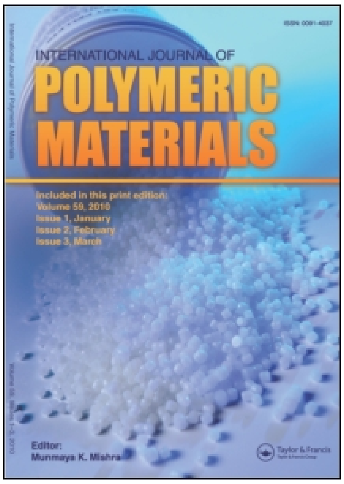

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Comparative Studies of Ash-AQ and Soda-AQ Lignins from Oil Palm EFB Fibre

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Three ash-AQ and three soda-AQ lignin preparations were obtained from the corresponding supernatants of black liquors after isolation of the polysaccharide degradation products and ash by precipitation at pH 3.0, 2.0, and 1.5, respectively. A comparison study of the lignin preparations was made in terms of yield, purity, content of associated polysaccharides, molecular weight, structural feature, and thermal stability. The yield of ash-AQ and soda-AQ lignins increased from 1.13 to 1.19 and 0.98 to 1.06 with decreasing precipitation pH from 3.0 to 1.5, respectively. Both of ash-AQ and soda-AQ lignins showed approximately molecular weights of $\overline{M}_w$, ranging between 3,580 and 3,930 g mol^{-1}, and had a similarly structural features and almost same physico-chemical properties except for the more condensed structure in ash-AQ lignin preparations. The results obtained by alkaline nitrobenzene oxidation revealed that all the lignin preparations composed of large amounts of non-condensed syringyl units and small amounts of non-condensed guaiacyl units together with minor quantities of *p*-hydroxyphenyl units.

Keywords: Ash-AQ lignin; Soda-AQ lignin; Oil palm empty fruit bunch; Phenolic acids and aldehydes; Degree of condensation; *p*-hydroxybenzoic acid

INTRODUCTION

In recent years there has been an increased focus on the environmental safety of conventional pulping process. In pursuit of the minimum impact mill, several new process strategies such as low-kappa pulping, oxygen-alkali delignification, and organosolv pulping, have won

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increased support and are now in widespread use [1, 2]. More recently, the researchers in our pulp and paper group found that the ash, obtained by burning EFB at 600°C in a muffle furnace and mainly composed of potassium carbonate, in a aqueous solution can be successfully used as a cooking liquor for pulping. It was found that this cooking liquor with a high pH can produce good quality of chemical or semi-chemical pulp. This makes it possible to use such a cooking liquor as a direct substitute for traditional soda-AQ, kraft or sulphite cooking processes, and to develop an environmentally safe and economically feasible pulping process.

Delignification, which facilitates disintegration of wood into fibrous components and eliminates colouring substances, constitutes the main process involved in chemical pulping and lignin-degrading bleaching [3,4]. Based on knowledge about alkaline delignification of woody materials, alkaline impregnation affects swelling and the formation of a certain tunnel-network in the cell walls, facilitating the removal of reaction products from the lignocellulosic matrix [5]. During the initial delignification stage in alkaline pulping, phenolic α-*O*-4 linkages in lignin are cleaved and some phenolic β-*O*-4 linkages are cleaved, followed by the diffusion of extractable lignin components. Meanwhile, hemicelluloses were deacetylated and a considerable amount of hemicelluloses was dissolved in this stage. The dominating reaction during the bulk stage is the cleavage of non-phenolic β-*O*-4 linkages, and most of the lignins were degraded or dissolved in the cooking liquor accompanying with dissolution and degradation of the remaining hemicelluloses. The residual delignification stage has been assigned to cleavage of carbon-carbon linkages in lignin and to carbohydrate degradation, releasing lignin-carbohydrate fragments [5, 6].

Lignins are the major by-products in the black liquor of the pulping, together with significant amounts of hemicellulosic degradation products and minor quantities of wax, lipids, and inorganics. More recently, there is a strongly increasing interest in the utilization of lignins produced from the chemical pulping as a raw materials source for production of higher value-added products such as useful low-molecular weight chemicals and polymeric materials [7]. Among the important advantages of these lignins often mentioned are their high reactivity, solubility, and relatively free of chemically linked polysaccharides [2]. For a purpose of obtaining more clear fundamental knowledge of the structure features and the physico-chemical properties of the lignin polymers, degraded during the ash-anthraquinone (AQ) pulping of oil palm empty fruit bunch (EFB) fibre, a comparative study of the lignin preparations with those derived from soda-AQ pulping process was performed. The characteristics of the lignins in terms of yield, purity, molecular weight distribution, alkaline nitrobenzene oxidation, ultraviolet (UV), Fourier transform infrared (FT-IR), carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR), gel permeation chromatography (GPC), and thermogravimetric analysis (TGA). The effect of precipitation pH on the lignin yield and its heterogeneity is also reported.

