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Selective Phenolation of Lignins Using Cellulose Supports for Functionality Control

Mitsuru Aoyagi, Satoko Yonekura and Masamitsu Funaoka
Graduate School of Bioresources, Mie University, Japan Science and Technology Agency (JST), Solution Oriented Research of Science and Technology (SORST)
Fax: +81-59-231-9517, e-mail: aoyagi@bio.mie-u.ac.jp

Hinoki cypress (*Chamaecyparis obtusa*)-lignophenol(*p*-cresol type, LC1) has been directly synthesized from milled wood of Hinoki cypress through the phase-separation system, which was surface reaction of lignocellulosics between concentrated acid and phenol under mild conditions. As resulting lignophenol has rich phenolic hydroxyl groups by grafted phenols, various derivatives were easily designed from lignophenol. Second phenolation for hydroxymethylated LC1(HM-LC1) by the phase-separation system were not carried out sufficiently because of aggregations in aqueous media such as acids. But with cellulose supports for HM-LC1, aggregations were physically restricted and reactions occurred on the surfaces of HM-LC1. Moreover sufficient reactions on un-reacted parts of HM-LC1 interacted with supports were also carried out after hydrolysis of celluloses. By these second phenolations of lignophenol with cellulose supports in acidic media, second phenolated LC (LC2) was obtained with high yield over 95 %. Using this technique, new developing molecular designs such as controls of network density keeping recycling switches are expected.
Key words: lignin, lignophenol, phenolation, reaction support, heterogeneous reaction

1. INTRODUCTION

Lignophenol has been synthesized through the phase-separation system, which is composed of the surface reaction between concentrated acid and phenol, directly from native lignin in lignocellulosics (Fig.1). lignophenol has 1,1-bis(aryl)propane-2-*O*-arylether type structures with the latent phenolic activity (arylether type linkages) based on native lignin. Although native lignin has slight amounts of phenolic hydroxyl groups, lignophenol has a lot of ones based on grafted phenols. Particular characteristics of lignophenol will be deeply influenced by grafted phenols. Therefore it is possible to synthesize a new lignophenol which is suitable to purposes [1-5].

In addition to selection of the first grafting phenols, it can be modified the characteristics of lignophenol by combination of second phenol to other lignophenol as a basic material through the phase-separation system. Due to the second phenolation of lignophenol various new properties such as recyclability or intermolecular network will be developed.

The phenolations for technical lignins have been tried but the treatments were achieved under high energy conditions under heterogeneous media to increase efficiencies of reactions [6-8]. But it is important to be treated under mild conditions to keep recyclability and activity of native lignin because active sites are delicate for variations of circumstances.

Since lignophenol was easily dissolved in acetone, THF, DMF and NaOHaq., homogeneous reactions such as acetylation, hydroxymethylation and epoxylation will be carried out easily. However, lignophenol with grafting especially a hydrophobic phenol aggregated in an aqueous medium, for example. In consequence, phenolation was only occurred at the surface of aggregations in this heterogeneous reaction phase. To prevent from decrease of reaction efficiencies, cellulose supports were tried to use. In the process of synthesis, cellulose support is expected to act in two ways, (1) to restrict aggregation and (2) to keep reaction surface.

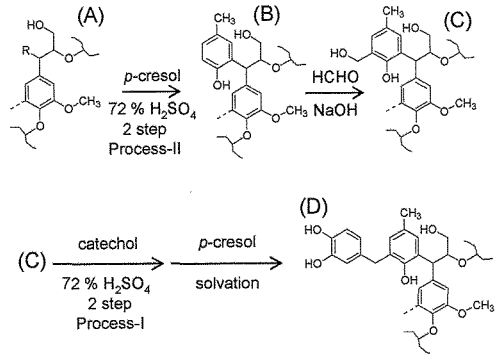

Fig.1 Schematic model for modification of lignin. (A)Native lignin, (B) softwood lignophenol (*p*-cresol type, LP1) synthesized through the phase-separation system, two step method, process-II, (C) hydroxymethylated LP(HM-LP) and (D) LP grafted catechol (LP2) through the phase-separation system, two step method, process-I.

Generally, hydroxymethylated (HM)-lignophenol are used as precursors for phenolic resin of resol type. But the benzyl positions of HM-lignophenol will act as reactive points for phenol grafting through the phase-separation reaction.

