# EFFECT OF CELLULOSIC MATERIAL FROM OIL PALM EMPTY FRUIT BUNCHES (OPEFB) ON THE REINFORCEMENT PROPERTIES OF RECYCLED PAPER

# KHAIRUL HAFIZUDDIN BIN ABDUL RAHMAN

# **UNIVERSITI SAINS MALAYSIA**

2017

# EFFECT OF CELLULOSIC MATERIAL FROM OIL PALM EMPTY FRUIT BUNCHES (OPEFB) ON THE REINFORCEMENT PROPERTIES OF RECYCLED PAPER

by

# KHAIRUL HAFIZUDDIN BIN ABDUL RAHMAN

Thesis submitted in fulfillment of the requirement

for the degree of

**Master of Science** 

December 2017

#### ACKNOWLEDGEMENT

Assalamualaikum W.B.T....

First of all, I would like to thank the Almighty ALLAH Blessing me and favor in guiding and helping me to finish this final report. Without Him, I can't finish this research in Effect of Cellulosic Material from Oil Palm Empty Fruit Bunches (OPEFB) on The Reinforcement Properties of Recycled Paper.

I also want to thanks so much to Professor Wan Rosli bin Wan Daud for become as supervisor and giving all his energy, expertise, experience and knowledge just for me to finish this research. As an expert person in Pulp and Paper Technology, his guiding is very important to me to complete this master research. Not forget to my laboratory partner Dr. Rohaizu Roslan and Dr. Eti Indarti for her guide and support from start until finish my research.

I also like to address our gratitude and appreciation to lecturer and staff Division of Bio-resources, Paper and Coating Technology, School of Industrial Technology, Universiti Sains Malaysia for their help and corporation.

Last but not least, to my parent Abdul Rahman bin Mohd Yusof and Norlida binti Zainal and all my siblings, thanks for their moral support to gave my best in this study. Also to my partner Nurazynie binti Herman who have been very helpful and supportive. Further gratitude is also extended to my entire friend from Universiti Sains Malaysia for support throughout the duration of this study, I really appreciate it.

#### Thank you....!

# TABLE OF CONTENTS

ACKN	OWLEDGEMENT	ii
TABL	E OF CONTENTS	iii
LIST	LIST OF FIGURES	
LIST	LIST OF TABLES	
LIST	OF ABBREVIATIONS	XV
LIST	OF SYMBOLS	xvii
ABST	RAK	xviii
ABST	RACT	xix
СНАР	TER 1 : INTRODUCTION	1
1.1	Project Background	1
1.2	Problem Statement	3
1.3	Objective	4
CHAP	CHAPTER 2 : LITERATURE REVIEW	
2.1	Oil Palm	5
	2.1.1 Oil Palm Biomass	7
	2.1.2 Oil Palm Empty Fruit Bunches (OPEFB)	8

		2.1.2(a)	Cellulose	10
		2.1.2(b)	Hemicellulose	13
		2.1.2(c)	Lignin	14
2.2	Pulp I	Production		16
	2.2.1	Soda Pulp	ing	17
2.3	Bleac	hing		20
2.4	Beatir	ıg		21
	2.4.1	Effect of l	Beating on Stock Properties	22
	2.4.2	Effect of l	Beating on Fiber Properties	23
	2.4.3	Effect of l	Beating on Paper Properties	25
		2.4.3(a)	Effect of Beating on Physical Properties of Paper	26
		2.4.3(b)	Effect of Beating on Mechanical Properties of Paper	26
		2.4.3(c)	Effect of Beating on Optical Properties of Paper	28
2.5	Cellul (OPE		rials from Oil Palm Empty Fruit Bunches	29
	2.5.1	Unbleachd OPEFB	ed Pulp (UB) OPEFB and Bleached Pulp (OZP)	31

	2.5.2 Microcrystalline Cellulose (MCC) OPEFB	32
	2.5.3 Tempo-Mediated Oxidation fiber (TEMPO) OPEFB	33
2.6	Blending with Cellulosic Material	35
2.7	Paper Properties	37
	2.7.1 Physical Properties of Paper	37
	2.7.2 Mechanical Properties of Paper	38
	2.7.3 Optical Properties of Paper	40
CHAPTER 3 : METHODOLOGY		
3.1	Preparation of Recycled Fiber	44
3.2	Preparation of OPEFB Pulp	44
	3.2.1 Oil Palm Empty Fruit Bunches (OPEFB)	44
	3.2.2 Pre-Hydrolysis	45
	3.2.3 Soda Pulping (OPEFB-UB)	46
	3.2.4 Bleaching Process (OPEFB-OZP)	47
	3.2.4(a) Oxygen Bleaching (O)	47
	3.2.4(b) Ozone Bleaching (Z)	47
	3.2.4(c) Peroxide Bleaching (P)	48

3.3	Prepa	ration of Pure Cellulose	49
	3.3.1	Microcrystalline Cellulose (MCC) OPEFB	49
	3.3.2	TEMPO-Mediated Oxidation (TEMPO) Pulp OPEFB	49
		3.3.2(a) TEMPO-Oxidation Reaction	49
		3.3.2(b) Post-Oxidation with NaClO2	50
3.4	Prepa	ration of Handsheet	51
	3.4.1	Optimizing Beating	51
	3.4.2	Blending on Recycled Fiber with Beaten Unbleached OPEFB and Beaten Bleached OPEFB	52
	3.4.3	Blending on Recycled Fiber with Pure Cellulose	52
	3.4.4	Handsheet Making	52
3.5	Morp	hological Analysis	55
	3.5.1	Fiber Length Determination	55
	3.5.2	Transmission Electron Microscope (TEM)	55
	3.5.3	Scanning Electron Microscope with Energy Dispersive X- Ray (SEM-EDX)	55
3.6	Hands	sheet Testing	57
	3.6.1	Physical Testing	57

