

**ISOLATION OF LIGNIN FROM OIL PALM EMPTY FRUIT BUNCH
(OPEFB) BY USING ORGANOSOLV METHOD**

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ABSTRACT

This research focus on the isolation of lignin component from lignocellulosic biomass of oil palm empty fruit bunch (OPEFB) using the organosolv method. Lignin has a unique structure where it consist of varies aromatic compound in their polymeric chain lignin that capable to copolymerize alternative units that derive from incomplete monolignol biosynthesis in plants. Nowadays, trending in lignin research was to focus the integration into lignin polymer and also improve the lignin degradation. Among the pretreatment methods to isolate lignin from its lignocellulosic biomass, the organosolv method process is the promising pretreatment method for biorefinery approach. Common organosolv methods consist of cooking lignocellulosic biomass in aqueous ethanol solvent at high temperature and carry out in a pressurized reactor. However, in this study, modification on organosolv method has been made where this reaction was carry out by refluxing at ambient pressure and lower temperature. Two parameters have been studied during the process: i) Extraction times (4-8 hour) ii) Ethanol concentrations (65-75% vol.). From the results, extraction time and ethanol concentration gives large effects to delignification. While delignification is decreased by lower extraction time and higher solvent concentration, pulp yield increased and thus decreased the yield of lignin. Extension of time leads to a decrease of the pulp yield and increase the lignin yield. For overall ethanol concentration, it can be shown that there is no significant effect in their trend. Mostly, the highest lignin yield was recorded at extraction time of 8 hour with 6.73% lignin yield (65% ethanol vol.), 8.91% lignin yield (70% ethanol vol.). However, for 75% ethanol vol., the highest was at 6 hour with 5.44% lignin yield. For solvent concentration effect, overall maximum lignin yield was observed at 70% ethanol. The highest lignin yield isolated at maximum extraction time (8 hour) was at 70% ethanol concentration with 8.91% lignin yield followed by 65% with 6.73% and 75% at 4.66% only. From this trend, it can be shown that a further increase ethanol concentration at 70% vol. reduces the lignin yield. Solvent concentration and extraction time gives an intense impact to this process as these parameters able to lead to much economical process condition to isolate high yield of lignin.

ABSTRAK

Kajian ini memberi tumpuan kepada pengasingan komponen lignin daripada biojisim lignoselulosa kelapa sawit tandan buah kosong (OPEFB) menggunakan kaedah organosolv. Lignin mempunyai struktur yang unik di mana ia terdiri daripada sebatian aromatik berbeza dalam rantaian polimer lignin mereka yang mampu untuk copolymerize unit alternatif yang berasal dari tidak lengkap monolignol biosintesis dalam tumbuh-tumbuhan. Pada masa kini, trend dalam penyelidikan lignin adalah untuk memberi tumpuan integrasi ke polimer lignin dan juga meningkatkan degradasi lignin. Antara kaedah rawatan untuk mengasingkan lignin daripada biojisim lignoselulosa, ialah proses kaedah organosolv di mana ia adalah kaedah rawatan yang menjanjikan untuk pendekatan biorefinery. Kaedah organosolv biasa terdiri daripada memasak biojisim lignoselulosa dalam akueus etanol pada suhu yang tinggi dan dijalankan dalam reaktor tekanan tinggi. Walau bagaimanapun, dalam kajian ini, pengubahsuaian kaedah organosolv telah dibuat di mana tindak balas ini adalah dilaksanakan oleh refluxing pada tekanan ambien dan suhu yang lebih rendah. Dua parameter telah dikaji semasa proses tersebut: i) Masa pengekstrakan (4-8 jam) ii) kepekatan etanol (65-75% vol). Daripada keputusan, masa pengekstrakan dan kepekatan etanol memberi kesan besar kepada delignifikasi. Walaupun delignifikasi dikurangkan dengan masa pengeluaran yang lebih rendah dan kepekatan pelarut yang lebih tinggi, hasil pulpa meningkat dan dengan itu mengurangkan hasil lignin. Pelanjutan masa membawa kepada penurunan hasil pulpa dan meningkatkan hasil lignin. Untuk kepekatan etanol keseluruhan, ia boleh ditunjukkan bahawa tidak ada kesan yang ketara dalam aliran mereka. Kebanyakannya, hasil lignin tertinggi dicatatkan pada masa pengekstrakan 8 jam dengan 6.73% hasil lignin (65% etanol vol.), 8.91% hasil lignin (70% etanol vol.). Walau bagaimanapun, bagi 75% etanol vol., Yang paling tinggi adalah pada 6 jam dengan hasil lignin 5.44%. Untuk kesan kepekatan pelarut, hasil lignin maksimum keseluruhan diperhatikan pada 70% etanol. Hasil lignin tertinggi diasingkan pada masa pengekstrakan maksimum (8 jam) adalah pada kepekatan etanol 70% dengan hasil lignin 8.91% diikuti oleh 65% dengan 6.73% dan 75% pada 4.66% sahaja. Dari trend ini, ia boleh menunjukkan bahawa meningkatkan lagi kepekatan etanol pada 70% vol. mengurangkan hasil lignin. Kepekatan pelarut dan masa perahan memberi kesan hebat kepada proses ini sebagai parameter ini dapat membawa kepada banyak keadaan proses ekonomi untuk mengasingkan hasil yang tinggi daripada lignin