Here, cellulose support for lignophenol to resistance for aggregation was used for second phase-separation treatment. The characteristics of resulting lignophenol were estimated.

2. EXPERIMENTAL

2.1 Synthesis of lignophenols

Hinoki cypress (*Chamaecyparis obtusa*) was used as a softwood material for the phase-separation system. The woody material was milled for 80 mesh passed.

Extractives in the material were removed by acetone at room temperature for 72 hrs. The milled wood (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 determined by Klason method. After evaporation of acetone, 72 % H_2SO_4 aq. solution was immersed into the material adsorbed with *p*-cresol at 30 °C. Then the mixture was stirred vigorously for 60 min soon after mixing. After 60 min, the reaction 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, the mixture was extracted by acetone. The lignophenol in acetone was refined by thrown into diethyl ether (EtOEt) under vigorously stirring at 0 °C. After evaporating and drying on P_2O_5, Hinoki cypress-lignophenol (*p*-cresol type, LC1) was obtained (Fig.1B) [3-4].

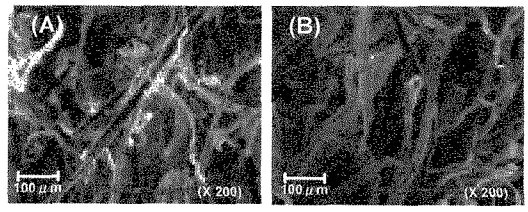

Fig.2 SEM images for kraft pulp. (A) Beaten bulp with freeness 100 and (B) freeness 400.

2.2 Preparation of vanishing reaction support

Kraft pulp was dispersed in de-ionized water. The suspension was beaten to freeness 100, 400, 600, 700 estimated using Canadian freeness-tester. After drying on the P_2O_5, BET surface area was measured by Surface Area and Poresize Analyzer NOVA 4200e (Quantachrome Inc.).

2.3 Synthesis of derivatives

Hydroxymethylated lignophenol (HM-LC1) was synthesized in 0.5 M NaOH solution by mixing 20 mol of formaldehyde for a amount of aromatic rings in lignophenol at 60 °C under N_2 atomosphere with a stirring system and a reflux condenser. After 3 hrs reaction, 1.0 M HCl was dropped into the mixture at 5 °C to pH = 2.0. The resulting precipitation was washed to pH = 5.0. After the insoluble residue was dried over P_2O_5, HM-LP was obtained (Fig.1C). Acetylated lignophenol was synthesized in 1.0 mL of pyridine with 1.0 mL of acetic anhydride under room temperature. After 48 hrs, the reaction mixture was dropped into chilled de-ionized water under stirring. The resulting precipitation was washed once by chilled water. After drying on P_2O_5, acetylated lignophenol was obtained.

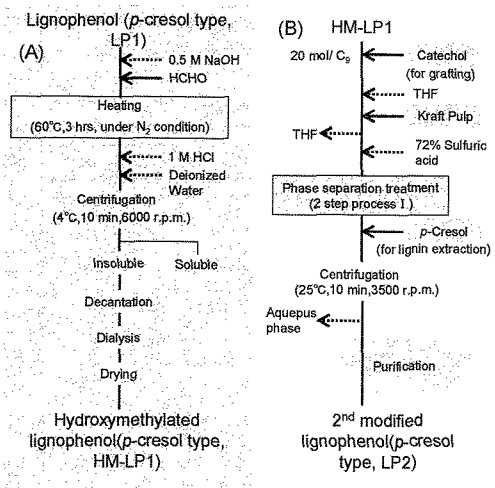

Fig.3 Synthesis flow of (A) hydroxymethylated lignophenol (*p*-cresol type, HM-LP1) and (B) second modified lignophenol (*p*-cresol type, LP2) through the phase-separation system, 2step method with process-I.

2.4 Second phenol grafting

Second phenol grafting lignophenol (*p*-cresol type, LC2) was synthesized from HM-LC1 with or without reaction supports through the phase-separation system (Two-step method, process-I, Fig.3). HM-LC1 (0.15 g) and catechol (1.05 g) were adsorbed on 1.50 g of dry Kraft pulp (freeness 100, 400, 600 and 700) in 35.0 mL of THF. After evaporation of THF the resulting compound was reacted through the phase-separation system (2 step method, process-I) with 20.0 mL of 72 % H_2SO_4 under 30 °C. After 30 min, 20.0 mL of *p*-cresol was added to the reaction mixture as an extracting solvent under stirring. After 20 min, the organic layer and aqueous layer were separated by centrifugation (3 500 rpm). The organic layer was washed by EtOEt. Insoluble moiety was refined in the same way as LC1. After evaporation and dry on P_2O_5, lignophenol, the second phenol grafted (LC2) was obtained (Fig.1D).

