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Comparison of the decomposition behaviors of hardwood and softwood in supercritical methanol

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Abstract The chemical conversion of Japanese beech (*Fagus crenata* Blume) and Japanese cedar (*Cryptomeria japonica* D. Don) woods in supercritical methanol was studied using the supercritical fluid biomass conversion system with a batch-type reaction vessel. Under conditions of 270°C/27 MPa, beech wood was decomposed and liquefied to a greater extent than cedar wood, and the difference observed was thought to originate mainly from differences in the intrinsic properties of the lignin structures of hardwood and softwood. However, such a difference was not observed at 350°C/43 MPa, and more than 90% of both beech and cedar woods were effectively decomposed and liquefied after 30 min of treatment. This result indicates that the supercritical methanol treatment is expected to be an efficient tool for converting the woody biomass to lower-molecular-weight products, such as liquid fuels and useful chemicals.

Key words Chemical conversion · Supercritical methanol · Hardwood · Softwood · Lignin · Cellulose

Introduction

Due to global warming caused by excessive use of fossil fuel resources, renewable biomass resources will become more important in the future as alternatives to fossil fuels. In addition, according to our recent investigation,¹ 240 million tons of biomass wastes such as the lignocellulosics are gen-

erated annually in Japan, of which 65 million tons are not used effectively. Therefore, technology that can convert them to valuable liquid fuels and chemicals will be important for solving our energy and environmental problems. Recently, the use of supercritical fluid has been thought to be attractive for chemical conversion of biomass resources.^{2–5}

Therefore, supercritical water (>374°C/>22.1 MPa) treatment of biomass resources has been studied to convert them to useful chemicals.^{2,4,6,7} Pyrolysis was found to be depressed to some extent by controlling the reaction conditions.⁴ However, hydrolysis products such as glucose were further decomposed rapidly in supercritical water due to its high critical temperature. On the other hand, the critical temperature (T_c 239°C) and critical pressure (P_c 8.09 MPa) of methanol, which are lower than those of water, offer milder conditions for the reaction. McDonald et al. reported that supercritical methanol extraction of Western red cedar (*Thuja plicata* D. Don) at 350°C/28 MPa yielded 70% of the extracted oil in which approximately 5% of the products were identified to be phenols and levoglucosan.⁸ Furthermore, Poirer et al. studied the supercritical methanol extraction of aspen (*Populus tremuloides* Michx), and the effects of three variables of the solvent (temperature, pressure, flow rate) on oil yield have been investigated by statistical analysis.⁹ However, the decomposition behaviors of each component of wood and its cell wall components (cellulose, hemicelluloses, lignin) in supercritical methanol remain unclear.

Therefore, Ishikawa and Saka studied the decomposition behaviors of cellulose samples of avicel (microcrystalline cellulose), cotton linters, and dissolving pulp.¹⁰ In this study the decomposition behaviors of woody biomass in supercritical methanol were examined, focusing on the wood cell wall components, especially lignin from hardwood and softwood. The advantages of this study are that the methanol with reaction products can be used as liquid fuel because methanol itself is a good fuel. Furthermore, the liquid fuel from biomass resources alone can be created using biomethanol as the supercritical solvent synthesized by pyrolysis of biomass resources.

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Materials and methods

Supercritical methanol treatment

As woody biomass samples, wood flours (80 mesh pass) from Japanese beech (*Fagus crenata* Blume) as hardwood and Japanese cedar (*Cryptomeria japonica* D. Don) as softwood were subjected to supercritical methanol treatment. High-performance liquid chromatography (HPLC)-grade methanol was used as the solvent. Supercritical methanol treatment was conducted using a biomass conversion system with a batch-type reaction vessel described elsewhere.^{6,7,10} The 5-mL reaction vessel is made of Inconel-625. This system can cover ranges of pressure and temperature up to 280 MPa and 500°C, respectively, with a constant density of 0.79 g/ml. To start the treatment, approximately 4.9 ml of methanol was placed with 150 mg of the wood flour in the 5-ml reaction vessel, which was then immersed in a molten tin bath preheated to an adequate temperature and maintained under supercritical conditions (>239°C/>8.09 MPa) for 1–30 min. After an adequate reaction time, the reaction vessel was moved to a waterbath to quench the reaction. The obtained reaction mixture was then filtered with a 0.2- μ m membrane filter to separate the methanol-soluble portion and the methanol-insoluble residue.