		3.6.1(a)	Grammage	57
		3.6.1(b)	Thickness	58
		3.6.1(c)	Density	58
	3.6.2	Mechanic	al Testing	59
		3.6.2(a)	Tensile Test	60
		3.6.2(b)	Tearing Test	60
		3.6.2(c)	Bursting Test	61
		3.6.2(d)	Folding Endurance Test	62
	3.6.3	Optical Te	esting	63
		3.6.3(a)	Brightness Test	63
		3.6.3(b)	Opacity Test	64
3.7	Statist	tical Analys	is	65
	3.7.1	R-Squared	l (R2) Analysis	65
СНАР	TER 4	: RESULT	'S AND DISCUSSION	66
4.1		B (Beating	ating Revolutions on Unbleached and Bleached Revolution – 0, 3000, 6000, 9000, 12000, 15000	67
	4.1.1	Morpholo	gy	67

	4.1.2	Pulp Freen	ness	69
	4.1.3	Paper Den	sity	71
	4.1.4	Mechanica	al Properties	72
		4.1.4(a)	Tensile Strength	72
		4.1.4(b)	Bursting Strength	75
		4.1.4(c)	Tearing Strength	76
		4.1.4(d)	The Tear-Tensile Relationship	77
	4.1.5	Optical Pr	operties	79
4.2	Effect	of Blendin	g on Recycled Fiber (RF) with OPEFB Pulp	81
	4.2.1	Pulp Freen	ness	83
	4.2.2	Paper Den	sity	84
	4.2.3	Mechanica	al Properties	85
		4.2.3(a)	Tensile Strength	85
		4.2.3(b)	Bursting Strength	87
		4.2.3(c)	Tearing Strength	88
4.3			g on Recycled Fiber (RF) with Micro-Crystalline npo-Oxidized Fiber	90
	4.3.1	Pulp Freer	iess	91

		4.3.2	Paper Der	nsity	93
		4.3.3	Mechanic	al Properties	94
			4.3.3(a)	Tensile Strength	94
			4.3.3(b)	Bursting Strength	97
			4.3.3(c)	Tearing Strength	98
	4.4	-		Various Types of OPEFB Cellulosic Materials as otential for Recycled Fiber	103
	CHAP	TER 5	: CONCLU	USION AND RECOMMENDATION	103
	5.1	Concl	usion		103
	5.2	Recor	nmendation	I	106
REFERENCES			107		
	APPENDICES				

## LIST OF PUBLICATION

## LIST OF FIGURES

## Page

Figure 1.1	The general effects of recycling (Wanrosli et al., 2005)	1
Figure 2.1	Oil palm tree (MPOB, 2008)	5
Figure 2.2	Global oil palm production 2015 (MPOB, 2016)	6
Figure 2.3	Cellulose structure (Sjostrom, 1993)	11
Figure 2.4	Schematic of molecular organization within a cellulose microfibril (Biermann, 1996)	12
Figure 2.5	Microscopic and submicroscopic structure of cellulose (Smook, 1992)	12
Figure 2.6	Hemicellulose monomers (Smook, 1992)	13
Figure 2.7	Cross section lignin impregnated wood (ILI, 2017)	14
Figure 2.8	Lignin subunits (Smook, 1992)	15
Figure 2.9	Beater machine (PFI mill)	22
Figure 2.10	External fibrillation with different beating (Gao et al., 2008) a) 0 rev., (b) 5000 rev., (c) 10,000 rev., (d) 15,000	23
Figure 2.11	OPEFB fiber fibrillated (Wenhua Gao et al., 2008)	24
Figure 2.12	Hydrogen bonding (Claudio-da-Silva et al., 1982)	30
Figure 2.13	OH groups to form H-bonds	32
Figure 2.14	2,2,6,6-tetramethylpiperidine-1-oxy (Saito, 2006)	33
Figure 2.15	The introduction of the additional carboxylic groups into the fibers will allow more H bonding to occur (Saito, 2006)	34

Figure 2.16	Hydrogen bonding (H-bond) (Claudio-da-Silva et al., 1982)	36
Figure 3.1	Experimental outline	43
Figure 3.2	PFI mill beater	51
Figure 3.3	Canadian Standard Freeness (CSF) test	53
Figure 3.4	Handsheet making machine	54
Figure 3.5	Scanning Electron Microscopic (SEM)	56
Figure 3.6	Thickness testing machine	58
Figure 3.7	Division of sheet for testing	59
Figure 3.8	Tensile strength tester	60
Figure 3.9	Elmendorf tearing tester	61
Figure 3.10	Mullen burst tester	61
Figure 3.11	Folding testing machine	62
Figure 3.12	Optical properties testing machine	63
Figure 4.1	Effects of PFI beating revolutions on fiber length	68
Figure 4.2	SEM images of bleached OPEFB pulps (a) before beating, (b) after beating	68
Figure 4.3	Effect of PFI beating revolutions on freeness	70
Figure 4.4	Effect of PFI Beating Revolutions on Sheet Density. (Green lines indicate the greater effect of OPEFB- OZP at higher levels of beating)	72
Figure 4.5	Effect of PFI beating revolutions on tensile index (Green circle indicates the region of difference in	74

beating response)

Figure 4.6	Effect of PFI beating revolutions on burst index	75
Figure 4.7	Effect of PFI beating revolutions on tear index	76
Figure 4.8	Tear-tensile relationship	78
Figure 4.9	Effect of PFI beating revolutions on optical properties	80
Figure 4.10	Effect of tensile index on unbeaten OPEFB pulp addition	81
Figure 4.11	Tensile index of RF in comparison to OPEFB-UB and OPEFB-OZP	82
Figure 4.12	Effect of CSF freeness on pulp addition	83
Figure 4.13	Effect of density on pulp addition	84
Figure 4.14	Effect of tensile index on pulp addition	85
Figure 4.15	Effect of burst index on pulp addition	87
Figure 4.16	Effect of tear index on pulp addition	88
Figure 4.17	Effect of freeness on cellulosic material addition	91
Figure 4.18	Morphological of Tempo fibers (a) SEM of TEMPO indicating its fibrous nature, b) TEM of TEMPO indicating the presence of NCC )	92
Figure 4.19	Effect of density on cellulosic material addition	93
Figure 4.20	Effect of tensile index on cellulosic material addition	94
Figure 4.21	Interfiber hydrogen bonding between the two cellulose fibers (Arrow shows the C3-OH of one cellulose chain and the C6-OH of the neighboring cellulose chain) (Isogai et al, 2011).	95

