

**EFFECT OF EMPTY FRUIT BUNCHES (EFB)  
BASED LIGNIN ON THE PROPERTIES OF EPOXY  
EFB FIBER COMPOSITE**

**MARLIANA BINTI MOHD MAHADAR**

**UNIVERSITI SAINS MALAYSIA**

**2011**

**EFFECT OF EMPTY FRUIT BUNCHES (EFB) BASED  
LIGNIN ON THE PROPERTIES OF EPOXY EFB FIBER  
COMPOSITE**

**by**

**MARLIANA BINTI MOHD MAHADAR**

**Thesis submitted in fulfillment of the requirements  
for the degree of  
Master of Science**

**JULY 2011**

## ACKNOWLEDGEMENT

### **In the name of Allah who is most grateful and merciful**

This appreciation is dedicated to those who have closely contributed their valuable assistance, cooperation and support towards the completion of this final project.

Firstly, I like to take this opportunity to show my thank fullness towards Almighty Allah S.W.T. for rendering upon me such a tremendous moment with determination and courage through the period of time leading to the completing of this final project and thank to my beloved family for their continuous support and encouragement..

I am pleased to express my great appreciation to Professor Dr Abdul Khalil Shawkataly, my supervisor due to his encouragement on the advice, comments and suggestion which had expended the valuable information throughout my graduate study. I would like to thank to my co-supervisor, Dr Issam Ahmed Mohammed for wiling to provide knowledge and assist in understanding the problem.

Not forget, sincere gratitude to Mr. Azhar, Mr. Raja, Mr. Abu, Mr. Shamsul, Mr. Ahmad Mrs. Hasni and Mrs. Aida for their assistance and co-operation in lab works and technical support during my graduate study. Also to my husband Mohamad Haafiz Mohamad Kassim, who give me the strength to keep up with study, encourage and helping me that leading towards the success of this project.

Last but not least, I want pay tribute to Hamzah Sendut 1 Library for supplied the references book that help in finishing my final thesis. I also like to acknowledge Institute of Postgraduate Studies, Universiti Sains Malaysia for financial support.

The appreciation also goes to my entire friend for their support. Lastly, at this moment I also wanted to convey my gratefulness to all individual who is involved either directly or indirectly during the times towards the success of this project.

## TABLE OF CONTENTS

<b>TITLE</b>	<b>PAGE</b>
<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>TABLE OF CONTENT</b>	<b>iii</b>
<b>LIST OF TABLES</b>	<b>vii</b>
<b>LIST OF FIGURES</b>	<b>viii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xi</b>
<b>ABSTRAK</b>	<b>xii</b>
<b>ABSTRACT</b>	<b>xiii</b>
<b>CHAPTER</b>	
<b>1 INTRODUCTION</b>	
1.1 General	1
1.2 Justification	4
1.2 Objectives	5
<b>2 LITERATURE REVIEW</b>	
2.1 Raw material	6
2.1.1 Oil Palm Tree	6
2.1.2 Oil Palm and Environment	10
2.1.3 Empty Fruit Bunch (EFB)	11
2.1.4 Chemical Compositions of Oil Palm Empty Fruit Bunch (OPEFB)	12



### 3 MATERIAL AND METHOD

3.1 Material	53
3.1.1 Oil Palm Empty Fruit Bunch (OPEFB)	53
3.2 Methodology	53
3.2.1 Preparation of lignin	53
3.2.1.1 Soda-AQ pulping	53
3.2.1.2 Isolation and purification of lignin from black Liquor	54
3.2.1.3 Characterization of lignin	55
3.2.1.3.1 Fourier Transform Infrared Spectroscopy (FTIR)	55
3.2.1.3.2 Carbon-Hydrogen-Nitrogen (CHN) Elemental Analysis	56
3.2.1.3.3 Gel Permeation Chromatography (GPC)	57
3.2.1.3.4 Thermogravimetric Analysis (TGA)	57
3.2.2 Preparation of Epoxy Resin	58
3.2.2.1 Molecular weight	59
3.2.3 Preparation of Composite	60
3.2.3.1 Characterization of Composites	61
3.2.3.1.1 Tensile Test (ASTM D 638-03)	61
3.2.3.1.2 Flexural Test (ASTM D 790-03)	62
3.2.3.1.3 Impact Test (ASTM D6110-05a)	64
3.2.3.1.4 Water Absorption (ASTM D 570)	64
3.2.3.1.5 Thermogravimetric Analysis (TGA)	65
3.2.3.1.6 Scanning Electron Microscope (SEM)	66

<b>4</b>	<b>RESULT AND DISCUSSION</b>	
4.1	Characterization of lignin	67
4.1.1	Yield of lignin	68
4.1.2	Fourier Transform Infrared Spectroscopy (FTIR)	69
4.1.3	Carbon-Hydrogen-Nitrogen (CHN)	71
4.1.4	Gel Permeation Chromatography (GPC)	72
4.1.5	Thermogravimetric Analysis (TGA)	74
4.2	Characterization of Composite	77
4.2.1	Fourier Transform Infrared Spectroscopy (FTIR)	78
4.2.2	Mechanical Properties	81
4.2.2.1	Tensile Properties	81
4.2.2.1.1	Tensile strength	81
4.2.2.1.2	Tensile Modulus	85
4.2.2.1.3	Elongation at Break	86
4.2.2.2	Flexural Properties	88
4.2.2.2.1	Flexural Strength	88
4.2.2.2.2	Flexural Modulus	90
4.2.2.3	Impact Properties	91
4.2.3	Physical Properties.	93
4.2.3.1	Water Absorption	93
4.2.4	Surface morphology (SEM)	95
4.3	Thermal properties of composites	99
<b>5</b>	<b>CONCLUSION AND RECOMMENDATION</b>	<b>108</b>
	<b>REFERENCES</b>	<b>111</b>
	<b>APPENDIX</b>	<b>125</b>