Analytical methods

The methanol-soluble portion was directly analyzed by HPLC carried out with a Shimadzu LC-10A apparatus under the following conditions: (1) Column STR ODS-II; flow rate 1.0 ml/min; eluent CH₃OH/H₂O, 20/80→100/0 (0–60 min); detector UV₂₈₀; temperature 40°C. (2) Column ULTRON PS-80P; flow rate 0.8 ml/min; eluent H₂O; detector refractive index detector (RID); temperature 40°C. Some reaction products were separated using the HPLC system and analyzed by proton nuclear magnetic resonance

(¹H-NMR) spectroscopy, by which the spectra were recorded in CDCl₃ using a Varian AC-300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. Gel permeation chromatography (GPC) was also carried out for the methanol-soluble portion with the Shimadzu LC-10A apparatus under the following conditions: column Shodex KF-801 connected with KF-802, KF-802.5, and KF-803 in the series; flow rate 0.6 ml/min; eluent tetrahydrofuran (THF); detector UV₂₈₀; temperature 50°C.

For the methanol-insoluble residue the Klason lignin content and the acid-soluble lignin were determined.¹¹ The yield of the nitrobenzene oxidation products of the lignin in the alkaline solution was also determined for the methanol-insoluble residue according to the described methods.¹² In addition, the amounts of constituent monosaccharides in the methanol-insoluble residue were determined by HPLC analysis for the clear filtrate from acid hydrolyzates in the Klason lignin determination under the conditions mentioned above. The cellulose and hemicellulose contents in the methanol-insoluble residue were then estimated based on the amounts of glucose and other monosaccharides, respectively.

Results and discussion

Decomposition behaviors

Figure 1 shows the changes in the methanol-insoluble residues of beech and cedar woods treated in supercritical methanol at various conditions. At the low temperatures of 255°C and 270°C, the amount of the residue remained constant after 5 min of treatment. For example, about 65% of beech wood remained methanol-insoluble at 270°C/27 MPa. However, at the high temperature of 350°C, decomposition of woods proceeded as the treatment was extended; finally, more than 90% of the wood was decomposed and liquefied

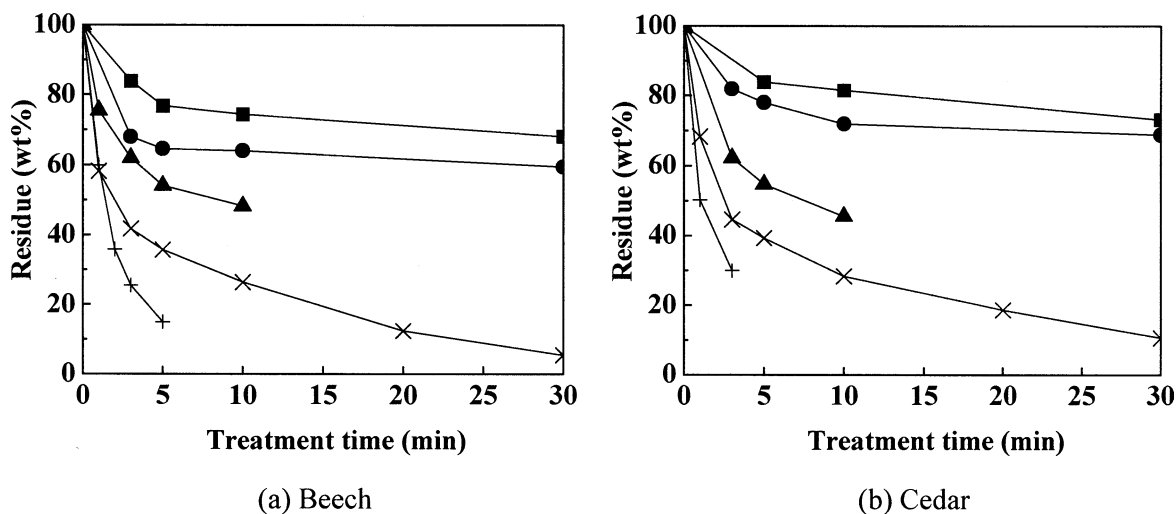


Fig. 1a,b. Changes in residue mass of **a** beech and **b** cedar woods treated in supercritical methanol at various conditions. Squares, 255°C/24 MPa; circles, 270°C/27 MPa; triangles, 325°C/36 MPa; crosses, 350°C/43 MPa; plus symbols, 375°C/50 MPa

