

Characteristics of Oil Palm EFB (Empty Fruit Bunch of *Elaeis guineensis*) Lignin

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In order to utilize EFB lignin successively following the ecosystem, the characteristics of EFB lignin were discussed in detail. EFB lignophenol was synthesized through the phase-separation system. The pyrogram of EFB lignophenol shows the peaks of phenol, *p*-cresol, guaiacol and syringol. The FT-IR spectrum of EFB lignophenol shows a peak at 1714 cm⁻¹ assigned to esters. EFB lignophenol was subjected to mild alkaline treatment to give guaiacyl - syringyl lignins and *p*-hydroxybenzoic acid. The thermal stabilities of EFB lignophenol after mild alkaline treatment were increased. GC/MS analysis and above results showed that EFB lignophenol includes esterified *p*-hydroxybenzoic acid. The amounts of attached *p*-hydroxybenzoic acid were 9.6% of EFB lignophenol (0.23 mol/C₉ in EFB lignophenol) and 1.8% of EFB extractives-free meals (0.15 mol/C₉ in klason lignin). The difference in frequencies of *p*-hydroxybenzoic acid suggests the heterogeneous incorporation of *p*-hydroxybenzoic acid into lignin.

Key words: Oil Palm, EFB (Empty Fruit Bunch), Phase-Separation System, Lignophenol, Resource Circulation

1. INTRODUCTION

Oil Palm EFB (Empty Fruit Bunch of *Elaeis guineensis*) is one of byproducts from oil palm industry. EFB composed of cellulose, hemicellulose and lignin has been utilized only as fuels and mulches. In the previous work [1], the potential of EFB as aromatic and aliphatic resources through the phase-separation system [2, 3] has been discussed. In order to successively utilize EFB from composite to molecular levels, following the carbon cycle in the ecosystem, detailed molecular information of EFB lignin is required. In this work, the characteristics of EFB core lignin and attached units were investigated.

2. EXPERIMENTAL

2.1 Synthesis of EFB lignophenol

EFB lignophenol was synthesized by 2 step process II of phase-separation system composed of *p*-cresol and 72 % H₂SO₄. In order to solvate lignin, extractives-free EFB meals (50 g) were covered with acetone solution containing 3 mol/C₉ of *p*-cresol uniformly. After 24 hrs, acetone was removed at room temperature. Seventy-two % H₂SO₄ (500 mL) was added to cresol solvated EFB meals, and stirred vigorously for 60 min. The reaction mixture was added to excess amount of deionized water. The precipitates (lignophenol - carbohydrate complex) were collected by centrifugation, washed up to pH 6-7 and freeze-dried. EFB lignophenol was extracted with acetone from the resulting composites. The combined lignophenol - acetone solution was concentrated, and added dropwise to excess amount of diethyl ether with vigorous stirring. The precipitate (EFB lignophenol) was collected by centrifugation and dried over P₂O₅ after evaporating the solvent.

2.2 Preparation of EFB core-lignophenol and

determination of *p*-hydroxyphenyl units.

EFB lignophenol (150 mg) was dissolved in 60 mL of 1 N NaOH and stirred under N₂ flow at 40°C for 72 hrs. The solution was acidified up to pH 4 with 1 N HCl. The precipitate (EFB core-lignophenol) was collected by centrifugation. EFB core-lignophenol was washed with small amount of hot water up to pH 7, and dried over P₂O₅. The water soluble part was saturated with NaCl and extracted with diethyl ether [4]. The ether soluble part was dried over anhydrous Na₂SO₄, concentrated, trimethylsilylated and analyzed by GC/MS [a Shimadzu GC/MS-QP 5050A, column: 007-1 (Quadrex, 50 m × 0.25 mm × 0.25 μm), carrier gas: He].

In case of quantitative analysis, β-naphthol was used as an internal standard. The ether soluble part was analyzed by gas chromatography [GC-17A with flame ionization detector, column: 007-1 (Quadrex, 50 m × 0.25 mm × 0.25 μm), carrier gas: He].

2.3 Determination of *p*-hydroxyphenyl units in EFB meals

Extractives-free EFB meals (1 g) were treated with 1 N NaOH under N₂ flow at 40°C for 96 hrs. The insoluble materials were collected by centrifugation and washed with hot water up to pH 7. The alkaline soluble part was acidified with 1 N HCl, saturated with NaCl and extracted with diethyl ether. After drying with anhydrous Na₂SO₄ and filtration, the ether soluble part was concentrated, trimethylsilylated and analyzed by GC/MS. In case of quantitative analysis, β-naphthol was used as an internal standard.