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LIST OF ABBREVIATIONS

AFEX	Ammonia fiber explosion
BTX	Butane, Toluene, Xylene
EOL	Ethanol-organosolv lignin
HMF	Hemi-furfural
ILs	Ionic liquids
LHW	Liquid hot water
MPOB	Malaysian Palm Oil Board
NMR	Nuclear magnetic resonance
POEFB	Palm oil empty fruit bunch
OPF	Oil palm fronds
T _g	Glassy transition temperature

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Lignin, a heterogeneous and highly cross-linked macromolecule (El Hage *et al.*, 2010) is the most abundant aromatic biopolymer in nature. This aromatic nature is capable in becoming a potential renewable source of aromatic chemicals and also others production with higher added value (Huijgen *et al.*, 2014). Lignin is the major structural constituent of lignocellulosic biomass. Lignocellulosic biomass consist of lignin, which is the polymer of aromatic compounds and also sugar polymers, where include of cellulose (a linear polymer of glucose) and hemicellulose (a branched copolymer of C5 and C6 sugars). The lignocellulosic biomass current application had forces the growth of pretreatment technologies which are required to separate them. There is been a lot of pretreatment methods have developed but most of the time, the structure of isolated lignin usually rely on the type of method being applied. Hence, the pretreatment methods affects the quality and also purity of lignin structure.

Among the pretreatment methods to isolate lignin from its lignocellulosic biomass, the organosolv method process is the promising pretreatment method for biorefinery approach (Huijgen *et al.*, 2014). Others method such as Kraft lignin, which is acquired by cooking in soda–sodium sulfide liquor has the weakness that it contains large amounts of sulfur compounds including lignosulfates and effect the purity of lignin produce. Eventhough it is the most commonly used method to obtain

chemical pulp, it still resulted with low yield, high uses of bleaching reagents and release of gaseous sulfur compounds during cooking (de la Torre *et al.*, 2013).

Organosolv method has been optimized for delignification for many types of lignocellulosic biomass like hardwood (e.g. poplar), softwood (e.g. pine) and also herbaceous (e.g. miscanthus, wheat straw). Organosolv method could offer cellulose-rich pulps with a better enzymatic digestibility and also yields large amount of high quality and purity lignin where this lignin could be further use in the field of composites or even biodegradable polymers (El Hage *et al.*, 2010). The organosolv process uses an organic solvent as delignifying agent and mostly use ethanol as the solvent. It produces cellulose and possible to recover by-products from the black liquors that contains hemicellulose degradation products and dissolved lignin where both sulfur-free (de la Torre *et al.*, 2013).

Nowadays, renewable lignocellulosic feedstocks like agricultural crop residues offers a right choice as feedstocks for pulp and also cellulose-fiber based products in order to reduce agriculture residues accumulation (Alriols *et al.*, 2009). In South East Asia, oil palm empty fruit bunch (OPEFB) being the main waste from the palm oil industry. This agroindustrial byproduct have been measured as a potential low-cost and plenty cellulosic biomass for use as an alternative and renewable bioresource existing for the biorefinery field (Hong *et al.*, 2013). About 15 million tons per year of OPEFB are produced in Malaysia and being burned thus creating pollution and economical problems. Oil palm empty fruit bunch (OPEFB), a lignocellulosic residue generated during oil extraction process was used as raw material for lignin production in this study. Mostly, the large quantities of these residues are unutilized and offer several studies to support the prospect of this OPEFB as raw materials in variety of applications (Alriols *et al.*, 2009).

In this work, a complete approach for establish a system in separating and isolating high yield of lignin from lignocellulosic residue was developed. This study attempts to develop an organosolv pretreatment process under mild conditions in separating lignocellulosic components from OPEFB and isolating the lignin through precipitation. The aim of this study was to find the best condition to achieve the high

yield of lignin from OPEFB through organosolv method. The organosolv method required a list of parameters that needed to be study to achieve high yield of lignin including the solvent concentration and also the extraction time.

