Carbohydrate Polymers 86 (2011) 112–119

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

Mohamad Nasir Mohamad Ibrahim[a,*], Norhidaya Zakaria[a], Coswald Stephen Sipaut[b], Othman Sulaiman[c], Rokiah Hashim[c]

[a] School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia
[b] School of Engineering and Technology Information, Universiti Malaysia Sabah, 88999 Sabah, Malaysia
[c] School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia

ARTICLE INFO

Article history:
Received 21 January 2011
Received in revised form 23 March 2011
Accepted 9 April 2011
Available online 19 April 2011

Keywords:
Kraft lignin
Soda lignin
Phenol formaldehyde
Oil palm biomass
Oil palm empty fruit bunch

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.

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 proportionately 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).

---

[*] Corresponding author. Tel.: +60 4 6533554; fax: +60 4 6574854.
E-mail address: mnm@usm.my (M.N. Mohamad Ibrahim).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.04.018

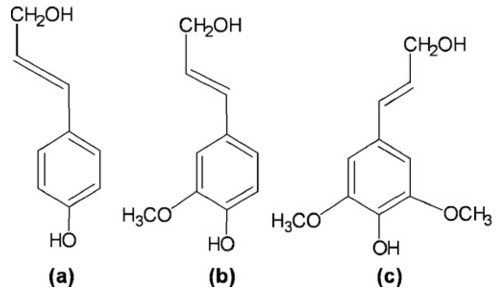

Fig. 1. Three major phenylpropanoid units of lignin: (a) trans-p-coumaryl alcohol, (b) trans-coniferyl alcohol and (c) trans-sinapyl alcohol.

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.

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

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).

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

2.3.2. *Ash content analysis*

Crucibles were dried at 105 °C until constant weight was obtained. Approximately 0.5 g lignin samples was weighed into the crucibles and calcined at 900 °C for 4 h. The ash content was calculated by determining the weight percentage of sample in the crucibles as burning process completed.

2.3.3. *FTIR analysis*

FTIR spectra of both lignin samples were performed in a Perkin Elmer model System 2000 instrument. Each spectrum was recorded in a frequency range of 400–4000 cm^{-1} using potassium bromide (KBr) disc. The KBr was previously oven-dried to reduce the interference of water.

2.3.4. *Mannich reactivity test*

The Mannich reactivity test was carried out to determine unsubstituted C-3 and C-5 in lignin as described by Mansouri and Salvadó (2006).

2.3.5. *Acetylation for GPC and ^{1}H NMR analysis*

Lignin samples were subjected to acetylation in order to enhance their solubility in organic solvent in GPC and ^{1}H NMR analysis. During the acetylation process, all the hydroxyl functional groups will be substituted by new acetyl groups. Acetylation was performed using Vázquez et al.'s (1999) method.

2.3.6. *GPC analysis*

The molecular weight distribution of lignin and acetylated lignin was determined by gel permeation chromatography (GPC). Tetrahydrofuran (HPLC grade) was used as a mobile phase with a flow rate of 1.0 mL min^{-1} using Water 1525 Binary HPLC Pump. Three Water Stryragel columns of doubled of HR 5E THF and HR 4E THF as well as a Water 2414 Refractive Index detector were used. The columns were calibrated using narrow molecular weight monodisperse polystyrene standard ranging from 580 to 8,500,000 g/mol in the eluent. The molecular weight and molecular number must be considered relative because they were compared with polystyrene standard. Both lignins were dissolved in the eluent at a concentration of 1 mg mL^{-1}. The solution was filtered using 0.45 μm filter. Then 20 μL of the filtered solution was injected into HPLC system.

2.3.7. *UV analyses*

UV analyses of both lignins in dioxane and alkaline solution were conducted. Briefly, 7 mg of lignins was weighed and dissolved in 5 mL of dioxane–water solution (9:1, v/v). Similarly, 7 mg lignin was dissolved in 5 mL pH 12 NaOH solution. Both solutions followed by refers to the lignin in dioxane solution and lignin in alkaline (NaOH) solution. And both solutions had been diluted to 50-fold dilution (Zhao, Dai, & Liu, 2009). The spectra were recorded using UV Perkin Elmer Lambda 25.

2.3.8. *^{1}H NMR analysis*

^{1}H NMR analysis of acetylated lignin samples was conducted by following the procedure described by Froass, Ragauskas, and Jiang (1998) with some modifications. Acetylated lignin (0.10 g) and pentaflourobenzaldehyde (PFB) (6.4 μL of PFB as internal standard) were dissolved in 1.0 mL of $CDCl_3$. PFB was selected as an internal standard because it can be dissolved in $CDCl_3$ and an involatile chemical. PFB also has single signal in the ^{1}H NMR and not overlap with lignin signals. The addition of PFB in the NMR sample gave an appropriate method by which the moles of the functional group of lignin could be determined. In this study however, estimation of the functional group using NMR method is more dependent on the changes in the structure of lignin component than to obtain it precisely. This is due to the signal overlapping and the complexity of lignin structure. The ^{1}H NMR spectrum was recorded using a Bruker 400 MHz Ultrashield spectrometer. The phenolic content was estimated according to Eq. (2).

$$\text{Ar–OH} \quad (\text{mmol/g of lignin}) = \frac{(I_{\text{Ar–OH}}/3) \times (1/I_{\text{PFB}}) \times M_{\text{PFB}} \times 1000}{W_{\text{L}} - (I_{\text{Ac}}/3) \times (1/I_{\text{PFB}}) \times M_{\text{PFB}} \times 42} \qquad (2)$$

where Ar–OH is the content of phenolic hydroxyl group, mmol/g; $I_{\text{Ar-OH}}$ is the integration of protons of the functional group (δ 2.50–2.17 ppm for acetyl group corresponding to Ar–OH); 3 is the number of proton of acetyl and methoxyl groups; 1 is the number of protons on PFB; I_{PFB} is the integration of PFB (δ 10.4–10.2 ppm); M_{PFB} is the mol of PFB used in internal standard; W_{L} is the weight of lignin in gram; I_{Ac} is the integration of protons of total acetyl groups corresponding to Ar–OH and Alk-OH (δ 2.50–1.70 ppm); 42 is the formula weight of acetyl group minus one (43 − 1).

