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Stable Oligomer Formation from Lignin by Pyrolysis of Softwood in an Aprotic Solvent with a Hydrogen Donor

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Pyrolysis of Japanese cedar wood in diphenoxybenzene (an aprotic solvent) with a hydrogen donor was investigated between 270–380 °C. Under these conditions, re-condensation via radical and quinone methide intermediates was efficiently suppressed and a thermally stable oligomer was obtained. The oligomer was stable even after the treatment time was extended. Yields of lignin-derived products at 270 °C were limited to approximately 20 wt%, but increased to >80 wt% (lignin basis) at the higher temperatures. The oligomer yield increased directly with the extent of the cellulose degradation at 350 °C. Based on the NMR analysis results, the ether bonds in lignin were largely cleaved, but condensed linkages such as β-aryl and β-β and 5-5′ types remained. The γ-hydroxypropyl group was identified as a typical side chain, formed by hydrogenation of the double bond of a coniferyl alcohol-type structure.

Introduction

Lignin is an amorphous aromatic polymer composed of phenylpropane units linked by ether (C–O) and condensed (C–C) bonds. There are three types of aromatic nuclei in phenylpropane units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S). The proportions of these units vary with the plant species. Japanese cedar (*Cryptomeria japonica*), a softwood, contains almost only G-type units. Because lignin accounts for 20–35% of lignocellulosic biomass, it could be used as a renewable resource for the production of aromatic chemicals. However, it is difficult to do this because of the lack of an efficient conversion process for lignin. Pyrolysis is a promising way to convert lignin.

Ether bonds, such as α-*O*-4 and β-*O*-4, are easily cleaved at approximately 350 °C, where efficient devolatilization of lignin occurs. By contrast, condensed bonds, such as β-aryl, β-β, and 5-5′ linkages, are stable against depolymerization of lignin macromolecules.[1,2] Because the content of ether bonds is generally greater than that of condensed bonds, lignin is expected to be largely depolymerized at 350 °C. However, the yield of depolymerization products from lignin pyrolysis is generally much lower than expected, and solid char is the main product.[3,4] This can be explained by the high re-condensation reactivity of the pyrolysis products.

Investigations using lignin model compounds are effective for clarifying the molecular mechanisms of the cleavage of lignin ether bonds and the subsequent re-condensation. The effects of aromatic substituents, introduced at the *para* position of the ether oxygen of model dimers and trimers, clearly indicate heterolysis and homolysis mechanisms for α-*O*-4 type bonds in phenolic terminal and non-phenolic intermediate units, respectively.[5] The β-*O*-4 type linkages are cleaved homolytically, but the reactivity depends on the chemical structure of the model dimer.[6] Reactivity differences have been explained with a quinone methide pathway[7] and radical chain[7,8] mechanisms as proposed for the homolytic cleavage of the β-ether bonds. The resulting radical species polymerize by the radical coupling mechanism.

With the abstraction of hydrogen, radical species resulting from the cleavage of the ether bonds are stabilized as phenols such as coniferyl alcohol [3-(4-hydroxy-3-methoxyphenyl)-2-propen-1-ol]. However, coniferyl alcohol is unstable above 250 °C, where it efficiently re-condenses and eventually converts to char.[9] Therefore, the yield of coniferyl alcohol is low in lignin pyrolysis. A quinone methide mechanism has been proposed for the condensation.[10] Compounds with a conjugated C=C double bond at the *para* position to the phenolic OH group tend to condense by a similar mechanism. Along with the condensation, the side chain of coniferyl alcohol is converted to produce various compounds such as coniferyl aldehyde, dihydroconiferyl alcohol, isoeugenol, and vinyl guaiacol.[9]

As a method of suppressing the two polymerization mechanisms, Kotake et al. proposed pyrolysis with aprotic solvents and hydrogen (H) donors.[11,12] Quinone methide formation would be suppressed in the aprotic solvent, while the H donor would stabilize radical species formed by pyrolysis. They also indicated that coexisting wood polysaccharides would act as H donors for stabilization of lignin-derived radicals. Under these conditions, the monomer yield increased from 2–3 wt% to 16 wt% (lignin basis), with the main monomers being dihydroconiferyl alcohol and isoeugenol. Nevertheless, most of the products were oligomers that have not yet been charac-

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terized. Characterization of this fraction is important to improve the proposed pyrolysis conditions.

In this study, the formation of oligomers during pyrolysis of Japanese cedar wood using 1,3-diphenoxybenzene (DPB) as the aprotic solvent and 1,2,3,10b-tetrahydrofluoranthene as the H donor at 270–380 °C was investigated. The chemical characteristics of the oligomers were determined and the role of wood polysaccharides in the cell wall was evaluated. The pyrolysis conditions are similar to those used in Kotake's research.[11]

Results and Discussion

Characterization of separated fractions

^{1}H NMR spectra were measured for water-soluble (Figure 1a), hexane-soluble (Figure 1b), and purified EtOAc-soluble (Figure 1c) fractions obtained at 350 °C with a 5 min treatment time. Spectra were also measured for acetate derivatives of the purified EtOAc-soluble fraction (Figure 1d) and milled wood lignin (MWL) isolated from Japanese cedar (Figure 1e).

In the spectrum of the water-soluble fraction (Figure 1a), many signals were observed between 1.5–3 ppm and 3.5–4.5 ppm. These peaks were assigned to saturated alkyl protons and RO-C<u>H</u>, respectively. The signals observed in the low magnetic field region above 6 ppm, which is where signals for aromatic and other double bond protons are located, were relatively small. Two signals at 5.40 and 5.46 ppm were assigned to the C1-protons of levomannosan (1,6-anhydro-β-D-mannopyranose) and levoglucosan (1,6-anhydro-β-D-glucopyranose), both of which are typical pyrolysis products from wood polysaccharides in softwoods. Saturated alkyl groups (1.5–3 ppm) may be contained in the polar components, such as sugar-related products, because they are soluble in water.

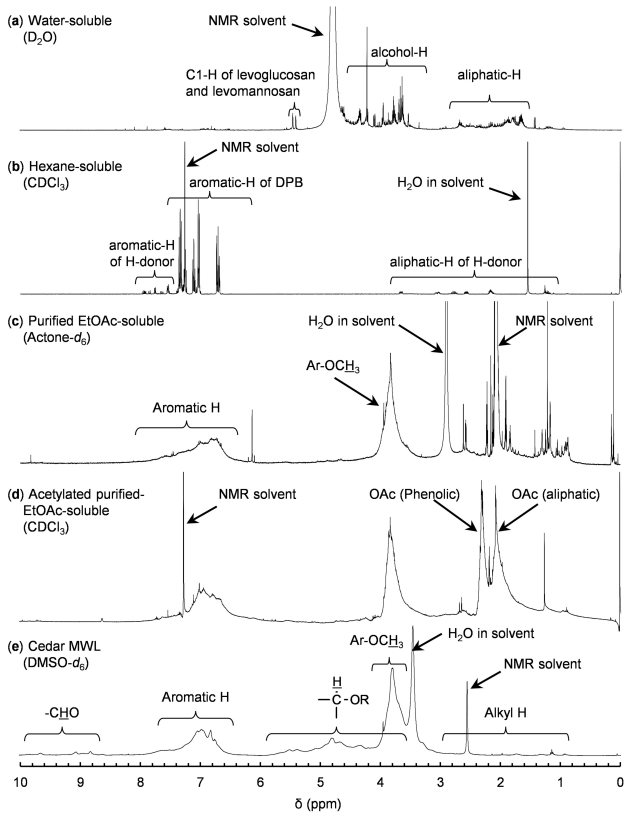

Figure 1. ^{1}H NMR spectra of various fractions obtained from wood pyrolysis in the presence of an aromatic solvent and a hydrogen donor at 350 °C for 5 min. (a) Water-soluble fraction, (b) hexane-soluble fraction, and (c) purified EtOAc-soluble fraction. (d) Acetylated derivatives of purified EtOAc-soluble fraction, and (e) milled wood lignin from Japanese cedar wood.