Figure 4.22	TEMPO-oxidation of OPEFB-fiber (Isogai et al, 2011)	96
Figure 4.23	Molecular configuration of (a) OPEFB-MCCand (b) OPEFB-TEMPO (Isogai et al, 2011)	97
Figure 4.24	Effect of burst index on cellulosic material addition	97
Figure 4.25	Effect of tear index on cellulosic material addition	98
Figure 4.26	Effect on tensile index for various OPEFB cellulosic materials additions	100
Figure 4.27	Effect on scattering coefficient for various OPEFB cellulosic materials additions	101

## LIST OF TABLES

## Page

Table 2.1	Wastes from palm oil production in 2015 (MPOB, 2016)	7
Table 2.2	Composition of oil palm empty fruit bunch from different sources (After normalization).	9
Table 2.3	Degree of polymerization values (Biermann, 1996)	11
Table 2.4	General classification of pulping process (Smook, 1992)	17
Table 3.1	List of chemicals used	42
Table 3.2	Pre-hydrolysis condition	45
Table 3.3	Soda pulping condition	46

## LIST OF ABBREVIATIONS

OPEFB	Oil Palm Empty Fruit Bunches
OPEFB-UB	Unbleached OPEFB
OPEFB-OZP	Bleached OPEFB
OPEFB-MCC	Microcrystalline cellulose OPEFB
OPEFB-TEMPO	Tempo-mediated oxidation OPEFB
MCC	Microcrystalline cellulose
MFC	Microfibrillated cellulose
NCC	Nanocrystalline cellulose
0	Oxygen
Z	Ozone
Р	Peroxide
SEM	Scanning electron microscopy
OCC	Old corrugated container
RF	Recycled fiber
LWA	Length weighted average
CSF	Canadian standard freeness
TAPPI	Technical Association of the Pulp and Paper Industry
LODP	Levelling-off the degree of polymerization
С	Carbon
Н	Hydrogen

0	Oxygen
CO <sub>2</sub>	Carbon dioxide
CaO	Calcium oxide
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
NaOH	Sodium hydroxide
СООН	Carboxylic acid
ОН	Hydroxide
H-bonds	Hydrogen bonds
TCF	Totally chlorine free

# LIST OF SYMBOLS

mm	Millimeter
ml	Milliliter
nm	Nanometer
μm	Micrometer
sec	Second
%	Percent
°C	Degree celsius
kV	Kilo volt
psi	Pound per square inches
psi g	Pound per square inches Grams
g	Grams
g kg	Grams Kilogram
g kg g/cm <sup>3</sup>	Grams Kilogram Unit of density
g kg g/cm <sup>3</sup> g/m <sup>2</sup>	Grams Kilogram Unit of density Unit of grammage

# KESAN BAHAN SELULOSIK DARI TANDAN KOSONG BUAH KELAPA SAWIT (OPEFB) TERHADAP PENINGKATAN SIFAT KERTAS KITAR SEMULA

### ABSTRAK

Penggunaan gentian kitar semula dalam industri kertas Malaysia adalah merupakan keperluan ekonomi dan persekitaran kerana kebolehdapatan pulpa dara yang terhad. Walaubagaimanapun, dengan setiap proses kitar semula, kekuatan kertas akan berkurang, maka kaedah yang berbeza digunakan untuk meningkatkan potensi kekuatannya. Pelbagai bentuk bahan selulosik kelapa sawit dihasilkan iaitu OPEFB-UB, OPEFB-OZP, OPEFB-MCC dan OPEFB-TEMPO, digunakan untuk meningkatkan sifat kekuatan kertas kitar semula yang diperolehi daripada kotak beralun lama (OCC). Potensi penguatan bahan-bahan selulosik dibandingkan dengan penilaian hubungan tegangan-peratusan tambahan yang mana menunjukkan bahawa semua bahan selulosik OPEFB memberi kesan positif dengan korelasi yang kuat sebagai petunjuk nilai R<sup>2</sup> hampir 1. Antara empat jenis selulosik OPEFB, OPEFB-TEMPO mempunyai potensi terbesar, diikuti oleh OPEFB-MCC, OPEFB-UB dan OPEFB-OZP. Potensi kekuatan luar biasa OPEFB-TEMPO ditunjukkan oleh fakta bahawa hanya dengan penambahan sebanyak 10% OPEFB-TEMPO, kesannya hampir bersamaan dengan 40% OPEFB-UB atau 80% OPEFB-OZP. Bagi OPEFB-MCC, pengaruhnya sedikit lebih rendah di mana tambahan 10% bersamaan dengan kira-kira 24% OPEFB-UB dan 50% OPEFB-OZP. Melalui pemerhatian, peningkatan ikatan interfiber yang selanjutnya bekerjasama dengan kebergantungan peratus penambahan-pekali berselerak di mana OPEFB-TEMPO memperlihatkan pekali penyebaran paling rendah, diikuti oleh OPEFB-MCC, OPEFB-UB dan OPEFB-OZP.