1.2 MOTIVATION

Nowadays, renewable lignocellulosic feedstocks like agricultural crop residues offers a right choice as feedstocks for pulp and also cellulose-fiber based products in order to reduce agriculture residues accumulation (Alriols *et al.*, 2009). In South East Asia, empty fruit bunch (EFB) being the main waste from the palm oil industry. This agroindustrial byproduct have been measured as a potential low-cost and plenty cellulosic biomass for use as an alternative and renewable bioresource existing for the biorefinery field (Hong *et al.*, 2013). About 15 million tons per year of EFB are produced in Malaysia and being burned thus creating pollution and economical problems. Mostly, the large quantities of these residues are unutilized and offer several studies to support the prospect of this OPEFB as raw materials in variety of applications (Alriols *et al.*, 2009). About 25% of OPEFB are produced for every FFB entered to the oil extraction processes. Nowadays, OPEFB solid wastes have become a major issue in biorefineries that using palm oil as their feedstocks. OPEFB use as fuel are limited due to the high content of moisture even though it is use as a fertilizer for oil plantation and a material for growing mushrooms (Narapakdeesakul *et al.*, 2013).

OPEFB is a lignocellulosic residue of palm oil mill that creates environmental problem and has low economic value that become the major waste stream of palm oil production that usually used as fertilizers, disposed in landfills, and also been burned in incinerators (Jeon *et al.*, 2014). This OPEFB fiber that is one of the massively biomass being produced in Malaysia able to maintain the sustainability resource for the production of value-added fiber-based products like pulp, paper, fiber board, panels and now, OPEFB also are capable in converting into cellulosic ethanol. Researches have been made and prove that OPEFB can be converted into glucose and xylose successfully for bioethanol production (Ying *et al.*, 2014) and they support the chance of using OPEFB as raw material in range of applications like

power generation, composites formulation and papermaking (Alriols *et al.*, 2009). Another potential solution that can be used in order to resolve this issue was to isolate the lignin from OPEFB lignocellulosic biomass and synthesizing those lignin into another valuable product such as vanillin.

Lignin is the world's second most abundant renewable carbon source, after cellulose. It is an aromatic polymer that usually deposited mostly in the walls of secondarily thickened cells (Vanholme *et al.*, 2010). Lignin has a unique structure where it consist of varies aromatic compound in their polymeric chain lignin that capable to copolymerize alternative units that derive from incomplete monolignol biosynthesis in plants. Nowadays, trending in lignin research was to focus the integration into lignin polymer and also improve the lignin degradation. Conventionally, lignin has been noticed as a waste material or a low value by-product of pulping. But, the chemical industries are widening their end user markets leading to requirements for a feedstock base that can satisfy the needs of these new end products and fill them with novel properties (Stewart, 2008). Lignin has a unique structure and chemical properties that can be viewed as a major aromatic resource of bio-based economy. Besides, the potential of lignin has just started to be explored by the industry that believe lignin could be the main renewable and aromatic resource for the chemical industry, according to growth strategy firm Frost & Sullivan (Jennifer Elks, 2014).

Lignin are the renewable source of aromatics fo a variety of chemicals (Wildschut *et al.*, 2012) such as phenol(ics) and BTX (Butane, Toluene, Xylene), phenolic resins, polyurethanes, epoxy resins, and carbon fibres (Huijgen *et al.*, 2014). Economics of biomass conversion would be improved and also overcome the problem of waste lignin disposal with any production of value-added lignin derived product. Based on Zakzeski *et al.*, 2010 , lignin streams could also have proteins, inorganic salts, and other potential poisons that generally complicate catalysis. There are a few number of lignin advantages has or can become integrated into materials industries and can suggest a bright future for lignin-based products since it is compatible with a wide range of industrial chemicals. The presence of aromatic rings in lignin structure offering strength as well as good mechanical properties and opportunity of a wide-ranging of chemical revolutions. Facile preparation of graft copolymers could be done by the

existing of other reactive functional groups. This also provides a good rheological and viscoelastic properties for a structural material and good film-forming ability (Doherty *et al.*, 2011).

1.3 PROBLEM STATEMENT

However, the difficulties in polymerize and upgrading lignin into useful fuels or chemicals being the main reason why this valuable aromatic polymer is often burned for process heat. Nowadays, through biorefinery approach, lignin can be isolated from the residue and can have a great potential to become a resource for fuels and higher added value of chemical production instead of being noticed as a waste material or a low valued by-product of pulping (Zakzeski *et al.*, 2010). However, the step where lignin is separated from cellulose, is the main key to economic conversion of lignocellulosic biomass. Efficiency of the lignin is solubilised or else purified towards the enzymatic depolymerisation of cellulose is the most important factor in the choice of pretreatment technology. It is decided that the economic feasibility of biofuel production will depend on adding value to the by-products, including lignin. Thus, it is needed to guarantee that the quality of the lignin is not degraded.