## LIST OF TABLES

Tables	Pages
Table 2.1: Chemical composition of OPEFB	13
Table 2.2 Pulping Reaction that Modify Lignin	20
Table 2.3. Glass Transition (Tg) of Lignin-PF resins	29
Table 3.1 Epoxy-lignin resin properties	61
Table 4.1 The average yields of lignin were recorded based on g/100 ml black liquor used	68
Table 4.2 Summary of IR bands associated with different types of bonds	70
Table 4.3 CHN of extracted EFB lignin	72
Table 4.4 Molecular weight average ( $M_w$ ), number average ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) of soda lignin from EFB fiber	72
Table 4.5 Thermal properties of EFB-lignin	74
Table 4.6 Tensile properties of composites	82
Table 4.7 Flexural properties of composites	89
Table 4.8 Thermal properties of EFB fiber, lignin and epoxy	100
Table 4.9 Thermal properties of EFB/lignin epoxy composites	106



## LIST OF FIGURES

Figures	Pages
Figure 2.1: Oil Palm Tree	7
Figure 2.2: Oil palm fresh fruit bunch and the structure of the palm fruit	8
Figure 2.3 (a) Fresh fruit bunch (b) Empty fruit bunch (c) Fibrous form	12
Figure 2.4: Chemical structures of three alcoholic precursors of lignin	16
Figure 2.5: Telescopic representation of a conifer tracheid. <i>p</i> -Coumaryl alcohol is preferentially deposited in the middle lamella and coniferyl alcohol in the secondary wall	17
Figure 2.6: The molecular structure of lignin	18
Figure 2.7: Cure conversion peaks for lignin-PF resin samples	30
Figure 2.8: Formation of a composite material using fibers and resin	39
Figure 2.9: Cross-link of thermoset materials	41
Figure 2.10: Epoxide group	43
Figure 2.11 Structure of DGEBA	43
Figure 2.12: Classification of Lignocellulosic Fiber	49
Figure 3.1 Soda lignin powder	55
Figure 3.2 Epoxy resin	59
Figure 4.1: Comparison FTIR spectra of lignin: (A) Commercial lignin and (B) Soda AQ Lignin	71
Figure 4.2: TG curves EFB based lignin under N <sub>2</sub> atmosphere at 20 °C/min	75
Figure 4.3: DTG curves EFB based under N <sub>2</sub> atmosphere at 20 °C/min	77

Figure 4.4: Comparison FTIR spectra of EFB based lignin (A), epoxy resin (B) and EFB/epoxy-lignin composite (C)	79
Figure 4.5 Comparison FTIR spectra of composites	80
Figure 4.6: Idealized network formation during curing reaction of epoxy-lignin system (where R represents $-OCH_3$ ; and R' represents $-CH=CH-CHO$ , etc)	80
Figure 4.7: Tensile strength of oil palm EFB composites	82
Figure 4.8: Scanning electron micrographs of the tensile-fractured surface of the oil palm fiber-reinforced composite EP-L15  The clean surface of oil palm fibers indicates better adhesion between the fibers and matrix  (magnification 50 X).	83
Figure 4.9: Scanning electron micrographs of the tensile-fractured surface of the oil palm fiber-reinforced composite EP-L30  (magnification 100 X).	84
Figure 4.10: Tensile modulus of oil palm EFB composites	85
Figure 4.11: Elongation at break of oil palm EFB composites	87
Figure 4.12: Flexural strength of oil palm EFB composites	88
Figure 4.13: Flexural modulus of oil palm EFB composites	90
Figure 4.14: Impact strength of oil palm EFB composites	92
Figure 4.15: Water absorption of Oil Palm EFB Composites	94
Figure 4.16: SEM micrograph of the oil palm empty fruit bunch fiber	96

Figure 4.17 A-D: SEM micrographs of epoxy composites at different magnification: A and C = Amine cured EFB/epoxy composite- EPAC; B and D = Typical lignin cured EFB/epoxy composite- EP-L20. The arrows indicate the pores on the fracture surface	97-98
Figure 4.18 TGA curves of EFB fiber, EFB based lignin and epoxy-amine cured polymer (EPA) under N <sub>2</sub> atmosphere at 20 °C/min	99
Figure 4.19 DTG curves of EFB fiber, EFB based lignin and epoxy-amine cured polymer (EPA) under N <sub>2</sub> atmosphere at 20 °C/min	101
Figure 4.20: TGA curves of natural fiber (EFB) reinforced lignin-epoxy composites.	103
Figure 4.21: DTG curves of composites under N <sub>2</sub> atmosphere at 20 °C/min	106

## **LIST OF ABBREVIATES**

OPEFB	Oil palm empty fruit bunch
EFB	Empty fruit bunch
EPAC	Epoxy amine composite
EP-L15	Epoxy-lignin composite
SEM	Scanning electron microscopy
GPC	Gel Permeation Chromatography
AQ	Antraquinone

**KESAN LIGNIN BERASASKAN DARIPADA TANDAN KOSONG BUAH  
KELAPA SAWIT (EFB) TERHADAP SIFAT KOMPOSIT EPOKSI  
DIPERKUATKAN GENTIAN EFB**

**ABSTRAK**

Resin epoksi merupakan matriks yang sangat penting dalam komposit polimer termoset. Objektif utama kajian ini adalah untuk menghasilkan dan mencirikan lignin dari likur hitam untuk digunakan sebagai agen pematangan bagi resin epoksi. Lignin yang diperolehi daripada pemulpaan tandan kosong buah kelapa sawit (EFB) digunakan sebagai agen pematangan dalam komposit epoksi. Struktur kimia lignin disahkan dengan menggunakan analisis CHN, spektroskopi FTIR, GPC dan analisis terma. Komposit epoksi yang diperkuatkan dengan gentian tandan kelapa sawit dihasilkan dengan menggunakan kandungan lignin yang berbeza (15%, 20%, 25% dan 30%). Pengaruh lignin ke atas sifat terma dan morfologi komposit diteliti dan dibandingkan dengan komposit yang dimatangkan oleh isophorone diamina. Sifat mekanikal dan fizikal komposit diperkuat gentian EFB seperti kekuatan tensil, kekuatan fleksural, kekuatan hentaman dan penyerapan air turut dikaji. Lignin sebagai agen pematangan telah meningkatkan kestabilan terma dan struktur mikro diamati dari permukaan patah komposit yang dikaitkan dengan interaksi serat-matriks yang baik. Secara umumnya, hasil kajian menunjukkan bahawa epoksi diperkuatkan komposit EFB dengan kandungan lignin 25% digunakan untuk pematangan menghasilkan matriks yang lebih baik dan memberikan nilai optimum berbanding dengan formulasi lain yang telah disahkan oleh sifat-sifat mekanik, fizikal, terma dan morfologi.