EXPERIMENTAL

Isolation of Lignins

The black liquors produced in ash-AQ and soda-AQ pulping processes had pH values of 13.9 and 12.9, and densities 1.14 and 1.04 (g/ml), respectively. The lignins were isolated by a two step precipitation method proposed in our laboratory [8] and as described below. The black liquor was subjected to neutralization to pH 7.0 with 6 M HCl and subsequently concentrated. The ash and polysaccharide degradation products were precipitated by pouring the concentrated liquor into 4 volumes of 95% ethanol. After evaporation of ethanol, the lignins were obtained from the corresponding black liquor by addition drop by drop of 6 M HCl under vigorous stirring to pH 3.0, 2.0, and 1.5 (room temperature), respectively. After filtration, the lignin preparations were washed with acidified water (pH 2.0) and then airdried. A flow scheme for isolation of the lignins from the corresponding black liquors is illustrated in Figure 1.

Physico-chemical and Structural Characterization of the Lignins

The methods of alkaline nitrobenzene oxidation, determination of phenolic acids and aldehydes with high performance liquid chromatography (HPLC), measurement of molecular weight with GPC, and the UV, FT-IR, and ^{13}C-NMR spectroscopy studies of the isolated lignin

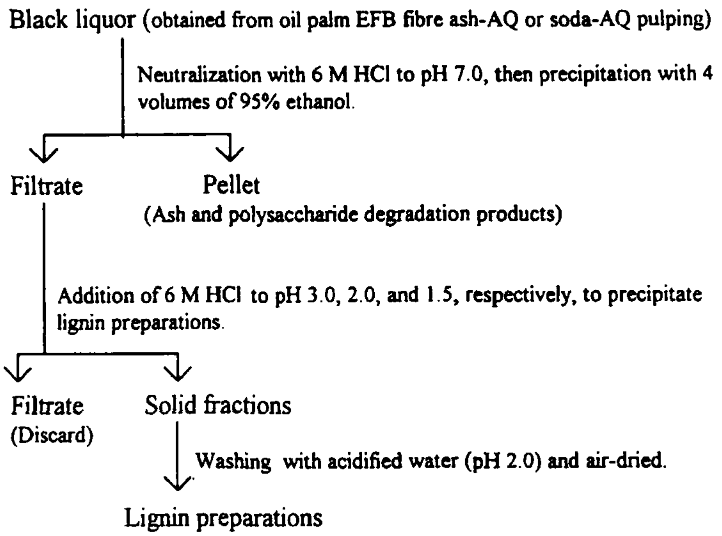

FIGURE 1 Scheme for isolation of lignin preparations from the black liquor of oil palm EFB fibre ash-AQ or soda-AQ pulping.

preparations have been described in previous papers [9 – 11]. The content of neutral sugars from associated hemicelluloses were analyzed as their alditol-acetate derivatives by gas chromatography (GC) after acid hydrolysis [12].

Thermogravimetric analysis of the lignin fractions was performed with a simultaneous thermal analyzer (STA 625). This apparatus provides for a continuous measurement of sample weight at a range of temperatures between ambient and 600°C. Samples of approximately 10 mg weight were heated in a platinum crucible to 600°C at a heating rate of 10°C min^{-1}. Provision was made for electronic differentiation of the weight signal to give the rate of weight loss.

RESULTS AND DISCUSSION

Yield and Purity

Similar procedures were used to isolate the degraded lignins from the black liquors of ash-AQ and soda-AQ pulping, respectively. The yield (g/100 ml) of lignin, recovered from the corresponding black liquors of oil palm EFB fibre pulping by precipitation at different pH after isolation of the polysaccharide degradation products and ash, is listed in Table I. Obviously, the yield of lignin depended on the precipitation pH. As can be seen in Table I, a decrease of precipitation pH from 3.0 to 2.0 and to 1.5 resulted in increasing yield of recovered lignin from 1.13 to 1.18 and to 1.19 (from ash-AQ pulping), and from 0.98 to 1.04 and to 1.06 (from soda-AQ pulping), respectively. This result indicated that an optimum precipitation pH was occurred at 2.0 – 1.5.