The signals mentioned in Figure 1a were not observed in the spectrum of the purified EtOAc-soluble fraction (Figure 1c). In this spectrum, methoxyl and aromatic protons were observed as broad signals at 3.5–4 ppm and 6.5–8 ppm, respectively. These broad signals indicated that the main component of this fraction was the lignin-derived oligomer. This was also demonstrated by gel-permeation chromatography (GPC) analysis (see below). Therefore, the carbohydrate-derived products were efficiently removed from wood pyrolysis products by extraction with a binary mixture of EtOAc/H_2O. The signals at 1–3 ppm originated from the saturated alkyl chain described below.

The major components of the hexane-soluble fraction were DPB and the H donor used for the pyrolysis (Figure 1b). These signals were not observed in the spectrum of the purified EtOAc-soluble fraction (Figure 1c), which indicated that washing with hexane effectively removed DPB and the H donor. No signals other than those for DPB and H donor were observed in the spectrum for the hexane-soluble fraction (Figure 1b), but gas chromatography mass spectrometry analysis of this fraction indicated that lignin-derived monomers were present in this fraction (Figure S1, Supporting Information). Van den Bosch[13] also reported that hexane extraction could separate monomers from lignin-derived pyrolysis products to leave oligomers as residue.

Effect of temperature on formation behavior

Temperature is the most important variable for thermal degradation of lignin in wood. Primary pyrolysis reactions of lignin occur over a wide temperature range of 200–400 °C but become significant around 320–350 °C.[14] Therefore, we studied the formation behavior of lignin-derived products and other fractions first at five different temperatures (270, 300, 320, 350, and 380 °C, Figure 2). Because the estimated boiling points of DPB and the H donor are 374 °C and 354 °C,[15] respectively, when the reactor temperature was set to 380 °C, the actual treatment temperature for the wood was lower than 380 °C under normal pressure.

The degradation behavior varied greatly depending on the treatment temperature. At 270 °C, the yield of the purified EtOAc-soluble (lignin) fraction was approximately 20 wt% (lignin basis) after treatment for 10 min. This yield did not increase even when the treatment time was extended to 60 min. These results indicate that approximately 20% of lignin in softwood is reactive even at a relatively low temperature, whereas the rest of the lignin in wood is not converted into soluble products.

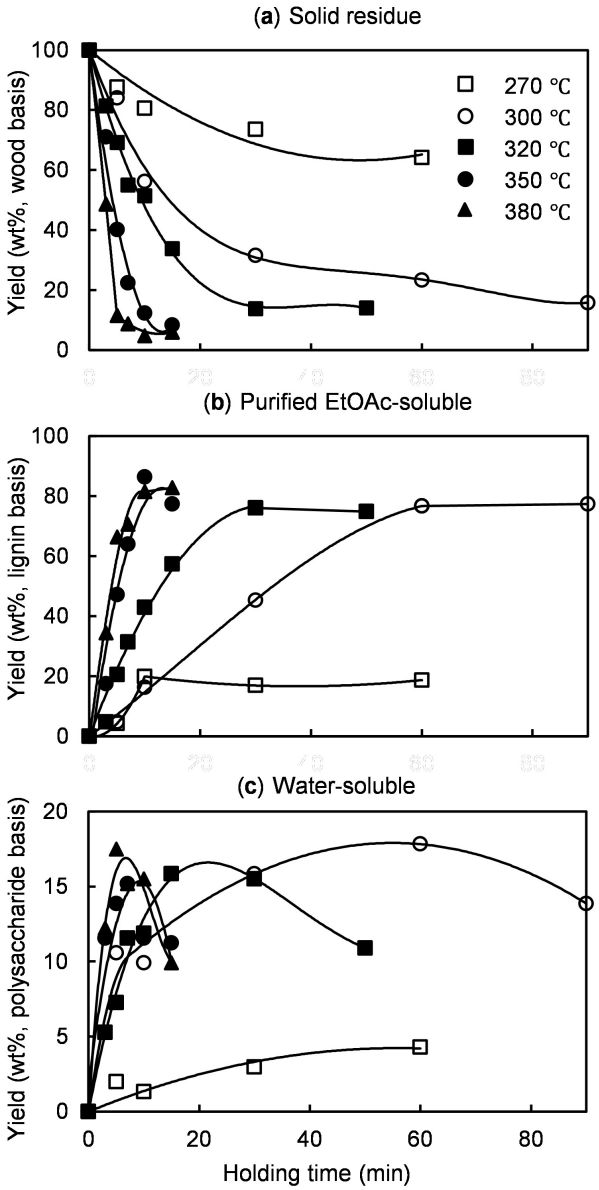

Figure 2. The yields of different fractions from wood pyrolysis in the presence of DPB and a hydrogen donor at 270–380 °C. Wood (50 mg), DPB (200 mg), and H donor (50 mg). (a) Solid residue, (b) purified EtOAc-soluble fraction, and (c) water-soluble fraction.

Increasing the temperature to 300 °C increased the yield of oligomers, which reached approximately 80 wt% with heating times of 60 and 90 min. The required heating time decreased to 30 min at 320 °C and 10 min at 350 °C. There was little variation in the heating time at temperatures above 350 °C. These results agree with thermogravimetric analysis of the pyrolysis reactivity of lignin.[14] Interestingly, the yield of lignin-derived products between 300–380 °C tended to level off at approximately 80 wt%; increasing the heating time did not decline such yields. These results indicate that most of the lignin in Japanese cedar wood was recovered as a very stable oligomer even at high temperatures.

By contrast, the yield of the water-soluble (polysaccharide) fraction was relatively low (< 20 wt%, polysaccharide basis). Furthermore, the yields tended to decrease as the treatment time increased, especially at temperatures above 300 °C. Therefore, products derived from polysaccharide were unstable under such conditions.

Molecular weight distribution of lignin-derived products

The molecular weight distribution of lignin-derived products (purified EtOAc-soluble fraction) was evaluated by GPC. The chromatogram of the lignin-derived products obtained after treatment at 350 °C for 5 min (Figure 3a) was compared with those of the lignin-derived products obtained in the absence of a H donor (Figure 3b) and in nitrogen (Figure 3c). The broad signal of the lignin-derived products (Figure 3a) showed a peak at approximately 10 min, which corresponded to 1,270 Da for polystyrene (GPC column exclusion limit: 1,500 Da at 9.5 min). Assuming that all monomeric units are coniferyl alcohol (MW 180.2), this is equivalent to a heptamer and indicates that the obtained lignin-derived products are oligomers. This feature was observed for all lignin-derived products (Figure 4) obtained under the pyrolysis conditions shown in Figure 2. Therefore, the molecular weight distribution is fairly similar regardless of the pyrolysis temperature (270–380 °C) and treatment time.

The GPC profile (Figure 4) tended to slightly shift to the higher MW region as the yield of lignin-derived products increased. This indicated that the MW range was determined by the yield. These results also indicate that re-condensation of lignin-derived products did not occur actively in DPB and the H donor.