# **EFFECT OF EMPTY FRUIT BUNCHES (EFB) BASED LIGNIN ON THE PROPERTIES OF EPOXY EFB FIBER COMPOSITE**

## **ABSTRACT**

Epoxy resin is an important matrix resins for thermosetting polymer composites. The objectives of this study were to extracts and characterize lignin from black liquor to be used as curing agent in epoxy resin application. Lignin obtained from pulping of oil palm biomass empty fruit bunches (EFB) fibers, were used as curing agent in green epoxy composites. The chemical structures and properties of lignin were confirmed by CHN analyses, FTIR, GPC and thermal analysis. Epoxy-lignin composites, with varying lignin content (15%, 20%, 25% and 30%), reinforced with EFB fiber were prepared. The effect of EFB based lignin on thermal and morphology properties of the composites were investigated and compared with the composites cured with isophorone diamine curing agent. The mechanical and physical properties such as tensile, flexural, impact properties and water absorption of EFB reinforced epoxy-lignin composite were also studied. The improved thermal stability and the observed microstructure of the fractured surface of the composites were attributed to good fiber-matrix interaction, induced by the curing agent. In general, the results showed that the epoxy reinforced EFB composites cured with 25% lignin content proved to be a better matrix and gave optimum value compared with other formulations which was confirmed by its mechanical, thermal and morphological properties.

## CHAPTER 1

### INTRODUCTION

#### 1.1 General

The plantation of oil palm (*Elaeis Guineensis*) is growing rapidly in Malaysia since late 1960s due to land settlement schemes introduced by the government. Palm oil industry generates vast amount of oil palm biomass mainly from milling and crushing palm kernel. The great establishment of oil palm industry was also accompanied by the generation of abundant oil palm biomass residues such as trunks, fronds, shell, mesocarps and empty fruit bunch (EFB). Oil palm (*Elaeis guineensis*) empty fruit bunch (OPEFB) was a lignocellulosic waste generated during palm oil extraction process is a good source of cellulose, lignin and hemicelluloses which can be used in many industrial processes. Over 15 million tons of EFB waste residue is generated annually in Malaysia (Alriols *et al.*, 2009; Abdul Khalil *et al.*, 2007).

This waste is mostly disposed through combustion or land filling, creating considerable pollution and economical problems. In order to overcome the problem such as curbing pest breeding in the plantation and open burning of the oil palm residues, owing to the left and unused biomass, many researches had started to study the feasibility of the utilization of the material by converting it into value added products including pulp and paper (Wan Rosli *et al.*, 1998). Therefore, utilization of this organic waste in any industrial process would be of immense environmental and economical benefits to society.

Several processes have been used to extract lignin or/and to produce pulp and paper from lignocellulosic materials. Soda pulping is one of the most relevant and widely used for delignification of non-woody materials. The process of producing cellulosic pulp from oil palm biomass and other non-wood fibers requires delignification with sodium hydroxide under pressure. This liberates the cellulosic fiber and produces a large quantity of toxic black liquor which is discharged into water bodies without proper treatment (Sun & Tomkinson, 2001; Mohamad Ibrahim *et al.*, 2004). As a consequence of the pulping process, lignin is dissolved from the raw material, being separated in the form of a liquor rich in phenolic compounds that represents the process effluent. This effluent is dark brown or black in colour.

The black liquor contains a wide variety of compounds (chemicals and derived from lignin). It is very complex, contains high alkalinity and high dissolved solids such as lignin residues, degraded carbohydrates and inorganic constituent (Sjostrom, 1981). Although the pulping chemical in the highly proposed soda pulping process is only sodium hydroxide (with or without anthraquinone as catalyst), the discharging of this spent liquor/black liquor into the downstream without proper treatment will definitely bring serious water pollution in term of biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), colour unit, pH, odour and etc. (Smook, 1992). The pulp and paper industries normally burn the lignin dissolved in the black liquor for energy generation (Garcia *et al.*, 2009).



Oil palm biomass consists of about 20% lignin. This lignin, obtained from the black liquor produced during pulping, is considered as pollutant and it is known to contain about 50% of lignin (Zaied & Bellakhal, 2009). However, the lignin can be isolated and used as the starting material for a series of useful products.

Lignin is a natural phenolic polymer which is occurring in higher plant tissues and is the second most abundant natural polymers after cellulose. It composed of one-third of the material found in plant cell walls and an important component of plant secondary cell walls. It is a complex polymer of phenylpropanoid units that is cross-linked to other components, including cellulose, within the wall. The integration of lignin into the cell wall strengthens and maintains the structure of the cell. Lignin serves to affect water transport, protect trees against chemical and biological attack, and provide structural integrity. Due to their very complex structure, lignins are amorphous polymers with rather limited industrial use. Traditionally lignin has been viewed as a waste material or a low value by-product of pulp and paper industry with its utilization predominantly limited to use as a fuel to fire the pulping boilers (Stewart, 2008).

Lignin as a heterogeneous biopolymer of extreme complexity, whose exact chemical composition is not known, hence recent efforts at developing lignin-based polymer blends and composites have lead to conflicting reports regarding the benefits of lignin incorporation into polymers (Mishra *et al.*, 2007). Also, the extensive cross-linking and strong intermolecular interactions prevent its utilization in solid material system. Consequently, lignin is often deficient in areas where homogeneity of chemical

functionalities and molecular weight distribution is required. It is therefore essential that rigorous intensive research on lignin modification and application would be of utmost importance. Moreover, studies by Simionescu *et al.*, (1993) showed that significant lignin loads could be incorporated into the epoxy resin whilst still maintaining good electrical (volume and surface resistivity, dielectric constant, loss in dielectric tangent angle and dielectric rigidity) and mechanical properties, and high impact toughness compared to the lignin-free phenol epoxy resins.

## **1.2 Justification**

Epoxy resin is a widely used polymer matrix for advanced composites where good stiffness, dimensional stability, excellent mechanical properties and chemical resistance is required (Sui *et al.*, 2009). The mechanical properties of this un-reinforced epoxy polymer matrix may not be sufficient for some end-use applications. Therefore, other materials such as filler/reinforcement may be incorporated to enhance the performance characteristics. The use of various form of curing agent/hardener has also been reported to influence the properties of such polymers. Several approaches of incorporating lignin into epoxy resins, aimed at partially replacing petroleum-based materials, have been reported in literatures (Cazacu & Popa, 2003; Stewart, 2008).