2.5Characterization of lignophenols

The structure of LC was characterized by Gel Permeation Chromatography (GPC), ^{1}H-NMR and Thermal Mechanical Analysis (TMA). GPC was carried out by LC-10 (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 increase of 2 °Cmin^{-1}, using penetrating technique for a measurement. UV-Vis spectroscopy was carried out on an UV-560 (JASCO Co.). FT-IR spectroscopy was also carried out on a Spectrum GX (Perkin Elmer Co.), using the KBr pellet technique for sample preparation.

3 RESULTS AND DISCUSSION

3.1 Effect of reaction supports

After second phenol grafting for HM-LC1 through the phase-separation system, LC2 was obtained with high yield with reaction support of Kraft pulp. The yields were over 95 % based on HM-LC1 because aggregation of HM-LC1 has not occurred in acidic medium (Fig.4).

Table I Relationship between freeness and BET surface area.

freeness	surface area (m^2/g)
100	4.2
400	2.1
600	1.3
700	0.9

This result indicated the reaction supports prevented from aggregation efficiently. Moreover, the resulting LC2 was perfectly dissolved into *p*-cresol. Since the insoluble residue was important indicator for aggregation, this result supported effectiveness of reaction support under heterogeneous condition.

As shown in Table I, the BET surface area of freeness100 is over 4 times than freeness700. But no correlation between the yield and freeness of Kraft pulp was observed. The difference in yield was only within 3.6 %. This result implied that structures of pulp related to freeness are larger scale than lignophenol. Therefore, hydrolysis was not rate-determining step because of high yields of LC2 and fast hydrolysis of cellulose.

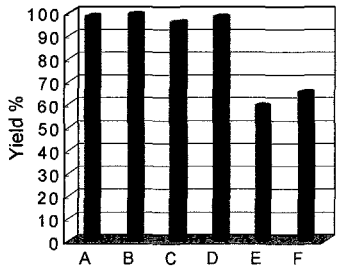

Fig.4 Yields for second grafting reactions for hydroxymethylated Hinoki cypress-lignophenol (*p*-cresol type, HM-LC1). The grafting phenol was catechol. A: with reaction support of pulp with freeness 100, B: freeness 400, C: freeness 600, D: freeness 700, E: Without spreading reaction mixtures in THF and F: without supports.

In contrast, without reaction support, LC2 was synthesized with only 60 % of yield (Fig.4F). Since aggregation was occurred by immersing into acidic media, efficient phenol grafting was not proceeded because reaction area was decreased. In fact, observation confirmed that insoluble moiety for *p*-cresol was produced after reaction. Similar result was obtained by insufficient mixing HM-LC1, catechol and Kraft pulp without THF (Fig4E). This indicated that homogeneous composites of these components are needed for efficient reaction.

3.2 Average molecular weight

Average molecular weights (M_w) of LC1 and HM-LC1 were 21 631 and 19 812, respectively (Fig.5). With reaction supports, M_w increased for 20 %. These results

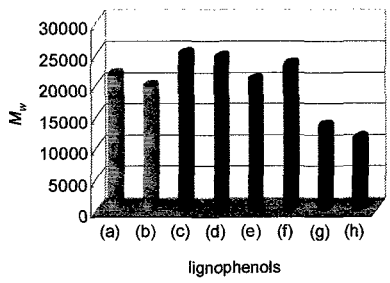

Fig.5 Avarage molecular weight of lignophenols estimated by GPC. (a)LC1, (b)HM-LC1, (c)LC2 with pulp of freeness100, (d)LC2 with freeness400, (e)LC2 with freeness600, (f) LC2 with freeness700, (g)LC2 with freeness 100 mixed by bulk and (h) LC2 without cellulose support. GPC analysis was carried out in THF using polystylene standards at 40 °C, 1.0 mLmin^{-1}.

