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Response of Lignophenol under High Energy Condition

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Hinoki cypress (*Chamaecyparis obtusa*) –lignophenol (*p*-cresol type, HCLC) has been directly synthesized from lignocellulosics through the phase-separation system composed of concentrated acids and phenols under mild conditions. Thermal responses of HCLC were estimated by FT-IR, GPC, UV-Vis, TMA, TG, DSC and ^{1}H-NMR. The HCLC annealed up to 180 °C have large molecular weight distribution estimated by GPC. The results showed both de-polymerization through the cleavage of unstable C_1-aryl ethers and polymerization through attacks of adjacent phenolic units to resulting reactive points on C_1 occurred in the same time on the molecules. Although an exothermal peak of HCLC was detected by DSC, HCLC annealed up to 200 °C, exothermal peaks were vanished with focusing of the M_w to about 4 000. These heat resistant materials with new conjugated structures, which were produced by eliminations of aliphatic hydroxyl groups, held recycle designs. In fact, HCLC annealed up to 300 °C, the M_w were focused to 1 000-2 500 by phenol switching under alkaline conditions at 140-170 °C. Thus annealed HCLC over 200 °C kept particular structures of lignophenol, especially both grafting *p*-cresol and C_2-*O*-aryl type linkages without random thermal decompositions.
Key words: lignin, lignophenol, annealing, thermal response, recycle

1. INTRODUCTION

Recently, biomass has attracted much attention as a substitution for fossil resources such as petroleum. Lignocellulosics are good resources for source of both phenolic and aliphatic materials. But it was impossible to separate lignin without damages because native lignin, which is an aromatic resource, has high sensitivity for change of circumstances. At the results of separation processes with high heating under high pressure, reactivity of lignin is vanished because of random polymerization. Therefore lignin has not been utilized efficiently.

In 1988, novel separation method for components of lignocellulosics under mild condition has developed by Funaoka *et al* [1]. Through the phase-separation system composed of a heterogeneous surface reaction between a concentrated acid and a phenol analog, lignocellulosics is easily converted to carbohydrates in acid and phenolic lignin-based polymers (lignophenols) under 1 atm at room temperature (Fig.1) [1-3]. Lignophenols has 1,1-bis(aryl)propane-2-*O*-arylether type structures. This structure has switching functionality by hydroxyl groups on *ortho*-positions of phenols. By switching functionality, both arylcoumaran type structures (second derivative-I) and stylbene type structures (second derivative-II) were formed by neighboring group participation and aryl migration under alkaline conditions, respectively (Fig.1) [4-5].

The information for thermal responses is important for stabilities of products and efficiencies for molds. Although thermal responses of lignin have been discussed on only industrial lignins, the ones of lignophenol have not been estimated sufficiently. To investigate the thermal responses of lignophenol, characteristics of lignophenol annealed under N_2 flow were estimated by GPC, ^{1}H-NMR, UV-Vis, FT-IR, TMA, DSC and TG.

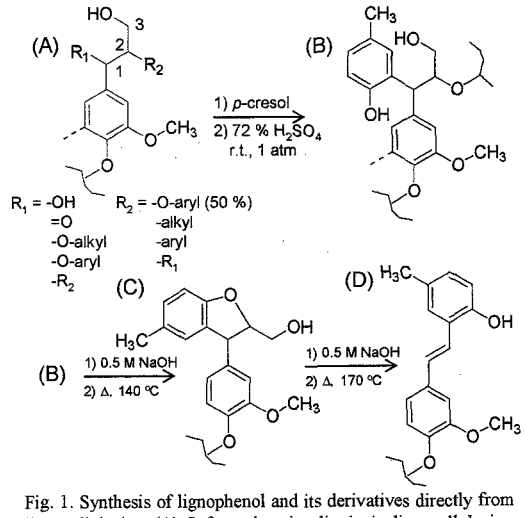

Fig. 1. Synthesis of lignophenol and its derivatives directly from lignocellulosics. (A) Softwood native lignin in lignocellulosics, (B) lignophenols (*p*-cresol type), (C)second derivative-I after neiboring group participation (phenol switching) and (D) second derivative-II after aryl migration.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols

Hinoki cypress (HC, *Chamaecyparis obtusa*) was selected as softwood (gymnosperm) material for the phase-separation system. The woody material was milled for 80 mesh passed. Extractives in the materials were removed by benzene / ethanol = 2 / 1 (v/v) with Soxhlet system for 72 hrs. Hinoki cypress-lignophenol (*p*-cresol type, HCLC) has been synthesized following the phase-separation system (Fig.1), using two-step method (process II) [4]. The material (500 g) was

thrown into acetone solution of *p*-cresol with concentration of 3 mol / phenylpropane units (C_9 units), which were subunits of native lignin. After evaporating acetone, 72 % H_2SO_4 aq. solution was immersed into the material adsorbed by *p*-cresol at 30 °C. Then the mixture was stirred vigorously for 60 min soon after mixing. After 60 min, the mixture was thrown into 20 L of de-ionized water with vigorously stirring by a homogenizer for 5 min. Then the purple precipitation was washed until pH = 5. After drying the precipitation, lignophenol was extracted by acetone. The lignophenol in acetone was refined by thrown into diethyl ether (EtOEt) under vigorously stirring in chilled conditions. After evaporating and drying on P_2O_5, HCLC was obtained.

2.2 Characterization of lignophenols

The structure of lignophenol was characterized by Gel Permeation Chromatography (GPC), ^{1}H-NMR and Thermo mechanical Analysis (TMA). GPC was carried out by LC-10 system (Shimadzu Co.) with four columns (KF801, KF802, KF803 and KF804, Shodex Co.), using tetrahydrofuran (THF) after distillation as eluent. M_w and M_n were determined based on standard polystyrene. ^{1}H-NMR spectrum was measured by JNM-A500 (JEOL Co.) in $CDCl_3$ or $CDCl_3$ / C_5D_5N = 3 / 1 (v / v). TMA was also carried out by TMA-SS (SII Inc.) in the temperature range 50-280 °C at a rate of 2 °Cmin^{-1}, using penetrating technique for a measurement. UV-Vis spectroscopy was carried out on a UV-560 (JASCO Co.). Ionization difference spectrum was measured by methylcellosolve and NaOH solutions. FT-IR spectroscopy was also carried out on a Spectrum GX (Perkin Elmer Co.), using the KBr pellet technique for sample preparation. Differential Scanning Calorimetry (DSC) analysis was carried out using DSC-60 (Shimadzu Co.) in 5 mmϕ Al pan and Al lid under 50 mLmin^{-1} of N_2 flow. Measurement was achieved at a rate 2 °Cmin^{-1}. Thermogravimetry (TG) was carried out TG/DTA-6200 (SII Inc.) at a rate 2 °Cmin^{-1} under 300 mLmin^{-1} of N_2 flow.

2.3 Annealing of lignophenol

Annealing of HCLC was carried out under 150 mLmin^{-1} of N_2 stream. HCLC was annealed at 2 °Cmin^{-1}to determined temperatures.

2.4 Functionality control

Second derivative-I of HCLC was synthesized in a 0.5 M NaOH solution at 140 °C in a SUS autoclave. After 1 hr, the reaction mixture was neutralized by 1.0 M HCl to pH = 2.0. The insoluble moiety was washed by chilled de-ionized water for two times. The product was dried on P_2O_5. Second derivative-II of HCLC was synthesized in the same way except reaction temperature. Derivative-II was derived at 170 °C

3. RESULTS AND DISCUSSION

3.1 Molecular size after annealing

Fig.2 illustrated GPC profiles of HCLC after 180-300 °C annealing. Both decrease and increase of M_w was observed in the same time for only HCLC heated up to 180 °C. Decrease of M_w indicated that C_1-*O*-arylether type structures cleft. The structures were reactive points