Table 2
Results of ash and moisture contents, elemental composition, protein content, double bond equivalent (DBE) of kraft lignin and soda lignin (% (w/w) on dry matter).

Type of lignins	Kraft lignin	Soda lignin
Ash content (%)	0.14 (22.26%)	0.55 (16.54%)
Moisture content (%)	1.6396	1.916
Elemental analysis (%)		
Carbon	56.7655	57.1154
Hydrogen	5.5932	6.6339
Oxygen	35.9384	35.2331
Nitrogen	0.7611	1.0176
Sulfur	0.9417	ND
% protein	4.757	6.350
DBE	4.679	3.727

Values in parenthesis are ash content before treated with hot water.

2.3.9. *Thermal analysis*

The thermal behaviors of the lignins were studied by thermogravimetric analysis (TGA) using a Perkin Elmer TGA 7 thermogravimetric analyser. Scans were recorded from 30 to 800 °C with a heating rate of 20 °C min^{-1} under nitrogen atmosphere. The glass transition temperatures (T_g) were obtained using a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC). The samples were heated up to 200 °C with a heating rate of 20 °C min^{-1}. T_g can be defined as the midpoint of the temperature range at which changes in heat capacity occur. The glass transition temperature (T_g) of an amorphous phase of material is the critical temperature at which the material changes its behavior from glassy to rubbery or vice versa (Young & Lovell, 1991).

2.3.10. *Field emission scanning electron microscopy (FESEM)*

The lignin samples were coated with gold before the surface of the lignin was visualized using a field emission scanning electron microscope, model LEO Supra 50Vp ultra-high resolution.

3. Results and discussion

3.1. *Analysis of yield of kraft and soda lignins*

The ash content and moisture content of kraft lignin and soda lignin are presented in Table 2, including the results of their elemental composition. The double bond equivalent and percentage of protein derived from the results of elemental analysis are also shown. The result shows that the ash content of kraft and soda lignins is relatively low and this content is reduced after treatment with hot water. It might be possible that before the hot water treatment, the lignin was attached to sugar, silicon and wax. Both lignins had relatively high dry matter because the moisture content was less than 2.0%.

Table 2 also reveals that both the lignins had similar C, H and O contents. This similarity of the elemental composition may be due

Table 3
FTIR absorption bands and assignments for kraft and soda lignins.

Band (cm^{-1})	Assignments	Kraft	Soda
		Band location (cm^{-1})	
3400–3405	O–H stretching (phenolic OH and aliphatic OH)	3404	3402
2960–2925	C–H stretching (CH_3 and CH_2 groups)	2937	2933
2850–2840	C–H stretching (OCH_3)	2841	2848
1705–1715	C=O stretching (unconjugated ketone, carbonyl and ester groups)	1709	1712
~1600	C–C stretching (aromatic skeleton)	1606	1603
1513	C–C stretching (aromatic skeleton)	1513	1513
1460	C–H deformation (asymmetric in $–CH_3$ and $–CH_2$)	1461	1462
1425	C–C stretching (aromatic skeleton) with C–H in-plane deformation	1426	1425
1326	C–O stretching (syringyl)	1327	1329
~1220	C–O(H) + C–O(Ar) (phenolic OH and ether in syringyl and guaiacyl)	1211	1216
1115	Ar–CH in plane deformation (syringyl)	1113	1114
~1030	C–O(H) + C–O(C) (first order aliphatic OH and ether)	1033	1026
915	C–H out of plane (aromatic ring)	914	916
831	C–H out of plane	831	831

to same resource of pulping material. The sulfur content in kraft lignin may be derived from hydrosulfide anions during the pulping process of empty fruit bunch fiber. Nitrogen content has been detected for both lignins. The presence of nitrogen content may be due to the formation of protein–lignin complexes during delignification process (Zhao et al., 2009). The protein residues attached to both lignins suggest a strong chemical bond between precipitated lignin and protein in non-woody plant such as empty fruit bunch fiber. This finding also shows that the proteins are difficult to remove by acid precipitation and reveals that proteins linked to lignin in the starting plant material are still attached with lignin fragments during the pulping process. Table 2 also shows that kraft lignin has lower nitrogen content in precipitation compared to soda lignin, suggesting that the precipitation of kraft lignin portions is less contaminated.

The number of double bond equivalent (DBE) in both lignins implies the degree to which the lignins condensed and the presence of aromatic ring structure. From Table 2, it can be seen that the number of DBEs in kraft lignin was slightly higher than that in soda lignin. It was expected that severe cracking would occur during the kraft pulping process. This cracking was attributed to the reaction of hydroxide and hydrosulfide with the lignin, which causes the kraft lignin structure to acquire higher double bonds compared to soda lignin.

3.2. FTIR spectroscopy

To investigate the structural changes taking place during the pulping process, FTIR spectra of kraft and soda lignins obtained from the black liquor were recorded. Fig. 2 shows the FTIR spectra for both lignins. The corresponding assignments and bands for both lignins are presented in Table 3. Fig. 2 reveals that the functional groups presented in both lignins were similar to each other. The assignments of the bands are reported according to other literature findings (Anglès, Reguant, Garcia-Valls, & Salvadò, 2003; Tejado et al., 2007).

