Potential of Oil Palm EFB
(Empty Fruit Bunch of *Elaeis guineensis*) as Industrial Raw Materials

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Empty fruit bunch (EFB) of *Elaeis guineensis* is one of by-products in the oil palm industry and has been used as fuels and mulch. In the present work, in order to utilize EFB as organic resources in place of petro-resources, the potential of EFB was investigated, using the phase-separation process, in comparison with woody materials. The yields of EFB- and hardwood lignophenols reached to the maximum by the phase –separation treatment for 10 min and decreased gradually after that, while the yields of softwood lignophenols increased gradually up to 60 min. This is due to the difference in the frequency of condensed structures in lignin molecules between with and without syringyl units. The compositions of carbohydrates from EFB through the phase-separation system were similar to those from hardwood, in which glucose and xylose were obtained as main constituents. The average molecular weights, amounts of grafted phenol and phase transition points of EFB lignophenols were about 8,000 (Mw), 0.7 mol/C_9, 150°C, respectively. Through the treatment with 0.5 N NaOH at 170°C, the molecular weight of lignophenol was decreased to about 800 (Mw). This was caused by the neighboring group participation reaction of grafted cresol in EFB lignophenol.

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

1. INTRODUCTION

EFB (Empty Fruit Bunch of *Elaeis guineensis*) has been discharged from oil palm industry. The amount of EFB is about 14 million t / year [1]. Most of traditional studies on EFB are of carbohydrate utilization, such as pulp and paper [2, 3]. During the utilization process of EFB including high energy input, lignin is highly modified to be inactivated. Consequently EFB lignin has not been utilized in molecular level as functional materials, being only utilized as mulch and energy resources in palm oil industry. These utilizations disturb the carbon balance between solid and gaseous states. In order to create sustainable human society, the material flow system following the oil palm circulation in the ecosystem is required.

The phase-separation system developed in funaoka lab, Mie university Japan is a key technology for utilizing both lignin and carbohydrates successively [4, 5]. First, wood meals are completely soaked in phenol derivatives. To the phenol-sorpted wood meals, concentrated acid is added and the mixture is stirred vigorously at room temperature. The reaction occurs at the interface between the organic and aqueous phases. During this process, C α -aryl ethers of native lignin are cleaved and then phenol derivatives is grafted selectively into C α -positions, leading to linear type polymers. Carbohydrates are hydrolyzed to give oligomers, dimers and monomers.

In the present work, conversion and separation of EFB components into functional materials through the phase-separation system were carried out, and the potential of oil palm plantation field as new spots sustainably providing industrial raw materials in place of petroleum was discussed in comparison with woody materials.

2. EXPERIMENTAL
2.1 Preparations of EFB and wood meals.

EFB was washed with a large amount of deionized water and dried. Air-dried EFB was ground by Wiley mill to pass an 80 mesh screen. To remove extractives, EFB was extracted with ethanol-benzene (1/2, v/v) for 48 hrs, using Soxhlet apparatus. In order to measure lignin contents of EFB, extractives-free EFB meals (1g) were treated with 72 wt % sulfuric acid (15 mL) at 20 °C for 4 hrs. The reactant mixture was diluted to 3 wt % of sulfuric acid and boiled for 2 hrs. The insoluble materials were separated by centrifugation and washed with hot water until pH 7. The acid-insoluble lignin content was calculated by subtracting the ash and protein. The protein content was calculated from N content. The acid soluble lignin content of EFB was measured by UM-205 (Tappi Standard). Lignin contents of extractives-free wood meals (Softwood: Douglas fir, *Pseudotsuga menziesii*, Hardwood: Birch, *Betula platyphylla*), were estimated by Klason method [6].