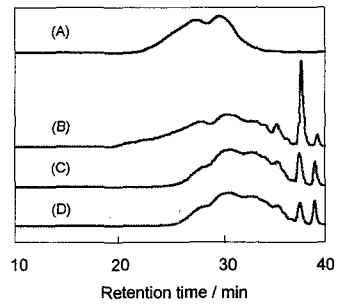

Fig. 2 Profiles of gel permeation chromatography for lignophenols. (A) Hinoki cypress-lignophenol (*p*-cresol type, HCLC), M_w = 24 100, (B) HCLC annealed up to 180 °C, M_w = 45 816, (C) up to 200 °C, M_w = 4 049 and (D) up to 230 °C, M_w = 4 377. Measurements were carried out by Shodex KF801, KF802, KF803 and KF804 columns, THF as eluent with standard polystylene as reference.

of native lignin. Because solid-liquid transition temperature of HCLC was 174.5 °C measured by TMA, the reactions were occurred by mobilizations of molecules. Although 70 % of the reactive sites were reacted by grafting of *p*-cresol through the phase-separation system, 30 % was remained in the structures of HCLC. In fact, a ratio of grafting *p*-cresol of HCLC was 72.0 % estimated by ^{1}H-NMR. Since annealed HCLC at both 200 and 230 °C kept the peak 30 min in Fig.2(C) and (D) respectively, main structures of HCLC, which were C2-*O*-aryl type linkages, were stored. Therefore cleavages of C_1-*O*-arylethers were easily occurred when HCLC was annealed over melting temperature without destroying C2-*O*-aryl main chains. Because C2-*O*-aryl type linkages were interunit-linkages of native lignin, which produced three-dimensional structures, the cleavages led to decreases of molecular sizes. However, reactive carbocations on C_1 were produced after cleavages of C_1-*O*-arylether linkages. If nucleophillic moieties such as hydroxyl groups existed near the cations, new ether type linkages on C_1 were occurred (Fig.3). Probably lone pairs of oxygen atoms of phenolic hydroxyl groups, aliphatic hydroxyl groups, methoxyl groups and ether type structures reacted in these ways. But resulting linkages also cleft in the same ways. This reversible system was observed at 180 °C. Therefore under higher energy conditions, only decreases of M_w were shown by HCLC heated over 200 °C (Fig.2C, D). Under higher energy conditions, de-polymerizations were prior to nucleophillic polymerization. Interestingly, M_w of HCLC approached to 4 000. In the production process of native lignin in plant cells, native lignin was formed by radical coupling

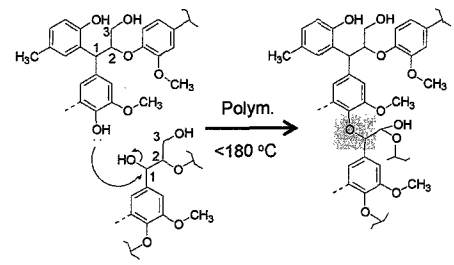

Fig. 3 A schematic model for production of C_1-*O*-arylether linkage by annealing under N_2 up to 180 °C.

of precursors of lignin such as coniferyl alcohol to polymers consisted of about 14 monomers with M_w = 4 000. This result implies that the stable moieties of lignin in lignophenol are stored after annealing by blocking reactive benzyl positions by grafting phenols.

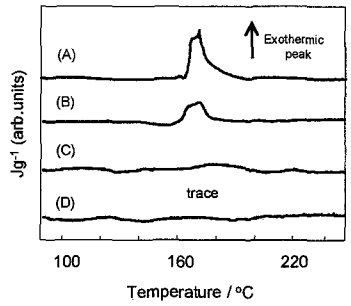

Fig. 4 Profiles of Differential scanning carolimetry for lignophenols. (A) Hinoki cypress-lignophenol (p-cresol type, HCLC), (B) HCLC, annealed up to 180 °C, (C) up to 200 °C and (D) up to 230 °C. Measurements were carried out under N_2 at heat rates 2 °Cmin^{-1}.

3.2 Thermal properties of lignophenol

As demonstrated in Fig.4, exothermal peaks of DSC were observed at 171 °C in both HCLC without annealing and HCLC heated up to 180 °C. But these peaks have not been observed after annealing over 200 °C. This indicated that reactive sites were exhausted over 200 °C perfectly. According to previous studies on DSC analysis on industrial lignins, exothermal peaks were not shown [6-8]. This indicated reactive benzyl positions of native lignin were exhausted after separation from lignocellulosics under high temperature and high pressure. On the other hand, the reactive points remained in lignophenol after preparation, the exothermal peaks are observed. Generally, the exothermal peaks of biomaterials, such as protein or nucleothides, showed decompositions of the structures. But lignophenol, on the contrary, obtained thermal stability after annealing.

