New EFB Refining System Using Structural Units of EFB Lignin

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In order to achieve sustainable conversion of lignocellulosics through the phase-separation process, p-hydroxybenzoic acid (p-HBA) attached to core lignin through ester linkage was used as a reagent for lignin conversion. During the phase-separation treatment with p-HBA, the viscosity of reaction mixture was higher, compared with the phase-separation treatment with p-cresol. By centrifugation of the reaction mixture, the thick interfacial solid materials were formed. The yields of lignophenol, its low molecular weight fraction (separated to the organic layer) and the interfacial solid fraction were about 30%, 30% and 40%, respectively. In case of phase-separation treatment with p-cresol, the yields of lignophenol and its low molecular weight fraction (separated to the organic layer) were about 73% and 27%, respectively. The peak ratio of phenol to guaiacol plus syringol in the pyrogram of lignophenol (p-HBA type) was higher than those of lignophenol (p-cresol type) and Klasson lignin. The peak of non-conjugated carbonyl group in the FT-IR spectrum of lignophenol (p-HBA type) was higher than that of the material synthesized without p-HBA. These results indicated that p-HBA was grafted to EFB lignin. The lignophenol (p-HBA type) had higher thermal stability, compared with lignophenols (p-Cresol type). The interfacial solid material between the organic and aqueous layers had higher thermal stability than sulfuric acid lignin. These results suggest the formation of lignin network through p-HBA.

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

1. INTRODUCTION

EFB (Empty Fruit Bunch, Elaeis guineensis) has been discharged from palm oil industry. The amount is 14 million tons / year [1]. The potential of EFB as industrial raw materials and the characteristics of EFB lignin have been formulated through the phase-separation system [2-3]. EFB core-lignin consists of guaiacyl and syringyl units, p-hydroxybenzoic acid (p-HBA) is linked to the side chain of EFB lignin through ester linkage. The ester linkages were hydrolyzed easily. This result shows that p-HBA can be collected from original EFB meals and EFB lignophenol (lignin derivative synthesized by the phase-separation system). In place of phenols obtained from petroleum, if p-HBA obtained from EFB itself can be used for the conversion and separation of lignin and carbohydrate, the amount of the used petroleum can be reduced.

In this study, the possibility of sustainable phase-separation system composed of p-HBA and acid was investigated.

2. EXPERIMENTAL

2.1 Preparation of alkaline treated EFB.

EFB meals (extractives-free, 80 mesh pass) were treated with 1.0 N NaOH [10 mg of lignin content / 4 mL of 1.0 N NaOH solution] under N₂ condition at 40°C for 96 hrs. After that, EFB meals were washed with hot water to pH 7 and dried at 40 °C. The alkaline treated EFB were milled by mill [Retsch, ZM 100, 60 mesh screen]. The lignin contents of alkaline treated EFB were estimated [4].

2.2 Preparations of lignin derivatives.

2.2.1 Conversion of alkaline treated EFB with p-HBA (2 step process 1).

Three mol / C₀ of p-HBA were solvated to alkaline treated EFB meals with acetone. Seventy-two wt % sulfuric acid [1g of meals / 10 mL of the acid] was added to the solvated meals and the reaction mixture was stirred vigorously. After 40 min, 10 mL of p-cresol was added. The total reaction time was 60 min. The reaction mixture was centrifuged. The organic phase was added drop wise to 250 mL of diethyl ether. The precipitate was dissolved with 80 mL of acetone. The insoluble fraction was removed by centrifugation and filtration. The soluble fraction was concentrated under reduced pressure until 10 mL. The concentrated acetone solution was added drop wise to 200 mL of diethyl ether. The insoluble fraction (1st ligno-p-HBA) was collected by centrifugation and dried with P₂O₅.

The interfacial phase (1st interfacial solid material) was added to excess deionized water and collected by centrifugation. The material was washed with deionized water until no smelling p-cresol and dried with P₂O₅. In order to remove sugars and non-polymerized lignin part of the washed material, the material was treated by 1step process of the phase-separation system composed of p-cresol and 72 wt % sulfuric acid [2]. 2nd ligno-p-HBA was separated and purified from the organic phase as described above. The 2nd interfacial solid material was separated from the interface phase as described above.

2.2.2 Conversion of alkaline treated EFB with p-cresol (1 step process).

In order to compare the roles of phenol derivatives for conversion of lignin, the alkaline treated EFB was converted by 1 step process composed of p-cresol and 72 wt % sulfuric acid. The lignophenol was separated and purified from the organic phase.

2.2.3 Conversion of alkaline treated EFB without

731
In order to compare the roles of \( p \)-HBA for lignin conversions, the alkali treated EFB was treated with 72 wt % sulfuric acid, followed by \( p \)-cresol treatment. The lignin derivative was separated and purified from the organic phase.

2.2.4 Conversion of alkali treated EFB with only 72 wt % sulfuric acid (Klason method).

In order to compare the characteristics of the polymerized materials, the EFB Klason lignin was prepared by Klason method. The remained precipitate was collected by filtration.