2.2 Preparation of lignophenols

Phenol derivative (*p*-cresol, 10 mL) was added samples (1g) with stirring. After 5 min, twenty mL of 72 wt % sulfuric acid were added and stirred vigorously at 30 °C for prescribed time. The reaction mixture was centrifuged. The organic phase was added dropwise to 250 mL of diethyl ether. The precipitates were dissolved in 80 mL of acetone. The insoluble materials were removed by centrifugation and filtration. The soluble fraction was concentrated under reduced pressure until 10 mL. The concentrated acetone solution was added dropwise to 200 mL of diethyl ether. The precipitates were collected by centrifugation and dried over P_2O_5 .

2.3 Sugar analyses

2.3.1 Water soluble carbohydrates.

A small amount of the water layers after the phase-separation treatment were neutralized with $Ba(OH)_2$. The suspensions were centrifuged and the supernatants were filtrated. The molecular weight distributions of water soluble carbohydrates were determined using three columns (Asahipak GS-520HQ, GS-320HQ and GS-220HQ) and RI.

2.3.2 Sugar compositions.

The water layers after the phase-separation treatment were diluted with distilled water to 3 % and boiled for 4 hrs. After cooling, ribose (for wood) or maltose (for EFB) was added as an internal standard. The small amount of acid solutions were neutralized with $Ba(OH)_2$. The suspensions were centrifuged and the supernatants were filtrated. The sugar compositions were determined on LC-10 system with a column (Shim-pack ISA-07/S2504). Potassium borate buffers were used as eluent.

2.4 Structural features of EFB lignophenols

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

The molecular weight distributions 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 eluent.

In order to estimate grafted p-cresol contents, ^{1}H-NMR spectra were recorded on a JNM-A500 FT-NMR SYSTEM and ALPHA FT-NMR Spectrometer (JEOL, 500MHz). The solutions of original lignophenols in C_5D_5N-$CDCl_3$ (1/3, v/v) containing TMS as the internal reference were used.

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 °C/min, 50 °C-250°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).

2.5 Switching function of lignophenol

Lignophenols (5 mg) were dissolved in 0.5 N NaOH (2 mL) in stainless steel bottle and then treated at 120 °C, 140 °C and 170 °C. After reactions, the bottles were cooled. The alkaline solutions were acidified with 1 N HCl to pH 2. The precipitates were collected by centrifugation, washed with small amount of water and dried under P_2O_5. Average molecular weights of lignophenols (2nd derivatives) were estimated by GPC.

3. RESULT AND DISCUSSION

3.1 Yields of lignophenol and sugars

The yields of lignophenols were estimated, basing on lignin contents (Table1, Fig. 1, Fig. 2). With about 10 min of treatment time, the yields of EFB and Birch lignophenols reached the maximum. While the yield of Douglas fir lignophenol increased gradually up to 60 min. This results show that EFB and Birch lignins have flexible molecular structures, due to the presence of guaiacyl and syringyl units leading to less condensed

structures. The maximum yield of EFB lignophenol was 71.3 % of lignin, lower than those of wood lignophenols. The yield of p-cresol free lignophenol was 51.5 % of lignin. This result shows that about the half of EFB lignin was converted into ether soluble low molecular weight lignophenols.

Table1 Moisture and lignin contents of lignocellulosics

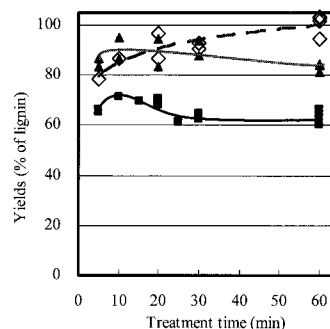| Sample	Moisture content(%)	Lignin contents (% of extractives-free meals)		
		Acid-insoluble lignin	Acid-soluble lignin	Total
EFB (of *Elaeis guineensis*)	7.73	18.4	1.99	20.4
Birch (*Betula platyphylla*)	6.90	25.0	1.85	26.8
Douglas fir (*Pseudotsuga menziesii*)	7.84	27.8	0.29	28.1

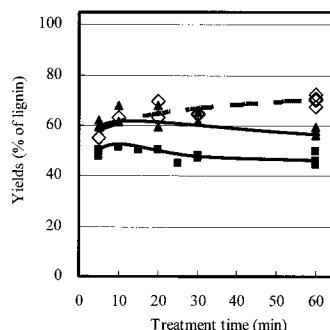Fig. 1 Yields of lignophenols. [■ :EFB, ▲:Birch, ◇:Douglas fir.]