2.4 Analyses of EFB lignophenol and EFB core-lignophenol

FT-IR spectra (KBr disks) of lignophenols were determined on Spectrum TM GX FT-IR Spectroscopy (PERKIN ELMER). In order to measure molecular

weight, gel permeation chromatograms of lignophenols were determined on LC-10 system with four columns (KF801, KF802, KF803 and KF804) and UV detector (280 nm). Tetrahydrofuran was used as the eluent. In order to estimate grafted *p*-cresol contents, $^1\text{H-NMR}$ spectra of original and acetylated lignophenol were determined in $\text{C}_5\text{D}_5\text{N-CDCl}_3$ (1/3, v/v) and CDCl_3 on a JNM-A500 FT-NMR SYSTEM and ALPHA FT-NMR Spectrometer (JEOL, 500MHz). UV-Vis (in methyl cellosolve) spectra of lignophenols were determined by a JASCO V-560 spectrophotometer. TMA profiles of lignophenols were determined by a Seiko Instruments Inc TMA / SS6100 (Rate: $2^\circ\text{C}/\text{min}$, 50°C - 250°C , Flow: N_2). TG profiles of lignophenols were determined by a Seiko Instruments Inc TG / DTA 6200 (Rate: $2^\circ\text{C}/\text{min}$, 50°C - 450°C , Flow: N_2). In order to estimate compositions of lignophenols, lignophenols were pyrolyzed at 500°C for 12 s, using a pyrolyzer (Frontier Lab., PY-2020D) coupled to a gas chromatograph with EI-MS detector (Shimadzu GC/MS-QP5050A, Carrier gas: He). The gas chromatographs were fitted with an 007-1 column programmed from 90 to 280°C at $4^\circ\text{C}/\text{min}$.

2.6 Switching function of lignophenol

Lignophenols (5 mg) were dissolved in 0.5 N NaOH (2 mL) and treated at 120°C , 140°C and 170°C . After reactions, the reaction mixture was acidified with 1 N HCl to pH 2. The precipitations were collected by centrifugation, washed with small amount of water and dried under P_2O_5 . The average molecular weights of lignophenols (2nd derivatives) were estimated by GPC.

3. RESULT AND DISCUSSION

3.1 Structural features of EFB core-lignophenol

The yields of EFB lignophenol and EFB core-lignophenol were 65.8% of EFB lignin and 80.3% of EFB lignophenol, respectively. FT-IR spectrum of EFB core-lignophenol does not have a peak at 1714 cm^{-1} assigned to ester linkages. This shows ester linkages in EFB lignophenol were hydrolyzed. The spectrum was similar to that of hardwood lignophenol (Fig. 1). Furthermore a peak of phenol to *p*-cresol in pyrogram of EFB core-lignophenol was decreased (Fig. 2). The peak ratio [guaiacol / syringol (area / area)] of EFB lignophenol and EFB core-lignophenol were 0.46 and 0.42, respectively. The $^1\text{H-NMR}$ spectrum of EFB core-lignophenol was similar to that of hardwood lignophenol (Fig. 3, b). These results show that the core-lignin of EFB lignophenol consists of guaiacyl and syringyl units.

The amount of phenolic hydroxyl group in EFB core-lignophenol was lower than that of EFB lignophenol, while the amount of aliphatic hydroxyl group was higher than that of EFB lignophenol (Table 1). The decrease of phenolic hydroxyl group was also confirmed by the differential ionization spectra of EFB lignophenol and EFB core-lignophenol (Fig. 4).