Tertiary amines, polyfunctional amines and acid anhydrides are widely used as curing agents for epoxy resins. These curing agents are toxic and are capable of causing severe irritation, serious rash or an asthmatic response in sensitive persons. Therefore this study was carried out to develop an environmental-friendly curing agent from bio-

resource material. The lignin recovered from the black liquor is widely recognized to be used as binder for adhesives or as additive such as oil well drilling additives, concrete additives, agricultural chemicals and industrial binders turning the lignin-rich black liquor to value-added products which will assist the development of pulp and paper industry in Malaysia.

### **1.3 Objectives**

The main objectives of this research are summarized below:

- I. To extract and characterize the properties of lignin from oil palm biomass as a curing agent in the preparation of epoxy resin.
- II. To investigate the physical and mechanical properties of the new epoxy resin reinforced composites.
- III. To study the influence of lignin on thermal properties of the composites.

## **CHAPTER 2**

### **LITERATURE RIVIEW**

#### **2.1 Raw Material**

Wood is principal sources of cellulosic fiber widely used as raw material for production of pulp and paper in the world. Presently, wood provides about 93% of the world's virgin fiber requirement, while non-wood sources provide the reminder (Smook, 1992). However, increasing concerns over future fiber supplies and potential increases in wood costs have caused the pulp and paper industry to search for alternative fiber sources such as non-wood fiber plants. Within the mixed of non-wood fibers, oil palm (*Elaeis guineensis*) is one that shows great potential as a papermaking raw material, particularly for Indonesia and Malaysia. Besides palm oil, the industry also generates massive amounts of lignocellulosic residues such as trunks, fronds and the empty fruit bunches (EFB), with an estimated amount of 30 million tonnes (MPOB, 2010).

##### **2.1.1 Oil Palm Tree**

The oil palm tree (*Elaeis guineensis*) was a tropical species that originated from West Africa where it was growing wild but now developed into an agricultural crop in many parts of the world including South East Asia and Central America. It was first introduced to Malaya in early 1870's as an ornamental plant. In 1917 the first commercial planting took place in Tennamaran Estate in Selangor, laying the foundations for the vast oil palm plantations and palm oil industry in Malaysia. The cultivation of oil palm rapidly increased beginning in the sixties under the government's

agricultural diversification programme which was 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. The oil palm plantations in Malaysia are largely based on the estate management system and small holders' scheme (MPOC, 2010).



Figure 2.1: Oil Palm Tree (Source: MPOC, 2010)

Oil palm is known as monoecious crops as it bears both male and female flowers on the same tree. The palm fruit develops in dense bunches weighing 10 kilograms (kg) or more and containing more than a thousand individual fruits similar in size to a small plum. Palm oil is obtained from the flesh of the fruit and formed part of the food supply. Generally the fruitlet is dark purple, almost black and the colour turns to orange red

when ripe. Each fruit is made up of oily fleshy outer layer (mesocarp), consists of a hard kernel (seed) inside a shell (endocarp) which also rich in oil (MPOC, 2010).

Botanically, oil palm is classified thusly:

Kingdom : Plantae  
Sub-Kingdom : Tracheopionta  
Division : Angiospermae  
Class : Monocotyledones  
Subclass : Arecidae  
Order : Arecales  
Family : Arecaceae  
Genus : Elaeis



Figure 2.2: Oil palm fresh fruit bunch and the structure of the palm fruit (Source: MPOC, 2010)

The past few decades have seen the rapid growth of the oil palm industry in Malaysia in terms of cultivated area and volume of production. Today, oil palm dominates the landscape throughout the country and the industry has become major

contributor to Malaysia's export earnings. The increase in palm oil production has been driven by strong and increasing global demand for oils and fats (Teoh, 2000). Its commercial value lies mainly in the oil that can be obtained from the mesocarp of the fruit - palm oil and the kernel of the nut - palm kernel oil. Palm oil is used mainly for cooking (cooking oil, margarine, shortening, etc.) and has non-food applications (soap, detergent, cosmetics, etc.)

To date, 4.69 million hectares of land in Malaysia is under oil palm cultivation; producing 17.73 million tonnes of palm oil and 2.13 tonnes of palm kernel oil. Malaysia is one the largest producers and exporters of palm oil in the world, accounting for 11% of the world's oils & fats production and 27% of export trade of oils & fats (MPOC 2010). The oil consists of only 10% of the total biomes produced in the plantation. The remainder consists of huge amount of lignocellulosic materials such as oil palm fronds, trunks and empty fruit bunches. The projection figures of these residues are as follows:

- 7.0 million tonnes of oil palm trunks.
- 26.2 million tonnes of oil palm fronds.
- 23% of Empty Fruit Bunch (EFB) per tonne of Fresh Fruit Bunch (FFB) processed in oil palm mill (ASEAN, 2010).

The total oil palm planted area in the country increased by 4.5% in 2009. Among the regions, Sarawak registered the largest increase in planted area with a growth of 12.8%, followed by Peninsular Malaysia 3.3% and Sabah 2.1%. Sabah is still the largest oil palm planted state, accounting for 1.36 million hectares or 29% of the total planted area in the country (Mohd Basri, 2010).

### **2.1.2 Oil Palm and Environment**

Freshly felled oil palm trunks cannot be burnt easily in the field due to its high moisture content. Leaving these residues in the field without further processing will not only physically hinder the process of planting but also serve as natural habitat and breeding ground for oil palm pests such as Rhinoceros beetles and fungus *Ganoderma*. On the hand, fungus *Ganoderma* will cause Basal Stem Rot (BSR) disease which is the most destructive disease in oil palm. It is lethal and incurable for more than 50 years now. Basal Stem Rot (BSR) is fast becoming a major threat to oil palm cultivation and palm oil production in Malaysia.

