ORIGINAL ARTICLE

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Liquefaction of beech wood in various supercritical alcohols

Abstract The liquefaction of Japanese beech (*Fagus crenata* Blume) was studied with various straight-chain alcohols in subcritical and supercritical states using a batch-type reaction vessel to obtain liquid fuel from lignocellulosics. Under the reaction condition of 270°C, beech wood was liquefied to some extent in all alcohols with about 50%–65% insoluble residue left after treatment for 30 min. Under the condition of 350°C, however, more than 90% of wood was decomposed and liquefied in all alcohols. Alcohols with longer alkyl chains liquefied lignocellulosics in shorter reaction times. Because many kinds of alcohols, such as methanol and ethanol, can be produced from biomass, 100% biomass-based liquid fuel can be prepared by supercritical alcohol technology when using such bioalcohols.

Key words Supercritical fluid · Alcohol · Japanese beech · Lignin · Cellulose

Introduction

Due to human activities of mass production, mass consumption, and mass waste since the early twentieth century, environmental issues such as global warming and acid rain have become increasingly serious in the world. In current environmental situations, environmentally friendly biomass resources such as lignocellulosics should be utilized effectively as an alternative to fossil resources. Although biomass resources are renewable, carbon-neutral, and remarkably massive in amount, they are very bulky and difficult to transport, handle, and store. Therefore, an appropriate methodology is required to convert them into low molecular weight products such as liquid fuels and valuable chemicals.

Supercritical fluid is a candidate for the chemical conversion of lignocellulosics due to its unique properties. As is well known, supercritical water (critical temperature; $Tc = 374°C$, critical pressure; $Pc = 22.1$ MPa) treatment for cellulosic samples has been studied by various groups to obtain saccharides for subsequent fermentation to ethanol.[1–5] However, these hydrolyzed products are further decomposed into various volatile and gaseous compounds in the severe conditions of supercritical water.[6–9]

On the other hand, alcohols such as methanol ($Tc = 239°C$, $Pc = 8.09$ MPa) and ethanol ($Tc = 243°C$, $Pc = 6.38$ MPa) have also been studied for supercritical fluid treatment of lignocellulosics.[10–12] Because these alcohols have lower critical temperatures and pressures than those of water, they can offer milder conditions for the reaction. In addition, these alcohols are expected to readily dissolve relatively high molecular weight products from cellulose, hemicelluloses, and lignin due to their low dielectric constants when compared with that of water.

Actually, McDonald et al.[10] and Poier et al.[11] have reported good conversion of woody biomass into liquefied products by supercritical methanol treatment. In previous works, furthermore, our research group has studied wood liquefaction and decomposition behaviors of its components; cellulose, hemicelluloses, and lignin in supercritical methanol, finding that more than 90% of wood could be decomposed and liquefied under the conditions of 350°C/43 MPa.[13–16] However, a prolonged treatment of about 30 min was required for the liquefaction of wood with methanol.[15]

Regarding other alcohols, Köll et al.[17] conducted a study of delignification by using methanol, ethanol, 1-propanol, and other organic solvents in their supercritical states at around 250°–280°C, and reported that the highest ratio of lignin/carbohydrate degradation was achieved with ethanol. However, because only few studies have been made on

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wood liquefaction in supercritical alcohols, knowledge of it is currently limited.

In this study, therefore, the possibility of wood liquefaction with various alcohols at sub/supercritical states was investigated to achieve a high conversion rate with appropriate reaction conditions. The obtained liquid products would be used directly as liquid fuel because alcohol itself is a good fuel. In addition, many kinds of alcohols can be produced from biomass; for example, methanol can be synthesized from hydrogen and carbon monoxide gasified from biomass, ethanol and butanol can be fermented from biomass saccharides, and octanol and decanol can be obtained by hydrogen reduction of vegetable oils. Thus, 100% biomass-based liquid fuel and chemicals can be created when using such bioalcohols. Additionally, different alcohols have different fuel properties; those with longer alkyl chains have higher calorific values and cetane numbers. Therefore, various types of biofuels can be achieved by changing the type of alcohol.

