Chemical and thermal properties of lignins from oil palm biomass as a substitute for phenol in a phenol formaldehyde resin production

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ABSTRACT

Lignins were extracted from oil palm empty fruit bunch after kraft and soda pulping process. The aim of this study was to characterise the chemical and thermal properties of these lignins as well as determine their suitability for partial incorporation into phenol formaldehyde resin. The analytical methods used were CHN analyser, FTIR spectroscopy, UV spectroscopy, TGA, DSC, GPC, ^{1}H NMR and FESEM. The elemental analysis results showed that both lignins had similar contents of C, H and O. FTIR spectra also revealed that both lignins have similar functional groups. Nevertheless, both lignins showed different compositions in terms of molecular weight distribution (M_n, M_w and polydispersity), reactive site through Mannich reactivity analysis, surface morphology and T_g value. The phenolic hydroxyl group content in kraft and soda lignins is 4.1076 mmol/g and 2.5830 mmol/g, respectively. The TGA thermogram showed both lignins had high thermal stability. Based on these analyses, kraft lignin from oil palm empty fruit bunch showed tremendous potential as a partial substitute for phenol in phenol formaldehyde resin production.

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1. Introduction

An oil palm empty fruit bunch (OPEFB) is a form of fibrous lignocellulosic residue generated in signification quantities in the palm oil industry (Tanaka, Wan Rosli, Magara, Ikeda, & Hosoya, 2004). Approximately 15 million tons of this agriculture waste is generated by oil palm milling operation annually and part of it is burned in incinerators (Rahman, Choudhury, Ahmad, & Kamaruddin, 2007). Malaysia is currently one of the world's top producers of oil palm products. The amount of lignocellulosic waste has increased proportionally with increases in oil palm cultivation acreage (Sulaiman et al., 2009). This incineration of the lignocellulosic waste is environmentally pernicious and unhealthy to inhabitants within the vicinity. Concerns about the effects of lignocellulosic waste to human and natural environment have prompted initiatives to recycle the lignocellulosic waste. Such initiatives have been incentivized by the abundance of this resource, its inherent renewability, its low cost and its relatively low toxicity.

Many studies have been conducted to use this renewable resource as a raw material such as in polymer blended composite manufacturing (Rozman, Ahmadhilmi, & Abubakar, 2004), the cellulase production (Umi Kalsom, Ariff, & Zulkifli, 1997) and the production of various chemicals (Rahman et al., 2007). The high content of α-cellulose in this lignocellulosic waste also makes it a potentially viable raw material for applications in the paper manufacturing industry (Akamatsu, Husin, Kamishima, & Hassan, 1987; Khoo & Lee, 1991; Wan Rosli, Law, & Valade, 1998). Through this alternative and its potential in the future of pulp and paper industry, it can decrease the deforestation rate in the country.

Alkaline pulping process such as kraft pulping and soda pulping is known as potential pulping process for non-woody materials (Garcia et al., 2009; Zhinan & Raimo, 2001). Essentially, both processes function to liberate lignin, hemicelluloses and cellulose to enhance the quality of the pulp (Akamatsu et al., 1987; Wan Rosli et al., 1998). Kraft pulping is a dominant pulping process in the world. This process enables pulping of different tree species, recovers and reuses all pulping chemicals and produces a high quality paper. However, there is a growing interest in applying soda pulping for non-woody based material in papermaking such as empty fruit bunch fiber (Wan Rosli, Law, Zainuddin, & Asro, 2004; Wan Rosli, Zainuddin, & Roslan, 2005).
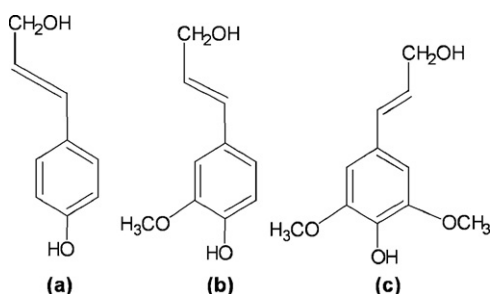
Fig. 1. Three major phenylpropanoid units of lignin: (a) trans-p-coumaryl alcohol, (b) trans-coniferyl alcohol and (c) trans-sinapyl alcohol.

Table 1
Chemical compositions of oil palm empty fruit bunch.

	(Ghazali et al., 2006) (%)	(Law et al., 2007) (%)
Extractives	3.7 ± 0.3	3.7 ± 0.3
Holocellulose	82.4 ± 1.4	82.4 ± 1.4
Hemicellulose	37.0	28.0
Lignin	18.8 ± 0.3	18.8 ± 0.3
Ash	1.3 ± 0.2	1.3 ± 0.2

Both pulping processes generate large amounts of a by-product known as black liquor. The pulp and paper industry normally burns the lignin dissolved in the black liquor for energy generation (El Hage et al., 2009; Garcia et al., 2009). However, the lignin which has been separated from hemicelluloses and cellulose during pulping process can be utilised as a starting material, due to its variable functional groups. These functional groups could lead to tremendous potential reactive sites for chemical and biochemical modifications.