The UV spectra of the six lignin preparations showed similar absorptions and exhibited the basic UV spectrum of typical lignins with a maximum at 236 nm. For a example, Figure 2 shows the UV

TABLE I Yield (g/100 ml) of lignin preparations obtained by precipitation at different pH from the supernatant of black liquor after isolation of ash and polysaccharide degradation products

Pulping process/lignin precipitation pH	*Yield (g/100 ml)*
Ash-AQ pulping	
Precipitation at pH 3.0	1.13
Precipitation at pH 2.0	1.18
Precipitation at pH 1.5	1.19
Soda-AQ pulping	
Precipitation at pH 3.0	0.98
Precipitation at pH 2.0	1.04
Precipitation at pH 1.5	1.06

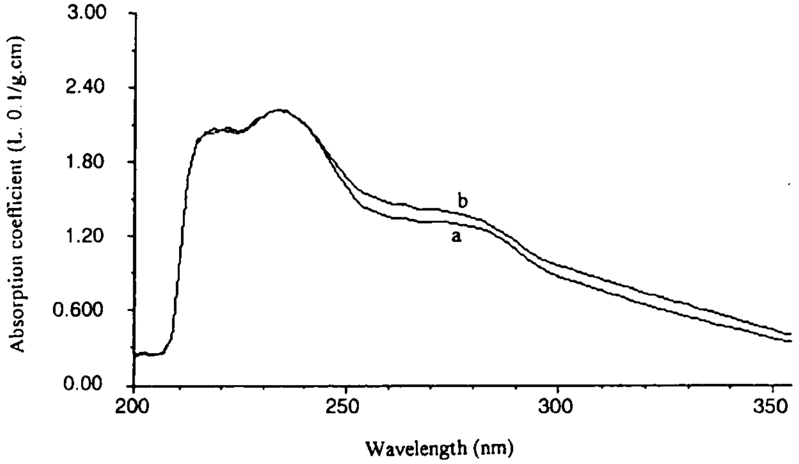

FIGURE 2 UV spectra of lignin preparations obtained by precipitation at pH 2.0 (spectrum *a* from soda-AQ pulping, spectrum *b* from ash-AQ pulping) from the supernatant of black liquor after isolation of ash and polysaccharide degradation products.

spectra of lignin preparations obtained by precipitation at pH 2.0 (spectrum *a* from soda-AQ pulping, spectrum *b* from ash-AQ pulping) from the supernatant of black liquor after isolation of ash and polysaccharide degradation products. The second maximum at 278 nm originated from the nonconjugated phenolic groups in lignin [13]. This similar absorption intensity of the lignins revealed that the six isolated lignin preparations had approximate purity. Further analysis of the liberated neutral sugars as their alditol-acetate derivatives by GC after hydrolysis with 2 M trifluoroacetic acid at 120°C for 2 h showed that all the six lignin preparation were relatively free of the bound polysaccharides.

Alkaline Nitrobenzene Oxidation

To gain insight into the structure of lignin such as composition of original lignin polymer and its degree of condensation, the isolated six lignin preparations were investigated by alkaline nitrobenzene oxidation at 170°C for 3 h, and the content of phenolic acids and aldehydes is given in Table II. The yield of phenolics ranged 15.0% in ash-AQ lignins and 18.8–20.5% in soda-AQ lignins, indicating that three ash-AQ lignin preparations had a similar degree of condensation. Similar trend was found between the three soda-AQ lignin fractions. However, a distinctly lower yield of three ash-AQ lignin preparations implied that these lignins comprised of higher amounts of condensed structures than those in three soda-AQ lignin fractions. Syringaldehyde, derived from noncondensed syringyl units, was identified to be the major product, comprising approximately 50% of the total phenolic monomers in all the six lignin preparations. Vanillin, originated from the noncondensed guaiacyl units, appeared as the second major phenolic component, comprising 23.8–27.7% of the total phenolic acids and aldehydes. The molar ratios of *S* (the relatively total moles of syringaldehyde, syringic acid, and acetosyringone) to *V* (the relatively total moles of vanillin and vanillic acid), and to *H* (the relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid) was found to be almost in same order, 6:3–4:1, indicating a similar composition of the original lignins.