# EFFECT OF CELLULOSIC MATERIAL FROM OIL PALM EMPTY FRUIT BUNCHES (OPEFB) ON THE REINFORCEMENT PROPERTIES OF RECYCLED PAPER

#### ABSTRACT

The use of recycled fibers in the Malaysian paper industry has been an economic and environmental necessity due to the limited availability of virgin fiber. However, with each recycling, the paper strength decreases, hence different methods are employed to increase its strength potentials. Various forms of oil palm cellulosic materials viz. OPEFB-UB, OPEFB-OZP, OPEFB-MCC and OPEFB-TEMPO were used to enhanced the strength properties of the recycled paper that were obtained from the old corrugated container (OCC). The reinforcement potential of the cellulosic materials was compared by an evaluation of the tensile-percent addition relationship which shows that all OPEFB cellulosic materials gave a positive impact with strong correlations as indicative from the  $R^2$  values of almost 1. Amongst the four types of OPEFB cellulosics, OPEFB-TEMPO has the greatest potential, followed by OPEFB-MCC, OPEFB-UB and OPEFB-OZP. The overwhelming strength potential of OPEFB-TEMPO is shown by the fact that by just an addition of 10 % of OPEFB-TEMPO, its impact is almost equivalent to that of 40 % OPEFB-UB or 80 % of OPEFB-OZP. As for OPEFB-MCC, the influence is slightly lower in which a 10 % addition corresponds to about 24 % of OPEFB-UB and 50 % of OPEFB-OZP. This observation has been ascribed to the enhancement of interfiber bonding which is further collaborated with the scattering coefficient-percent addition dependency whereby OPEFB-TEMPO showed the lowest scattering coefficient, followed by OPEFB-MCC, OPEFB-UB and OPEFB-OZP.

xix

### **CHAPTER 1**

## **INTRODUCTION**

#### 1.1 Project Background

Papermaking in Malaysia is essentially based on recycled fibers where out of the 19 paper mills, only one mill utilizes virgin fibers. The situation arises due to the limited availability of virgin fibers for paper production and thus has become an economic necessity. One of the major issues faced by mills using recycled fibers is the diminishing strength of papers with recycling except for tear; an example of such effect can be seen in Figure 1.1.

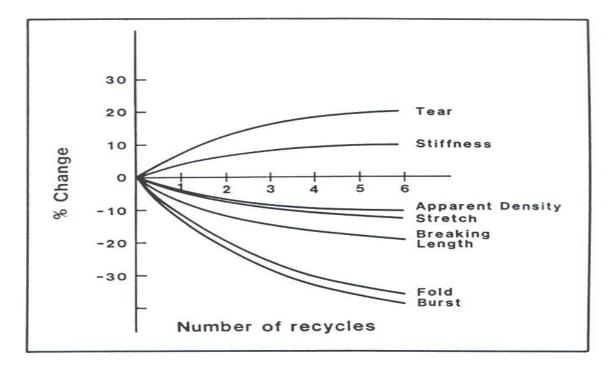


Fig. 1.1 : The general effects of recycling (Wanrosli et al., 2005)

The single most important factor for this reduction is due to the loss of interfiber bonding between fibers (hydrogen bonds), a phenomenon known as hornification. Different methods are currently used in the paper industry such as mechanical beating and refining, use of chemical additives, physical fractionation, and blending with virgin fibers (Wanrosli et al, 2005) to recover or minimize the loss of recyclability of these recycle fibers. Blending of virgin pulp with recycled fibers, which is of interest in this investigation, is a physical upgrading treatment, which relies on the interaction between the two types of fibers. Mills occasionally use softwood fibers to impart additional strength to papers made from recycled paper.

#### **1.2 Problem Statement**

Malaysia being the second world's largest oil palm producer generates massive amounts of lignocellulosic residues. It is reported that Malaysia generated approximately 95 million tonnes of dry oil palm lignocellulosic biomass (OPLB) which includes trunks, fronds, and empty fruit bunches (OPEFB) in 2015 with an expected increase to 100 million tonnes by 2020, with annual production expected to increase in line with the growing worldwide demand for palm oils (Bazmi et al., 2011). These residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass that can be used to blend with recycled fibers so as to increase the strength of the resultant paper. The basis of this improvement is the partial replacement of the inactive recycled fibers with the more active virgin fibers and in the process creating new hydrogen bonds leading to the increase of the paper's strength. Apart from being unbleached fibers, these virgin fibers can also be bleached into bleached fibers. Through various treatments, the fibers can be converted into other forms; of particular interest in this research are the microcrystalline cellulose and oxidized cellulose which is obtained via the TEMPOoxidation procedure. These forms of cellulosic materials are expected to respond differently towards the development of paper strength properties by virtue of its capability to form additional hydrogen bonds.

### 1.3 Objective

This research investigates the use of cellulosic material from OPEFB as reinforcement agents in papermaking that uses recycled fiber. To achieve this aim, the following objectives were studied:

- a) To study the effects of beating of unbleached and bleached OPEFB pulp
- b) To study the effects of paper properties upon the addition beaten pulp of unbleached and bleached OPEFB
- c) To study the effects of paper properties upon the addition of microcrystalline cellulose and TEMPO-oxidized pulp OPEFB
- d) To compare the effects of the additions of the different cellulosic materials on the paper properties

### CHAPTER 2

#### LITERATURE RIVIEW

#### 2.1 Oil Palm

Oil palm (*Elaeis guineensis*) (Fig. 2.1) is one of the most important agriculture plants in Malaysia and one of the non-wood fibers. It's originated from West Africa where it was growing wild and later developed into an agricultural crop. Early 1870's, this plants was first introduced to Malaysia as an ornamental plant and the first commercial Oil Palm estate in Malaysia was set up in 1917 at Tennamaran Estate, Selangor. The cultivation of oil palm rapidly increased beginning in the sixties under the government's agricultural diversification program which was to reduce the country's economic dependence on rubber land and tin. The Oil Palm plantations in Malaysia are largely based on the estate government system and small holder scheme (MPOB, 2008).



Fig. 2.1 : Oil palm tree (MPOB, 2008)

Statistic for 2015 from Malaysia Palm Oil Board (MPOB), 5.74 million hectares of land in Malaysia is under Oil Palm cultivation, then producing 17.73 million tonnes of Palm Oil and 2.13 tonnes of Palm Kernel Oil. From the Figure 2.2, Malaysia is one the largest producers and exporters of Palm Oil in the world, accounting for 32 % equal to 19.9 million tonnes Palm Oil production in 2015 (MPOB, 2016). The industry provides employment to more than half a million people and livelihood to an estimated one million people.