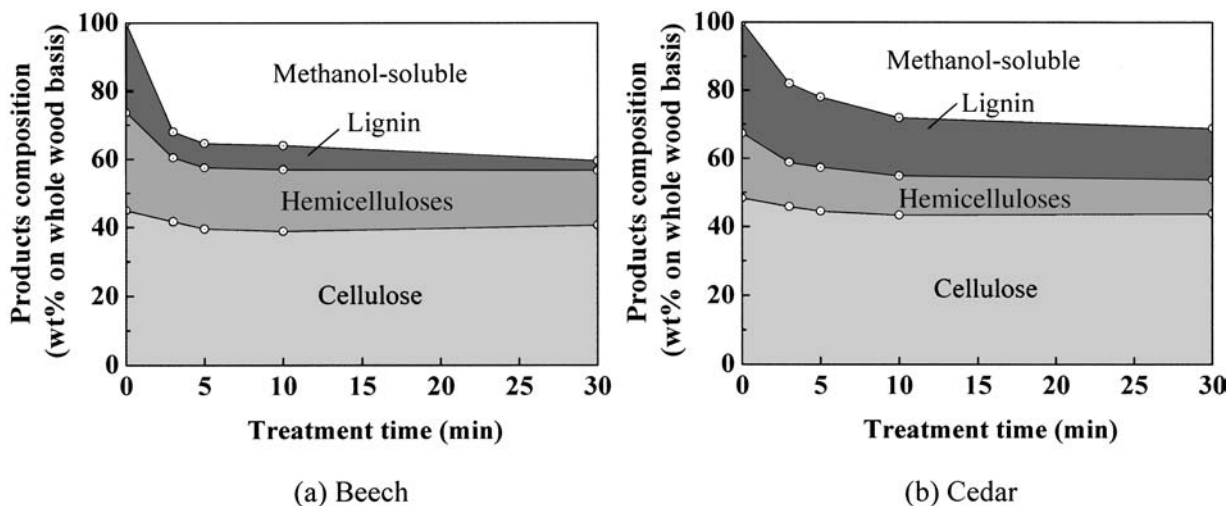


Fig. 2a,b. Product composition of a beech and b cedar woods treated in supercritical methanol at 270°C/27MPa

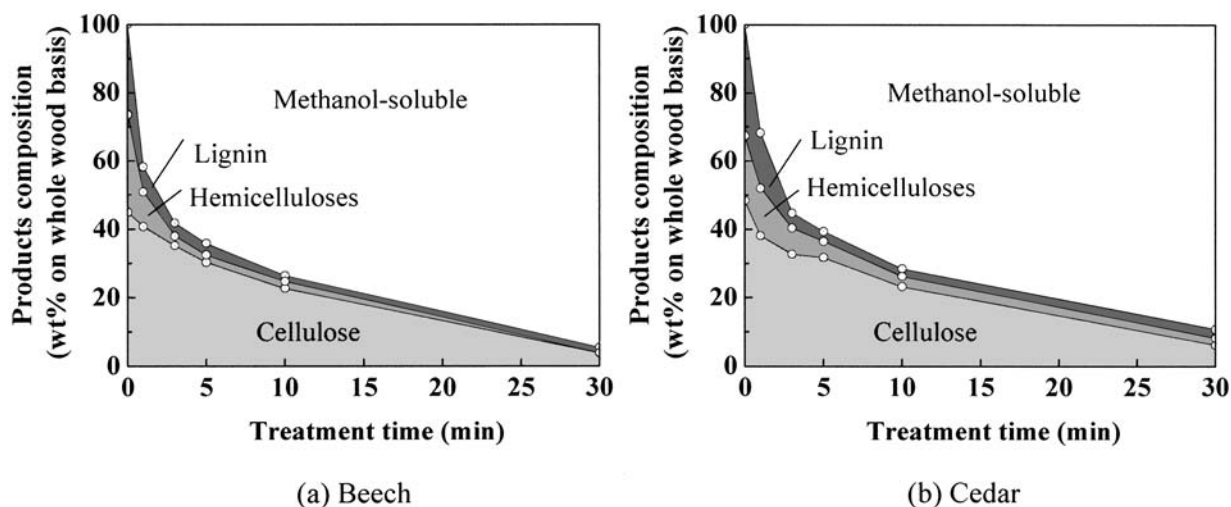


Fig. 3a,b. Product composition of a beech and b cedar woods treated in supercritical methanol at 350°C/43MPa

in methanol after 30 min. The only difference observed between beech and cedar was that it was slightly easier to liquefy beech wood than cedar.