TABLE II The content (% lignin sample, w/w) of phenolic acids and aldehydes from alkaline nitrobenzene oxidation of the lignin preparations isolated from the black liquor

Phenolic acids and aldehydes	*Precipitation pH (Ash-AQ pulping)*[a]			*Precipitation pH (Soda-AQ pulping)*[b]		
	3.0	2.0	1.5	3.0	2.0	1.5
p-Hydroxybenzoic acid	0.78	0.79	0.74	0.98	1.10	1.01
p-Hydroxybenzaldehyde	0.31	0.38	0.40	0.41	0.42	0.46
Vanillic acid	0.42	0.45	0.47	0.48	0.59	0.62
Syringic acid	1.58	1.54	1.62	1.53	1.68	1.75
Vanillin	3.70	3.56	3.60	5.20	5.53	5.08
Syringaldehyde	7.41	7.42	7.42	9.28	10.08	9.83
p-Coumaric acid	0.22	0.21	0.20	0.29	0.38	0.27
Acetosyringone	0.35	0.32	0.28	0.38	0.32	0.25
Ferulic acid	0.21	0.28	0.30	0.23	0.40	0.28
Total	14.98	14.95	15.03	18.78	20.50	19.55
Molar ratio (S:V:H)[c]	6:3:1	6:3:1	6:3:1	6:4:1	6:4:1	6:3:1

[a] The lignin preparations obtained by precipitation at different pH from the supernatant of the black liquor of oil palm EFB ash-AQ pulping after isolation of the ash and polysaccharides degradation products.

[b] The lignin preparations obtained by precipitation at different pH from the supernatant of the black liquor of oil palm EFB soda-AQ pulping after isolation of the polysaccharides degradation products.

[c] *S* represents the relatively total moles of syringaldehyde, syringic acid, and acetosyringone; *V* represents the relatively total moles of vanillin and vanillic acid; and *H* represents the relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid.

Molecular Weight Distribution

Table III shows the weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights and polydispersity ($\overline{M}_w/\overline{M}_n$) of both ash-AQ and soda-AQ lignin preparations. Due to the unavailable pure and structurally verified lignin model compounds with molecular weights higher than about 1,000 g mol^{-1}, polystyrene standards were used for calibration, and the values of $\overline{M}_w$ and $\overline{M}_n$ presented in Table III should therefore be considered as relative molecular weights. Apparently, there was no significant difference in the effect of precipitation pH on the weight-average and number-average molecular weights and polydispersity of each lignin preparations. Additionally, both ash-AQ and soda-AQ lignins showed similar molecular weights of $\overline{M}_w$, ranging between 3,580 and 3,930 g mol^{-1}. Similar feature was observed in the values of polydispersity. All the six lignin preparations showed relatively narrow molecular weight distribution as shown by $\overline{M}_w/\overline{M}_n < 3$. The molecular weight distribution of the lignin preparation, precipitated at pH 1.5 from the supernatant of the black liquor of oil palm EFB fibre ash-AQ pulping after isolation of ash and polysaccharide

TABLE III Weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights and polydispersity ($\overline{M}_w/\overline{M}_n$) of the lignin preparations isolated from the black liquor of oil palm EFB fibre pulping

	Precipitation pH (Ash-AQ pulping)[a]			*Precipitation pH (Soda-AQ pulping)*[b]		
	3.0	2.0	1.5	3.0	2.0	1.5
$\overline{M}_w$	3,680	3,580	3,700	3,880	3,830	3,930
$\overline{M}_n$	1,500	1,440	1,470	1,550	1,560	1,560
$\overline{M}_w/\overline{M}_n$	2.46	2.49	2.52	2.50	2.48	2.52

[a] The lignin preparations obtained by precipitation at different pH from the supernatant of the black liquor of oil palm EFB ash-AQ pulping after isolation of the ash and polysaccharides degradation products.

[b] The lignin preparations obtained by precipitation at different pH from the supernatant of the black liquor of oil palm EFB soda-AQ pulping after isolation of the polysaccharides degradation products.