Lignin pre-treatment is the main key early step in this biorefinery operation as it separate the major components of biomass and related materials. Besides, it also degrades the extended polymer into smaller compounds (Zakzeski *et al.*, 2010). However, the potential application of lignin are largely biased by its purity, molecular size and distribution and also amounts of different chemical functional groups. Isolation of lignin from its lignocellulosic components is done under conditions where lignin is progressively degrade to lower molecular weight fragments, causes in alterations to its physicochemical properties (Doherty *et al.*, 2011). For that reason, an efficient pretreatment technologies are necessary for isolate lignin as the the method of isolation will have an significant impact on composition and properties of lignin (Guo *et al.*, 2013). This isolation or pretreatment methods affect in the consistent types of lignin with high quality and purity that are highly desirable.

Among the pretreatment methods to isolate lignin from its lignocellulosic biomass, the organosolv method process is the promising pretreatment method for biorefinery approach (Huijgen *et al.*, 2014). Organosolv method could offer cellulose-rich pulps with a better enzymatic digestibility and also yields large amount of high quality and purity lignin where this lignin could be further use in the field of composites or even biodegradable polymers (El Hage *et al.*, 2010).

1.4 OBJECTIVE

The objective of this study were:

- i. To isolate lignin from OPEFB using organosolv method.
- ii. To study the effect of solvent concentration and extraction time to lignin yield.

1.5 SCOPE

The scopes of this study were:

- i. To isolate lignin by using organosolv method. Lignin was isolated from OPEFB by using organosolv method in which ethanol will be used as the solvent and the reaction will be carried out under mild conditions at ambient pressure and moderate heat.
- ii. To study the effect of ethanol concentrations on lignin yield. The solvent concentrations (65-75% w/w aqueous ethanol) were used as parameters for this study to identify the effect of solvent concentration in achieve high yield of lignin isolation.
- iii. To study the effect of extraction time on lignin yield. Extraction time (4 hour, 6 hour and 8 hour) also was studied as parameters for each solvent concentration to know the effect of extraction time in reaching high yield of lignin isolation.

CHAPTER 2

LITERATURE REVIEW

2.1 LIGNOCELLULOSES BIOMASS

Lignocelluloses biomass largely found in residues collected from agricultural, forestry, municipal and other activities is comprised of carbohydrate polymers (cellulose and hemicellulose), aromatic polymers (lignin) and other compounds (xylose, tannin, arabinose) (Laurichesse & Avérous, 2014). It is a flexible renewable source of chemicals and fuels can be found in large quantities, environmentally safe and relatively at lower costs. Due to its valuable use, it has forced the growth of pretreatment technologies which are required to separate them. The general composition of lignocellulosic biomass can be figured out as Figure 2.1-1 below.

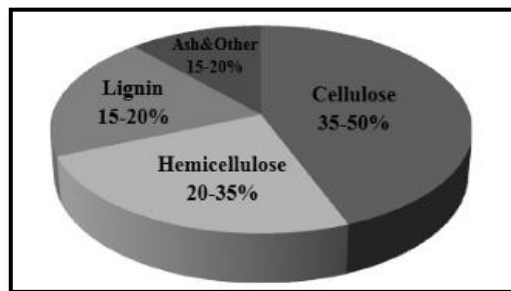


Figure 2.1-1 General composition of lignocellulosic biomass

Source: Haghghi *et al.*, 2013

2.1.1 Carbohydrate polymers

The carbohydrate polymers that consist of cellulose and hemicellulose are fermentable after hydrolysis, which makes lignocellulosic biomass a suitable feedstock for biofuels production like bioethanol (Zheng *et al.*, 2014).

Cellulose is the main constituent of lignocellulose cell walls that can be found in a form of linear polysaccharide polymer of glucose disaccharide (D-glucose) that is sturdily allied via β -(1, 4) glycosidic bonds. High tensile strength in microfibrils is due to interlinked of hydrogen bonds and van der Waals forces in the cellulose chains (Zheng *et al.*, 2014). The hydroxyl groups those are present in the cellulose chains, resulting to the formation of a number of intra- and intermolecular hydrogen bonds that make it insoluble in water and most organic solvents (Haghighi *et al.*, 2013). The different levels of the crystallinity in cellulose structure forming two different sections which are low crystallinity (amorphous) and high crystallinity (crystalline) which is higher crystallinity index will makes the biodegradation of cellulose becomes more difficult (Zheng *et al.*, 2014).