Both lignins show bands at ~1600, 1515 and 1425 cm^{-1} which is corresponding to aromatic ring vibrations of the phenyl-propane (C_9) skeleton. The band at ~1513 cm^{-1} assigned to aromatic skeletal vibrations coupled with C–H, in plane deformation. The band at ~1425 cm^{-1} contributes to aromatic ring vibrations, which are affected by the nature of the ring substituent and coupled to C–H in plane deformations. The presence of band at ~1460 cm^{-1}, assigned to C–H deformation (asymmetric) in methyl, methylene and methoxyl groups, confirms that both lignin aromatic structures did not change dramatically during the extraction procedure (Nadji et al., 2009).

In the area from 3400 to 2840 cm^{-1}, similar bands appeared for both lignins. A wide absorption band that appears at ~3400 cm^{-1} can be attributed to aromatic and aliphatic OH groups. The absorption peak between 3000 cm^{-1} and 2840 cm^{-1} can be assigned to C–H stretching in methyl, methylene and methoxyl groups. There were no significant differences of the spectra in the 1800–800 cm^{-1} wave number region for kraft and soda lignins. Bands between 1715 and 1705 cm^{-1}, shown for both lignins, were assigned to carbonyl stretching – unconjugated ketones and carbonyl groups. The band at 1675–1660 cm^{-1}, which is normally attributed to conjugated carbonyl stretching, was not found in both lignins. The bands at ~1326 and 1117 cm^{-1} were assigned to syringyl ring breathing with C–O stretching and aromatic C–H, in plane deformations, respectively. Bands at ~1220 cm^{-1} were attributed to syringyl and guaiacyl ring breathing with C–O stretching. The aromatic C–H in plane deformation for guaiacyl type lignin appears at ~1030 cm^{-1}. The peak at 831 cm^{-1} was typical for aromatic C–H out of plane bending. The presence of syringyl (S) and guaiacyl (G) bands for both lignins indicated that the lignin extracted from OPEFB is more similar to wood lignin than annual plant lignin, which is normally HGS lignin. This similarity was due to the absence of band of p-hydroxyl phenyl propane (H) at 1166 cm^{-1} in the spectra (Zhao et al., 2009).

The presence of guaiacyl-type (G) unit in both lignins confirmed that both lignins had potential active site for polymerisation. In phenol formaldehyde condensation reactions, phenol condenses initially with formaldehyde in the presence of alkaline to form methylolphenol (Pizzi, 1983). The initial attack may be at the 2-, 4- or 6-position as shown in Fig. 3. The second stage of the reac-

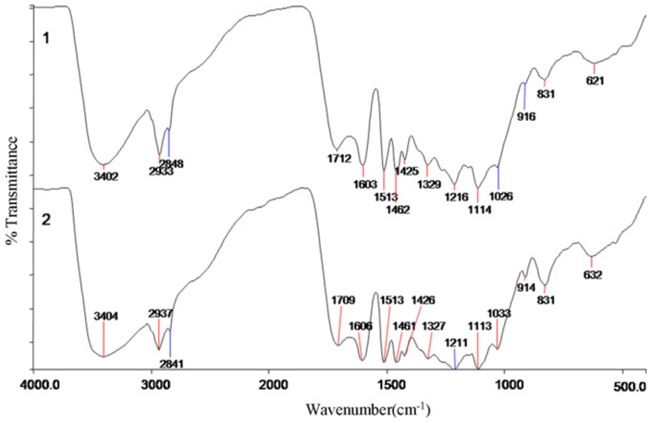

Fig. 2. FTIR spectra of soda lignin (1) and kraft lignin (2) with wave number: 4000–500 cm^{-1}.

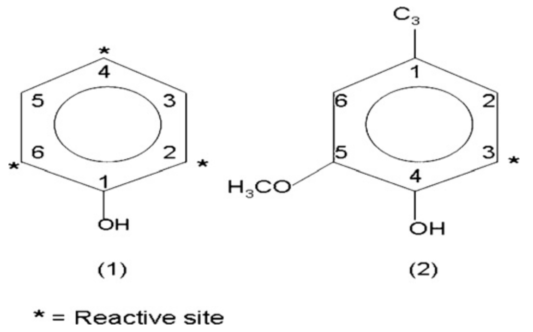

Fig. 3. (1) Phenol structure with three reactive sites: 2-, 4- and 6-position and (2) typical lignin structure with 1 reactive site: 3-position.

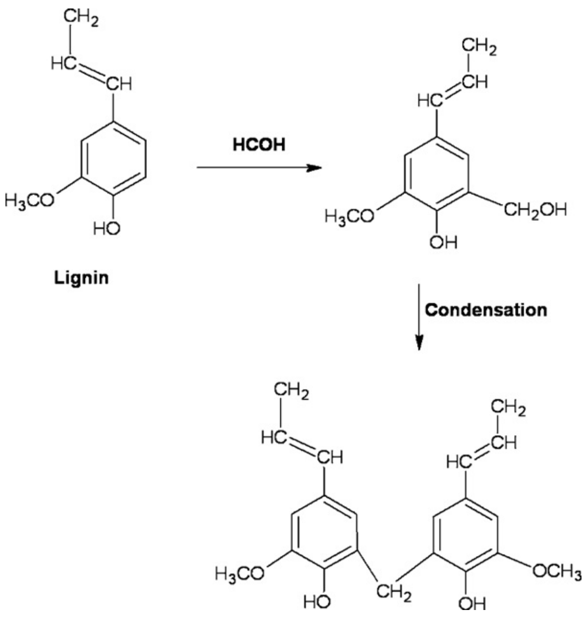

Fig. 4. Crosslingking between lignin and formaldehyde.

tion involved the reaction of methylol groups with other available phenol or methylolphenol, leading first to the formation of linear polymers and then to the formation of hard cure and highly branched structure.