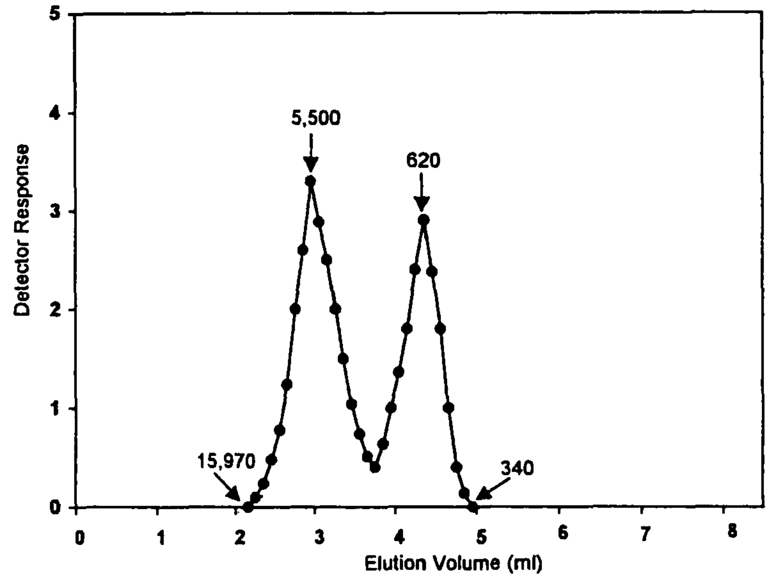

FIGURE 3 GPC molecular weight distribution of lignin preparation isolated at pH 1.5 from the supernatant of the black liquor of oil palm EFB fibre ash-AQ pulping after isolation of ash and polysaccharide degradation products.

degradation products (Fig. 3), ranged from biphenols to $\overline{M}_w$ nearly 16,000 g mol^{-1}. The distribution showed two elution maxima, corresponding to $\overline{M}_w$ of 5,500 and 620 g mol^{-1}, respectively. The much lower molecular weight eluted at peak II was largely due to the substantial fragmentation of the dissolved lignins by significant cleavage of β-aryl ether linkages during the ash-AQ pulping process.

FT-IR Spectra

The FT-IR spectra of the four lignin preparations, obtained by precipitation at pH 2.0 (spectrum *a* from ash-AQ pulping, spectrum *c* from soda-AQ pulping) and 1.5 (spectrum *b* from ash-AQ pulping, spectrum *d* from soda-AQ pulping) from the supernatant of the black liquor after isolation of ash and polysaccharides degradation products, are shown in Figure 4. The spectra showed the typical alkaline lignin spectra, and the absorption pattern and intensity were rather similar, indicating similar structure of the lignins. The band at 1713 cm^{-1} has been assigned to C=O stretching in nonconjugated ketone and carboxylic acid with the aromatic ring [1, 14]. Aromatic skeleton vibrations in the lignin preparations are assigned at 1609, 1514, and 1424 cm^{-1}. Absorption at 1462 cm^{-1} attributes to the aromatic methyl group vibrations. The intensive bands at 1330 (syringyl ring breathing with CO stretching) and 1118 cm^{-1} (aromatic CH in-

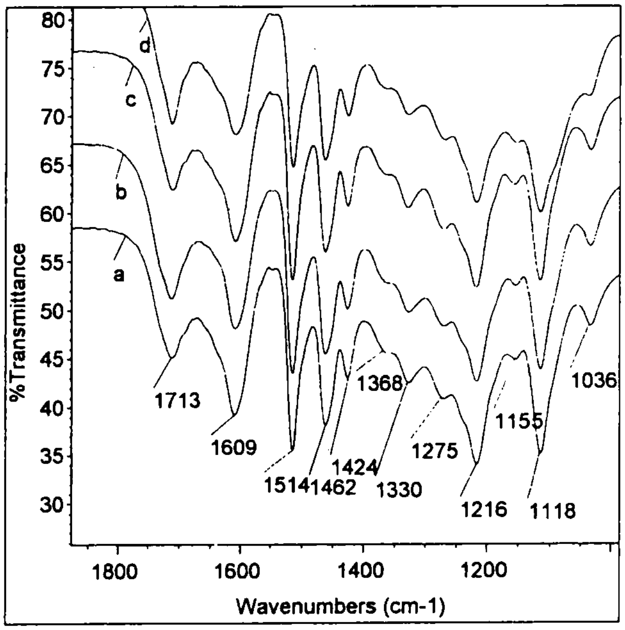

FIGURE 4 FT-IR spectra of lignin preparations, obtained by precipitation at pH 2.0 (spectrum *a* from ash-AQ pulping, spectrum *c* from soda-AQ pulping) and 1.5 (spectrum *b* from ash-AQ pulping, spectrum *d* from soda-AQ pulping) from the supernatant of the black liquors after isolation of ash and polysaccharides degradation products.

plane deformation, syringyl type) are originates from the syringyl units in lignin molecules, while the bands at 1275 (guaiacyl ring breathing with CO stretching), 1216 (guaiacyl ring breathing with CO stretching), 1155 (aromatic CH in-plane deformation, guaiacy type), and 1036 cm^{-1} (aromatic CH in-plane deformation, guaiacyl type) correspond to the guaiacyl units in lignin molecules [15].