Figure 2 shows the changes in the chemical composition of cellulose, hemicelluloses, and lignin in the residues of beech and cedar woods treated in supercritical methanol at 270°C/27MPa. It is clear that the lignin in beech was liquefied to a greater extent than that of cedar. Furthermore, the hemicelluloses of both woods were decomposed slightly in methanol, whereas cellulose was not under the given conditions. Therefore, the decomposition of lignin contributes mainly to the liquefaction of beech and cedar woods in supercritical methanol.

Under the conditions of 350°C/43MPa (Fig. 3), however, all three components (cellulose, hemicelluloses, lignin) were decomposed and liquefied effectively in methanol in both cases. For lignin, however, the residues of about 1%–3% on the original wood basis remained constant after 3 min of treatment. This suggests that these residues must

have specific structures that remain stable in supercritical methanol.

Decomposition of cellulose and lignin

Assuming that the decomposition of cellulose and lignin in supercritical methanol is a pseudo-first-order reaction, their decomposition rate constant (κ) in beech and cedar woods was evaluated by the following equation

$$X = e^{-\kappa t} \times 100 \text{ (wt\% on the original cellulose or lignin basis)}$$

where X is the residue of cellulose or lignin, and t is the treatment time (seconds). Figure 4 shows the obtained Arrhenius plots for the κ values of cellulose and lignin in cedar and beech woods. It is apparent that the κ of lignin in beech is larger than that in cedar at any of the temperatures

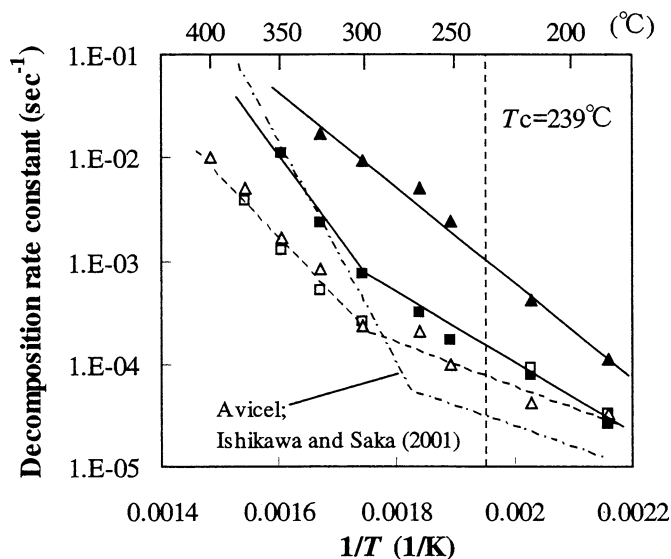


Fig. 4. Arrhenius plots for decomposition rate constants for cellulose and lignin in beech and cedar woods in subcritical and supercritical methanol. *Filled triangles*, beech lignin; *filled squares*, cedar lignin; *open triangles*, beech cellulose; *open squares*, cedar cellulose

studied, which in turn is larger than that of cellulose, especially at around 300°C.

However, the κ values of cellulose in both woods were almost equal and increased when the temperature rose above 300°C, which is about 60°C higher than the critical temperature (T_c) of methanol, as in Fig. 4. This trend is similar to that for avicel, a microcrystalline cellulose, studied previously.¹⁰ However, after supercritical water treatment, Sasaki et al. reported that the κ of the cellulose was drastically increased around the T_c of water.¹³ This discrepancy has not been clarified.

Figure 4 shows further that the κ of cellulose in woods is smaller than that of avicel at an elevated temperature. This observed difference possibly originates from the differences in the fibrillar structures of these samples; avicel is in powder form, whereas cellulose in wood is in fiber form. Therefore, avicel is more accessible to methanol molecules than is wood cellulose. Ishikawa and Saka¹⁰ reported that it is more difficult to liquefy cotton linters and dissolving pulp than avicel in supercritical methanol.