*Ganoderma* species attacks start from the palm roots and gradually spread to the bole of the stem, causing dry rot, thus preventing nutrients from being absorbed by the soft tissues. The palm will gradually lose its ability to produce fruits and eventually collapse. The failure to control this disease is due to the characteristics of *Ganoderma* spp. This fungus is soil borne pathogens which allowing the disease to reappear in oil palm estates which are doing their second or even third replanting. As a result it is a common practice to either poison the trunks before they are felled in order to increase the rate of decomposition or to shred the felled trunks into smaller pieces in order to ease their burning. These practices have given rise to many environmental problems such as air pollution for the industry (Susanto *et al.*, 2005; Mazliham *et al.*, 2007)



Besides trunks, a large amount of fronds is also generated during replanting. Currently, a certain amount of pruned fronds is used as interior mulching to conserve soil moisture in the plantations. However, this utilization has been found to attract rats, snakes, insect pests and thus limited its application. The incineration of EFB emits particulates into the surrounding atmosphere and indiscriminate dumping of EFB causes additional methane emission into the atmosphere. However, due to the pollution problem, incineration of EFB has been discouraged (Kamaruddin *et al.*, 2006). As a result a large quantity of lignocelluloses resource is still available for exploitation.

### **2.1.3 Empty Fruit Bunch (EFB)**

EFB is one of such solid waste generated in oil palm planted throughout Malaysia over 4 million hectares land, which remains unutilized commercially. Hence, it has been verified in engineering properties and construction products made from EFB satisfy the requirement of consumers' trend using products made from eco-friendly and natural waste. However, woody fibrous residues, which remain after oil is extracted, have not been effectively utilized so far (Wan Rosli & Tanaka, 2002). Several studies support the possibility of using EFB (Figure 2.3) as raw material in variety of application including composites formulation (Abdul Khalil *et al.*, 2007; Abdul Khalil *et al.*, 2001) and papermaking (Wan Rosli *et al.*, 1998; Tanaka *et al.*, 2004; Sun & Tomkinson, 2001). In papermaking industry, good quality pulps have been successfully gained through EFB kraft (Tanaka *et al.*, 2004), soda (Wan Rosli *et al.*, 2005) potassium hydroxide (Sun *et al.*, 1999) and organosolv pulping processes.

EFB are partly dried in the sun and later used as fuel, if not incinerated or applied to the fields. An economic use of EFB is to return them to the plantation as a mulch to enhance moisture retention and organic matter in the soil. On the other hand, the ash recovered from the incinerated EFB can also be sold or used as fertilizer in the palm plantations (Kamaruddin *et al.*, 2006).

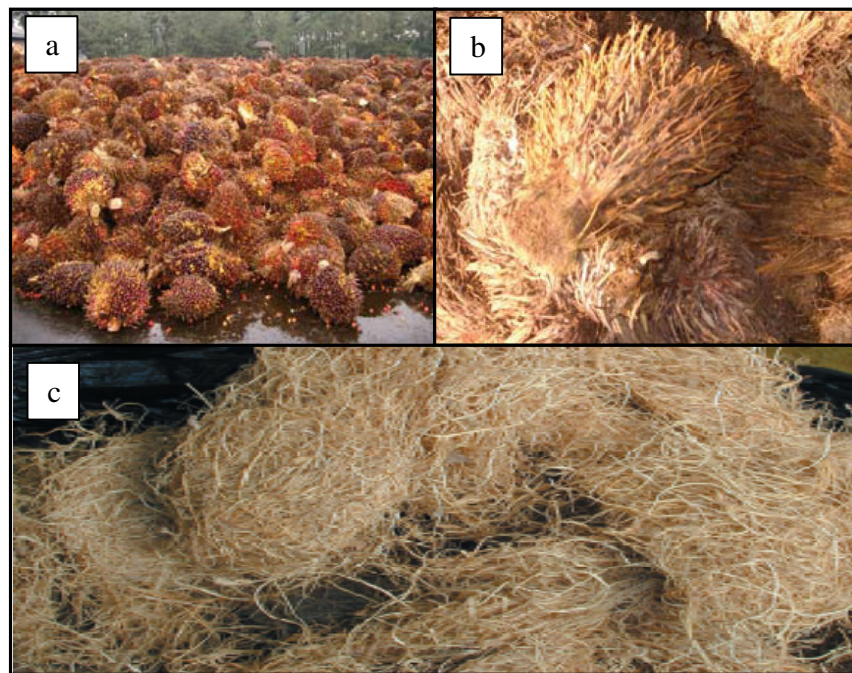


Figure 2.3: (a) Fresh fruit bunch (b) Empty fruit bunch (c) Fibrous form  
(Source: Wan Rosli & Tanaka, 2002)

#### 2.1.4 Chemical Compositions of Empty Fruit Bunch (EFB)

Lignocellulosics material such as wood and non-wood are three-dimensional composites, principally composed of macromolecules of cellulose, hemicelluloses, lignin and small amount of extractives and ash (Rowell, 1990). The three polymeric components, which occur in the cell wall of lignocellulosics, determine most of the

properties of lignocellulosics. The crystalline cellulose acts as the reinforcement while lignin predominantly acts as a matrix, making the cell wall matter a composite in nature (Ndazi *et al.*, 2006). The chemical compositions of lignocellulosic fibers vary according to the species, growing condition, method of fiber preparation and source of raw material. The chemical compositions of EFB are presented in Table 2.1.

Chemically, the EFB are rich in holocellulose (70%) and also high cellulose (42.7%) as illustrated in Table 2.1, both of which are important parameters in determining the suitability of a raw material for papermaking (Law *et al.*, 2007). The lignin content (18.8%) is lower than normally found in common hardwood, for example aspen of 18.1% and eucalyptus of 22% which is not surprising since oil palm trees are non-woody and the requirement for structural support is lower compared to that trees.

Table 2.1: Chemical composition of EFB

Composition	% Dry EFB
Holocellulose	70
Hemicellulose	32.5
Cellulose	42.7
Lignin	18.8
Extractives	3.7
Ash	1.3

Source: Law *et al.*, 2007; Khoo and Lee, 1991

## 2.2 Lignin

Lignin is a complex organic polymers produced by all vascular terrestrial plants and renewable natural products on earth which is second in abundance only to cellulose (Lewis and Lantzy, 1989; Lora and Glasser, 2002). The term lignin is derived from the Latin word “lignum” meaning wood was introduced by F. Schulze in 1865 (Sjostrom, 1981; Sarkanen and Ludwig, 1971). As one of the structural components of plants, lignin composing up to one-third of the material found in plant cell walls (Vinardell *et al.*, 2008) and often described as the material binding plant fibers together (Lewis and Lantzy, 1989).