Fig. 2 Yields of p-cresol free lignophenols. [■:EFB, ▲:Birch, ◇:Douglas fir.]

The GPC profile of water soluble carbohydrate of EFB was similar to that of Birch (Fig. 3). To estimate the variation of molecular weight distribution of carbohydrates, the chromatogram was divided into 8 units (I - VIII). The ratios of their peak areas were calculated. The ratio of peak I decreased with time, indicating that degradation of pentose derived from hemicellulose (Fig. 4).

The carbohydrates from EFB contained glucose, xylose, arabinose, galactose, mannose, ribose and rhamnose. The main constituents were glucose and xylose. This indicates that the hemicellulose of EFB consists of xylan. With about 10 min of treatment time, the yields of carbohydrates from EFB were 62.8 % of extractive free EFB meals and 83.4 % of carbohydrate of EFB (Fig. 5). During the phase-separation treatment, the viscosity of reaction mixture of EFB was decreased more rapidly, compared with woody materials, indicating that the interpenetrating polymer network structures in the cell wall were released more rapidly.
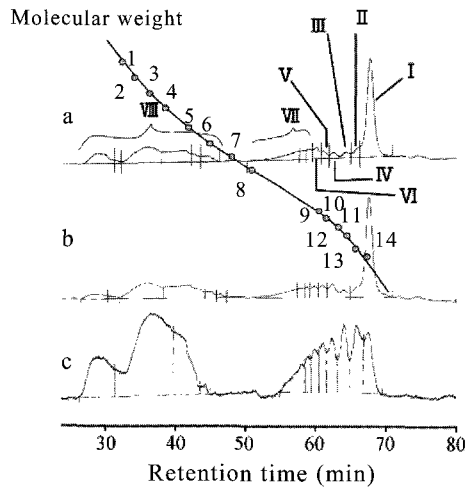
Fig. 3 GPC profiles of water soluble carbohydrates. [a: EFB, b: Birch, c: Douglas fir, Conditions: Phase-separation treatment time: 10 min, Peak I : Pentose, II :Hexose, III :Dimer, IV : Trimer and tetramer, V :Pentamer and hexamer, VI: Heptamer, VII: Oligomer (more than heptamer), VIII : High molecular weight part. Molecular weight: 1: 788,000, 2: 404,000, 3: 212,000, 4: 112,000, 5: 47,300, 6: 22,800, 7: 11,800, 8: 5,900, 9: 1,153, 10: 829, 11: 504, 12: 342, 13: 180, 14: 150.]
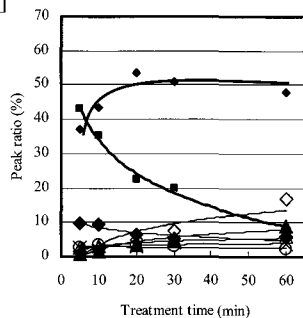

Fig. 4 Variations of molecular weights of carbohydrates in the water layer after the phase-separation treatment of EFB. [■ :peak I (Pentose), ◇: II (Hexose), ▲ :III (Dimer), △ :IV (Trimer and tetramer), × : V (Pentamer and hexamer), ○ : VI (Heptamer), ◆ : VII (Oligomer), ◆ :VIII (High molecular weight part).]
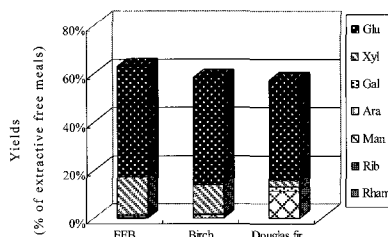
Fig. 5 Yields of carbohydrates of EFB through the phase-separation system. [Treatment time: 10min.]