Regarding the decomposition of lignin, the κ of lignin in beech is a larger value than that of cedar (Fig. 4). This observed difference would mainly originate from differences in the intrinsic properties of the lignin structures of hardwood and softwood. Figure 5 shows that the yield of nitrobenzene oxidation products, which is a measure of the number of ether linkages in lignin, decreased for the methanol-insoluble residue of woods as the duration of the supercritical treatment increased. Therefore, the methanol-insoluble residue has fewer ether linkages (e.g., β -O-4 and α -O-4 linkages) in the lignin. In addition, the lignin model compound study indicated that the condensed linkages of lignin (e.g., 5-5 and β -1 linkages) are stable during treatment with supercritical methanol, whereas the β -ether and α -ether linkages are rapidly cleaved.^{14,15} Therefore, it is sug-

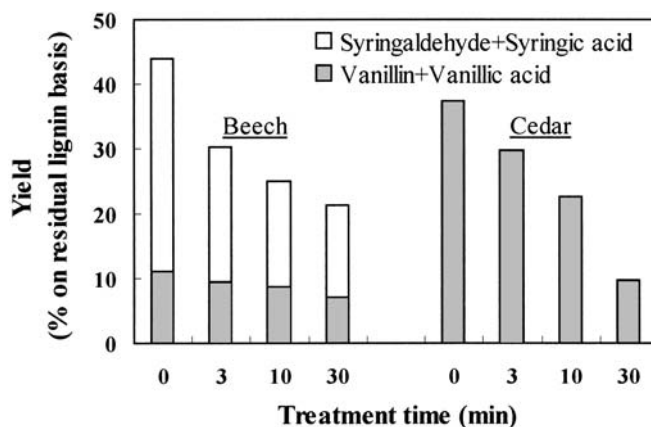


Fig. 5. Changes in the yields of alkaline nitrobenzene oxidation products of methanol-insoluble residue in beech and cedar woods treated in supercritical methanol at 270°C/27 MPa

gested that cleavage of ether linkages mainly contributes to the decomposition of lignin. This further indicates that lignin rich in ether linkages is more easily depolymerized in supercritical methanol than are the condensed types of lignin. Hardwood lignin, which is known to have more ether linkages is therefore readily depolymerized and liquefied compared with softwood lignin, as observed in Fig. 4.

Based on these lines of evidence, treatment temperatures higher than 300°C are necessary to decompose beech and cedar woods effectively. Moreover, thermal cracking of methanol is reported to occur at 370–380°C.¹⁶ Therefore, it can be concluded that the appropriate treatment temperature of wood is about 350°C.

Decomposed products of cellulose and lignin

Cellulose-derived products in the methanol-soluble portion were also studied. As a result, the main monomeric products from cellulose of both beech and cedar woods were identified by HPLC analysis to be methyl- β -D-glucoside, methyl- α -D-glucoside, and levoglucosan. 5-Hydroxymethylfurfural and furfural were also found in the methanol-soluble portion of both woods as minor products. According to the decomposition pathway proposed by Ishikawa and Saka,¹⁰ methanolysis of cellulose in supercritical methanol results in methylated cellotriose and methylated cellobiose, which are converted to methyl α - and β -D-glucosides. Subsequently, these are anomerized and, after prolonged treatment, decompose further to other products, such as levoglucosan and 5-hydroxymethylfurfural. Therefore, the main decomposition pathway of cellulose in woods must be the same as that of avicel in supercritical methanol.

Figure 6 shows the yield changes of methyl α -D-glucoside (MG- α), methyl β -D-glucoside (MG- β), and levoglucosan (LG) on the original cellulose basis as the supercritical treatment was extended at 350°C/43 MPa. The results obtained are similar for beech and cedar, and their yields increase gradually with the increased treatment time. How-