Lignin plays an important role such as internal transport of water, nutrients and metabolites throughout plant, impart rigidity to the cell walls and in woody parts which acts as permanent bonding agents between cells and protect trees against chemical and biological attack by impeding penetration of destructive enzymes into the cell wall (Sarkanen and Ludwig, 1971). The amount of lignin in plants varies widely according to the kind of plant. In the case of wood, the amount of lignin ranges from 19 - 30 %, and in the case of non-wood fiber, ranges from 8 – 22 %, when the amount is determined according to Klason lignin analysis which is dependent on the hydrolysis and solubilization of the carbohydrate component of the lignified material, leaving lignin as a residue (Sarkanen and Ludwig, 1971). Lignins are difficult to extract as a pure material, and they are present with cellulose and hemicellulose to various extents (Singh *et al.*, 2005).

Lignin is predominantly limited use as a fuel. Indeed it has been estimated only a small amount of lignin 1-2% is isolated from spent pulping liquors and used in a wide range of specialty products (Lora and Glasser, 2002; Stewart, 2008). Instead of that, lignin is a three dimensional, highly branched polymer, which contains a variety of functional groups, and is capable of undergoing a large number of modification reactions. Both aliphatic and aromatic hydroxyl groups are abundant in it and are potential reactive sites. Because of this multifunctionality, lignin can be considered as a natural polyol (Khan and Ashraf, 2007). Because lignins are very complex natural polymers with many random couplings, their exact chemical structure is not known (Vinardell *et al.*, 2008).

### **2.2.1 Lignin Structure**

The chemical nature of lignin is known largely from studies of its biosynthesis (Sarkanen and Ludwig, 1971), work pioneered by Freudenberg and his co-workers between about 1930 and 1965. Lignin is usually considered as a polyphenolic material having an amorphous structure where synthesized by an enzyme which initiates dehydrogenative polymerization of three monomeric aromatic alcohols p-coumaryl (I), coniferyl (II) and sinapyl alcohols (III) as illustrated in Figure 2.4 connected with carbon atoms in phenylpropanoid units, which form a randomized structure in a three-dimensional network inside the cell wall (Stephen and Carlton, 1992; Garcia *et al.*, 2009; Jung and Fahey, 1983; Boudet and Grima-Pettenati, 1996) whose substituents and linkages depend on the plant species (Vazquez *et al.*, 1997).

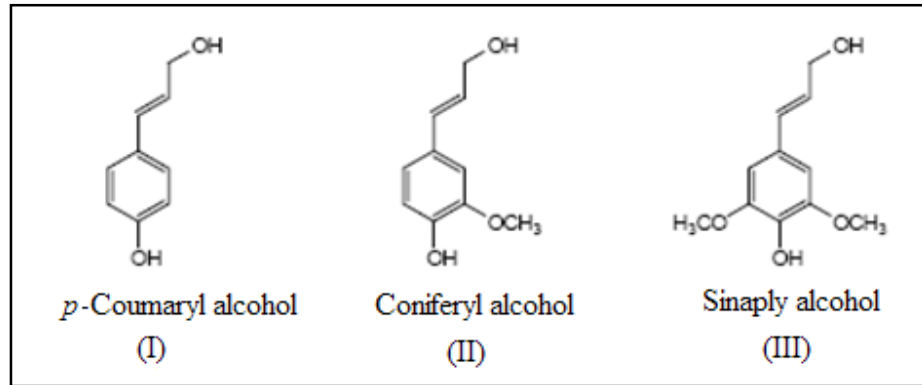


Figure 2.4: Chemical structures of three alcoholic precursors of lignin (Source: Davin and Lewis, 2005)

Variation in lignin concentrations among plant species is due to differences in the proportions of these alcohols. Generally, lignin in gymnosperms is predominantly composed of II units while angiosperm lignin is a mixture of II and III units, with lignin in the grasses additionally containing I units as illustrated in Figure 2.4 (Stephen and Carlton, 1992). The stems of woody angiosperms contain 18-25% lignin on a dry weight basis. Corresponding values for gymnosperms and monocotyledons are 25-35% and 10-30% lignin respectively. It commonly has been stated that the plant polymer lignin is the second most abundant organic compound on Earth, and that cellulose is the only other organic substances present in the biosphere in larger quantities than lignin.

The lignin concentration is high in the middle lamella and low in the secondary wall. Because of its thickness, at least 70% of the lignin in softwood is however, located in the secondary wall (Sjostrom, 1981). Lignin monomers are differentially targeted to discrete regions (lignin initiation sites) of various lignifying cell walls; for example, *p*-coumaryl alcohol is mainly targeted to the middle lamella and coniferyl alcohol to the secondary wall of the xylem elements as illustrated in Figure 2.5. Sinapyl alcohol, by

contrast, is targeted to discrete regions in fiber-forming cell walls (Davin and Lewis, 2005).

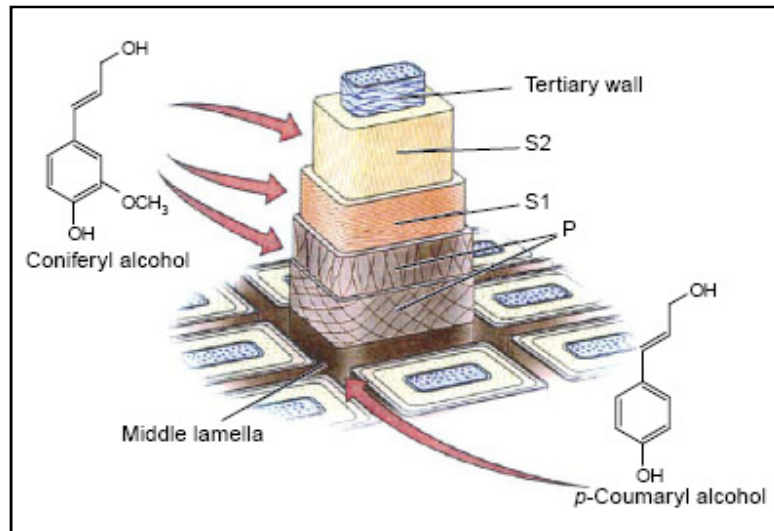


Figure 2.5: Telescopic representation of a conifer tracheid. *p*-Coumaryl alcohol is preferentially deposited in the middle lamella and coniferyl alcohol in the secondary wall. (Source: Davin and Lewis, 2005)

The content, composition and structure of lignin within cell walls, as well as the type and frequency of linkages between lignin and other wall polymers, influence the mechanical and industrial properties of plant fibres. Lignin is viewed not as a constitutionally defined compound, but as a composite of physically and chemically heterogeneous materials whose structure may be represented by model such as Figure 2.6 (Lin and Dence, 1992).