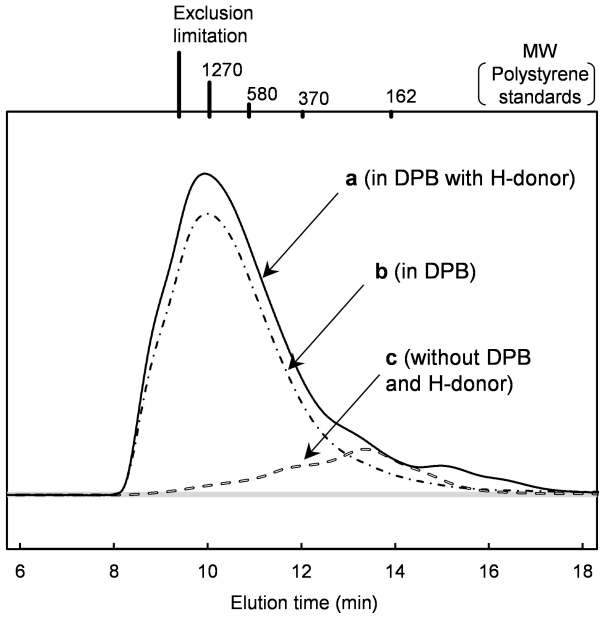

Figure 3. GPC chromatograms of purified EtOAc-soluble fractions obtained from Japanese cedar wood. (a) Dashed line: neat pyrolysis at 350 °C for 5 min under nitrogen, (b) dotted and dashed line: pyrolysis in an aromatic solvent (diphenoxybenzene, DPB), and (c) solid line: pyrolysis in DPB with a hydrogen donor (1,2,3,10b-tetrahydrofluoranthene).

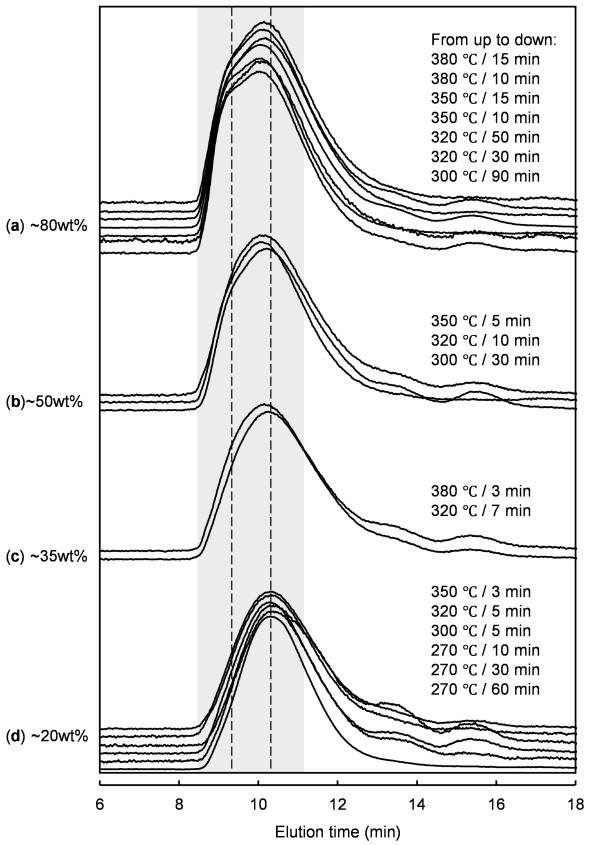

Figure 4. GPC chromatograms of the purified EtOAc-soluble fractions obtained from Japanese cedar wood pyrolysis in DPB with a hydrogen donor (1,2,3,10b-tetrahydrofluoranthene) after treatment at various temperatures and for different times. The results are grouped by the yield of lignin-derived oligomer.

Under nitrogen, the yield of lignin-derived products from Japanese cedar wood was only approximately 10 wt% (lignin basis), and the oligomer signal in the 9–12 min range was relatively very small. Thus, under neat pyrolysis conditions, most of the lignin-derived products re-condense and are converted to char, and only volatile monomers are recovered.

In DPB, the yield of lignin-derived products greatly increased from 10 wt% (under nitrogen) to 40 wt%, and the addition of the H donor further increased the yield to 52 wt% (Figure 3). These results indicate that aprotic solvents are more important than H donors in the production of low MW lignin-derived products from Japanese cedar wood. As discussed below, thermal degradation of wood polysaccharides may produce H donors that stabilize lignin-derived radicals. Both pyrolysis conditions using DPB show similar oligomer signals in Figure 3. As indicated by Kotake et al.,[11] quinone methide formation from lignin pyrolysis products would be effectively inhibited in DPB, an aprotic solvent, by suppressing the proton transfer required for the transformation.

NMR analysis of lignin-derived oligomer

The ^{1}H NMR spectra of the lignin-derived products obtained after treatment at 350 °C for 5 min (Figure 1c and d) were compared with that of Japanese cedar MWL (Figure 1e), to evaluate the chemical structure of oligomer derived from lignin. The MWL spectrum (Figure 1e) showed signals for H-C_α-OR and H-C_β-OR at 3.5–6 ppm.[16] These signals were much smaller in the spectra of the lignin-derived products (Figure 1c and d), which indicated that these structures containing α- and β-ether linkages almost disappeared. Aldehyde signals (8.5–10 ppm) in the MWL spectrum (Figure 1e) also disappeared in the spectra of the lignin-derived products (Figure 1c and d). By contrast, large signals assigned to saturated alkyl protons were observed between 0.5–3 ppm in the spectrum of lignin-derived products (Figure 1c). These results indicated that the α- and β-ether bonds were cleaved, and the side-chains were converted to saturated alkyls.

The ^{1}H-^{1}H COSY NMR spectra of the lignin-derived products obtained after treatment at 350 °C for 5 min and their acetyl derivatives (Figure 5) were used to evaluate the side chain structure. Dihydroconiferyl alcohol is reportedly produced by hydrogenation of the C=C double bond of coniferyl alcohol, a primary pyrolysis product, under pyrolysis conditions.[11] Signals assigned to the γ-hydroxypropyl side chain were observed in Figure 5a, and the C_γ–H signal shifted to a lower magnetic field in Figure 5b because of the electron-withdrawing effect of the acetyl group. These results confirm that γ-hydroxypropyl is a major alkyl side chain in the lignin-derived oligomer as suggested by the monomer composition.[11]

In the ^{1}H NMR spectrum (Figure 1d), acetyl methyl protons of aliphatic and phenolic hydroxyl groups were observed at 1.7–2.1 ppm and 2.1–2.3 ppm, respectively, because of the deshielding effect of the aromatic ring. As discussed below, other saturated alkyl signals overlapped with these signals, but the amounts of aliphatic and phenolic OH groups of the lignin-derived products could still be estimated. $CDCl_3$ was used for NMR spectroscopy of the acetylated derivatives (Figure 1d) to avoid overlap with the solvent signal (acetone: 2.05 ppm, $CHCl_3$: 7.26 ppm). The relative peak areas of aromatic, methoxy, phenolic, and aliphatic acetyl methyl protons were approximately 1:1:0.8:1 (Figure 1d). These values are not accurate because of signal overlap, but the relatively large aromatic proton signal indicates that re-condensation is not important because the guaiacyl unit contains three aromatic protons and three methoxy protons. Similarly, most repeating units contain a phenolic OH group and one OH group in the side chain (probably C_γ).

The signals at 2.5–3 ppm in the NMR spectra of the acetate derivatives of lignin-derived products increased in intensity when the treatment time was increased from 3 min to 10 min, and the yield of lignin-derived products reached 80 wt% (Figure 6). This indicates that large numbers of saturated alkyl side chains form in this period. As explained below, conversion of the vinyl ether structure was considered along with hydrogenation of the coniferyl alcohol type C=C double bond.