Hemicellulose can be found in secondary cell walls of a plant where it is branched with heterogeneous branched biopolymers encompassing of pentoses (β -D-xylose, α -L-arabinose), hexoses (β -D-mannose, β -D-glucose, α -D galactose) and acids (α -D-glucuronic, α -D-4-O-methyl- galacturonic and α -D-galacturonic acids) (Haghighi *et al.*, 2013). The lignocellulosic biomass matrixes are extremely firm with the help of hemicellulose that form the cellulose microfibrils network and interact with lignin. This properties make hemicelluloses highly resistant to biological, thermal, and chemical hydrolysis of their monomer compounds (Zheng *et al.*, 2014). Figure 2.1-2 shows the structure of cellulose and hemicellulose.

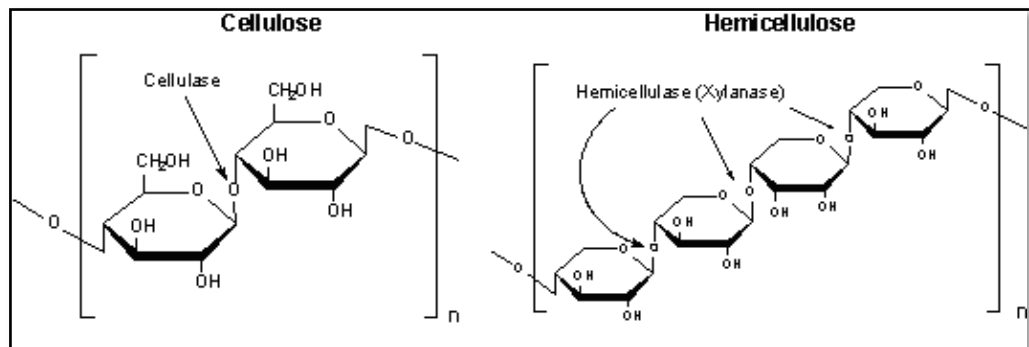


Figure 2.1-2 Cellulose and Hemicellulose structure

Source: Sigma Aldrich

2.1.2 Lignin polymer

Lignin is the second most abundant natural polymeric material in nature (El Hage *et al.*, 2010) composed of phenylpropane units that come from three aromatic alcohol precursors (monolignols) which are p-coumaryl, coniferyl and sinapyl alcohol (Huijgen *et al.*, 2014). Three structural moieties which are p-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) are formed through the cross linked of phenolic substructures that comes from these monolignols (Huijgen *et al.*, 2014). In woody plant, lignin are playing a main role in providing strength to the structure of cell walls besides monitoring fluid flow and defend against biochemical stresses by inhibiting enzymatic degradation of other components. Species and environment are the major factors that influence the lignin composition and contents.

Lignins is a polymer that consists of variety of functional groups such as aliphatic and phenolics hydroxyls, carboxylic, carbonyl and methoxyl groups that unique as a plant cell wall biopolymer due to its heterogeneity, lack of defined primary structure and aromatic functionality (Norgren & Edlund, 2014a). Lignin are able to play a main role as a new chemical feedstock down to its unique structure that contains a lot of chemical sites that offers different possibilities for chemical modification especially

in the formation of aromatic chemicals. According to Guo *et al.*, 2013, lignin that have been extracted from the residue in the biorefinery operation can be used in high-value added chemicals which would create higher profits for bio-ethanol industry. The structures of the building block monomeric aromatic precursors of lignin can be shown as Figure 2.1-3 below.

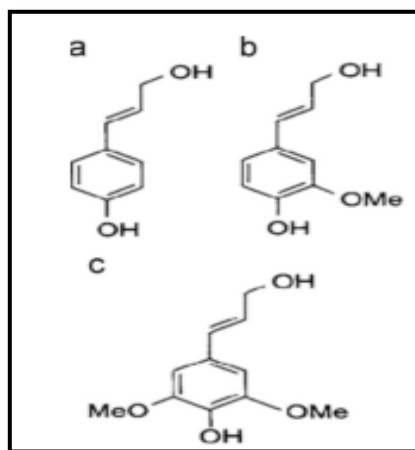


Figure 2.1-3 Structures of the building block monomeric aromatic precursors of lignin (a) monolignols p-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohols

Source: Ghaffar & Fan, 2014

2.1.2.1 Applications of lignin

The aromatic nature in lignin makes it a potential renewable source of aromatic chemicals and higher valuable products. Lignin have been found to be a right choice as a source of chemicals in the production of phenolics, BTX (Butane, Toluene, Xylene), vanillin, simple and hydroxylated aromatics, quinines, aldehydes, aliphatic acids, and many others chemical compounds. Besides, the ability of lignin to act as a neutralizer or inhibitor in oxidation process has been specified by Hussin *et al.*, 2014. It was also discovered that antioxidant properties shown by lignin can give extensive uses as anti-microbial, anti-aging agents and corrosion inhibitors (Hussin *et al.*, 2014). Lignin uses

can be categorized into two different groups which are, (i) without further chemical modification, (ii) with chemical modification. Chemical modification is to formulate a large series of chemicals, building blocks and also polymers that can be divide into three categories which are, (i) fragmentation, (ii) modification by adding new chemical active sites, (iii) hydroxyl function modifications (Laurichesse and Averous, 2014).