Fig.5 showed TG curves for HCLC. Both 5 % and 10 % weight losses were observed at 161 °C and 240 °C, respectively. In contrast, HCLC heated over 230 °C showed 200 °C and 270 °C, respectively. Because of vanishing of reactive sites, C_1-*O*-arylether linkages, thermal stability was improved by rearrangements after annealing in spite of biomaterials, which are generally

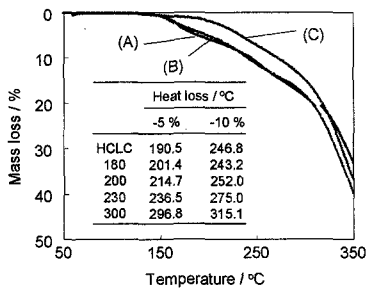

Fig. 5 Profiles of thermal gravity analysis for lignophenols. (A) Hinoki cypress-lignophenol (*p*-cresol type, HCLC), (B) HCLC annealed up to 180 °C and (C) up to 230 °C. Measurements were carried out under N_2 at rate 2 °C.(inset) Table of both 5 % and 10 % heat loss after annealing at 180, 200, 230 and 300 °C.

weak for heat.

After annealing, high solubility of HCLC was stored. Therefore these thermal resistance materials will be modified or utilized easily.

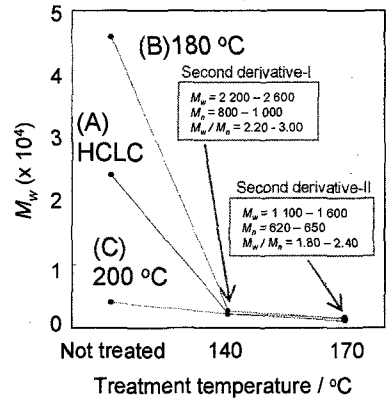

Fig. 6 Changes of average molecular weights of HCLC estimated by GPC. (A)HCLC, (B) HCLC annealed at 180 °C and (C) HCLC annealed at 200 °C. Second derivative-I and II were synthesized in alkaline media at 140 and 170 °C, respectively.

3.3 Functionality control after annealing

Fig.6 showed variation of M_w after functionality controls with switching devices in HCLC molecules. These results implied that C_2-*O*-arylether type structures, which were main linkages of HCLC, were kept after annealing over 200 °C.

These results implied that both grafted *p*-cresol and main chains of HCLC have not been destroyed over 200 °C. Because the switching functionality of lignophenols acts by nucleophollic attacks by only phenolate oxygens on *ortho*-positioned on C_1 under alkaline media, Fig.6 showed these mechanisms were stored in annealed HCLC. Therefore HCLC kept particular sustainability and recyclability of lignophenol after annealing.

3.4 New conjugated system

The spectrum of acetylated HCLC (Fig.7A) showed characteristic peaks for acetyl groups at 1763 cm^{-1} and 1742 cm^{-1}. These two peaks corresponded to phenolic and aliphatic esters of HCLC, respectively. In fact, the

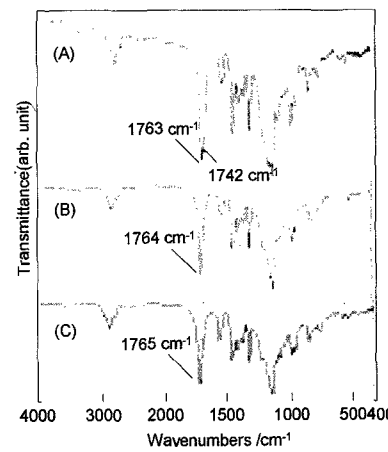

Fig. 7 FT-IR spectra of Hinoki cypress-lignophenol(*p*-cresol type, HCLC). (A)HCLC, (B)HCLC annealed to 180 °C under N_2 and (C)HCLC annealed to 200 °C.