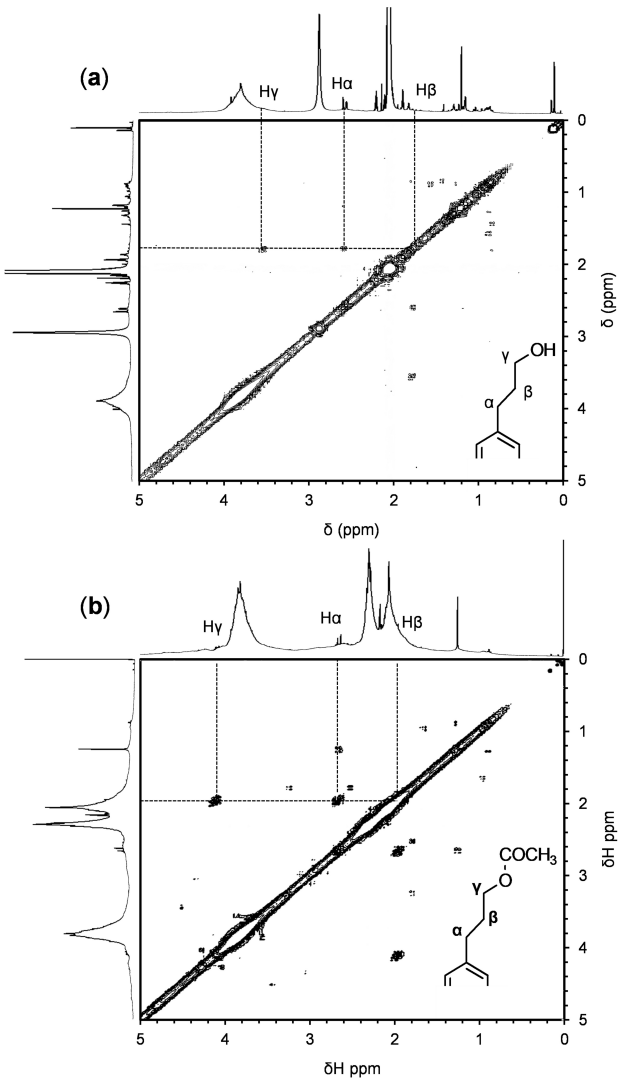

Figure 5. ^{1}H-^{1}H COSY NMR spectra of (a) the purified EtOAc-soluble fraction obtained after treatment at 350 °C for 5 min (NMR solvent: acetone-d_6) and (b) its acetylated derivatives (NMR solvent: $CDCl_3$).

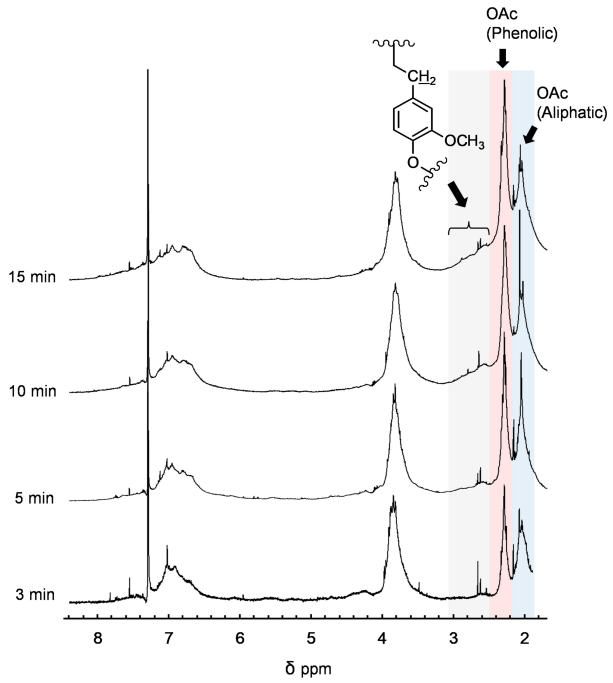

Figure 6. ^{1}H NMR spectra of acetylated purified EtOAc-soluble fractions obtained after treatment at 350 °C for various times.

The relative peak area of the aromatic/aliphatic acetyl methyl protons also slightly increased in this period, which indicated that ether bond cleavage occurred even in the treatment period between 5 and 10 min. When the yield of lignin-derived products reached approximately 80 wt%, the spectra were very similar regardless of the pyrolysis temperature or processing time (Figure S2). The spectrum for the product obtained after treatment at 270 °C for 60 min (yield 20 wt%) was similar to that for the product obtained after treatment at 350 °C for 5 min (yield 52 wt%), which indicated that the chemical structure of lignin-derived products was determined by the yield even at a low temperature of 270 °C. These results led to a hypothesis that the chemical structure of lignin-derived products correlated with the pyrolysis reactivity of lignin in wood, because the HSQC NMR spectra of lignin-derived oligomers obtained after treatment at 270 °C for 60 min (Figure S3) and 350 °C for 5 min (Figure 7b) were also quite similar.

The HSQC NMR spectra of Japanese cedar MWL and lignin-derived products obtained after treatment at 350 °C for 5 min or 10 min are shown in Figure 7. The chemical structures assigned to the signals are shown in Figure 8. In the δ_C/δ_H 50–90/3–6 ppm region of the MWL spectrum (Figure 7a), signals assigned to the side chains of guaiacylglycerol-β-guaiacyl ether (β-*O*-4) (**A**), phenylcoumaran (β-5) (**B**), pinoresinol (β-β) (**C**), dibenzodioxocin (**D**), and coniferyl alcohol (**F**) type structures were observed (Figure 8).[16,17] These signals were weak in the spectrum of the lignin-derived products obtained after treatment for 5 min (Figure 7b) and not present in the spectrum of the lignin-derived products obtained after treatment for 10 min (Figure 7c), which supports the above conclusion that α- and β-ether bonds are cleaved within 10 min.

In the alkyl region of the lignin-derived product (δ_C/δ_H 20–50/1.5–3.5 ppm) (Figures 7b and c), several new signals were observed. Signals assigned to the γ-hydroxypropyl side chain (**K**)[18] formed by hydrogenation of **F** were observed, and the signal for **F** disappeared in the spectrum for the product obtained after treatment for 10 min. In addition to these signals, pyrolysis produced large signals at δ_C/δ_H 35–40/2.4–2.7 ppm, labeled as **B'**$_\alpha$ and **C'**$_\alpha$. According to the literature, these signals can be assigned to structures derived from phenylcoumaran (**B**) and pinoresinol (**C**),[19,20] with cleavage and rearrangement of the side-chain ring structures (Figure 8). Conversion of **B** to **B'** and **C** to **C'** would occur during pyrolysis, and this explains the increase in signal strength in the 1.8–3 ppm region with treatment times of up to 10 min (Figure 6). However, these conversions do not contribute to the depolymerization of lignin macromolecules.