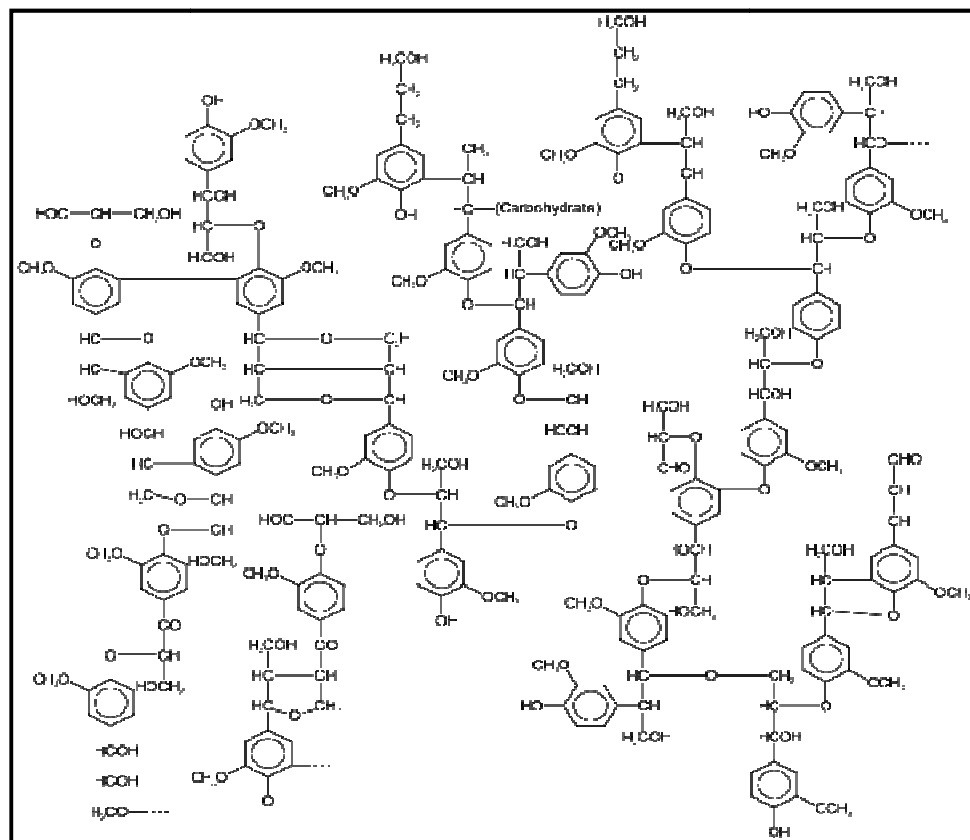


Figure 2.6: The molecular structure of lignin (Source: Lin and Dence, 1992)

### 2.2.2 Isolation of Lignin

The isolation of lignin methods conveniently divided into two classes, those that depend on the removal by hydrolysis of the cellulose and other components leaving the lignin as an insoluble residue and those that depend on the removal of lignin from the cellulose and the other substances with which it is associated (Max, 1995). Pulping is one of the methods that can be used to remove the lignin from the cellulose. During the pulping process, lignin is solubilized by degradation and/or derivatization, thereby



freeing cellulose fibers for the manufacture of paper and other products (Lundquist *et al.*, 1977).

The composition of lignin obtained as a by-product of the wood pulping industry (Canetti and Bertini, 2007; Vazquez *et al.*, 1997) depends not only on the wood pulped but also on the pulping process and the procedure used to isolate the lignin from the pulping liquor (Vazquez *et al.*, 1997). In chemical pulping, wood chips are treated in one or more stages with reagents in solution that are designed to remove some or most of the lignin from the wood, generally in an altered form. Heat and pressure accelerate the reactions involved and aid penetration of the chemicals into the wood. Most of the reactions used are unfortunately of low selectivity: the removal of lignin is incomplete and degradation of the plant fibers occurs (Harkin, 1966).

Industrially produced lignins are readily available and thus have been used extensively in biodegradation research. The two major pulping processes on a worldwide basis are the kraft process and the sulfite process. Millions of tons of kraft lignin and lignin sulfonates are produced annually by the pulping industry (Crawford, 1981). In the last decades, new delignification processes have been developed which produce low-molecular weight lignins, soluble in common solvents. Among these processes, the most prominent are the organosolv and steam explosion refineries to remove lignins from plants.

The solubilized lignins are chemically modified forms of natural lignin. Some of the important pulping reactions that modify lignin are shown in Table 2.2.

Table 2.2 Pulping Reaction that Modify Lignin

Kraft Process	Acid Sulfite Process
1. Cleavage of $\alpha$ -aryl ether bonds	1. Introduction of sulfonic acid group into $\alpha$ -positions on side chains.
2. Cleavage of phenolic $\beta$ -aryl ether bonds with extensive depolymerization	2. Opening of pinoresinol structures
3. Limited demethylation of methoxyl groups forming catechol structures	3. Some aryl-alkyl ether cleavages
4. Shortening of some side chains	4. Various condensation reactions, particularly at the $\alpha$ -positions of side chain
5. Various ill-defined condensation Reaction	5. Introduction of quinonoid structures
6. Introduction of quinonoid structures	

Source: Gierer (1970)

### 2.2.2.1 Soda Pulping

Sulfur-free lignins are an emerging class of lignin products. Having no sulfur and being of moderate macromolecular size, these lignins resemble more closely the structure of native lignin, and they exhibit distinct properties relative to kraft and sulfite lignins. This opens up new avenues for utilization. One of the sources of sulfur-free

lignin is soda pulping. Soda pulping is particularly of alternative biomass resources, such as agricultural harvesting residues and non-wood fiber crops (Lora & Glasser, 2002).