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is one of the valuable product that can be produced through lignin oxidation and likely to become a bio-based building block for polymer chemistry. Borregaard Company is the second largest vanillin producer in the world that use a vanillin-from-lignin process (Fache *et al.*, 2014). Vanillin is the most well-known and valuable product that is mainly used as a flavorings and as a chemical feedstock in the pharmaceutical industry (Laurichesse and Averous, 2014). Figure 2.1-4 shows the structure of vanillin.

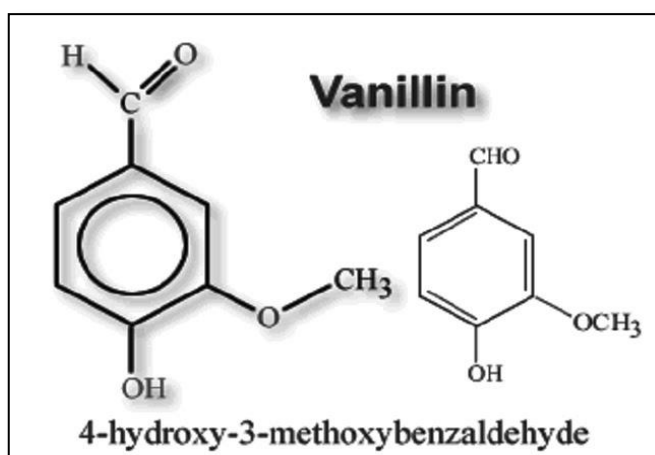


Figure 2.1-4 Vannilin structure model

Utilization of lignin derivatives have booming the industrial recently as society realize the necessity in replacing oil-based and non-renewable surface active and polymeric materials. Lignin are also being used for the controlled release of fertilizers where it is modified for slow release fertilizers and herbicides in agriculture besides act as a base for different materials application in the fields of bioplastics, nanocomposites and nanoparticles. A more advances uses of lignin are function as adsorbents in solution, protective UV-absorbents, dispersants, and in electro-chemical applications (Norgren & Edlund, 2014).

2.2 OIL PALM EMPTY FRUIT BUNCH (OPEFB) AS LIGNOCELLULOSIC FEEDSTOCK

Annually, oil palm empty fruit bunches (OPEFB) produces about 19.8 million tonnes of biomass on a wet basis or 6.93 million tonnes on a dry basis in Malaysia. This offers massive incomes for the transformation into value-added products since the cellulosic biomass is unlimited, renewable, ecofriendly, and a derivatizable biopolymer (Nazir *et al.*, 2013).

OPEFB is a lignocellulosic residue of palm oil mill that creates environmental problem and has low economic value that become the major waste stream of palm oil production that usually used as fertilizers, disposed in landfills, and also been burned in incinerators (Jeon *et al.*, 2014). This OPEFB fiber that is one of the massively biomass being produced in Malaysia able to maintain the sustainability resource for the production of value-added fiber-based products like pulp, paper, fiber board, panels and now, OPEFB also are capable in converting into cellulosic ethanol. Researches have been made and prove that OPEFB can be converted into glucose and xylose successfully for bioethanol production (Ying *et al.*, 2014) and they support the chance of using OPEFB as raw material in range of applications like power generation, composites formulation and papermaking (Alriols *et al.*, 2009).

About 25% of OPEFB are produced for every fresh fruit bunch entered to the oil extraction processes. Nowadays, OPEFB solid wastes have become a major issue in

biorefineries that using palm oil as their feedstocks. OPEFB use as fuel are limited due to the high contain of moisture even though it is use as a fertilizer for oil plantation and a material for growing mushrooms (Narapakdeesakul *et al.*, 2013).