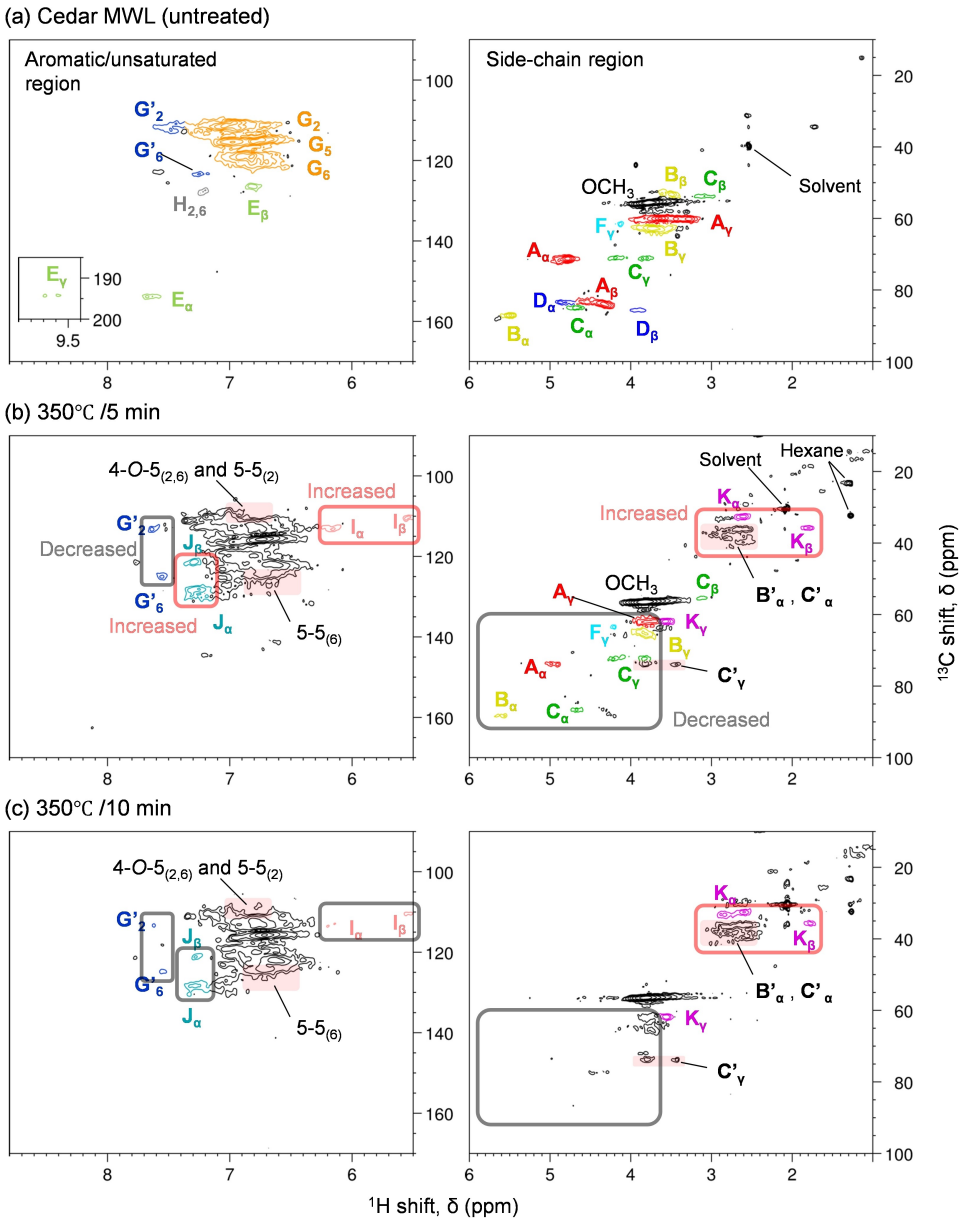

Figure 7. HSQC NMR spectra of (a) Japanese cedar MWL (solvent: DMSO-d_6), and purified EtOAc-soluble fractions obtained after treatment at 350 °C for (b) 5 min and (c) 10 min.

The spectra in the aromatic/unsaturated region slightly changed for the lignin-derived products. The signals assigned to the conjugated aldehyde (**E**) and benzaldehyde (**H**) disappeared in the spectra for the products obtained after treatment at 350 °C for 5 min or 10 min (Figure 7). Instead, signals appeared for vinyl ether (**I**),[21] stilbene (**J**),[22] and 5-5′ (**D′**).[18,20] Stilbenes are reportedly formed by pyrolytic degradation of the β-aryl type condensed structure.[2,23] Large stilbene signals were observed in the spectrum for the product obtained after treatment for 5 min, and the signal strength was not lessened greatly in the spectrum for the product obtained after treatment for 10 min. This indicates that the stilbene C=C double bonds are stable under the current pyrolysis conditions, even though the coniferyl alcohol type C=C bonds are efficiently hydrogenated as mentioned above.

Vinyl ether is reportedly formed from the β-ether structure.[2,23] Clear signals were observed for vinyl ether in the spectrum of the product obtained after treatment for 5 min. The signal intensity was much lower in the spectrum of the product obtained after treatment for 10 min. Thus, this structure was degraded during the 5–10 min treatment period. Vinyl ether, particularly in the phenolic terminal unit, is reportedly hydrolyzed during heat treatment in nitrogen to form a β-carbonyl structure.[24] This transformation would occur under the current pyrolysis conditions and increase the content of phenolic OH groups as described above.

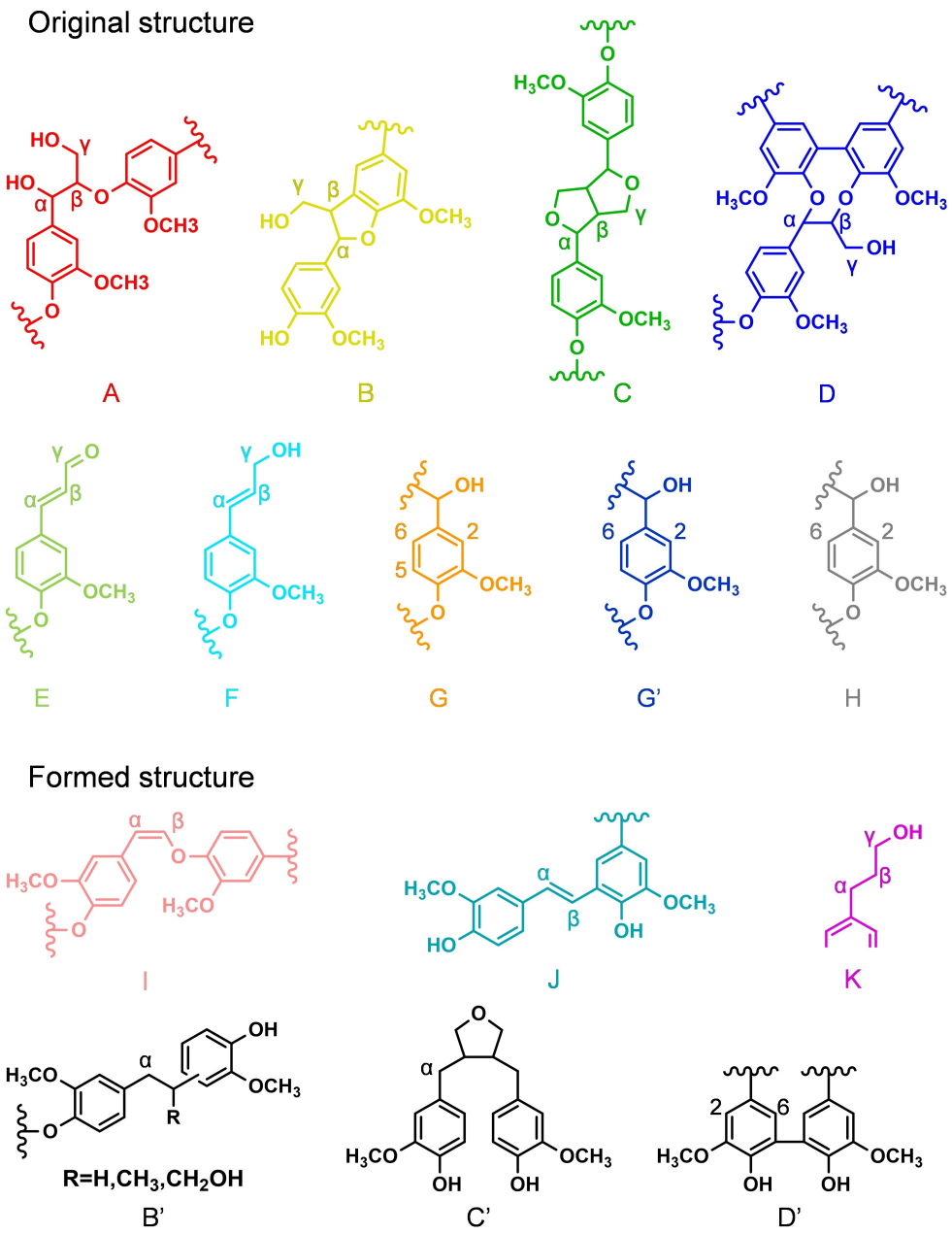

Figure 8. Chemical structures identified from the HSQC NMR spectra.