^{13}C-NMR Spectra

To further investigate the structural differences between ash-AQ and soda-AQ lignins, solid-state ^{13}C-NMR spectrum of soda-AQ lignin isolated at pH 3.0 (Fig. 5) and solution-state ^{13}C-NMR spectra of

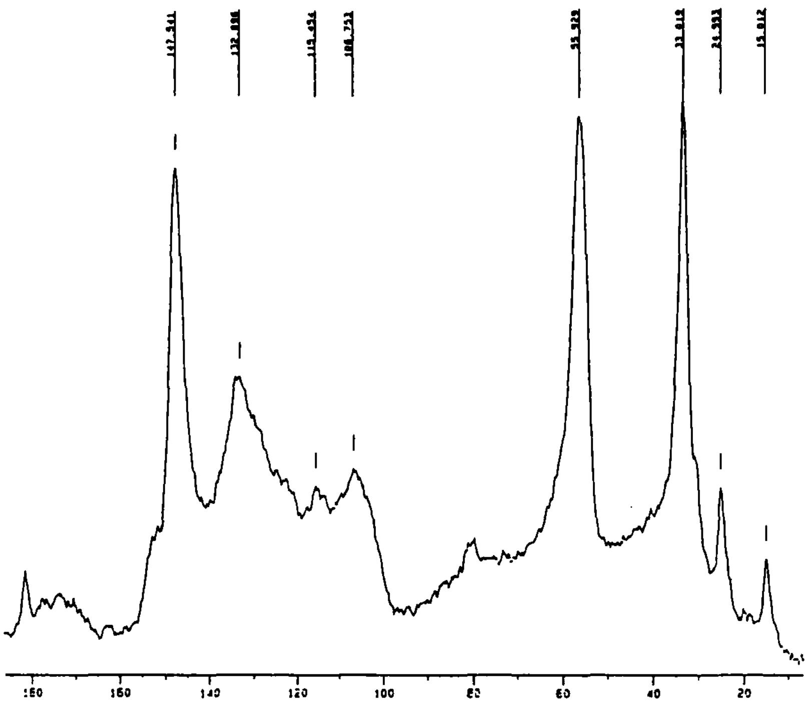

FIGURE 5 Solid-state ^{13}C-NMR spectrum of lignin preparation isolated by precipitation at pH 3.0 from the supernatant of black liquor of oil palm EFB fibre soda-AQ pulping after isolation of polysaccharide degradation products.

soda-AQ lignin preparation precipitated at pH 2.0 (Fig. 6) and ash-AQ lignin preparation obtained by precipitation at pH 2.0 (Fig. 7) were recorded. Most of the assignments could be made according to the spectra of straw and wood lignins from the literature [13, 16–19]. The most striking feature of the lignins was the relatively free of chemically linked neutral polysaccharides or below the detection limit for ^{13}C-NMR. However, the lignin preparations contained noticeable amounts of uronic acids as shown by a signal at 174.6–174.7 ppm for C-6 in methyl uronates (C=O in aliphatic acids or esters) [20].

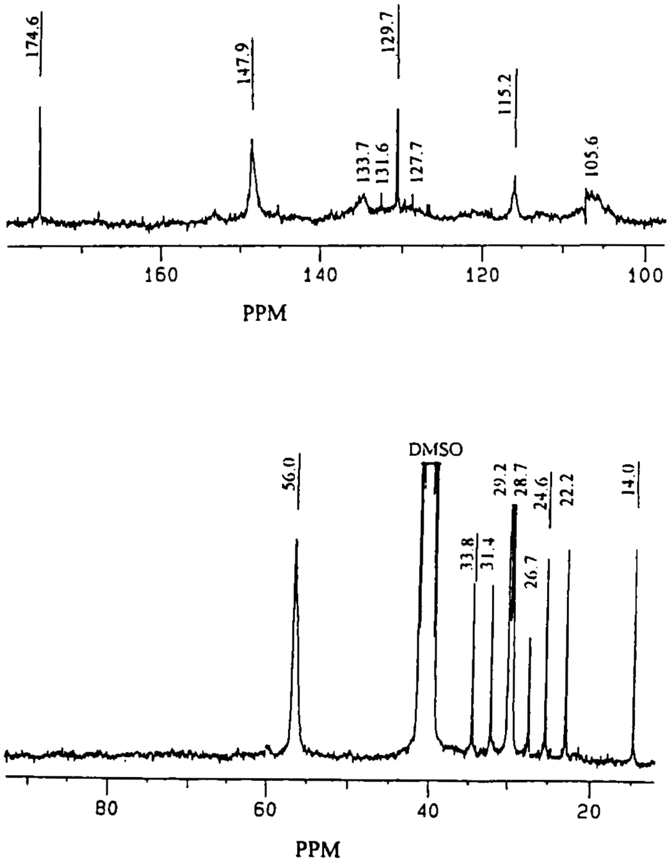

FIGURE 6 Solution-state ^{13}C-NMR spectrum of lignin preparation isolated by precipitation at pH 2.0 from the supernatant of black liquor of oil palm EFB fibre soda-AQ pulping after isolation of polysaccharide degradation products.