Lignin is a major cell wall component in plants; it provides support for the plant, contributes to the transport of nutrients and water and protects against attack by microorganisms (Buranov & Mazza, 2008). Lignin is an amorphous polymer built up by oxidative coupling of three major phenylpropanoid units namely trans-p-coumaryl alcohol, trans-coniferyl alcohol and trans-sinapyl alcohol, which form a randomised structure in a three-dimensional network inside the cell wall as shown in Fig. 1. The phenylpropane units are commonly classified into three main types which differ in the amount of methoxyl groups: p-hydoxyphenyl (H), guaiacyl (G) and syringyl (S) lignin (Lewis & Yamamoto, 1990). These basic units are primarily attached to different types of aryl–aryl ether type and have more than 10 different types of linkages (Brunow, Lundquist, & Gellerstedt, 1999). The existence of a variety of functional groups in the structure of lignin structure enables this macromolecule to undergo a large number of modifications. Some studies show that some parts of a lignin structure resemble phenol, making this material an attractive potential substitute for phenol in wood adhesive resin (Alonso et al., 2001; Vázquez, Freire, Bona, Gonzalez, & Antorrena, 1999).

The scarcity of petroleum-based material could affect the production of the most dominant wood adhesive (Sulaiman et al., 2009). Thus, research and development focused on this matter seem to be appropriate to decrease dependence on petroleum-based materials. However, the variations in the types of pulping materials and pulping conditions produce different lignin properties. Furthermore, lignin composition is different not only among plants but also between parts of the same plant (Gosselink et al., 2004). To utilise these lignins as a replacement in phenol formaldehyde resin synthesis optimally, it is therefore necessary to determine their suitability by examining their chemical and thermal properties. Currently, only a few studies concentrated in characterisations on lignin specifically for phenolic resin replacement and most of these have focused on lignin from softwood and hardwood (Mansouri & Salvadó, 2006; Tejado, Peña, Labidi, Echeverria, & Mondragon, 2007).

The aim of this study was to characterise the different types of lignin, which were extracted from OPEFB that was derived from different pulping processes, for their suitability for partial incorporation into phenolic resins such as phenol formaldehyde resin.

2. Materials and methods

2.1. Raw materials and pulping condition

The OPEFB fiber used for kraft and soda pulping was obtained from Sabutek Sdn. Bhd., Malaysia. The typical chemical composition of OPEFB is presented Table 1 (Ghazali, Wan Rosli, & Law, 2006; Law, Wan Rosli, & Ghazali, 2007). Both pulping processes were carried out in a 10-L digester. For kraft pulping, a 19% of active alkali and a 25% of sulfidity with water to fiber ratio of 8 was used. The digester was heated from room temperature to 170 °C for 1 h and continued at 170 °C for 2 h. The contents in the digester were stirred by rotating the digester controlled via a motor. For soda pulping, 25% of active alkali with no percentage of sulfidity was applied and same condition was used. After cooking, the pulp and black liquor were mixed. The pulp was washed and separated by screening though a sieve and black liquor was collected.

2.2. Extraction and purification of lignin

The pH of kraft and soda black liquor was measured as 13.69 and 13.36 respectively. Both lignins gave the same density value of 1.04 g/mL. Lignin was precipitated from the concentrated black liquor by acidifying it until pH 2 using 20% (v/v) sulfuric acid. The precipitated lignins were filtered and washed with pH 2 water. Both lignins were then dried in a vacuum oven at 45 °C for 48 h (Mohamad Ibrahim, Chuah, & Rosli, 2004). The purification of both lignins was conducted by extracting the lignins in the soxhlet apparatus for 6 h with n-pentane to remove wax and lipids. The precipitate was filtered and washed with pH 2 water to remove the excess n-pentane and non-lignin phenolic compounds which may remain in the black liquor. The purified lignin was then dried further in the vacuum oven at 45 °C for another 48 h. Both lignins showed high content of ash and had been treated with hot water and pH 2 water to dissolve the residual sugars (Lin, 1992). The lignin was then dried in a vacuum oven at 45 °C for another 48 h before being ground and was filtered using 200 μm sieves and stored in plastic bottles for further analysis.

2.3. Analytical methods

2.3.1. Elemental analysis

In preparing lignins for further analysis, the lignin powder was obtained by drying the lignin samples at 105 °C in a vacuum oven until a constant weight was obtained. The content of carbon, hydrogen, nitrogen and sulfur was analysed using a Thermo Finnigan model Eager 300 analyser. The percentage of oxygen was calculated by subtracting the C, H, N and S contents from 100%. The percentage of proteins was calculated as $N(\%) \times 6.25$. Based on elemental composition, $C_aH_bO_cS_d$, the average of double bond equivalent (DBE) was calculated according to Eq. (1) (Robert, Michel, Gellerstedt, & Lindfors, 1984).

$$\text{DBE} = \frac{(2a + 2) - b}{2} \tag{1}$$