The 5–5′ signals originated from dibenzodioxocin (**D**) after cleavage of the α- and β-ether bonds.

On the basis of these results, the side chains of the condensed structures were transformed during the treatment, but these transformations do not contribute to depolymerization of the lignin macromolecules. This is the main reason for production of oligomers rather than monomers.

On the basis of the HSQC NMR analysis results, the changes in the ^{1}H NMR spectrum (Figure 6) could be interpreted as follows. The saturated side-chain H-C_α-OR and H-C_β-OR signals (4–5 ppm) almost disappeared even after treatment for only 3 min. Some of the β-ether and β-aryl structures were converted to vinyl ethers and stilbenes, respectively. These double bond signals overlapped with the aromatic proton signals, which resulted in slight overestimation of the peak areas of the aromatic protons. The vinyl ethers were cleaved after treatment for 10 min, which increased the signal intensity for phenolic acetyl methyl protons. The increase in the peak area of the signal at 2.5–3.5 ppm with treatment times of up to 10 min resulted primarily from ring-opening and ring-isomerization of the side chains of phenylcoumaran (**B**) and pinoresinol (**C**) structures.

Cell wall effect

Wood is made up of cells with thick cell walls, and each cell is connected by a middle lamella. The cell wall is a nanocomposite

of crystalline cellulose microfibrils surrounded by a matrix of hemicellulose and lignin.[25] Such nanostructures are expected to affect the thermal degradation of wood component polymers.

The recoveries of hydrolysable sugars from solid residues treated at 350 °C for up to 15 min were compared with the yields of lignin-derived oligomers (Figure 9). Japanese cedar contains the hemicelluloses glucomannan and xylan. The percentages of the undecomposed fraction were estimated from the recoveries of mannose and xylose. The yields of hydrolysable mannose, xylose, and glucose were 10.0, 6.0, and 48.5 wt% (wood basis). Assuming a glucomannan mannose/glucose ratio of 3:1,[26,27] 3.3 wt% glucose comes from glucomannan and the remaining 45.2 wt% comes from cellulose.

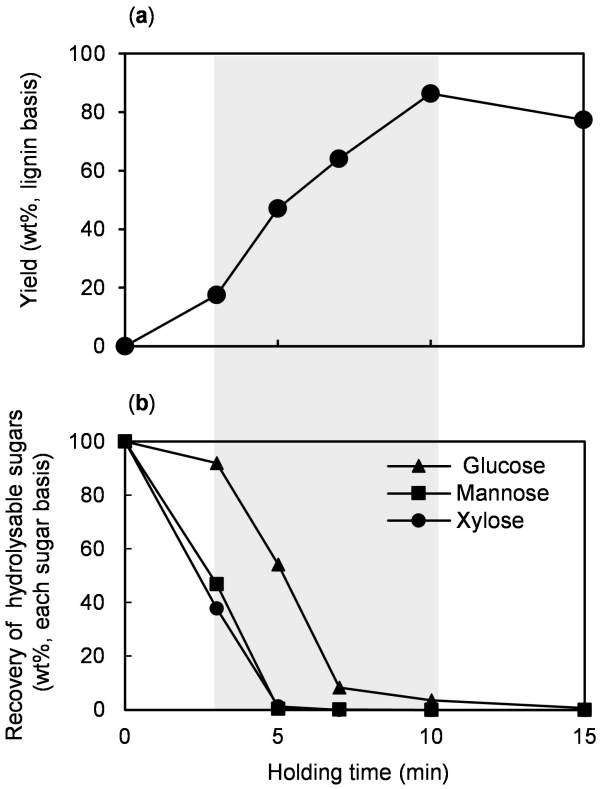

Figure 9. Correlation between (a) the yield of lignin-derived oligomer and (b) the yields of hydrolysable sugars in solid residues after treatment at 350 °C for various times.

After treatment for 3 min, approximately half of the glucomannan and xylan were degraded and/or removed, but most of the cellulose remained in the solid residue. The yield of lignin-derived oligomer was only 20 wt% at this point, and increased as the cellulose decomposed during the 3–10 min treatment period. These results indicate that the formation of lignin-derived oligomers is closely associated with the degradation of cellulose. Similar to the molecular weight distribution described in the GPC results (Figure 3), removal of the H donor did not change the HSQC NMR spectrum of the lignin-derived oligomer obtained after treatment at 350 °C for 5 min (Figure S4). Therefore, wood polysaccharides are expected to function as H donors that stabilize lignin-derived radicals. Conversely, this process may accelerate the thermal degradation of cellulose and hemicellulose.

Cellulose is stable at 270 °C, and the yield of lignin-derived products was limited to approximately 20 wt% even if the treatment time was extended (Figure 2). These results show that approximately 20% of lignin in wood is degraded to oligomers even if cellulose degradation does not proceed. One possible explanation is that the production of these lignin-derived products comes from middle lamella lignin (Figure 10), but further research is needed to confirm this. SEM-EDX has shown that 15–35% of lignin is present in the middle lamella of secondary walls.[28] However, cellulose degradation is required for degradation of the remaining bulk lignin and subsequent removal from the cell wall structure (Figure 10).

Conclusions

Pyrolysis of Japanese cedar wood was studied in an aromatic solvent with a H donor at 270–380 °C. Re-condensation was efficiently suppressed to form thermally stable oligomers with yields up to approximately 80 wt% (lignin basis) at temperatures above 300 °C. Extraction with EtOAc/water effectively separated the lignin-derived oligomers from wood polysaccharide-derived products. The yield of lignin-derived oligomer was limited to approximately 20 wt% (lignin basis) at 270 °C, which indicated that approximately 20% of lignin in the Japanese

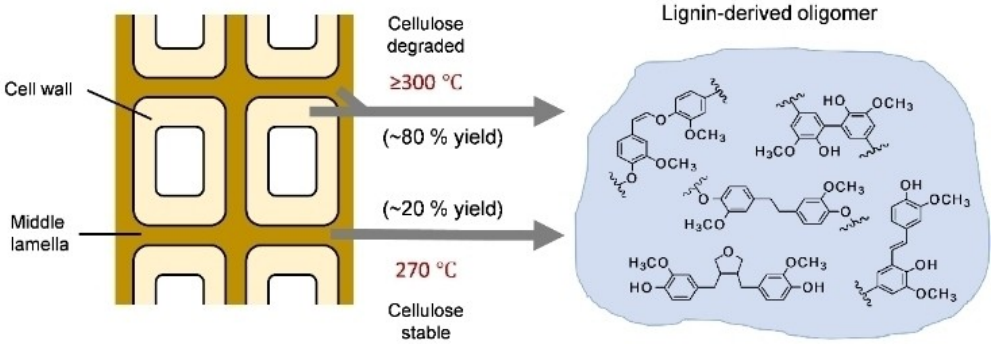

Figure 10. Effect of temperature on the production of oligomers from lignin in the cell wall during pyrolysis of Japanese cedar wood in an aromatic solvent with a hydrogen donor.