The similarity between G-type unit of lignin and phenol (Fig. 3) revealed that lignin could also react with formaldehyde and could be cross linked with formaldehyde in the same way as in the phenol formaldehyde condensation reaction, as shown in Fig. 4. Thus, the free 3-position of G-type units in both lignins gave significant values compared to S-type unit, which had both the 3-position and 5-position attached to the methoxyl group, preventing the occurrence of a polymerisation reaction.

3.3. Mannich reactivity

The active sites in lignin also could be determined through Mannich reactivity reaction. Fig. 5 depicts the step Mannich reaction took place. Kraft lignin has a slightly higher content of free 3-position than soda lignin, as shown in Table 4, which indicates that kraft lignin has better reactivity with formaldehyde in phenol formaldehyde polymerisation compared to soda lignin. This higher content also suggests that kraft lignin from OPEFB has a greater content of unsubstituted 3-position or G-type unit compared to soda lignin. Furthermore, the capacity of lignins as a substitute for phenol in phenol formaldehyde resins is related to the number of sites on lignin fragment that are reactive to formaldehyde (Pizzi, Flora-Ann, & Van der Klashorst, 1989).

Table 4
Unsubstituted C-3 and C-5 in kraft lignin and soda lignin.

Types of lignins	Kraft lignin	Soda lignin
Content of free 3-position (%)	3.88	3.50

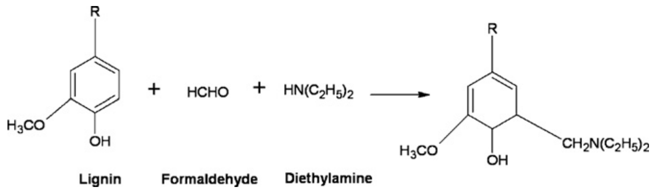

Fig. 5. Mannich reactivity reaction.

Table 5
Result of functional group in both lignins by ^{1}H NMR analysis.

Functional group	Kraft lignin	Soda lignin
OH phenolic (mmol/g)	4.1076	2.5830

3.4. UV and ^{1}H NMR analyses

The most significant functional group in lignin structure is the free phenolic group because in most chemical reactions involving lignin, phenolic phenylpropane units are preferentially attacked. The phenolic group was determined via UV and ^{1}H NMR analyses. The UV–visible spectra of kraft lignin and soda lignin in dioxane–water solution (neutral solution) (9:1, v/v) and pH 12 NaOH solution (alkaline solution) are shown in Fig. 6(a). Comparison of absorbance for both lignins in neutral and alkaline solutions was conducted due to the tendency of phenolic group to ionise in alkaline solution (Robert et al., 1984). Both lignins have a maximum absorption at ~240 nm and a second maximum absorption at about ~280 nm in dioxane–water solution. In alkaline solution, the maximum absorption appears at ~210 nm and a shoulder appears near ~240–250 nm and~280 nm. The scattering at 200–230 nm in dioxane–water solution was due to dioxane absorption (Hoareau, Trindade, Siegmund, Castellan, & Frollini, 2004). The absorbance of kraft lignin and soda lignin in dioxane–water was similar. However, in alkaline medium, kraft lignin showed higher absorbance than soda lignin. The UV analysis result was also supported by ^{1}H NMR analysis. Quantitative analysis of phenolic hydroxyl group in both lignins was determined by ^{1}H NMR spectra as shown in Fig. 6(b). From Table 5, it shows that kraft lignin possesses higher phenolic hydroxyl content compared to soda lignin. The higher absorbance in UV analysis and higher phenolic group content through ^{1}H NMR in kraft lignin are contributed by the cleaving of alkyl–aryl ether linkages during the kraft cook, which led to the formation of new phenolic end groups and indirectly increased the phenolic hydroxyl content in kraft lignin. Higher amount of phenolic hydroxyls in kraft lignin structure allowed the activation of free ring position which makes the kraft lignin more reactive toward formaldehyde than the soda lignin. The tendency of formaldehyde to attack at the free 3-position as depicted in Fig. 3 of the aromatic ring in lignin makes it able to form quinon methide intermediates (Mansouri & Salvadó, 2006). This also occurs in phenol formaldehyde polymerisation process.

3.5. GPC analysis

The molecular weight distribution of kraft lignin and soda lignin was analysed using gel permeation chromatography (GPC). The