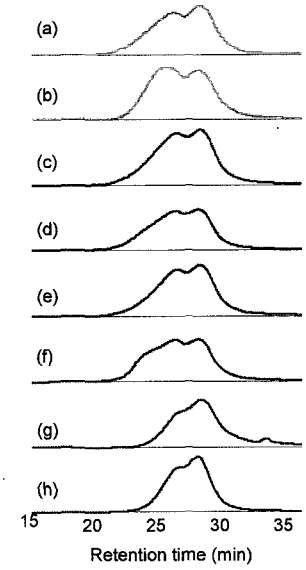

Fig.6 GPC profiles for lignophenols. (a)LC1, (b)HM-LC1, (c)LC2 with pulp of freeness100, (d)LC2 with freeness400, (e)LC2 with freeness600, (f) LC2 with freeness700, (g)LC2 with freeness 100 mixed by bulk and (h) LC2 without cellulose support. GPC analysis was carried out in THF using polystylene standards at 40 °C, 1.0 mLmin^{-1}.

indicated that both aggregation and polymerization were not occurred through the phase-separation system. Although no influences of freeness also were reflected on M_w, increases of dispersion ratio (M_w/M_n) were observed (Fig.6). As demonstrated in Fig.6, profiles of LC2 with cellulose supports were similar to LC1 with slight increases of high molecular fractions. Accordingly, LC2 with catechol was obtained sufficiently. However, high molecular weight was observed in the profile of LC2 with high freeness pulp (Fig.6f). These results implied polymerizations with acid catalyst partly occurred because small rates of hydrolysis with small surfaces for reactions. Therefore the effective grafting was expected with low freeness with large surface area (Table1). In contrast, M_w of LC2 without support decreased because polymeric regions were removed in the process of refinery by solvents. In fact, observations of insoluble moieties for THF confirmed that random polymerizations and high aggregations in acidic medium.

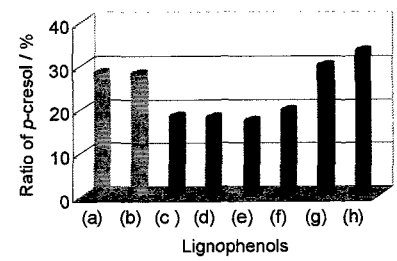

Fig.7 Ratio of *p*-cresol in lignophenols estimated by ^{1}H-NMR. (a)LC1, (b)HM-LC1, (c)LC2 with pulp of freeness100, (d)LC2 with freeness400, (e)LC2 with freeness600, (f) LC2 with freeness700, (g)LC2 with freeness 100 mixed by bulk and (h) LC2 without cellulose support.

3.3 Phenol contents

Fig.7 illustrated ratio of *p*-cresol in lignophenol molecules. LC1 and HM-LC1 showed same ratio of *p*-cresol. But the ratios for LP2 were decreased to 15 % because catechol was grafted efficiently. Because the amounts of catechol were same in freeness 100 to 700, no correlations were observed differences of pulp freeness. Since total weight of LC2 with support was increased due to catechol, ratios of *p*-cresol relatively decreased. Since after reaction most of active points in HM-LC1 were used, only few secondary *p*-cresols have been grafted. Therefore the ratios decreased from HM-LC1. On the other hand, the ratio for LC2 without support increased compared to both LC1 and HM-LC1, because *p*-cresol, which was added as extracting solvent, was grafted into HM-LC1. By aggregation only the surfaces of HM-LC1 were treated by catechol. But after dissolving by *p*-cresol, a part of aggregation was released into the solvent with high affinity. Since un-reacted active sites were solvated by *p*-cresol, the phase-separation treatment was occurred on the surface. Moreover, *p*-cresol was reacted frequently because the concentration of *p*-cresol was much larger than catechol. In consequence, the ratio of *p*-cresol increased after addition of *p*-cresol.

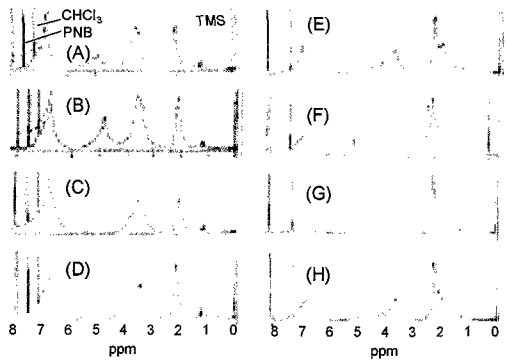

Fig.8 ^{1}H-NMR spectra for lignophenols and acehylated lignophenols. (A)LC1, (B)HM-LC1, (C)LC2 with pulp of freeness100, (D)LC2 without support, (E)acethylated LC1(A-LC1), (F) A-HM-LC1, (G)A-LC2 with freeness 100 and (H) A-LC2 without support.