cedar wood was reactive. Decomposition of cellulose was required to obtain lignin-derived oligomers from bulk lignin in wood (cell wall effect). Because wood polysaccharides act as H donors, the use of aromatic solvents is more important than the use of H donors in the production of lignin-derived oligomers. The α- and β-ether bonds were cleaved to form saturated alkyl side chains such as γ-hydroxypropyl, but condensed type β-β, β-aryl and 5-5′ bonds remained. The β-aryl type existed as a stilbene in the oligomer. Some β-ether bonds were cleaved via vinyl ether. The obtained lignin-derived oligomer was rich in phenolic and alcohol OH groups. This is advantageous for utilizing lignin-derived oligomers as polyols for biopolymer production.

Experimental Section

Materials

Japanese cedar wood (cellulose: 38.3 wt%, hemicellulose: 24.5 wt%, lignin: 33.3 wt%, and extractives: 3.4 wt%)[29] was ground into flour and sieved (< 150 μm), and then extracted with ethanol/benzene (2:1, *v/v*) to remove the extractives. MWL was prepared from Japanese cedar wood flour in accordance with an established method.[30] The contents of hydrolysable sugars in this MWL were glucose 0.6 wt%, xylose 0.7 wt%, mannose 0.3 wt%, and arabinose, 0.2 wt%. These sugars were derived from the carbohydrates remaining in the MWL.[31]

DPB, which has a melting point of 60.0 °C[32] and an estimated boiling point of 374.2 ± 25.0 °C,[15] was used as the aromatic solvent. 1,2,3,10b-Tetrahydrofluoranthene, which has a melting point of 72–73 °C[33] and an estimated boiling point of 353.5 ± 17.0 °C,[15] was used as the H donor. These compounds (Figure 11) were purchased from Tokyo Chemical Co., Ltd. (Tokyo, Japan) and were of guaranteed grade and used without purification.

Pyrolysis and product fractionation

Oven-dried extractive-free cedar wood flour (50 mg), DPB (200 mg), and H donor (50 mg) were placed in the bottom of a Pyrex tube reactor (internal diameter: 8.0 mm, glass thickness: 1.0 mm, length: approximately 300 mm) (Figure 12). The amount of DPB (200 mg) was the minimum amount sufficient to solvate the wood flour. The amount of the H donor (50 mg) was also sufficient to influence the lignin pyrolysis reactions, which was determined by the preliminary experiments using different loading levels of H donor. The inside air was replaced with N_2 through a three-way cock connected to an aspirator and a N_2 balloon. The tube reactor was preheated to around 100 °C until the DPB and H donor melted. Then, through a small hole in the upper wall, the lower two-thirds of the reactor was inserted into a muffle furnace preheated to a set temperature between 270 °C and 380 °C. After the specified treatment time at normal pressure, the reactor was removed from the furnace and

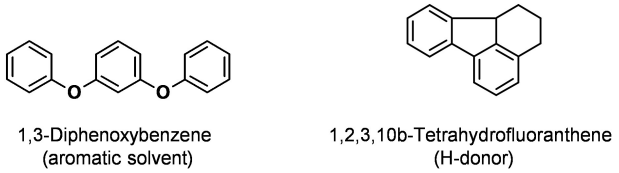

Figure 11. Aprotic solvent and hydrogen donor used in this study.

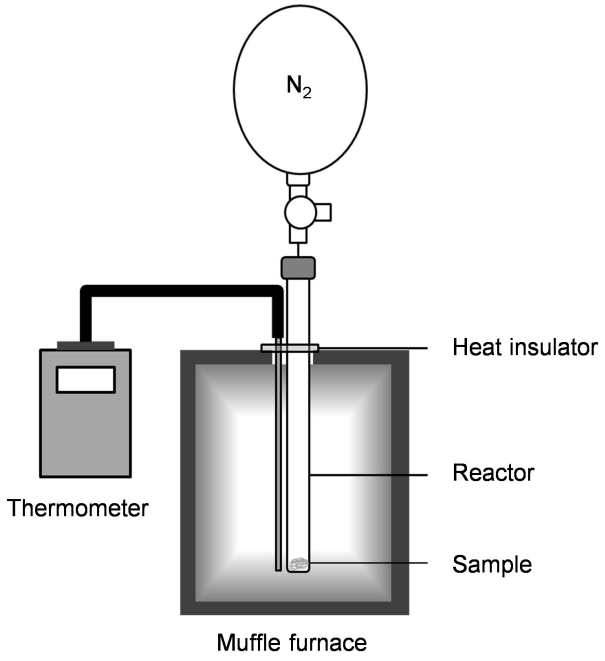

Figure 12. Experimental setup for pyrolysis.

cooled immediately under airflow for 1 min and then in flowing cold water for 1 min.

The pyrolysis products were separated into four fractions by extraction with binary solvent systems (Figure 13). In the first extraction step using ethyl acetate (EtOAc) and water (1:1, *v/v*), relatively polar carbohydrate-derived products were extracted into water. The EtOAc layer contained the hydrophobic lignin-derived products, DPB, and the H donor. Char and unreacted wood were separated as solid residue. The water layer was evaporated in

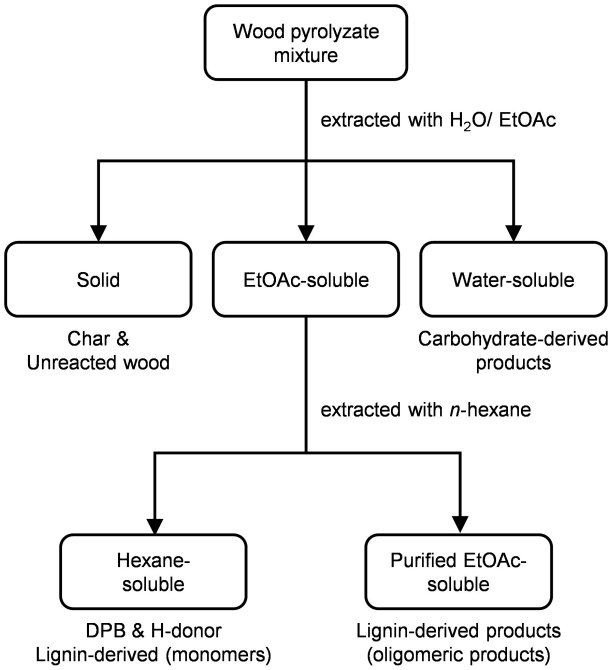

Figure 13. Separation process for the wood pyrolysate.

Table 1. Experimental conditions used for pyrolysis of Japanese cedar wood flour (50 mg).