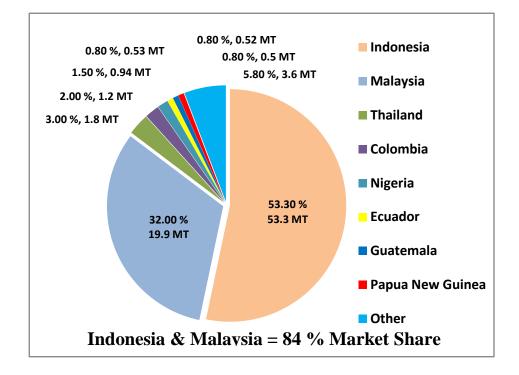


Fig. 2.2 : Global oil palm production 2015 (MPOB, 2016)

Moreover, the Oil Palm is the most productive oil crop and has become an important feedstock to the food industry for edible oil production, since the amount of oil produced per hectare per year is far greater than other vegetable oils like soybean, sunflower and rapeseed. Higher demand especially in food industry caused Oil Palm being a largest export and import among a country in the world. Number of export and import Oil Palm is increasing every year.

#### 2.1.1 Oil Palm Biomass

According to the official statistics until end 2015 from Malaysia Palm Oil Board (MPOB), Malaysian palm oil industry generated 83 million tonnes dry biomass wastes, and the estimated number is 85-100 million tonnes by 2020, including trunks, fronds, and empty fruit bunches (OPEFB), which are rich in fibers, and has yet to be fully utilized.

These include the Oil Palm Fronds (OPF) and Oil Palm Trunks (OPT) which are obtainable at the plantation site; Empty Fruit Bunches (EFB), Palm Kernel Shells, Mesocarp Fiber and Palm Oil Mill Effluent (POME) at the mill sites. Table 2.1 shows the breakdown of wastes from Oil Palm production for 2015. Currently, there is a massive quantity of Oil Palm biomass residue still perceived as waste byproducts. Thus, making oil palm biomass disposal is a great concern which gains criticism from the environmental groups regarding biodiversity and air pollution (Aljuboori, 2013).

Waste	Quantity ('000Tonnes)
Oil Palm Fronds (OPF)	58,000
Oil Palm Trunks (OPT)	17,000
Empty Fruit Bunches (EFB)	8,000
Palm Pressed Fiber (PPF)	8,000
Shell	4,000

Table 2.1:Wastes from palm oil production in 2015 (MPOB, 2016)

#### **2.1.2 Oil Palm Empty Fruit Bunches (OPEFB)**

In terms of this issue, Oil Palm biomass has being utilized as an economically useful alternative. For example, OPEFB has huge potential to be used as mulching and fertilizer in plantation, or contribute as a solution to the renewable energy at the mill site. In addition, OPEFB is now viewed as a feasible alternative to sources of fibers, which can be converted into paper making pulp with good printing properties and a good papermaking formation, yet to be extensively commercialized.

Realizing the potential of these Oil Palm biomasses, recently, there have been numerous ongoing efforts to increase profits from Oil Palm biomass fiber by producing fuel and bio-based chemicals, with an emphasis on its major component cellulose (Table 2.2). Additionally, Oil Palm biomass residue is a reliable resource because of its availability, continuity, non-hazardous, biodegradable material (Abdullah & Sulaiman, 2013). Oil palm fibers are also versatile, stable and can be processed into various dimensions and grades to fit specific applications.

In fact, several reviews and scientific papers have been published on the synthesis of cellulose and cellulose derivative from Oil Palm Empty Fruit Bunch, such as cellulose phosphate (Wanrosl et al., 2011; Wanrosli et al., 2013) and Microcrystalline Cellulose (Haafiz et al., 2013).

Besides oil palm biomass, cellulose can be produced from others lignocellulosic biomass and some potential feedstock including wood waste such as timber residues from saw mills; agriculture waste, such as straw and corn stover; grasses such as miscanthus and algae; and sugar bagasse (Okita et al., 2011; Verardi et al., 2012). However, industrially, the cellulose fiber is mostly derived from wood (softwood and hardwood) and relatively small amount in volume of non-woody fiber, which comes mainly from bagasse, bamboo, jute, ramie, hemp, flax and cotton. Nevertheless, non-woody fibers are important, particularly in the developing world, with low cost on importing wood pulp and beneficial since non-woody fibers produce an annual crop with a higher yield than wood (Jones & Wegner, 2009).

Table 2.2: Composition of oil palm empty fruit bunch from different sources<br/>(After normalization).

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Location	References
54	30	16	Dengkil, Selangor, Malaysia	Ariffin et al. (2008)
60	7	33	Indonesia	Kasim & Kasim (2013)
60	23	17	Teluk Intan, Perak, Malaysia	Wanrosli et al. (2004)
60	22	18	MPOB, Malaysia	Abdullah et al., (2011)
41	24	35	Sumatera, Indonesia.	Isroi et al. (2012)

Currently products made from lignocellulosic biomass feedstock only represent a minor fraction of the chemical industry products. However, the interest in the biobased products has increased because of the rapidly rising barrel cost, an increasing concern about the environment issue and the depletion of the fossil resources in the near future (Verardi et al., 2012). Therefore, utilizing these plentiful by-products to replace non-renewable material sources should be realized.

#### 2.1.2(a) Cellulose

Cellulose is a potential useful output for industrial exploitation, which represents a considerably valuable product for the oil palm biomass utilization. This will impact positively towards a more sustainable development, especially to resolve the issue on oil palm biomass residue in Malaysia. According to Smook (1992), in plant fibers it is the substances celluloses that determines the character of the fiber and permits its use in papermaking.

Cellulose is a carbohydrate, meaning that it is composed of Carbon (C), Hydrogen (H) and Oxygen (O), with the latter two elements in the same proportion as in water. Cellulose is also a natural polysaccharide, indicating that it contains many sugar units of glucose. Cellulose is the most abundant renewable biopolymer, naturally produced by plants, as well as by microorganisms. In wood, cellulose can be obtained by 42-52 % and mostly located in the secondary cell wall, while more than 90 % cellulose can be obtained from raw cotton and more than 60 % can be obtained from the oil palm empty fruit bunch (OPEFB).