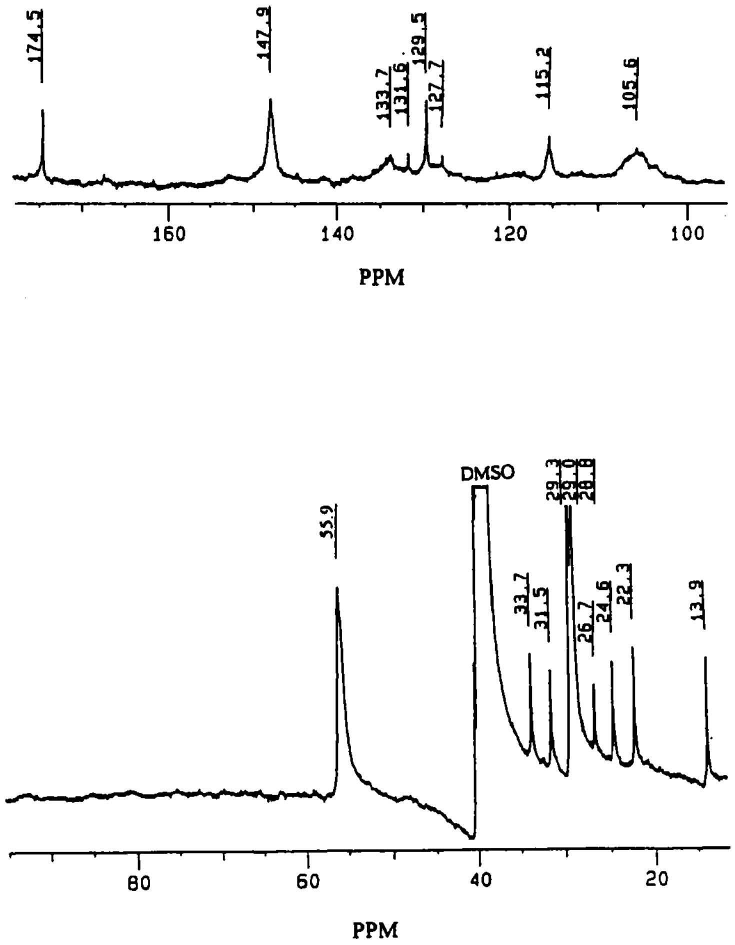

FIGURE 7 Solution-state ^{13}C-NMR spectrum of lignin preparation isolated by precipitation at pH 2.0 from the supernatant of black liquor of oil palm EFB fibre ash-AQ pulping after isolation of ash and polysaccharide degradation products.

In Figure 5, the intensive peak at 147.5 ppm corresponds to C-3/C-5 in non-etherified syringyl units and C-4 in guaiacyl units in lignin molecules. The C-1 in non-etherified syringyl and guaiacyl units was identified at 132.9 ppm. Two small peaks at 115.5 and 106.8 ppm are attributed to C-5 in guaiacyl units and C-2/C-6 in syringyl units, respectively. The sharp peak at 55.9 ppm is assigned to aryl methoxyl groups in syringyl and guaiacyl units. The signals from carbon in

—CH—, —CH_2—, and —CH_3— of lignin the side-chain structures can be observed at 33.0, 25.0, and 15.0 ppm, respectively.

No significant differences in peak intensity were found between ash-AQ and soda-AQ lignin preparation as shown in Figures 6 and 7, indicating a similar structure of the lignins from oil palm EFB fibre. The syringyl, guaiacyl, and *p*-hydroxyphenyl units in lignin structures were identified by signals at 147.9 (C-3/C-5 in nonetherified syringyl units), 133.7 (C-1 in nonetherified syringyl units), and 105.6 ppm (C-2/C-6 in syringyl units); 147.9 (C-4 in etherified guaiacyl units), 133.7 (C-1 in nonetherified guaiacyl units), and 115.3 ppm (C-5 in guaiacyl units); and 127.7 ppm (C-2/C-6 in *p*-hydroxyphenyl units), respectively. Esterified *p*-hydroxybenzoic acid was detected with two signals at 131.7 (C-3 in *p*-hydroxybenzoic acid) and 115.2 ppm (C-5 in *p*-hydroxybenzoic acid, overlapped with C-5 in guaiacyl units). The strong peak at 55.9 – 60.0 ppm originates from OCH_3 in syringyl and guaiacyl units. The signals assigned to γ-methyl and α- and β-methylene group in *n*-propyl side chains appeared in the spectra between 13.9 and 33.8 ppm. The almost absence of signals between 90 and 60 ppm suggested a substantial cleavage of β-*O*-4 ether intermonomer linkages in lignin structures during the ash-AQ and soda-AQ pulping processes under the conditions given.