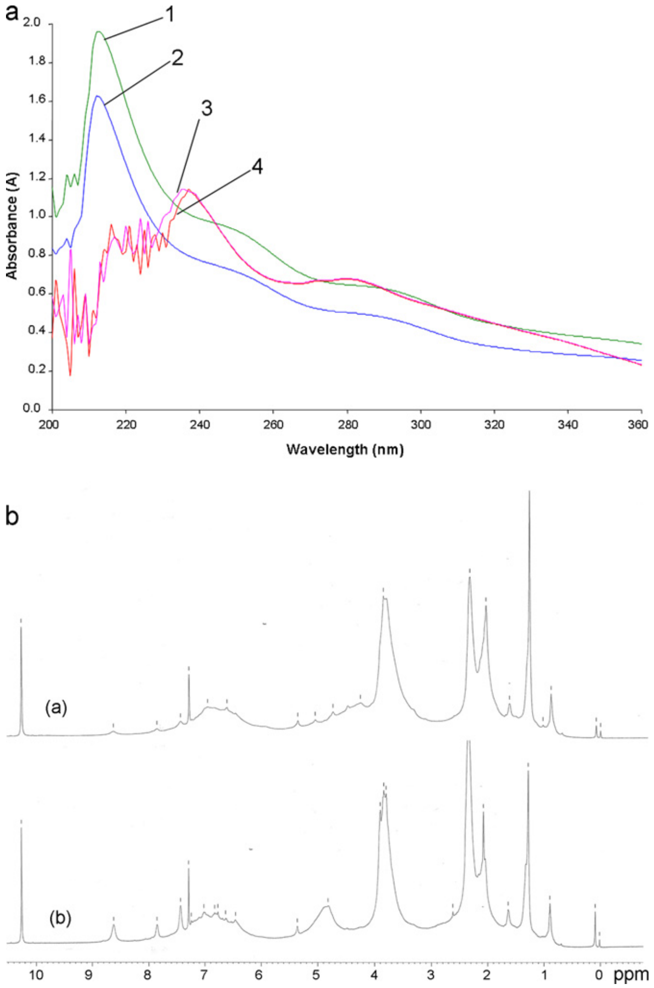

Fig. 6. (a) UV spectra of kraft and soda lignins. 1 – kraft lignin in pH 12 solution; 2 – soda lignin in pH 12 solution; 3 – soda lignin in dioxane–water (9:1) solution; 4 – kraft in dioxane–water (9:1) solution. (b) ^{1}H NMR spectra for acetylated (a) soda lignin and (b) kraft lignin.

result of molecular weight for both lignins could be compared because a polystyrene standard was used for calibration. The results of weight-average (M_w), number-average (M_n) molecular weight and polydispersity of kraft lignin and soda lignin before and after acetylation are presented in Table 6. It was observed that the molecular weights of both lignins before being acetylated are comparatively lower than those after acetylation. This observation indicates that the macromolecules of lignin were not completely dissolved in GPC eluent (tetrahydrofuran). Thus, acetylation should be carried out. For comparison, the molecular weights of acetylated lignins were examined.

From Table 6, it can be seen that M_w and M_n for kraft lignin is lower compared to soda lignin. This difference is due to the cooking process of the kraft pulp. During kraft cooking, the hydroxide and hydrosulfide anions reacted with the lignin causing the polymer to fragment into smaller water/alkali-soluble fragment. The fragmentation of the kraft lignin proceeded through the cleavage of α-aryl ether and β-aryl ether bonds. The severe process of kraft pulping leads the lignin to fragment into smaller molecular weights. This process also implies that the cleavage of α and β-O-4 bonds is the major process in kraft pulping process, as compared to the soda pulping process, because the phenolic content increased as the molecular weight of the lignin decreased. Higher M_w and M_n for soda lignin compared to kraft lignin suggest that soda lignin produces fragments with higher masses than kraft lignin.

Table 6
Results of weight-average (M_w), number-average (M_n) and polydispersity of kraft lignin and soda lignin before and after acetylation.

	Soda	Soda acetylated	Kraft	Kraft acetylated
M_w (g/mol)	1262	2873	1373	1807
M_n (g/mol)	988	1398	950	1101
M_w/M_n (polydispersity)	1.28	2.05	1.45	1.64

Table 7
Value of glass transition temperature (T_g) and maximum of thermal decomposition temperature DTG_{max}.

Samples	T_g (°C)	DTG_{max} (°C)
Kraft lignin	67.47	363.12
Soda lignin	71.64	347.09

Table 6 shows that the polydispersity for both lignins was relatively low, indicating that both lignins have a high fraction of low-molecular weight molecules. As for the polydispersity, both lignins possessed a narrow molecular weight distribution ($M_w/M_n < 2$). Compared to soda lignin, kraft lignin has a slightly lower polydispersity. This result suggests that kraft lignin is more suitable for condensates with phenol formaldehyde because it is more reactive than those with high molecular weight molecules (Pizzi & Mittal, 1994). The reaction of lignin with lower molecular weight (kraft lignin) with formaldehyde is preferred because it will enhance the rate of polymerisation process.

3.6. FESEM analysis

Fig. 7(a) and (b) presents the FESEM micrographs of kraft lignin and soda lignin, respectively. Both lignins have distinct difference in surface morphology. In Fig. 7(a), the surface morphology of kraft lignin shows large number of small pores that can be detected under 3000× magnification. It also shows rounded shapes with different sizes. Very few pores are present in soda lignin surface morphology as shown in Fig. 7(b). Different morphology in the lignin is due to the concentration process of the lignin from black liquor, which is done by evaporation. Due to their surface tension, the particles take a spherical form, which is thermodynamically stable (Fierro, Torné-Fernández, & Celzard, 2006).

The presence of vast quantities of small pores in kraft lignin surface enhances the chances of kraft lignin to incorporate with phenol formaldehyde because it promotes dispersion and penetration of the polymer into the lignin molecule. Thus, the polymerisation process between lignin, phenol and formaldehyde makes the lignin–phenol formaldehyde resin become a high-branched and strong cross-linked polymer. Lack of pores on the soda lignin surface reduced the tendency of polymerisation process between phenol formaldehyde and soda lignin.