The chemical formula for cellulose is  $(C_6H_{10}O_5)_n$ , where *n* is the number of repeating sugar units or the degree of polymerization (DP). Table 2.3 shows the value of degree of polymerization with the different sources of cellulose and treatment received. Most papermaking fibers have a weight-averaged DP in the 600 – 1500 range. Cellulose structure in Figure 2.3, recurring unit is actually two consecutive glucose anhydride units, known as cellobiose unit. Cellulose contains a large amount of free hydroxyl groups available for reaction located at C2, C3, and C6 respectively, where hydroxyl group of C6 is much more reactive than that of C2 and C3 (Qin et. al, 2011).

10

Table 2.3: Degree of polymerization values (Biermann, 1996)

Types	Degree of Polymerization
Native Cellulose (In Situ)	3500
Purified Cotton Linters	100 - 3000
Commercial Wood Pulps	600 -1500
Regenerated Cellulose (e.g., Rayon)	299 - 600

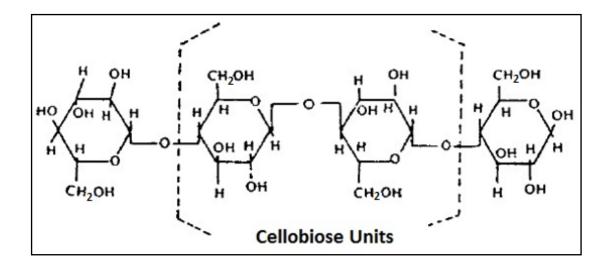


Fig. 2.3 : Cellulose structure (Sjostrom, 1993)

Polymeric linkage during cellulose synthesis is such that the chain forming an extended manner. As a consequence, cellulose molecules fit snugly together over long segment. Cellulose in plant fibers is found in several ordered levels of orientation, as illustrated in Figure 2.4. Where the molecules fit together over long segments regions of crystallinity develop which are difficult to penetrate by solvents or reagents. The relatively more amorphous regions are readily penetrated and are therefore more susceptible to hydrolysis reaction. Microscopic and submicroscopic Structure of Cellulose is shown in Figure 2.5.

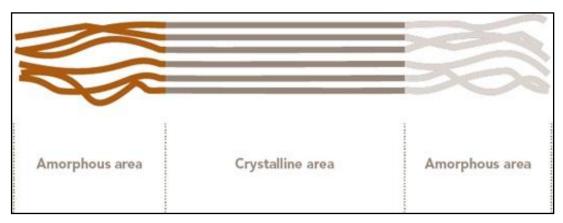


Fig. 2.4 : Schematic of molecular organization within a cellulose microfibril (Biermann, 1996)

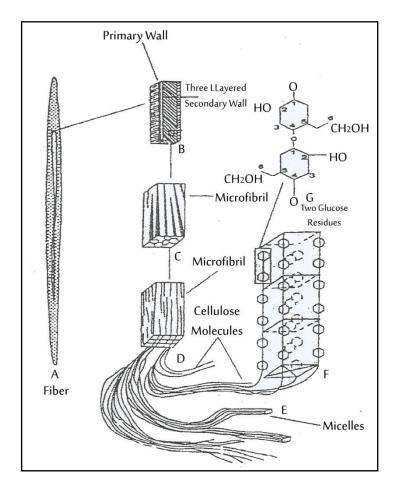


Fig. 2.5 : Microscopic and submicroscopic structure of cellulose (Smook, 1992)

#### **2.1.2(b) Hemicellulose**

According to Smook (1992), hemicelluloses are polymer of five different sugars of hexoses (glucose, mannose, and galactose) and pentoses (xylose and arabinose) shown in Figure 2.6. Depending on plant species, these sugars along with uronic acids from various polymeric structures; some are associated with the cellulosic portion of the plants, while the others are more closely associated with lignin.

During chemical treatment of wood to produced pulp, the amounts, locations and structures of the various hemicelluloses usually change dramatically. The hemicelluloses are more easily degraded and dissolved than celluloses, so their percentage is always less in the pulp than in the original wood.

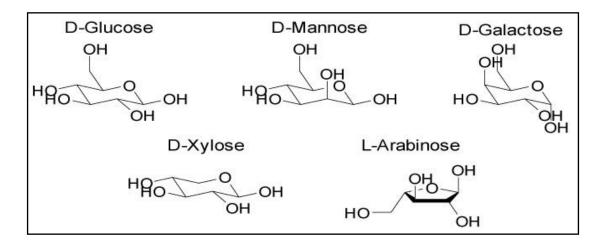


Fig. 2.6 : Hemicellulose monomers (Smook, 1992)

#### 2.1.2(c) Lignin

According to Smook (1992), the term "Holocellulose" is used to describe the total carbohydrate content of fibers. In addition to Holocellulose, woody plant materials contain an amorphous, highly polymerized substance called lignin. Lignin is an organic substance binding the cells, fibers and vessels which constitute wood and the lignified elements of plants, as in straw. After cellulose, it is the most abundant renewable carbon source on Earth.

Lignin principal role is to form the middle lamella, the intercellular material which cements the fibers together as shown in Figure 2.7. It is not possible to define the precise structure of lignin as a chemical molecule. All lignin show a certain variation in their chemical composition.

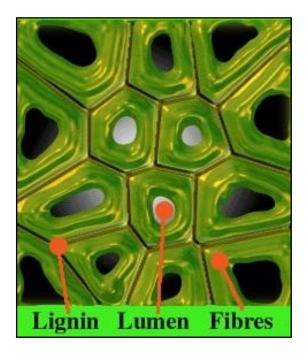


Fig. 2.7 : Cross section lignin impregnated wood (ILI, 2017)

However the definition common to all is a dendritic network polymer of phenyl propane basic units. Figure 2.8 shows the three linkages between the propane side chains and the benzene rings are broken during chemical pulping operations to free the cellulosic fibers.