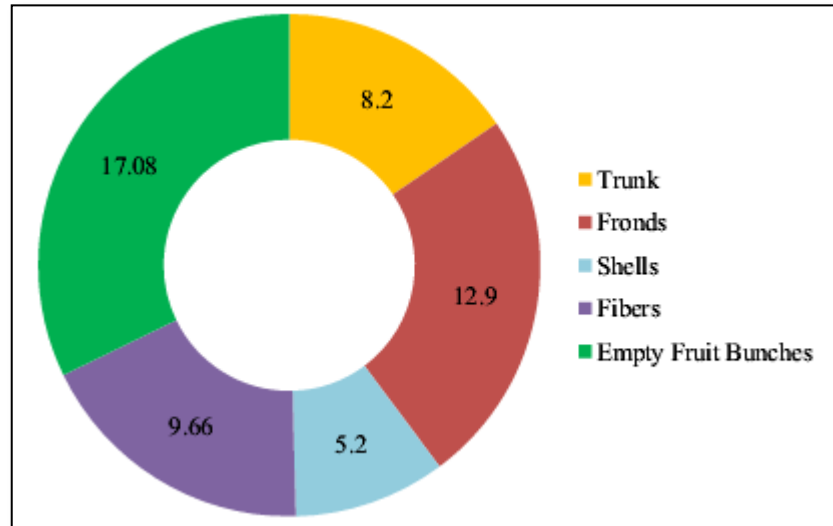


Figure 2.2-1 Palm biomass production in Malaysia (million tons per year)

Source: Mohammed *et al.*, 2011

Utilization of agricultural solid wastes into possible production products has not only helped the environment but also helps preserve natural resources. OPEFB can be an organic mulching that valuable to crop production. Mulching is a materials that being applied on the surface of soil to decrease soil temperature and protect soil moisture to improve growth and yield of plants besides providing variable amount of nutrients as they decompose. OPEFB mulching is benefit in improve the soil structure to a better aeration, improved water holding size, and increase the pH in soil pH. It also helps in reduces erosion on soil and nutrient losses besides moderates soil temperatures (Heriansyah, 2009).

Normally, OPEFB consist of 17 to 33% hemicellulose, 43 to 65% cellulose and 13 to 37% lignin on a dry weight basis (Palamae *et al.*, 2014). A OPEFB composition can be shown in Table 2.4-2 below.

Table 2.2-1 Composition of OPEFB

Number	Component	Content (wt%)
1	Lignin	24% - 26.6%
2	Cellulose	22.5% - 25.3%
3	Hemicellulose	24.5% - 27.8%
4	Moisture	8% - 10%
5	Other components	14% - 16%

Source: Nomanbhay et al., 2013

Research on OPEFB has been done by Ying *et al.*, 2014 to study the effect of various pretreatment methods for sugar production. The pre-treatments method was carried out in a 4-L stationary stainless steel digester (NAC Autoclave Co. Ltd., Japan), that completed with a microcomputer-controlled thermocouple. The pretreatment method was carried out by using different types of chemical which are water, acid and alkaline. After the pretreatment, the pre-treated fibers were washed and spin-dried before stored in a fridge for determining the yields based on the weight of oven-dried fiber. The original of OPEFB composition were analyzed by followings the standard procedures (Ying *et al.*, 2014).

Another research on OPEFB also was done by Nazir *et al.*, 2013 to extract and characterize the composition of cellulose in OPEFB. The pretreatment process were done by using solvent extraction method which the delignification on fibers were done in 200 mL 70% (v/v) ethanol, with a fiber to solvent ratio of 1:10 (g L⁻¹) using soxhlet apparatus for six hours (Nazir *et al.*, 2013).

Paper by Hong *et al.*, 2013 also study on the fractionation and delignification of empty fruit bunches (OPEFB) by conducting in a series of two steps under low reaction severity with the aim of reducing the neutralization of hydrolyzates. Through method which OPEFB undergo acid fractionation, the glucan content was increased to 62.4%, at

which point 86.9% of the hemicellulosic sugar and 20.5% of the lignin were extracted from the raw OPEFB (Hong *et al.*, 2013).

Jeon *et al.*, 2014 using a pilot-scale bioethanol plant to explored the opportunity in utilizing OPEFB as a renewable resource by study on overall biorefinery processes such as pretreatment, hydrolysis, fermentation, and purification. In this paper, the comparison between different pretreatment has been studied and CHEMEX pretreatment with sodium hydroxide has been reported to be applied in order to improve the enzymatic digestibility (Jeon *et al.*, 2014).

Narapakdeesakul *et al.*, 2013 worked on the synthesis of OPEFB lignin derivatives and their capability for the production of linerboard coating. He choose to use alkaline pretreatment method by cooking the OPEFB pieces with 20% NaOH solution (1:15 w/v) at 170°C for 120 min in a rotary digester (Narapakdeesakul *et al.*, 2013).

Nowadays, study on OPEFB lignocellulosic biomass has emerging tremendously due to its availability and related environmental issues in Malaysia. A lot of research has been working to find a new solution or opportunities in utilizing these abundances of OPEFB in Malaysia to transform into a much valuable product.