3.7. Thermal behavior

3.7.1. Differential scanning calorimetry

Amorphous polymers such as lignin undergo a transition from a glassy state to a rubbery state at some temperature. This temperature is referred to as glass transition temperature or T_g. It is one of the significant characteristics of a polymer as it relates its application and processing (Steven, 1999). DSC analysis is an established method for determining glass transition temperature of polymer. Table 7 shows the value of T_g of soda lignin is higher compared to kraft lignin. This is believed to be related to molecular weights and can be explained by free volume concept. The free volume is the space in a solid or liquid sample which is not occupied by polymer molecules (Young & Lovell, 1991). The glass transition could be described by such activation energies through the use of free

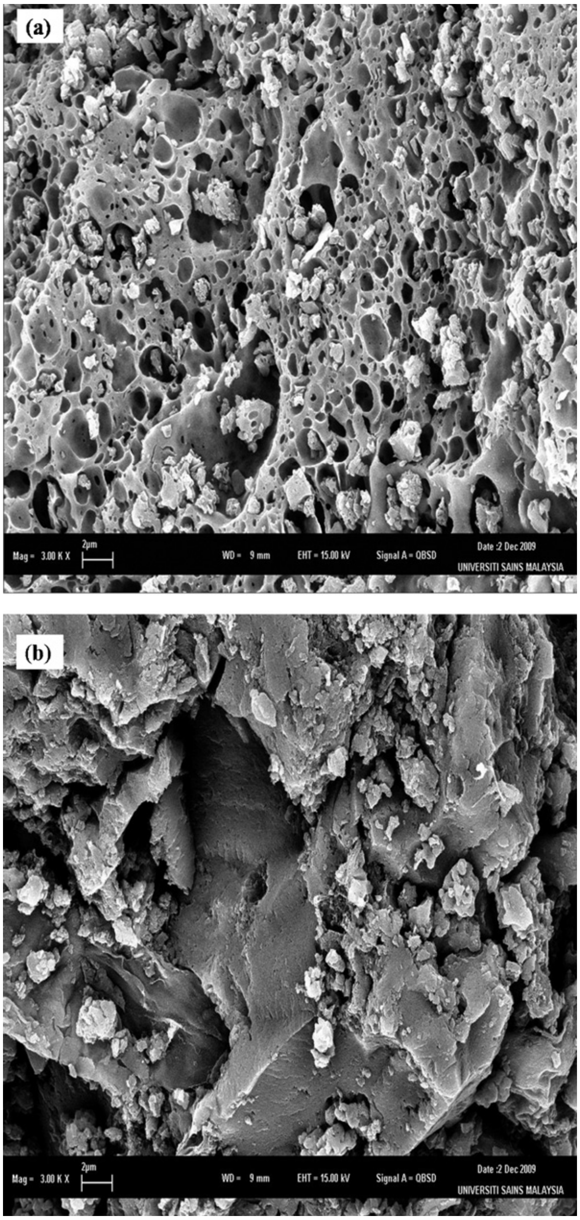

Fig. 7. FESEM micrographs of (a) kraft lignin and (b) soda lignin at 3000× magnification.

volume. T_g only appears when the main chain has enough energy for chain rotation. The chains in lignin initially vibrate when energy was supplied. Adding some more energy, the lignin chains rotate and create free volume. The higher molecular weight of soda lignin as shown in Table 7 suggests that soda lignin has few chain ends and low mobility volume. Thus more energy is required for rotation to occur, increasing the T_g value. Consequently, the free volume is limited and it increases the T_g value. These findings also indicate that the main chain of soda lignin is stiffer than that of kraft lignin, which is not conducive for incorporation with phenol formaldehyde resin when processed at lower temperature than their T_g value. When the main chain of soda is stiffer than that of kraft lignin, it reduces the chances of crosslink formation.

3.7.2. Thermal gravimetric analysis

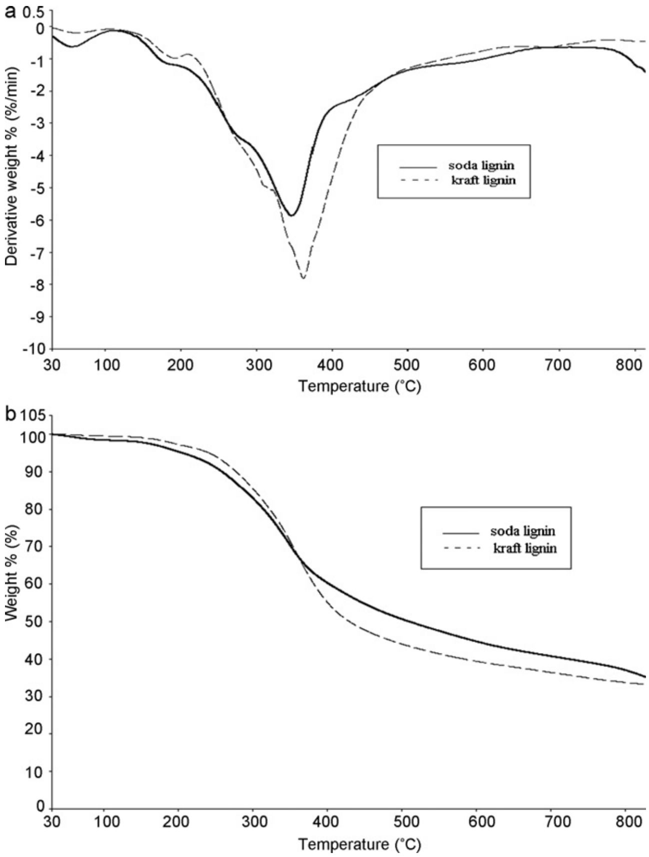

Fig. 8. DTG curves (a) and TG curves (b) for kraft lignin and soda lignin.

Thermal stability of the kraft lignin and soda lignin was investigated by thermogravimetric method. First derivative thermogravimetric (DTG) and thermogravimetric (TG) curves are presented in Fig. 8(a) and (b), respectively. TG curves indicate the weight loss of lignin samples in relation to the temperature of thermal degradation, while the first derivative of that curve (DTG) shows the corresponding rate of weight loss. The peak of this curve (DTG_{max}) is expressed as a single thermal decomposition temperature and can be used to express the thermal stability characteristics for any materials.