2.3 Analysis of lignin derivatives.

FT-IR spectra (KBr disks) of lignin derivatives were determined by Spectrum TM GX FT-IR Spectrometer (PERKIN ELMER). In order to measure molecular weight, gel permeation chromatograms of lignophenols were determined by 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 measure the compositions of lignophenols, GPC of original 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 -250°C (370°C), Flow: \( N_2 \)). TG profiles of lignophenols were determined by a Seiko Instruments Inc TG / DTA 6200 (Rate: 2°C/min, 50 -450°C, Flow: \( N_2 \)). In order to estimate the grafted \( p \)-cresol contents, \( ^1 \)H-NMR spectra of original lignophenols were determined in \( C_6D_6N-CDCl_3 \) (1/3, v/v) on a JNM-A500 FT-NMR SYSTEM and ALPHAp FT-NMR Spectrometer (JEOL, 500 MHz). 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 -250°C (370°C), Flow: \( N_2 \)). TG profiles of lignophenols were determined by a Seiko Instruments Inc TG / DTA 6200 (Rate: 2°C/min, 50 -450°C, Flow: \( N_2 \)). In order to estimate the compositions of lignophenols, lignophenols were pyrolyzed at 550°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°C/min.

2.4 Conversions of lignin derivatives by neighboring group participation reaction of grafted phenol derivatives.

Lignin derivatives (5 mg) were dissolved in 0.5 N NaOH (2 mL) and treated at 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 a 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

The viscosity of reaction mixture in the conversion with \( p \)-HBA was higher than that in the conversion with \( p \)-cresol. After centrifugation of the reaction mixture in the conversion with \( p \)-HBA, about 5 mm of the interface layer between the organic layer and aqueous layer appeared. The interfacial solid material did not disappear even after treated by 2nd phase-separation treatment. In case of the conversion with \( p \)-cresol, the centrifuge tube had a thin layer. But the layer disappeared after 80 min treatment. The yields of 1st ligno-\( p \)-HBA, 2nd ligno-\( p \)-HBA and 2nd interfacial solid material were 18.6%, 8.91% and 37.7% of alkaline treated EFB lignin (Acid insoluble lignin: 17.7%, Acid soluble lignin: 2.44%). In case of the conversion with \( p \)-cresol, the yield of lignophenol (\( p \)-cresol type) was 73.3% of the lignin. These results suggest that polymerized materials of lignin and \( p \)-HBA are formed in the conversion reaction. The amount of grafted cresol contents of 1st ligno-\( p \)-HBA and lignophenol (\( p \)-cresol type) were 14.0% and 27.4%, respectively.

The FT-IR spectrum of lignophenol (\( p \)-cresol type) from alkaline treated EFB did not have a peak of 1714 cm\(^{-1} \) assigned to ester linkages and was similar to that of hardwood lignophenol (Fig. 1). These results show that ester linkages of \( p \)-HBA and \( p \)-coumaric acid in EFB native lignin are hydrolyzed to give guaiacyl (G)-syringyl (S) type lignin. The peaks of about 1700 cm\(^{-1} \) assigned to non-conjugated carbonyl groups of lignin derivatives synthesized with \( p \)-HBA (Fig. 1, c, d, e and f) were higher than that of lignin derivative synthesized without \( p \)-HBA (Fig. 1, f). The pyrogram of 1st ligno-\( p \)-HBA mainly had the peaks of phenol, \( o \)-cresol, \( p \)-cresol guaiacol and syringol. The peak ratio of phenol for guaiacol plus syringol in the pyrogram of 1st ligno-\( p \)-HBA was higher than those of lignophenol (\( p \)-cresol type), Klason lignin and the lignin derivative synthesized without \( p \)-HBA (Fig. 2). These results indicate that \( p \)-HBA is grafted to EFB lignin at \( \alpha \)-position of \( p \)-HBA.
The TMA and TG profiles of 1st ligno-\textit{p}-HBA and lignophenol (\textit{p}-cresol type) were shown in Fig. 4. The phase transition points of 1st ligno-\textit{p}-HBA and lignophenol (\textit{p}-cresol type) were about 205 °C and 142 °C respectively. The 10% weight loss point of 1st ligno-\textit{p}-HBA and lignophenol (\textit{p}-cresol type) were about 253 °C and 224 °C, respectively. These results suggest that the amount of C-C linkage and the intermolecular interaction of 1st ligno-\textit{p}-HBA are higher than those of lignophenol (\textit{p}-cresol type). Judging from TG profile of 1st ligno-\textit{p}-HBA, the kickback around 300 °C in the TMA profile of 1st ligno-\textit{p}-HBA shows the decomposition of the molecule.
The GPC profiles and the variations of average molecular weights of 1st ligno-p-HBA and lignophenol (p-cresol type) were shown in Fig. 5 and Fig. 6, respectively. After 140°C and 170°C treatment of lignophenol (p-cresol) with 0.5 N NaOH, the molecular weight distribution was moved to right hand side with increasing treatment temperature, indicating the conversion into low molecular weight parts. In case of 1st ligno-p-HBA, the molecular weight distribution slightly changed. These results suggest that the lignin molecules are tied up by p-HBA and the network structures are formed through the phase-separation treatment.

In order to compare the characteristics of high polymerized materials, the TMA and TG profiles of 2nd interfacial material and sulfuric acid lignin were analyzed (Fig. 7 and Fig. 8). The volume of 2nd interfacial material slightly decreased with the decrease of weight. In case of sulfuric acid lignin, the volume dramatically decreased with the decrease of weight. These results suggest that as the lignin molecules are tied up by p-HBA, the degree of freedom of the lignin molecule decreases, and the amount of C-C linkage in the molecule and the intermolecular interaction increases (Fig. 9).

4. CONCLUSION
Through the phase-separation process with p-HBA, lignin / p-HBA hybrid (ligno-p-HBA) was synthesized. Lignin / p-HBA hybrids had higher thermal stabilities, compared with lignin / p-cresol hybrids, suggesting the formation of network structures through p-HBA.

5. ACKNOWLEDGEMENT
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6. REFERENCE
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