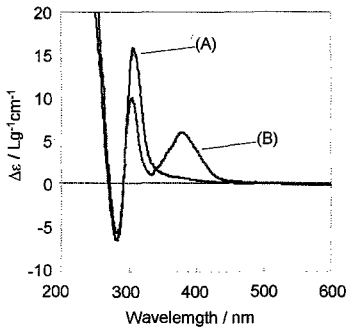

Fig. 8 Differential ionization spectra for lignophenols between neutral condition (2-methoxyethanol) and alkaline condition (2-methoxyethanol / NaOH) . (A) Hinoki cypress-lignophenol (*p*-cresol type, HCLC) and (B) HCLC, annealed up to 200 °C.

amounts of phenolic and aliphatic hydroxyl groups were 1.05 and 0.84 mol/C_9 estimated using ^{1}H-NMR, respectively. However the peaks of phenolic esters were observed with same intensities in HCLC after annealing (Fig.7B and 7C), aliphatic esters gradually decreased according to rise of temperature. This indicates that the aliphatic hydroxyl group with the C_3 carbon (Fig.1B) was released after annealing over 180 °C. Moreover, other structures of HCLC were damaged slightly as shown in Fig.7. Main structures of HCLC has not been destroyed at random because same spectra based on ether type linkages (1100-1300 cm^{-1}), hydroxyl groups and grafting *p*-cresol (800-820 cm^{-1}) were observed. Therefore drastic structural rearrangements were occurred on aliphatic moieties of lignin core units without decomposition of main structures.

Fig.8 illustrated ionization difference spectra for HCLC between neutral condition and alkaline condition. In addition to the results of FT-IR, variations of structural properties on electrons were observed.

Although only production of phenoxide ion was observed for HCLC, the electronic absorbance spectrum was varied in two ways after annealing up to 200 °C.

First, decrease of phenoxide ions at λ = 320 nm with blue shifts. This shows new conjugated structures produced after annealing. Although the ratio of phenolic hydroxyl groups for HCLC annealed up to 200 °C (9.5 wt%) is larger than HCLC (6.4 wt%) estimated by ^{1}H-NMR, the coefficient of absorbance of the annealed HCLC is smaller than HCLC in contrast. This indicates that configurations of electrons on the phenolic hydroxyl groups varied after ionization.

Second, increase of absorbance at λ = 375 nm. This increase of peaks depends on alkenyl type structures such as stylylarylether type structures (Fig.9). These C_2-enol aryl ether type structures were well discussed in pulping processes [9-12]. According to Gierer *et al*, these arrangements occurred without Na_2S [13]. These enol aryl ether type structures were produced by the removal of the C_3 aliphatic hydroxyl groups. These enol aryl ether structures link to C_1 positions stabilize both grafting phenols and lignin core units by new conjugation, quinoid type structures will increase. In consequence, the amounts of phenoxide ion in alkaline conditions decreased.

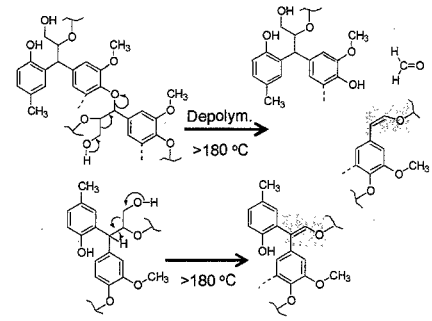

Fig. 9 Proposal mechanisms for rearrangements by eliminations of C3-aliphatic hydroxyl groups after annealing over 180 °C.

4. CONCLUSION

HCLC obtained thermal stability after annealing over 180 °C, because of exhausting reactive benzyl positions remained through the preparation. Thermal stability was confirmed by DSC and TG. The average molecular weights decreased with focusing to 4 000. The annealed HCLC kept phenolic moiety in the molecule with switching functionality for recycle. New conjugated structures produced by elimination of aliphatic hydroxyl groups. Since resulting HCLC annealed over 180 °C have both phenolic properties and thermal stabilities without destroying main chains of HCLC, the materials were expected to be applied to precursors for new stable materials.

5. REFERENCES

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