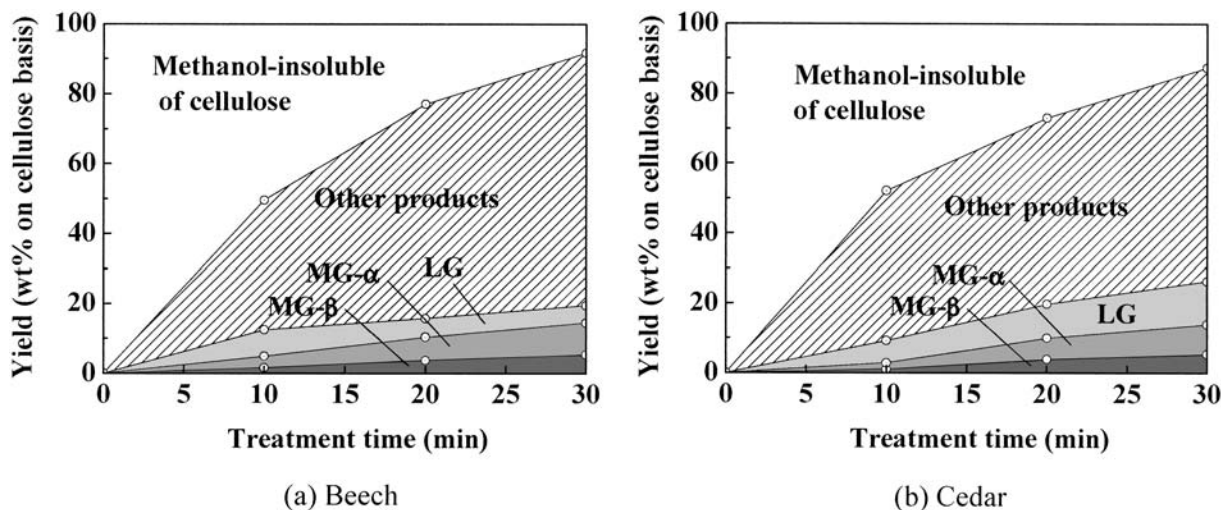


Fig. 6a,b. Changes in the yields on the cellulose basis of cellulose-derived products in methanol-soluble portions of **a** beech and **b** cedar woods treated in supercritical methanol at 350°C/43 MPa. *MG-β*, methyl-β-D-glucoside; *MG-α*, methyl-α-D-glucoside; *LG*, levoglucosan

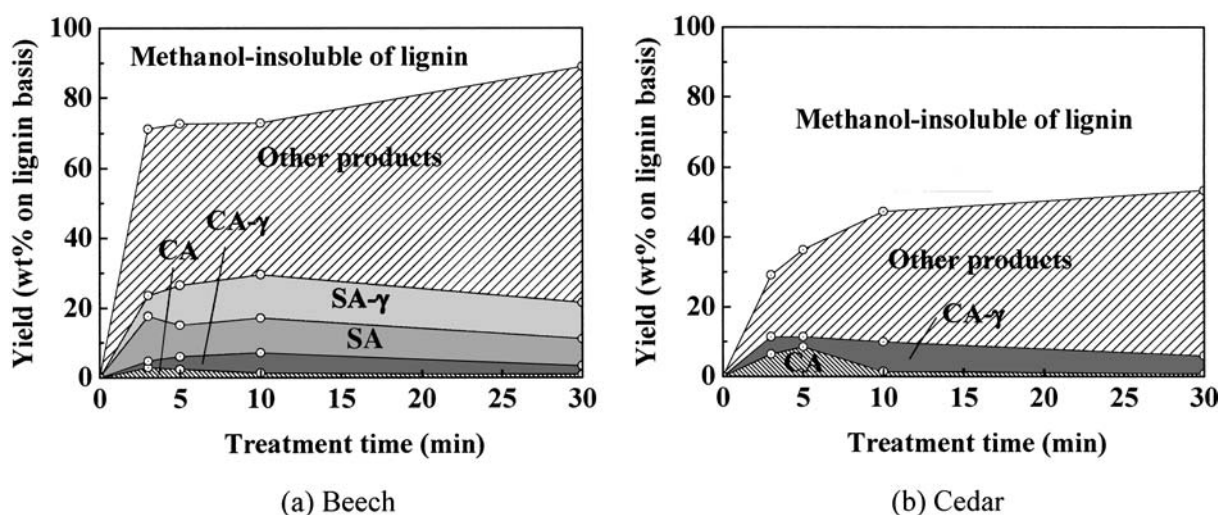


Fig. 7a,b. Changes in the yields on the lignin basis of lignin-derived products in methanol-soluble portions of **a** beech and **b** cedar woods treated in supercritical methanol at 270°C/27 MPa. *CA*, coniferyl alcohol; *CA-γ*, coniferyl alcohol γ -methyl ether; *SA*, sinapyl alcohol; *SA-γ*, sinapyl alcohol γ -methyl ether

ever, on a methanol-soluble portion basis the results were almost proportional at each treatment time.