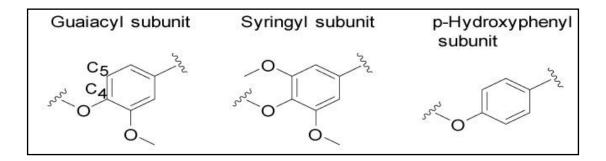


Fig. 2.8 : Lignin subunits (Smook, 1992)

Lignin is a one of the component in plants structural that binds the cellulose fibres together. Prior to papermaking process, the lignin must be removed from the pulp because it affects the performance and decreases the paper quality (Abdul Khalil et al., 2006). Lignin is considered to be an undesirable polymer that is removed during pulping process (Rodríquez et al., 2008). In addition, lower lignin content could be advantageous for use in pulp and paper making manufacturing, as fewer amounts of chemicals needed during pulping and bleaching process (Marques et al., 2010) and ultimately reducing hazard release to environment.

#### 2.2 Pulp Production

Manufacturing of pulp starts with raw material preparation (Smook, 1992; Biermann 1996). This includes debarking (when wood is used as raw material), chipping, and other processes such as strands (for example, when OPEFB is used as the raw material). The manufacture of pulp for paper and cardboard employs mechanical and chemical methods pulping. Pulping is the first step in paper making process. Pulping is the process to converting the raw material from wood or lignocellulosic Non-wood material to separated pulp fibers for papermaking. Pulping process is known as the process which the bonds within wood structure are ruptured either chemically or mechanically (Stellman, 1998). Pulping can be defined as any process which fibrous raw material is reduced to a fibrous mass (Smoke, 1992).

Method of pulping depend on product been made at the end. Each pulping process has its advantages and disadvantages (Smook 1992; Biermann 1996). The major advantage of mechanical pulping is its high yield of fibers up to 90%. Chemical pulping yields approximately 50% but offers higher strength properties and the fibers are more easily bleached because the mechanical pulping process does not remove lignin.

Three types of pulping process are mechanical pulping, chemical pulping and hybrid (combination mechanical and chemical). The mechanical pulping is the process wood is ground into fibers by disk refiner or grindstones. While the chemical pulping is the process the fibers are separated by chemically degrading and dissolving the lignin that binds them together. Table 2.4 shows general classification of pulping process.

16

### Table 2.4:General classification of pulping process (Smook, 1992)

Mechanical Pulping	Chemical Pulping	Hybrid
Pulping with mechanical energy (Little amount of chemical and heat).	and heat (Little or no	of mechanical and
High Yield (85-95 %)	Low Yield (40-55 %)	Intermediate Yield (55-85%)
Short, Impure Fiber (Weak and Unstable)		Intermediate Pulp Properties (Some Unique Properties)
Good Printing Quality	Poor Printing Quality	

#### 2.2.1 Soda Pulping

In this study, soda pulping is used as a pulping method and pre-hydrolysis is done before soda pulping to remove hemicellulose. Chemical pulping is used on most papers produced commercially in the world today (Smook 1992; Biermann 1996). Traditionally, this has involved a full chemical treatment in which the objective is to remove non-cellulose wood components leaving intact the cellulose fibers. In practice, separation of the components is never completely realized. Yet satisfactory compromises are reached in the processes which yields somewhere between 45 % and 55 % of the wood mass. Chemical pulps are made by cooking (digesting) the raw materials. Soda pulping utilized only strong alkaline solution of Sodium hydroxide (NaOH) as pulping chemical to delignify raw material. The raw material are cooked in closed digester with Sodium hydroxide as the base at pH around 13 - 14, 160°C - 170°C of temperature, 100 - 110 psi pressure of temperature for 3 - 8 hours of cooking time (Sell, 1992).

According to Sell (1992), soda pulping required long cooking time and yield dark colour pulp (dark brown) which still had significant lignin content. The soda pulping process had limited use for some fibrous raw material and during soda pulping process; NaOH mostly reacted with the lignin or the processing gas carbon dioxide ( $CO_2$ ). Meanwhile, sodium carbonate ( $Na_2CO_3$ ) is produced as the by product in the latter reaction. The recovery of NaOH from black liquor is accomplished by first evaporating the water in the black liquor, the other are solids consisting of organic residues and inorganic salts. The organic will be burnt as the residues can be combusted. On the other hand, NaOH can be recovered to a large extent by the treatment with lime (CaO), where this process called recausticization.

During soda cooking process, NaOH enable wood cells to swell better than water then results the cell walls were more accessible to pulping liquor. On the other hand, hydroxide ion (OH<sup>-</sup>) generated from NaOH reacted with lignin found in wood and caused the lignin to degraded into smaller soluble fragments (Ibrahim, 2000). When temperature reached about 100°C, the degradation of cellulose due to peeling reaction started and contributes to the yield loss problem. The degradation of cellulose started at the reducing end group, which a proton is extracted from the C-2 position and ketose is formed. After that,  $\beta$ -alkoxy elimination at C-4 become the new educing end on the remainder of the polymer was further peeling reaction taken place. Finally, the degradation of cellulose during the peeling reaction produced various hydroxyl acids that will consume the alkali and reduced the effective concentration of the pulping liquor (Sjostrom, 1993).

After pulp production, pulp is processed in wide variety of ways to remove impurities, and recycles any residual cooking liquor via the pulp washing process. Residual spent cooking liquor from chemical pulping is washed from the pulp using hydrapulper. Water comes out during washing process called brown stock. Efficient washing is critical to maximize return of cooking liquor to chemical recovery and to minimize carryover of cooking liquor. Excess cooking liquor increases consumption of bleaching chemicals. Specifically, the dissolved organic compounds contained in the liquor will bind to bleaching chemicals and thus increase bleach chemical consumption. Some pulp processing steps that remove pulp impurities are screening.

#### 2.3 Bleaching

Bleaching is the process that designed to react with lignin either converts it to a colorless form or removes it. Objective of bleaching to remove or convert to colorless form, maintain cellulose chain length and brighten the fibers. The color for unbleached pulp is predominantly caused by the lignin remaining in the fiber after pulping. Paper yellowing is a natural process of paper ageing which is caused by sunlight, moisture and air. Chemical pulps contain very little lignin while mechanical pulps contain most of the lignin which was present in the wood used to make the pulp. Lignin is the main source of color in pulp due to the presence of a variety of chromophores naturally present in the wood. Celluloses and hemicelluloses are white. So do not contribute to pulp color.