3.2 Structural features of EFB lignophenols

The colors of lignophenols obtained from EFB

through the phase-separation system were pinkish white. UV-vis spectrum of EFB lignophenol showed sharp peaks only at 280 and 300 nm, indicating that EFB lignophenol do not have conjugated structure (Fig. 6). FT-IR spectrum of EFB lignophenols showed a peak at 815 cm^{-1} assigned to out of plane vibrations for aromatic C-H (Fig. 7), showing that p-cresol was grafted into lignin. The spectrum of EFB lignophenol showed a peak at 1714 cm^{-1} assigned to C=O stretch in ester groups. The pyrogram of EFB lignophenol showed a peak of phenol as well as guaiacol and syringol (Fig. 8). These results suggest that carboxyl groups of p-hydroxyphenyl units are linked to EFB core-lignin through ester linkages.
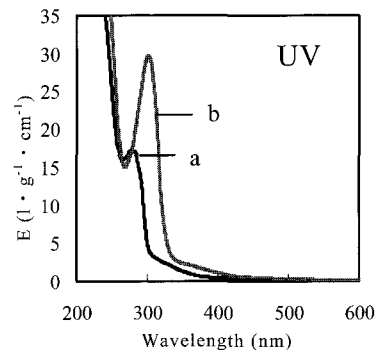

Fig. 6 Uv-Vis spectra of EFB lignophenol. [a: Neutral solution, b: Alkaline solution.]
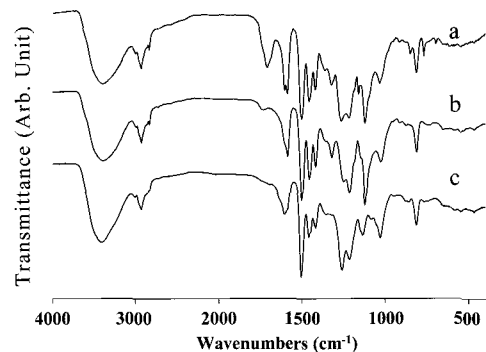

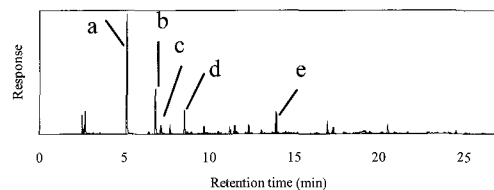Fig. 7 FT-IR spectra of lignophenols. [a: EFB, b: Birch, c: Douglas fir.]

Fig. 8 Pyrogram of EFB lignophenol. [a: Phenol, b: p-Cresol, c: Guaiacol, d: 2.4-dimethyl phenol, e: Syringol, Phase-separation treatment time: 60 min.]

The molecular weight distribution pattern of EFB lignophenol was similar to that of Birch lignophenol (Fig. 12). Dispersity index of EFB lignophenol (Mw/Mn: 1.65-2.32) was lower than woody lignophenols (Birch lignophenol: 2.24-2.63, Douglas fir

lignophenol: 3.54-4.18), indicating more regular molecular form. Variations of average molecular weight and grafted cresol contents of EFB lignophenols during the phase-separation treatment were not so high, compared with those of woody lignophenols (Fig. 9, Fig. 10). This indicates that the conversion of native lignin of EFB into lignophenol was more rapid, compared with woody materials.