Reaction conditions				Data presented		
Temperature (°C)	Time (min)	DPB (mg)	H-donor (mg)	GPC	1H-NMR	2D-HSQC
270	5	200	50	✓		
	10	200	50	✓		
	30	200	50	✓		
	60	200	50	✓	✓	✓
300	5	200	50	✓		
	10	200	50	✓		
	30	200	50	✓		
	60	200	50	✓	✓	
	90	200	50	✓		
320	3	200	50	✓		
	5	200	50	✓		
	7	200	50	✓		
	10	200	50	✓		
	15	200	50	✓		
	30	200	50	✓	✓	
	50	200	50	✓		
350	3	200	50	✓	✓	
	5	200	50	✓	✓	✓
	5	200	0	✓		✓
	5	0	0	✓		
	7	200	50	✓		
	10	200	50	✓	✓	✓
	15	200	50	✓	✓	
380	3	200	50	✓		
	5	200	50	✓		
	7	200	50	✓		
	10	200	50	✓	✓	
	15	200	50	✓		

vacuo. The EtOAc layer was evaporated in vacuo after dehydration over anhydrous Na_2SO_4. The EtOAc-soluble (lignin) fraction was further purified by washing with n-hexane. Each dried fraction was weighed on an electronic balance. Some samples were acetylated in acetic anhydride and pyridine at room temperature, followed by removal of the solvent and reagent through evaporation in vacuo.

Product analysis

GPC was conducted to analyze the molecular weight distribution of the purified EtOAc-soluble (lignin) fraction using a Shimadzu LC-10A system with a Shodex KF-801 column (exclusion limit molecular weight: 1,500 Da, polystyrene standard) at a flow rate of 0.6 mL min^{-1} and a temperature of 40 °C. Tetrahydrofuran was used as the eluent with a UV detector at 280 nm. The NMR spectra were measured by a Varian AC-400 (400 MHz) spectrometer (Varian, CA, USA). The chemical shifts and coupling constants (J) are reported in δ (ppm) and Hz, respectively.

The hydrolysable sugars in the solid residue were obtained by an acid hydrolysis process as described in our previous work.[34] After neutralization with an OnGuard II/A ion exchange column (Dionex, Sunnyvale, USA), the hydrolysates were quantified by high-performance anion-exchange chromatography (Prominence, Shimadzu Corp., Kyoto, Japan) with an electrochemical detector (DECADE Elite, Antec Scientific, Zoeterwoude, Netherlands). The column was a CarboPac PA1 (4×250 mm, Dionex) with a column temperature of 35 °C. The eluent was 0.2 M NaOH in ion-exchanged water at a flow rate of 1.0 mL min^{-1}, and the carrier gas was N_2.

Gas chromatography/mass spectrometry was performed to analyze the lignin-derived monomers in hexane-soluble portion by using Shimadzu 2010 Plus gas chromatograph (Shimadzu Corporation, Kyoto, Japan) coupled with a Shimadzu QP 2010 Ultra mass spectrometer (Shimadzu Corporation, Kyoto, Japan). The instrumental conditions consisted of: column, Agilent CPSil 8CB (length: 30 m, diameter: 0.25 mm); injector temperature, 250 °C; split ratio, 10; column temperature, 50 °C (1 min), 5 °C/min to 120 °C, 10 °C/min to 330 °C, 330 °C (5 min); carrier gas, helium; flow rate, 1.22 mL min^{-1}. The mass spectrometric scan parameters included a scan range of 35–500 m/z and a scan interval of 0.3 s.

Table 1 summarizes the experimental conditions used in this study and the analysis data presented in this article. Pyrolysis experiments at 350 °C were repeated twice to confirm the reproducibility, although the data presented in this paper were not treated statistically. The yields reported in this article are mean values.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: aprotic solvent · cell wall effect · hydrogen donor · stable oligomer · wood lignin pyrolysis

[1] T. Nakamura, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2008**, *81*, 173–182.
[2] H. Kawamoto, S. Horigoshi, S. Saka, *J. Wood Sci.* **2007**, *53*,168–174.
[3] J. Cho, S. Chu, P. J. Dauenhauer, G. W. Huber, *Green Chem.* **2012**, *14*, 428–439.
[4] B. Biswas, R. Singh, J. Kumar, A. Ali, B. B. Krishna, T. Bhaskar, *Bioresour. Technol.* **2016**, *213*, 319–326.
[5] H. Kawamoto, T. Nakamura, S. Saka, *Holzforschung* **2008**, *62*, 50–56.
[6] H. Kawamoto, M. Ryoritani, S. Saka, *J. Anal. Appl. Pyrolysis* **2008**, *81*, 88–94.
[7] T. Watanabe, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2015**, *112*, 23–28.
[8] T. Watanabe, H. Kawamoto, S. Saka, *Holzforschung* **2009**, *63*, 424–430.
[9] T. Kotake, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2013**, *104*, 573–584.
[10] T. Nakamura, H. Kawamoto, S. Saka, *J. Wood Chem. Technol.* **2007**, *27*, 121–133.
[11] T. Kotake, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2014**, *105*, 309–316.
[12] T. Kotake, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2015**, *113*, 57–64.
[13] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.-F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels, *Energy Environ. Sci.* **2015**, *8*, 1748–1763.
[14] M. Asmadi, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2011**, *92*, 417–425.
[15] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2019 ACD/Labs).
[16] C. Heitner, D. R. Dimmel, J. A. Schmidt, *Lignin and lignans: advances in chemistry*. CRC press, USA **2016**, Ch. 9.
[17] J. L. Wen, S. L. Sun, B. L. Xue, R. C. Sun, *Materials* **2013**, *6*, 359–391.
[18] S. Ralph, J. Ralph, L. L. Landucci, L. Landucci, "NMR data base of lignin and cell wall model compounds", can be found under https://www.glbrc.org/databases_and_software/nmrdatabase/NMR_DataBase_2009_Complete.pdf, **2009**.
[19] L. K. Sy, G. D. Brown, *J. Nat. Prod.* **1998**, *6*, 987–992.
[20] K. Van Aelst, E. Van Sinay, T. Vangeel, E. Cooreman, G. Van den Bossche, T. Renders, J. Van Aelst S Van den Bosch, B. F. Sels, *Chem. Sci.* **2020**, *11*, 11498–11508.
[21] C. Zhao, Z. Hu, L. Shi, C. Wang, F. Yue, S. Li, H. Zhang, F. Lu, *Green Chem.* **2020**, *22*, 7366–7375.
[22] C. S. Lancefield, H. J. Wienk, R. Boelens, B. M. Weckhuysen, P. C. A. Bruijnincx, *Chem. Sci.* **2018**, *9*, 6348–6360.
[23] E. Minami, H. Kawamoto, S. Saka, *J. Wood Sci.* **2003**, *49*, 158–165.
[24] K. Miyamoto, H. Kawamoto, *J. Anal. Appl. Pyrolysis* **2019**, *137*, 54–60.
[25] N. Terashima, K. Kitano, M. Kojima, M. Yoshida, H. Yamamoto, U. Westermark, *J. Wood Sci.* **2009**, *55*, 409–416.
[26] T. E. Timell, *Wood Sci. Technol.* **1967**, *1*, 45–70.
[27] A. Tyminski, T. E. Timell, *J. Am. Chem. Soc.* **1960**, *82*, 2823–2827.
[28] E. Higuchi, Takayoshi, Elsevier, **2012**, Ch. 3.
[29] H. Rabemanolontsoa, S. Ayada, S. Saka, *Biomass Bioenergy* **2011**, *35*, 4630–4635.
[30] A. Björkman, *Sven. Papperstidn.* **1956**, *59*, 477–485.
[31] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2007**, *78*, 328–336.
[32] K. J. Sax, W. S. Saari, C. L. Mahoney, J. M. Gordon, *J. Org. Chem.* **1960**, *25*, 1590–1595.
[33] E. Steinberg, G. A. Conrad, A. W. Ruddy, *J. Am. Chem. Soc.* **1954**, *76*, 5445–5447.
[34] T. Nomura, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **2017**, *126*, 209–217.

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