In this study, chemical pulps contains much less lignin then, the goal in bleaching chemical pulps is to remove essentially all of the residual lignin, hence the process is often referred to as delignification. In order to achieve sustainable development and to take the advantage of low Kappa number of the resulting unbleached pulp, the employment of Totally Chlorine-Free (TCF) bleaching become the prior consideration in producing full bleached cellulose pulp from EFB (Leh et al., 2008).

The sequence in Totally Chlorine-Free (TCF) is OZP sequences where Oxygen bleaching (O), Ozone bleaching (Z) and Peroxide bleaching (P). In order to complete the bleaching process all types bleaching OZP need to complete with sequence to get bleached (OZP) OPEFB pulps.

20

#### 2.4 Beating

Beating is one of the most important processes in papermaking. Beating can defined as the mechanical treatment of pulp that carried out in the presence of water and applied to the batch treatment of stock in a beater machine by passing the slurry of pulp fibers through a relatively narrow gap between revolving rotor and stationary stator (Casey, 1981). Beating will modify the structure of the fiber to obtain optimal properties for the demands of the particular papermaking furnish. A paper sheet made from virgin pulp which has not undergone a form of mechanical treatment is characterized by low strength, bulkiness and surface roughness, then not suitable for papermaking (Bhardwaj et al., 2004). These undesirable characteristics can be changed to a large extent by treating the pulp mechanically in a highly controlled manner.

The PFI mill (Fig. 2.9) is a beater featuring a high reproducibility, used for studying the relationship between beating degree of pulp and physical properties. This machine is basically an experimental beater widely used in the preparation stage of paper making. The beating of fibers consists of mechanical crushing and abrasion of fiber caused by contact with edge and faces of rapidly moving metal bars in the presence of polar penetrating liquid, such as water. Both mechanical and hydraulic forces are employed to alter the fiber characteristics. Beating mechanism: a constant load is given to the pulp circulating in between stainless steel roll and cylindrical mill house, which are rotating with a constant difference in circumferential velocity, applying mechanical effects such as shear and compression, thereby performing beating by frictional forces between fibers. The number of rotations is read on the counter. The beating degree is evaluated by the freeness tester.



Fig. 2.9 : Beater machine (PFI mill)

#### 2.4.1 Effect of Beating on Stock Properties

Beating will give affect on stock properties. It controls the rate at which water drain from papermaking fiber while they are being formed into a wet met on the drainage plate of the tester. A free pulp drains rapidly and slows, it's known as freeness of fibers. That happened because increased specific surface by fibrillation during beating and it gives a slow drainage rate. However slowing of drainage rate will produce a sheet with good formation (Casey, 1981). Fine formation comes from pieces of fiber wall depth from the fiber, creating secondary fine. These can consist of exposed cellulose fibrils from the secondary wall, and material from the primary wall and middle lamella, in case of slow drainage rate that cause fine formation of fiber.

#### 2.4.2 Effect of Beating on Fiber Properties

The PFI-mill beating is performed at 10% (w/w) medium concentrated pulp. Beating process brings changes to the structure and properties of fibers, such as fiber swelling, fiber shortening, internal and external fibrillation (Lecourt et al., 2010). Beating is physical actions towards the fibers that fractures and partially remove the primary wall, reduce average fiber length, increase the fiber flexibility due to internal fibrillation, external fibrillation of the fiber surface, fiber shortening or cutting, and fines formation. Beating also essential step in improving the bonding affinity between fibers in the web and is related to a fibrillation.

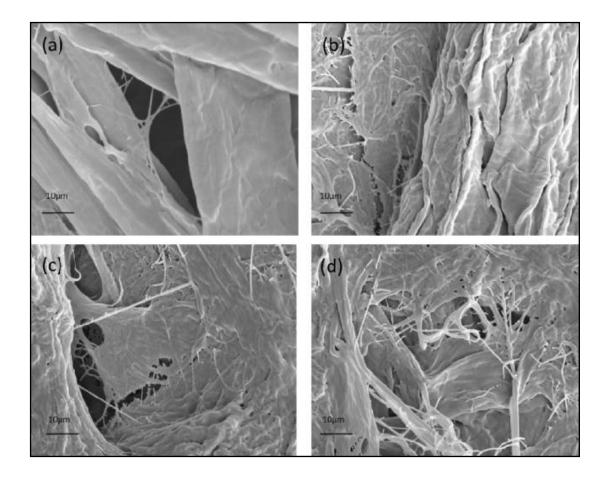


Fig. 2.10 : External fibrillation with different beating (Gao et al., 2008) a) 0 rev., (b) 5000 rev., (c) 10,000 rev., (d) 15,000

External fibrillation (Fig. 2.10) is a release of visible external fibrils from the fiber surface and commonly cause by beating which is increased the specific surface of fiber. Increase the surface area available for the absorption of water and a progressive enlargement of the fibril bundles occur. The outer layer of the fiber bonds are removed, exposing fibrils of the secondary wall. New external surfaces are created, which can participate in polyelectrolyte adsorption and inter-fiber bonding (Clark, 1985).

The flexibility of fiber increase during beating is attributing to an internal fibrillation (Fig. 2.11). The breaking down of adhesion between the fibrils in the fiber walls particularly in the secondary wall layer and the breaking down of the adhesion between secondary wall layer themselves. The beating process will cause production certain amount of fines fiber. The presence of fines fiber will affect the freeness of the stock and the properties of the sheet made from the stock such as air permeability.

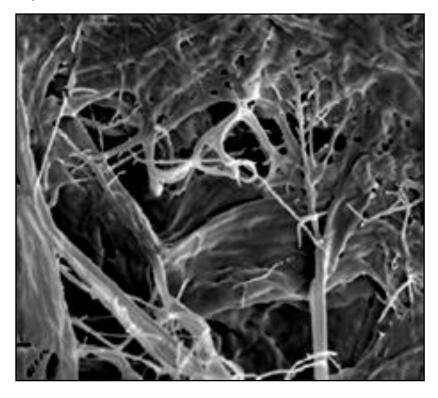


Fig. 2.11 : OPEFB fiber fibrillated (Gao et al., 2008)