Materials and methods

Supercritical alcohol treatment

As the woody biomass sample, wood flour of Japanese beech (*Fagus crenata* Blume) passed through 80 mesh (about 280 μm) was subjected to supercritical alcohol treatment. As solvents, six straight-chain monohydric alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-octanol, and 1-decanol) were purchased from Nacalai-tesque, Kyoto.

To start the treatment, approximately 4.9 ml of alcohol was placed with 150 mg of the wood flour in a 5 ml reaction vessel, which was then immersed in a molten tin bath preheated to 270°C or 350°C. The reaction pressure, which is uncontrollable in the batch-type reaction vessel, depended on reaction temperature and type of alcohol. The experimental conditions for the respective alcohols are shown in Table 1 with their critical points. After an adequate reaction time, the vessel was moved to a water bath to quench the reaction. The obtained reaction mixture was then filtered with a 0.2-μm membrane filter to separate the alcohol-soluble portion from the alcohol-insoluble residue.

Table 1. Critical points of various alcohols and reaction conditions in the batch-type vessel

Alcohol	Number of carbons	Critical point		Reaction condition (°C/MPa)	
		T_c (°C)	P_c (MPa)		
Methanol	1	239	8.09	270/27	350/43
Ethanol	2	243	6.38	270/20	350/25
1-Propanol	3	264	5.06	270/14	350/23
1-Butanol	4	287	4.90	270/12[a]	350/23
1-Octanol	8	383	2.86	270/8[a]	350/19[a]
1-Decanol	10	414	2.22	270/4[a]	350/6[a]

[a] Subcritical condition

Analytical methods

Analytical methods for the alcohol-insoluble residue and alcohol-soluble portion were the same as those in our previous work.[15] For the residue, Klason lignin content and acid-soluble lignin were determined, while the amounts of constituent monosaccharides were analyzed by high-performance liquid chromatography (HPLC) for the clear filtrate from acid hydrolyzates obtained in the Klason lignin determination process. The cellulose and hemicellulose contents in the alcohol-insoluble residue were then estimated, based on the amounts of glucose and other monosaccharides, respectively.

On the other hand, the alcohol-soluble portion was directly analyzed by gel permeation chromatography (GPC) and HPLC.[15] Some reaction products were isolated using preparative thin-layer chromatography (TLC) on silica gel plate (Kieselgel 60 F$_{254}$, Merck) and analyzed by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, in which the spectra were recorded in CDCl$_3$ using a Bruker AC-300 (300 MHz) spectrometer with tetramethylsilane as internal standard. Chemical shift δ (ppm) and coupling constant (Hz) of the isolated products were obtained as below.

Coniferyl alcohol γ-ethyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 1.25 (3H, t, $J = 7.0$, -CH$_3$), 3.54 (2H, q, $J = 7.0$, -OCH$_2$-), 3.90 (3H, s, -OCH$_3$), 4.12 (2H, d, $J = 6.2$, Cγ-H), 5.62 (1H, s, -OH), 6.15 (1H, dt, $J = 15.8, 6.2$, Cβ-H), 6.52 (1H, d, $J = 15.8$, Cα-H), 6.83–6.93 (3H, m, aromatic H).

Sinapyl alcohol γ-ethyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 1.25 (3H, t, $J = 7.0$, -CH$_3$), 3.55 (2H, q, $J = 7.0$, -OCH$_2$-), 3.90 (6H, s, -OCH$_3$), 4.12 (2H, d, $J = 6.3$, Cγ-H), 5.52 (1H, s, -OH), 6.17 (1H, dt, $J = 15.8, 6.2$, Cβ-H), 6.51 (1H, d, $J = 15.8$, Cα-H), 6.63(2H, s, aromatic H).