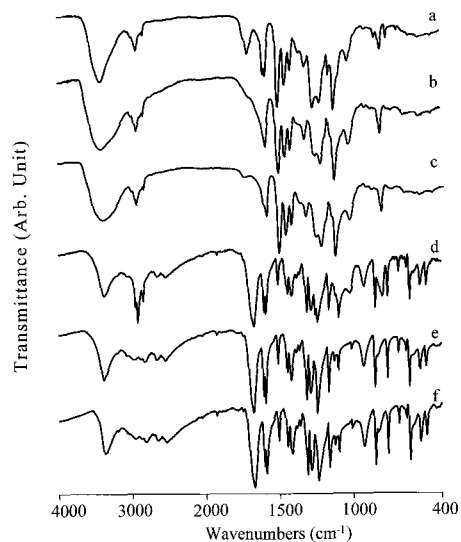


Fig. 1 FT-IR spectra of lignophenols and alkaline hydrolysis products. [a: EFB lignophenol, b: EFB core-lignophenol, c: Hardwood lignophenol, d: Alkaline hydrolysis product from EFB lignophenol, e: Product obtained after recrystallization of alkaline hydrolysis product with water, f: *p*-Hydroxybenzoic acid.]

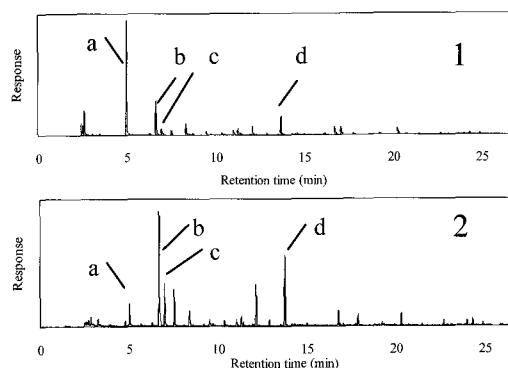


Fig. 2 Pyrograms of EFB lignophenols. [1: EFB lignophenol, 2: EFB core-lignophenol, a: Phenol, b: *p*-Cresol, c: Guaiacol, d: Syringol.]

The average molecular weight (\bar{M}_w) of EFB core-lignophenol was about 4,000. These results suggest that phenolic carboxylic acid is linked to the side chain of G-S type core lignin through ester linkage, and DP of lignin subunits formed by radical coupling in biosynthesis of EFB lignin is in the range of 13-14.

Table 1 Amounts of grafted cresol, average molecular weights and hydroxyl groups of lignophenols

Sample	Grafted cresol contents		Hydroxyl groups				Average molecular weights		
			Phenolic OH		Aliphatic OH				
	wt(%)	mol/C ₉	wt(%)	mol/C ₉	wt(%)	mol/C ₉	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
EFB lignophenol	26.2	0.72	7.58	1.31	3.06	0.56	6184	3522	1.76
EFB core-lignophenol	27.8	0.78	6.45	1.13	6.87	1.20	4074	2436	1.67

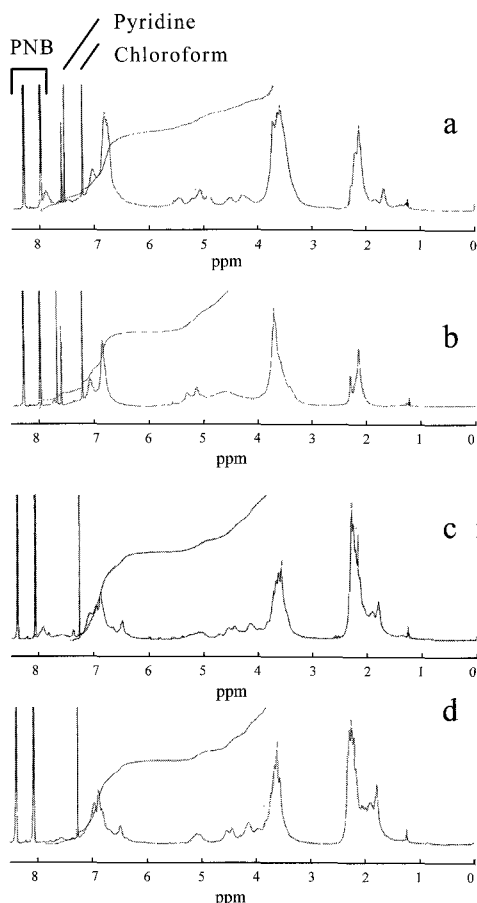


Fig. 3 $^1\text{H-NMR}$ spectra of lignophenols. [a: EFB lignophenol (original), b: EFB core-lignophenol (original), c: EFB lignophenol (acetylated), d: EFB core-lignophenol (acetylated).]