3.4 ^{1}H-NMR analysis

Fig.8 illustrated ^{1}H-NMR spectra of lignophenols and acetylated lignophenols. By comparison of these spectra based on signal of methoxyl proton (3.5 ppm), variations of both *p*-cresol and catechol were estimated at aromatic methyl proton (2.1 ppm) and phenolic acetyl proton (2.3 ppm), respectively. The ratio for signal of *p*-cresol over methoxyl groups, HM-LC1 was equal to LC1. The ratios of LC2 with support and of LC2 without support decreased and increased, respectively (Fig.8A-D). Moreover, amounts of phenolic acetoxyl proton of LC2 with support increased for LC1. This result simply indicated that the amounts of phenolic hydroxyl groups increased by grafting of only catechol (Fig.8G). Although spectrum of LC2 without support corresponded to only soluble moieties, these fractions were sufficiently treated by secondary phenolation with both catechol and *p*-cresol.

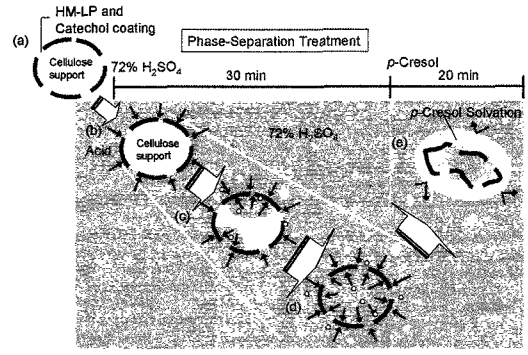

Fig.9 A schematic model for second phenol grafting reaction through the phase-separation system. (a) HM-LP1 and catecohl coated honogeneously, (b) reactions occurred at the surface, (c) gradual hydrolysis, (d) increase of reaction surface after hydrolysis and (e) solvation by *p*-cresol.

3.5 Principle of reaction

As shown in Fig.9, the second phenol grafting reaction was carried out by following the mechanism with increase of reaction surface with restriction of aggregation and hydrolysis of cellulose. Since HM-LC1 was composed in framework structures of pulps under homogeneous condition in THF, HM-LC1/pulp system is mimicked for lignocellulosics. Because of no influence for reaction rate and pulp freeness, it seems that interactions of lignophenol and pulp are mainly C_3-OH on C_9 units, the predominant aliphatic hydroxyl groups. Therefore fast reaction step of phenol grafting will be occurred. Since the phase-separation system has been carried out under aqueous condition, cellulose was gradually hydrolyzed.

4 CONCLUSION

By using vanishing support, secondary phenolations of lignophenols were easily succeeded with both high yields and high selectivity. For example, lignophenol (catechol type) was derived from HM-LC1 with 95 % of yield in spite of low yield about 10 % from lignocellulosics through the phase-separation system with 95 % H_3PO_4. This principle for heterogeneous reactions is expected to be adapted for other chemical synthesis.

5 REFERENCES

[1]M. Funaoka and I. Abe, *Tappi.*, 72(8), 145-149 (1989).
[2]M. Funaoka, M. Matsubara, N. Seki, S. Fukatsu, Biotechnology and Bioengineering, 46, 545-552(1995)
[3]M. Funaoka, S. Fukatsu, Holzforshung, 50, 245-257(1996)
[4]M. Funaoka, *Polym. Int.*, 47, 277-290(1998)
[5]M. Funaoka, *Macromol. Symp.*, 201, 213-221(2003)
[6]M. V. Alonso, M. Oliet, F. Rodriguez, J. Garcia, M. A. Gilarranz, J. J. Rodiguez, *Bioresource Technology*, 96, 1013-1018(2005), phenolation SA
[7]Y. Matsushita, M. Imai, T. Tamura, K. Fukushima, *J. Appl. Polym. Sci.*, 98, 2508-2513(2005), phenolation, acid
[8]M. V. Alonso, J. J. Rodiguez, M. Oliet, F. Rodriguez, J. Garcia, M. A. Gilarranz, *J. Appl. Polym. Sci.*, 82, 2661-2668(2001)

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