Coniferyl alcohol γ-propyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 0.95 (3H, t, $J = 7.4$, -CH$_3$), 1.56–1.7 (2H, m, -CH$_2$-), 3.44 (2H, t, $J = 6.8$, -OCH$_2$-), 3.90 (3H, s, -OCH$_3$), 4.11 (2H, d, $J = 6.2$, Cγ-H), 5.61 (1H, s, -OH), 6.15 (1H, dt, $J = 15.8, 6.2$, Cβ-H), 6.52 (1H, d, $J = 15.8$, Cα-H), 6.86–6.94 (3H, m, aromatic H).

Sinapyl alcohol γ-propyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 0.95 (3H, t, $J = 7.4$, -CH$_3$), 1.56–1.7 (2H, m, -CH$_2$-), 3.44 (2H, t, $J = 6.7$, -OCH$_2$-), 3.90 (6H, s, -OCH$_3$), 4.12 (2H, d, $J = 6.2$, Cγ-H), 5.51 (1H, s, -OH), 6.17 (1H, dt, $J = 15.8, 6.2$, Cβ-H), 6.51 (1H, d, $J = 15.8$, Cα-H), 6.63 (2H, s, aromatic H).

Coniferyl alcohol γ-butyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 0.93 (3H, t, $J = 7.3$, -CH$_3$), 1.32–1.46 (2H, m, -CH$_2$-), 1.56–1.65 (2H, m, -CH$_2$-), 3.48 (2H, t, $J = 6.6$, -OCH$_2$-), 3.90 (3H, s, -OCH$_3$), 4.11 (2H, d, $J = 6.2$, Cγ-H), 5.61 (1H, s, -OH), 6.15 (1H, dt, $J = 15.8, 6.2$, Cβ-H), 6.52 (1H, d, $J = 15.8$, Cα-H), 6.83–6.92 (3H, m, aromatic H).

Sinapyl alcohol γ-butyl ether (*trans*). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ: 0.93 (3H, t, $J = 7.4$, -CH$_3$), 1.33–1.47 (2H, m, -CH$_2$-), 1.56–1.65 (2H, m, -CH$_2$-), 3.48 (2H, t, $J = 6.5$,

Fig. 1. Changes in the residues of beech wood treated in various sub/supercritical alcohols at **a** 270°C and **b** 350°C. *Circles*, methanol; *squares*, ethanol; *triangles*, 1-propanol; *diamonds*, 1-butanol; *crosses*, 1-octanol; *pluses*, 1-decanol

(a) 270°C   (b) 350°C
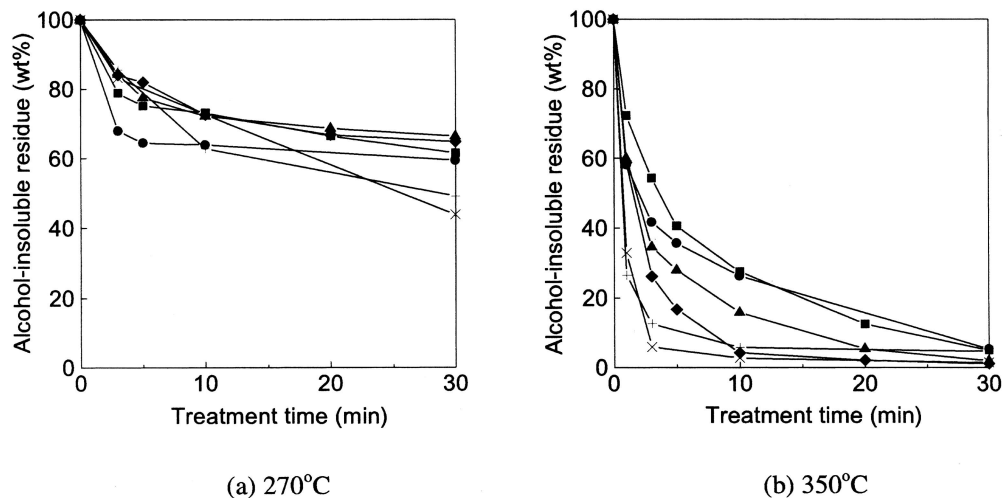
-OCH₂-), 3.90 (6H, s, -OCH₃), 4.11 (2H, d, J = 6.2, Cγ-H), 5.51 (1H, s, -OH), 6.16 (1H, dt, J = 15.8, 6.2, Cβ-H), 6.50 (1H, d, J = 15.8, Cα-H), 6.63 (2H, m, aromatic H).

