MCC), X-ray diffraction analyse (XRD) should be implemented to examine the changes in the crystalline structure during the preparation of microcrystalline cellulose (MCC).

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