Among the lignin-derived products in the methanol-soluble portion, the main monomeric products were identified to be (1) guaiacol, coniferyl alcohol, and its γ -methyl ether as guaiacyl lignin-derived products from both woods and (2) 2,6-dimethoxyphenol, sinapyl alcohol, and its γ -methyl ether as syringyl lignin-derived products from beech wood. Figure 7 shows the yields of coniferyl alcohol (*CA*), sinapyl alcohol (*SA*), and their γ -methyl ethers (*CA-γ* and *SA-γ*) on the original lignin basis under the conditions of 270°C/27 MPa. Coniferyl alcohol and sinapyl alcohol appeared at an early stage of treatment and then decreased. In turn, γ -methyl ethers of coniferyl alcohol and sinapyl alcohol appeared to be comparatively stable in supercritical methanol. This pathway was already eluci-

dated by the lignin model compound study, and conversions of coniferyl alcohol and sinapyl alcohol into their γ -methyl ethers are thought to be due to the acidic character of the supercritical methanol.¹⁴ The maximal total yields of the methanol-soluble compounds from beech and cedar woods were, respectively, 89 wt% and 53 wt% on a lignin basis.

It was demonstrated in the lignin model compound study^{14,15} that the condensed types of linkages, such as 5-5 and β -1, are stable during supercritical methanol treatment, whereas ether linkages such as β -O-4 and α -O-4 are readily cleaved. Therefore, the methanol-insoluble residues in Fig. 7 must be rich in condensed linkage. In addition, a large proportion of the methanol-insoluble residues in cedar is in good agreement with the fact that the lignin structure of softwood is more condensed than that of hardwood.

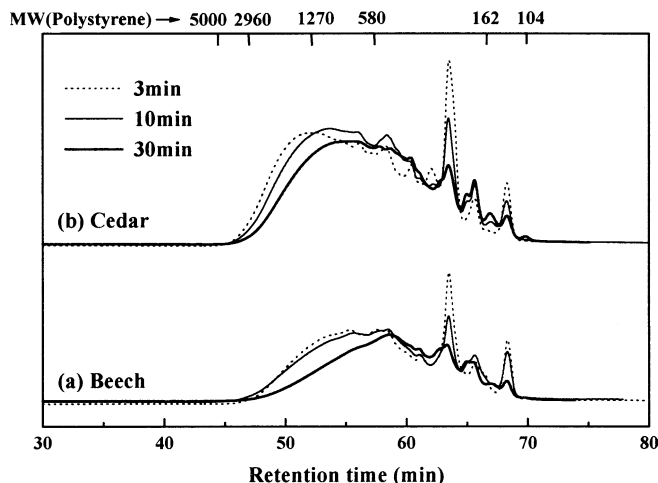


Fig. 8. Gel permeation chromatograms of methanol-soluble portions of **a** beech and **b** cedar woods treated in supercritical methanol at 350°C/43 MPa. Column Shodex KF-803 connected with KF-802.5, KF-802, and KF-801; flow rate 0.6 ml/min; eluent tetrahydrofuran (THF), detector UV₂₈₀; temperature 50°C. MW, molecular weight

Molecular weight distribution of the methanol-soluble portion

The main monomeric products in the methanol-soluble portion were identified as discussed above, but the minor products described by the other products in Fig. 6 and 7 are not clearly identified. Therefore, the molecular weight distribution of the methanol-soluble portion was studied by gas permeation chromatography (GPC). Figure 8 shows the GPC chromatograms of beech and cedar woods treated in supercritical methanol at 350°C/43 MPa. It is apparent that the distribution in beech wood is similar to that in cedar, in a range between 100 and 3000 molecular weight. Furthermore, the mean molecular weight decreased in both woods as the treatment was extended. Therefore, the products that liquefied in methanol would not be condensed and would decompose further into lower-molecular-weight products in supercritical methanol.

Conclusions

The chemical conversion of beech and cedar woods in supercritical methanol was studied using a supercritical fluid biomass conversion system. The conditions for the chemical conversion of woods were optimized at 350°C/43 MPa. Under these conditions beech wood was decomposed to a greater extent than cedar wood, but in both cases more than 90% of the wood was successfully decomposed

and liquefied in methanol. However, about 1%–3% of lignin, on the whole wood basis, was found to remain methanol-insoluble and so would be rich in the condensed types of linkage stable in supercritical methanol, as demonstrated in a study with lignin model compounds.^{14,15}

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