The initial weight lost for both lignins associated with water evaporation is shown in Fig. 8(a). The second weight lost with temperature between 300 °C and 310 °C indicated the degradation of hemicelluloses, which attached to lignin structure. The temperature with the maximum rate of weight loss for kraft lignin and soda lignin appeared at 363.12 °C and 347.09 °C, respectively, as shown in Table 7 and Fig. 8(a). The value of soda lignin is slightly lower than the value of soda lignin from ash-AQ pulping process reported by Sun, Tomkinson, and James (2000). Thermal degradation in this temperature range involves fragmentation of inter-unit linkages, releasing monoric phenols into the vapour phase (Elsaied & Nada, 1993). The DTG_{max} for kraft lignin was slightly higher than soda lignin as shown in Table 7 and was related to different content in C–C linkages for both lignins.

Fig. 8(b) shows that the thermal degradation of both lignins covers a wide temperature range between 105 °C and 800 °C. The temperature to 50% weight loss in kraft lignin and soda lignin was 429.5 °C and 508.3 °C, respectively. At 800 °C, about 33.7% and 36.9% of non-volatile residue for kraft and soda lignins, respectively, still remained in solid form and were not completely burned. This result reveals that both lignins are stable at high temperature, which is attributed by the high degree of branching and formation of highly condensed aromatic structure for both types of lignins. This thermal characteristic is reported to be similar to phenol formaldehyde resin (Tejado et al., 2007).

4. Conclusions

The chemical and thermal characterisations of kraft and soda lignins, extracted from oil palm biomass had been performed. The results demonstrate that the kraft lignin has a greater potential to partially substitute phenol in phenol formaldehyde resin compared to soda lignin. Mannich reactivity analysis shows that kraft lignin has a greater content of free 3-position in its lignin structure which indicates it has better reactivity to formaldehyde. This result is supported by UV and ^{1}H NMR analyses which revealed that kraft lignin has more phenolic group than soda lignin. M_w, M_n and polydispersity of the kraft lignin are lower than the soda lignin which helps the kraft lignin condense better with phenol formaldehyde compared to soda lignin. Large quantities of small pore in the kraft lignin surface enhance the chances for kraft lignin to incorporate with phenol formaldehyde during polymerisation process. Moreover, a lower T_g value and high thermal stability make kraft lignin suitable to condensate with phenol formaldehyde resin. This project is a doubled-edged enterprise that aims to recycle the waste from pulping industry as well as to turn it into a valuable material.

Acknowledgements

The authors gratefully acknowledge the financial support from Universiti Sains Malaysia through RU Grant (1001/PKIMIA/814018) and Incentive Grant for Post Graduate student (1001/PKIMIA/821117). Z. Norhidaya would like to express her gratitude to Universiti Sains Malaysia (USM) for her USM-Fellowship.

References

Akamatsu, I., Husin, M. B., Kamishima, H., & Hassan, A. H. (1987). Industrial utilization of oil palm (*Elaeis guneensis*) by-products. 1. Kraft-anthraquinone pulping of oil palm empty fruit bunches. *Cellulose Chemistry and Technology*, *21*, 67–75.

Alonso, M. V., Rodríguez, J. J., Oliet, M., Rodríguez, F., García, J., & Gilarranz, M. A. (2001). Characterization and structural modification of ammonic lignosulfonate by methylolation. *Journal of Applied Polymer Science*, *82*, 2661–2668.

Anglès, M. N., Reguant, J., Garcia-Valls, R., & Salvadò, J. R. (2003). Characteristics of lignin obtained from steam-exploded softwood with soda/anthraquinone pulping. *Wood Science and Technology*, *37*, 309–320.

Brunow, G., Lundquist, K., & Gellerstedt, G. (1999). Analytical methods in wood chemistry pulping and papermaking. In E. Sjöström, & R. Alén (Eds.), *Lignin* (pp. 77–124). Berlin/Heidelberg/New York: Springer-Verlag.

Buranov, A. U., & Mazza, G. (2008). Lignin in straw of herbaceous crops. *Industrial Crops and Products*, *28*, 237–259.

El Hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., & Ragauskas, A. (2009). Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. *Polymer Degradation and Stability*, *94*, 1632–1638.

Elsaied, H., & Nada, A. (1993). The thermal-behaviour of lignins from wasted black pulping liquors. *Polymer Degradation and Stability*, *40*, 417–421.

Fierro, V., Torné-Fernández, V., & Celzard, A. (2006). Kraft lignin as a precursor for microporous activated carbons prepared by impregnation with orthophosphoric acid: Synthesis and textural characterization. *Microporous and Mesoporous Materials*, *92*, 243–250.

Froass, P. M., Ragauskas, A. J., & Jiang, J. (1998). NMR studies. Part 3. Analysis of lignins from modern kraft pulping technologies. *Holzforchung*, *52*, 385–390.

Garcia, A., Toledano, A., Serrano, L., Egues, I., Gonzales, M., Marinn, F., et al. (2009). Characterization of lignins obtained by selective precipitation. *Separation and Purification Technology*, *68*, 193–198.

Ghazali, A., Wan Rosli, W. D., & Law, K. N. (2006). Alkaline peroxide mechanical pulping (APMP) of oil palm lignocellulosic. Part 2. Empty fruit bunch (EFB) responses to pretreatments. *APPITA Journal*, *59*, 65–70.

Gosselink, J. A., Abächerli, A., Semke, H., Malherbe, R., Käuper, P., Nadif, A., et al. (2004). Analytical protocols for characterisation of sulphur-free lignin. *Industrial Crops and Products*, *19*, 271–281.