2.3 LIGNIN EXTRACTION PROCESS

The unique structure of lignin are rely strongly on the original source and extraction method that being applied (Alriols *et al.*, 2009). The extraction process are highly impact the final lignin structure, purity and others properties. One of the successful studies has been done is Hardwood Alcell lignins which it is able to transformed into filament form suitable for carbon fibres without further any chemical modification after extracted through acid ethanolysis (Kadla *et al.*, 2002). Molar mass (polydispersity) and (total) OH content are physico-chemical lignin characteristics that are important for the use of lignins since in many application, lignins with high purity are preferred (Huijgen *et al.*, 2014).

The extraction process can be categorized into two types of process either sulfur process or sulfur-free processes. This can be shown as Figure 2.3-1 below.

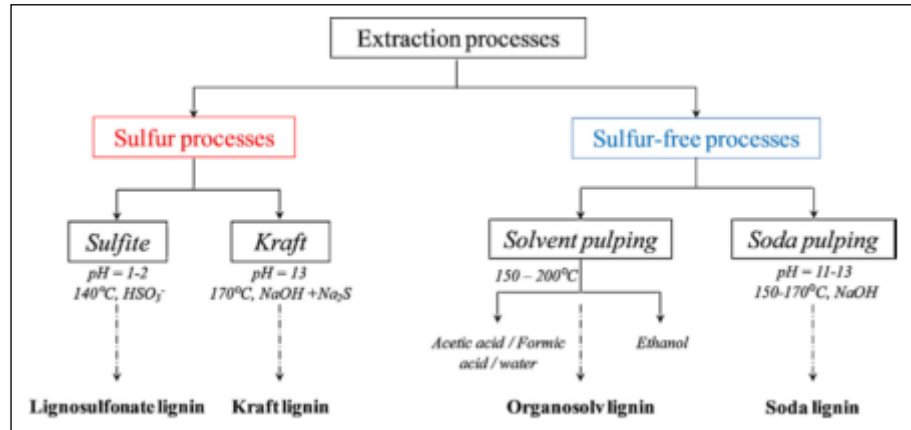


Figure 2.3-1 Different extraction processes to separate lignin from lignocellulosic biomass and the corresponding productions of technical lignins

Source: Laurichesse & Avérous, 2014

2.3.1 Kraft lignin

Kraft and lignosulfonates are both include in sulfur lignins which majorly refer to the lignin extraction from the cellulose. Kraft is the process that uses a mixture of chemicals containing sulfur such as sodium hydroxide and sodium sulfide whereas lignosulfonates lignin is produce from the cooking process with an aqueous sulfur dioxide and bases compound. Even though, Kraft process is the most extensively used choice to obtain chemical pulp and using a high sulfur content in their process, the extraction process is quiet efficient as it able to produce lignin with a high amount of condensed structure and high level of phenolic hydroxyl groups with so low sulfur content (Laurichesse & Avérous, 2014). However, it has the weakness that it holds significant amounts of sulfur compounds including lignosulfates. Besides, it produce such a low yield, great intake of bleaching reagents and release gaseous sulfur compounds during cooking and recovery of mineral residues from the liquors when burnt to ash (de la Torre *et al.*, 2013).

2.3.2 Lignosulfonate lignin

Lignosulfonate also contain a considerable amount of sulfur in the form of sulfonate groups that attached on the aliphatic side chains. Nevertheless, they denote this lignosulfonate lignins which are most exploited for several industrial applications since they produce a much higher average molar mass of lignin and always being contaminated by the cations used during process (Laurichesse & Avérous, 2014).

2.3.3 Soda lignin

Lignin extraction in soda pulping process are based on hydrolytic cleavage of native lignin but result in with relatively chemically unmodified lignin compared to others lignin types. However, this type of lignin can have a high silicate and nitrogen contents due to its extraction process (Laurichesse & Avérous, 2014).

2.3.4 Organosolv lignin

Generally, organosolv lignins are the most pure with highest quality (Laurichesse & Avérous, 2014). Organosolv lignins can be obtained by cooking lignocellulosic biomass in an (aqueous) organic solvent such as ethanol, acetone, methanol, acetic acid at elevated temperatures and under high pressure either in both autocatalytic (where there's no catalyst added) and catalytic (where there's present of catalyst use usually sulphuric acid) within a reaction time (Wildschut *et al.*, 2012). The advantages of organosolv lignin is it allowing utilization of all components of lignocellulosic biomass, and the process is generally considered environmentally friendly because it does not use the sulfides and harsh conditions as in the kraft or lignosulfonate processes. Besides, it has lower ash content, higher purity (due to lower carbohydrate content) which has important effects for its valorization to high-value chemicals, lower molecular weight and more hydrophobic (Doherty *et al.*, 2011). Lignin that produce from organosolv method also have been found to be suitable raw material for producing low molecular weight compounds like vanillin where this compound are majorly used in cosmetics and others valuable product (Alriols *et al.*, 2009).