Sulfur-free soda pulping is practiced widely around the world and offers a potentially more readily available source of lignins. Most alkali required for pulping to neutralize saccharinic acids which formed in the degradation of hemicelluloses. These degradation reactions happen at 100°C and the reaction is completed at around 150°C, where delignification becomes the main reaction. A minimum residual alkali in  $\text{pH} \geq 9$  is required to keep the dissolved lignin in solution. In alkaline pulping, penetration of chemical is much easier than in the acidic sulfite pulping. The diffusion of alkaline pulping liquor into the wood is at an approximately equal rate in all structural directions. The degree of swelling of the fibers also is considerably higher in alkali compare to acidic sulfite. The swelled fibers produce several hundred fold increase in the potentially reactive surface area which increases further as the delignification proceeds.

Besides the penetration pattern, the actual distribution of the cell wall components exerts a major effect on the practical rate of delignification. Studies on the organization of microfibrillar structure of cell wall also suggest that lignins in the cell wall and in the middle lamellae have different morphology. In sulfite pulping, the delignification proceeded with the same rate in the middle lamella and in the secondary cell wall; while in alkaline pulping, lignin was completely removed from the middle layer before any delignification could be observed in the cell wall. One of the difficulties

of this type of process technology when applied to non-wood fiber sources is that the soda spent pulping liquors often contain silica, which may co-precipitate with the lignin, rendering it of lower quality.

In summary, sulfur-free lignins, although known for many years, are gaining new interest as a result of a diversification of biomass processing schemes. With the disappearance of the popular organosolv lignins from commercial availability, nonwood alkali extraction lignins are beginning to receive industrial attention. Soda lignins may originate from many different plant sources and process variations. These soda lignins all have in common that they are of low molecular weight, high phenolic hydroxy content, and relatively low (but variable) glass transition temperature. However, their properties sometimes vary significantly (Lora & Glasser, 2002).

#### **2.2.2.2 Black Liquor**

Black liquor is a thick, dark liquid that is a byproduct of the process that transforms wood into pulp, which is then dried to make paper. One of the main ingredients in black liquor is lignin, which is the material in trees that binds wood fibers together and makes them rigid, and which must be removed from wood fibers to create paper.

The pulp and paper industry generates 500 billion pounds of black liquor annually. The process of producing cellulosic pulp from wood and non-wood fiber requires delignification with sodium hydroxide under pressure. This liberates the

cellulosic fiber and produces a large quantity of waste product, the black liquor which is discharged into waters without effective treatment. Black liquor is an environmentally unfriendly by-product of the paper pulping industry.

Pollution is therefore a major problem in some countries where non-wood and wood is used as the raw materials for papermaking. The tree glue, or lignin, which holds the wood fibers together in the tree, becomes part of the black liquor. This lignin can be filter out and impurities are removed through a special purification process. In pulp and paper mill, large volume of the spent liquor from the pulped could be recycled in order to recover lignin rather than discarded into waste. Precipitation of lignin from the black liquor was reported by a number of researchers using mineral acids (Sun *et al.*, 2000b; Sun & Tomkinson, 2001; Samir *et al.*, 2002; Mohamad Ibrahim *et al.*, 2005).

### **2.2.3 Utilization of Lignin**

Lignin and derivatives have the right chemistry to be used in making coatings and composites because they have small particle size, are hydrophobic and have the ability to form stable mixtures (Park *et al.*, 2008). The most important future application of lignin will be as a natural plastic in the field of general polymer application especially as adhesives for wood composite (Haars, *et al.*, 1989).

The conversion of wood cellulose into commercial products often involves using the by-product lignins as a low cost, in-house fuel at the pulp mill (Hoyt and Goheen, 1972). Little attention has been focused on the use of lignins as chemicals or the

conversion of lignins to higher value products (Allen *et. al.*, 1980) because these could be produced from inexpensive petroleum. The recent energy crisis and the scarcity of crude oil has prompted research activities to develop alternative and renewable feedstocks for polymers and petrochemicals. Lignin products which were viewed as uneconomical only a few years ago are starting to appear attractive. This has led to the rediscovery of lignins as a possible renewable source of materials if its isolation can be achieved without harming the cellulose component.

Lately, the research done on the utilization of lignin shifted from the degradation approach to the use of lignin in its polymeric form. The utilization of polymeric lignin in solid material systems has been reported to be constrained by adverse effects on mechanical properties, (resin) viscosity, cure rate and other important material characteristics (Falkehag, 1975; Kringstad, 1980). Chemical modification has been demonstrated to offer a potential route to tailoring mechanical properties for specific needs (Glasser and Hsu, 1977). Reductions in brittleness of isolated lignin polymers (Kringstad, 1980), and alteration of viscoelastic properties, which seem to control such factors as the abrasion resistance of lignin-reinforced styrene-butadiene rubber (SBR) (Falkehag, 1975) constitute worthwhile targets for chemical polymer modification.

Possibilities of lignin include use as stabilizers for oil in water emulsion, stabilizers for fire fighting foams, dye levelers, extenders in rubber compounding, dispersants in oil well drilling operations (Hoyt and Goheen, 1971), briquette binders, an additive in controlled release pesticides, an additive in ion exchange resins, extenders in

rubber compounding, soil stabilizer and dispersants in oil well drilling operations (Venter and Van der Klashorst, 1989).

In paper industry, lignin is found potentially of interest in paper-coating applications due to its capability to interact well with wood fibres and make paper hydrophobic. Lignin derivative has shown a hydrophobic behaviour on papers as well as good interaction with wood fibres, making it an interesting potential paper-coating chemical made from bioresources (Antonsson *et al.*, 2008). According to a study, lignins have been demonstrated as antioxidants, acting as free radical scavengers. This activity allows the use of lignins for cosmetic formulations such as topical applications. The study of the potential eye and skin irritation also demonstrated that all lignins are non-irritant for eye and skin after application (Vinardell *et al.*, 2008). Furthermore, this phenolic compound can act as a precursor for activated carbon (AC) production (Suhas *et al.*, 2006). Organosolv lignin also acts as filler in inks, varnishes and paints (Mohamed Naceur *et al.*, 2003).

The use of lignin as an adhesive and adhesive extender has also received attention. Lignin has been widely used for the preparation of phenol formaldehyde adhesives (Mozaffar *et al.*, 2004; Gosselink *et al.*, 2004). Since lignin is derived from a renewable waste stream of the paper and pulp industry, (partial) replacement of phenol formaldehyde by lignin could make the resin cheaper, environmentally friendlier and healthier for the worker (Gosselink *et al.*, 2004). Patents on the use of lignin as an adhesive for wood, paper, and other materials date back almost to the last century.