The phase-transition point of EFB lignophenol was about 150 ℃ (Fig. 11), higher than woody lignophenols. This is due to less amount of low molecular weight fractions which work as internal plasticizers.
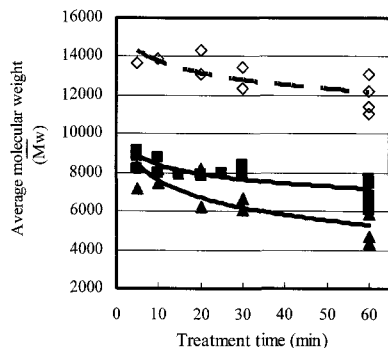

Fig. 9 Average molecular weights of lignophenols. [■:EFB, ▲:Birch, ◇:Douglas fir.]
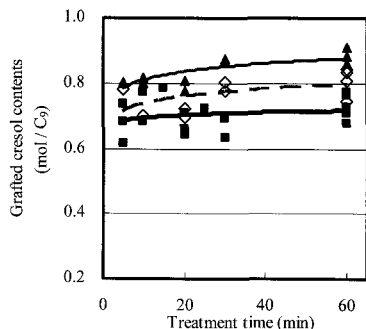

Fig. 10 Grafted cresol contents of lignophenols. [■:EFB, ▲:Birch, ◇:Douglas fir.]
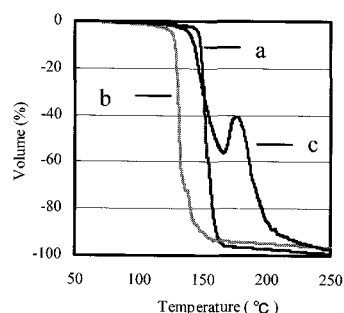

Fig. 11 TMA profiles of lignophenols. [a: EFB, b: Birch, c: Douglas fir, Phase-separation treatment time: 30 min.]
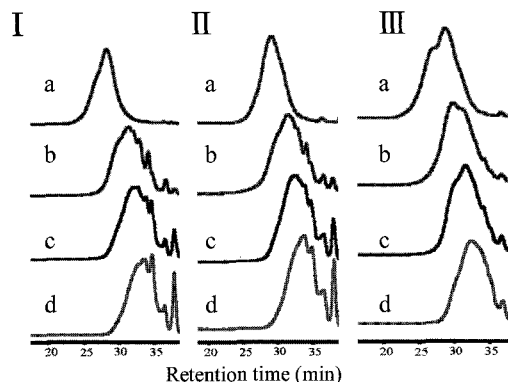

Fig. 12 GPC profiles of lignophenols and 2nd derivatives. [I : EFB, II : Birch, III: Douglas fir, Treatment temperature; a: Original (untreated), b: 120 ℃, c: 140 ℃, d: 170 ℃.]
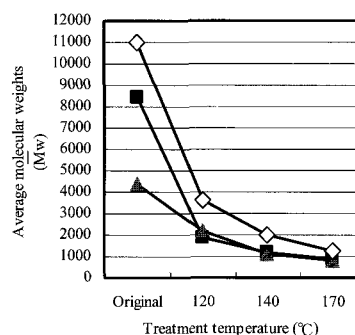

Fig. 13 Average molecular weights of lignophenols and 2nd derivatives. [■ :EFB, ▲:Birch, ◇:Douglas fir.]

Phenolic units grafted to $C\alpha$ positions work as intramolecular switching device by attacking to adjacent $C\beta$-carbon nucleophilically [5]. Each GPC pattern was shifted to right hand side with increasing treatment temperature, indicating the conversion to low molecular weight parts. Variation of average molecular weights of EFB lignophenols was the similar to hardwood lignophenols (Fig. 12, Fig. 13).

4. CONCLUSION

The native lignin and carbohydrates of EFB was converted into lignophenol and water soluble carbohydrates respectively more rapidly, compared with woody materials. The average molecular weights, amounts of grafted phenol and phase transition points of EFB lignophenols were about 8,000 (Mw), 0.7 mol/C_9, 150℃, respectively. EFB have the potential comparable to woody materials as raw materials for chemical industries.

5. REFERENCE

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