Hoareau, W., Trindade, W. G., Siegmund, B., Castellan, A., & Frollini, E. (2004). Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: Characterization and stability. *Polymer Degradation and Stability*, *86*, 567–576.

Khoo, K. C., & Lee, T. W. (1991). Pulp and paper from oil palm. *APPITA Journal*, *44*, 385–388.

Law, K. N., Wan Rosli, W. D., & Ghazali, A. (2007). Morphological and chemical nature of fiber strands of oil palm empty-fruitbunch (OPEFB). *Bioresources*, *2*, 351–362.

Lewis, N. G., & Yamamoto, E. (1990). Lignin: Occurrence, biogenesis and biodegradation. *Annual Review of Plant Physiology and Plant Molecular Biology*, *41*, 455–496.

Lin, S. Y. (1992). Commercial spent pulping liquors. In S. Y. Lin, & C. W. Dence (Eds.), *Methods in lignin chemistry* (pp. 75–80). Berlin: Springer-Verlag.

Mansouri, N. E., & Salvadó, J. (2006). Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Industrial Crops and Products*, *24*, 8–16.

Mohamad Ibrahim, M. N., Chuah, S. B., & Rosli, W. D. W. (2004). Characterization of lignin precipitated from the soda black liquor of oil palm empty fruit bunch fibers by various mineral acids. *Asian Journal on Science and Technology for Development*, *21*, 57–68.

Nadji, H., Diouf, P. N., Benaboura, A., Bedard, Y., Riedl, B., & Stevanovic, T. (2009). Comparative study of lignins isolated from Alfa grass (*Stipa tenacissima* L.). *Bioresource Technology*, *100*, 3585–3592.

Pizzi, A. (1983). Phenolic resin wood adhesives. Wood adhesives. In A. Pizzi (Ed.), *Wood adhesives: Chemistry and technology* (pp. 247–287). New York: Marcel Dekker Inc.

Pizzi, A., Flora-Ann, C., & Van der Klashorst, G. H. (1989). Soda bagasse lignin adhesives for particleboard. Preliminary results. In *Adhesives from renewable resources*. Washington: American Chemical Society., pp. 82–95.

Pizzi, A., & Mittal, K. L. (1994). *Handbook of adhesives technology*. New York: Marcel Dekker Inc.

Rahman, S. H., Choudhury, J. P., Ahmad, A. L., & Kamaruddin, A. H. (2007). Optimization studies on acid hydrolysis of oil palm empty fruit bunch fiber for production of xylose. *Bioresource Technology*, *98*, 554–559.

Robert, D. R., Michel, B., Gellerstedt, G., & Lindfors, L. (1984). Structural changes in lignin during kraft cooking. Part 3. On the structure of dissolved lignins. *Journal of Wood Chemistry and Technology*, *4*, 239–263.

Rozman, H. D., Ahmadhilmi, K. R., & Abubakar, A. (2004). Polyurethane (PU)-oil palm empty fruit bunch (EFB) composites: The effect of EFBG reinforcement in mat form and isocyanate treatment on the mechanical properties. *Polymer Testing*, *23*, 559–565.

Steven, M. P. (1999). *Polymer chemistry: An introduction* (1st ed.). New York: Oxford University Press.

Sulaiman, O., Salim, N., Hashim, R., Yusof, L. H. M., Razak, W., Yunus, N. Y. M., et al. (2009). Evaluation on the suitability of some adhesives for laminated veneer lumber from oil palm trunks. *Materials and Design*, *30*, 3572–3580.

Sun, R. C., Tomkinson, J., & James, B. (2000). Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. *Polymer Degradation and Stability*, *68*, 111–119.

Tanaka, R., Wan Rosli, W. D., Magara, K., Ikeda, T., & Hosoya, S. (2004). Chlorine-free bleaching of kraft pulp from oil palm empty fruit bunches. *Japan Agricultural Research Quarterly*, *38*, 275–279.

Tejado, A., Peña, C., Labidi, J., Echeverria, J. M., & Mondragon, I. (2007). Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis. *Bioresource Technology*, *98*, 1655–1663.

Umi Kalsom, M. S., Ariff, A. B., & Zulkifli, H. S. (1997). The treatment of oil palm empty fruit bunch fibre for subsequent use as substrate for cellulase production by *Chaetomium globosum Kunze*. *Bioresource Technology*, *62*, 1–9.

Vázquez, G., Freire, S., Bona, C. R., González, J., & Antorrena, G. (1999). Structures, and reactivities with formaldehyde, of some acetosolv pine lignins. *Journal of Wood Chemistry and Technology*, *19*, 357–378.

Wan Rosli, W. D., Law, K., & Valade, J. L. (1998). Chemical pulping of oil palm empty fruit bunches. *Cellulose Chemistry and Technology*, *32*, 133–143.

Wan Rosli, W. D., Law, K. N., Zainuddin, Z., & Asro, R. (2004). Effect of pulping variables on the characteristics of oil-palm frond-fiber. *Bioresource Technology*, *93*, 233–240.

Wan Rosli, W. D., Zainuddin, Z., & Roslan, S. (2005). Upgrading of recycled paper with oil palm fiber soda pulp. *Industrial Crops and Products*, *21*, 325–329.

Young, R. J., & Lovell, P. A. (1991). *Introduction to polymers* (2nd ed.). London: Chapman & Hall.

Zhao, X. B., Dai, L., & Liu, D. (2009). Characterization and comparison of acetosolv and milox lignin isolated from crofton weed stem. *Journal of Applied Polymer Science*, *114*, 1295–1302.

Zhinan, F., & Raimo, A. (2001). Soda-AQ pulping of reed canary grass. *Industrial Crops and Products*, *14*, 31–39.