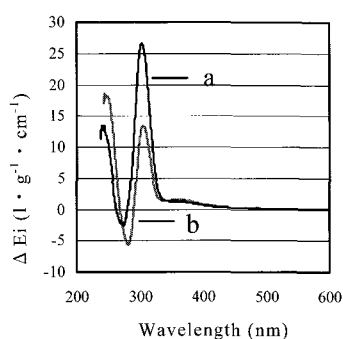


Fig. 4 Ionization differential spectra of lignophenols. [a: EFB lignophenol, b: EFB core-lignophenol.]

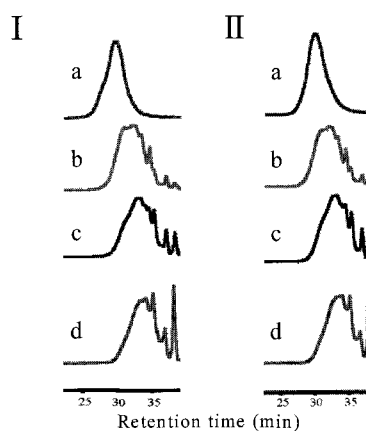


Fig. 5 GPC profiles of lignophenols and 2nd derivatives. [I: EFB lignophenol, II: EFB core-lignophenol, Treatment temperature; a: Original (untreated), b: 120 °C, c: 140 °C, d: 170 °C.]

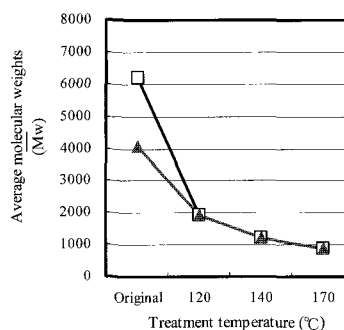


Fig. 6 Average molecular weights of lignophenols and 2nd derivatives. [□: EFB lignophenol, ▲: EFB core-lignophenol.]

After alkaline treatments at 120 °C, 140 °C and 170 °C of EFB core-lignophenols, the average molecular weights were decreased. The variation of average molecular weight was similar to that of EFB lignophenol, indicating the presence of 1,1-bis (aryl) propane units working as switching devices [3] (Fig. 5, Fig. 6)

3.2 The structure and frequency of *p*-hydroxyphenyl units

FT-IR spectrum of the alkaline hydrolysis product (Fig. 1, d) has a peak around 1674 cm^{-1} assigned to conjugated carboxyl groups. Furthermore the product obtained after recrystallization of alkaline hydrolysis product from EFB lignophenol with water was similar to that of *p*-hydroxybenzoic acid, suggesting that main constituent of the alkaline hydrolysis product is *p*-hydroxybenzoic acid.

Table 2 Yields of *p*-hydroxybenzoic acid, *p*-coumaric acid and ferulic acid.

Sample	<i>p</i> -Hydroxybenzoic acid			<i>p</i> -Coumaric acid			Ferulic acid		
	wt (% of sample)	wt (% of lignin)	mol / C ₉ in lignin	wt (% of sample)	wt (% of lignin)	mol / C ₉ in lignin	wt (% of sample)	wt (% of lignin)	mol / C ₉ in lignin
EFB meals	1.8	8.8	0.15	0.05	0.25	0.004	trace	trace	trace
EFB lignophenol	9.6	-	0.23	trace	trace	trace	-	-	-

The GC/MS chromatograms and mass spectra of alkaline hydrolysis product from EFB lignophenol and EFB meals were shown in Fig. 7 and Fig. 8. The alkaline hydrolysis product from EFB lignophenol contained *p*-hydroxybenzoic acid mostly. This result was also confirmed by FT-IR spectrum of alkaline hydrolysis product from EFB lignophenol after recrystallization (Fig. 1, e). The alkaline hydrolysis product from EFB meals contained *p*-hydroxybenzoic acid and *p*-coumaric acid.