Thermal Analysis

The thermal stability of the lignin preparations was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results revealed that all the lignin preparations exhibited similar thermograms, indicating an equal thermal stability of the lignins. Most lignin preparations observed showed their maximum rate of weight loss between 300°C and 450°C as compared to the hemicelluloses, which were degraded at a much faster rate than lignins between 200°C and 300°C [21 – 23]. As shown in Figure 8, the decomposition temperature at 10% weight loss appeared at 241°C. When the temperature raised to 300°C, the weight loss accounted for 16.3%, while at temperature of 435°C the weight loss increased significantly to 47.0%.

Pyrolytic degradation of lignin in the temperature region involved fragmentation of inter-unit linkages, releasing monomeric phenols

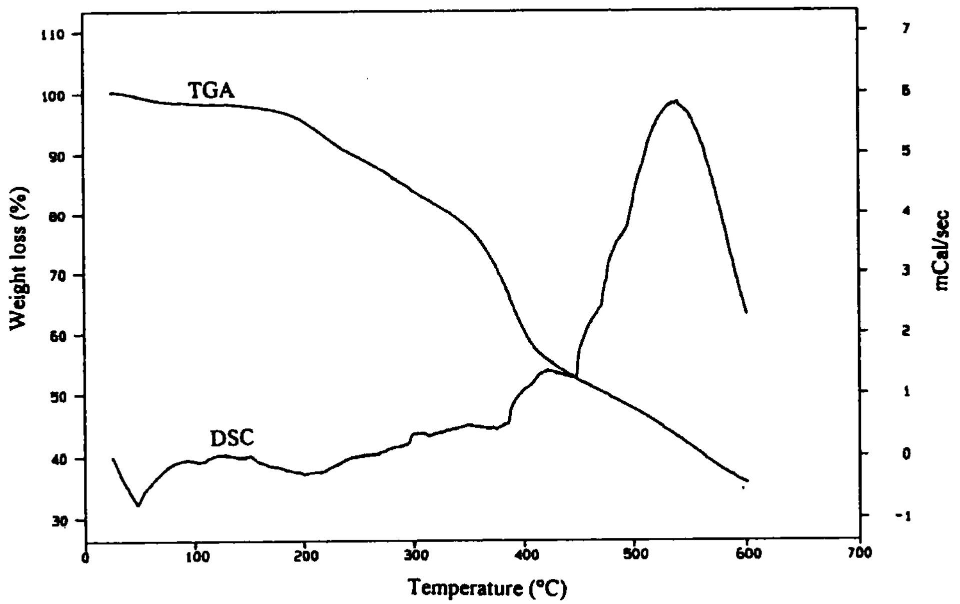

FIGURE 8 TGA/DSC curves of ash-AQ lignin preparation obtained by precipitation at pH 2.0 from the supernatant of black liquor after isolation of ash and polysaccharide degradation products.

into the vapour phase. The evolution of methanol from the lignin materials indicated the cleavage of methyl-aryl ether bonds at just below 400°C. Decomposition or condensation of aromatic ring was probable to take place at 400 – 600°C [21]. The non-volatile residue at 600°C was large, amounting to 36.2% of the lignin material (Fig. 8), which reflected a high degree of branching and substantial condensation of the lignin preparations.

Overall, the above results showed that ash-AQ and soda-AQ lignin preparations had a similar structure and physico-chemical properties except for the more condensed structure in ash-AQ lignin preparations. All the six lignin preparations were relatively free of associated neutral polysaccharides and were composed of large amounts of syringyl units together with small amounts of guaiacyl units and minor quantities of *p*-hydroxyphenyl units. *p*-Hydroxybenzoic and uronic acids were identified to be esterified at the side chains of lignin molecules. Additionally, a substantial cleavage of *β-O*-4 ether intermonomer linkages in lignin structures was found during the ash-AQ and soda-AQ pulping processes under the conditions given.

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