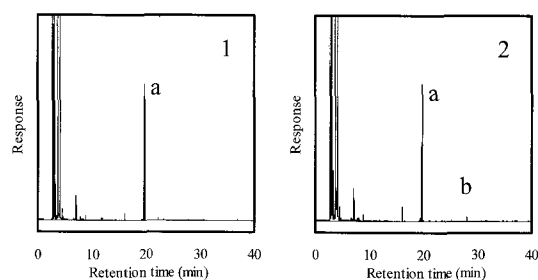


Fig. 7 GC/MS chromatograms of alkaline hydrolysis product from EFB lignophenol and EFB meals. [1: Alkaline hydrolysis product from EFB lignophenol, 2: Alkaline hydrolysis product from EFB meals, a: *p*-Hydroxybenzoic acid, b: *p*-Coumaric acid]

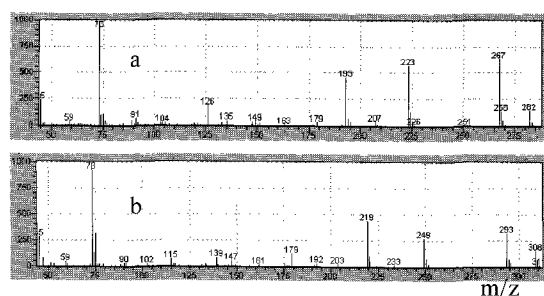


Fig. 8 Mass spectra of main peaks of alkaline hydrolysis products. [a: *p*-Hydroxybenzoic acid (Fig. 7, 1-a), b: *p*-Coumaric acid (Fig. 7, 2-b).]

The amounts of attached *p*-hydroxybenzoic acid were 9.6% of EFB lignophenol (0.23 mol/C₉ in EFB lignophenol) and 1.8% of EFB extractives-free meals (0.15 mol/C₉ in klason lignin). This result shows that ester linkages of *p*-hydroxybenzoic acid are not cleaved during phase-separation treatment because of solvation effect of phenol. EFB lignin was converted to ether insoluble lignophenol (about 70%) and ether soluble lignophenol (about 30%) through the phase-separation system. The difference in frequencies of *p*-hydroxybenzoic acid suggests the heterogeneous incorporation of *p*-hydroxybenzoic acid into lignin (Table 2).

3.3 The role of *p*-hydroxyphenyl units in EFB lignin

From the results of TMA and TG, the thermal stabilities of EFB core-lignophenol were higher than

those of EFB lignophenol (Fig. 9, Fig. 10). The phase-transition points and 10 % weight loss points of EFB lignophenol and EFB core-lignophenol were 162 °C and 192 °C, 235 °C and 254 °C, respectively. The pattern of TMA of homogeneous mixture of EFB core-lignophenol and *p*-hydroxybenzoic acid was similar to that of EFB lignophenol. This result shows that *p*-hydroxybenzoic acid works as internal plasticizer.

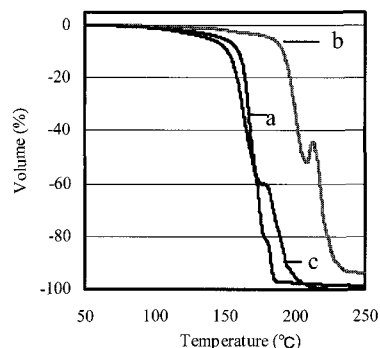


Fig. 9 TMA profiles of lignophenols. [a : EFB lignophenol, b: EFB core-lignophenol, c: Homogeneous mixture of EFB core-lignophenol (10.3 mg) and *p*-Hydroxybenzoic acid (1.08 mg).]

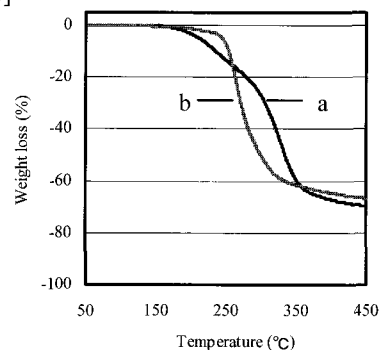


Fig. 10 TG profiles of lignophenols. [a : EFB lignophenol, b: EFB core-lignophenol.]

4. CONCLUSION

EFB core-lignin consists of guaiacyl and syringyl units, and carboxyl groups of *p*-hydroxybenzoic acid are linked to aliphatic groups of EFB core-lignin, showing that EFB lignin is classified with grass lignin. Furthermore it is easy to release *p*-hydroxybenzoic acid, showing that EFB lignin is successively structure-controllable. *p*-Hydroxybenzoic acid is valuable as an organic resource, medical supply and phenolic agents for sustainable phase-separation system without petroleum. EFB is superior to woody materials as industrial raw materials.

5. REFERENCE

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