Results and discussion

Decomposition behaviors of beech wood

Figure 1 shows the changes in the mass of alcohol-insoluble residues of beech wood after treatment in various supercritical alcohols at 270°C and 350°C. Under the condition of 270°C (a), beech wood was liquefied to some extent in all alcohols but 50%–65% of wood was recovered in all cases even after treatment for 30min. For shorter reaction times of less than 10min, the residue amount increased slightly with increasing length of the alcohol alkyl chain. In contrast, the amount of residue decreased with increased length of alcohol alkyl chain for prolonged reaction times over 10min. Under the condition of 350°C (b), however, beech wood was decomposed efficiently and more than 90% of wood was eventually liquefied for all alcohols. In addition, it was apparent that alcohols with longer alkyl chains exhibited faster wood liquefaction. In the case of methanol and ethanol, about 30min of treatment was required to liquefy 90% of the wood, while 20min, 10min, and only 3min of treatment were required for 1-propanol, 1-butanol, and 1-octanol, respectively. However, 1-decanol produced slightly more residue, than 1-octanol; thus, it can be concluded that 1-octanol is the most efficient alcohol for wood liquefaction among those used in this study.

Decomposition of wood components

Figures 2 and 3 show the chemical composition of cellulose, hemicelluloses, and lignin in alcohol-insoluble residues after treated in various alcohols at 270°C and 350°C, respectively. Under the condition of 270°C, it was found that cellulose was not decomposed in alcohols with short alkyl chains, whereas a small amount of cellulose could be lique-

fied in 1-octanol and 1-decanol. Furthermore, hemicelluloses and lignin were liquefied in all cases.

Under the condition of 350°C, on the other hand, cellulose was decomposed successfully and eventually liquefied in all alcohols. The hemicelluloses and lignin were almost decomposed and liquefied within a few minutes. It was also found that alcohols with the longer alkyl chains exhibited faster liquefaction of cellulose.

Assuming that the liquefaction of wood components is the pseudo-first-order reaction, the liquefaction rate constants (k) were evaluated for cellulose, hemicelluloses, and lignin, respectively. The results are shown in Fig. 4. The liquefaction rate constant of cellulose was increased when longer alkyl chain alcohols were used. In the case of methanol, the rate constant for cellulose liquefaction was estimated to be $1.25 \times 10^{-3} s^{-1}$, and increased to $28.7 \times 10^{-3} s^{-1}$ for 1-decanol, a value about 20 times higher than that for methanol. Similarly, the rate constant for hemicelluloses tended to increase with the length of alkyl chain of the alcohol, except for methanol. In contrast, lignin had almost the same rate constant for all alcohols except for 1-decanol, which seemed to promote formation of char-like substances.

Molecular weight distribution of the alcohol-soluble portion

Figure 5 shows the GPC chromatograms of the various alcohol-soluble portions after 30min of treatment at 350°C. Although the chromatograms were recorded using both an ultraviolet (UV) light detector and a refractive index (RI) detector, no difference was observed between the molecular weight distributions given by the two detectors.

The molecular weights of the liquefied products were in ranges below about 3500 for methanol, 7900 for ethanol, 8800 for 1-propanol, 11000 for 1-butanol, 38000 for 1-octanol, and 42000 for 1-decanol by comparison with polystyrene standards. This result indicates that alcohols with longer alkyl chains can dissolve higher molecular weight products, which cannot be liquefied in alcohols with shorter alkyl chains. Although the reason remained unclear why
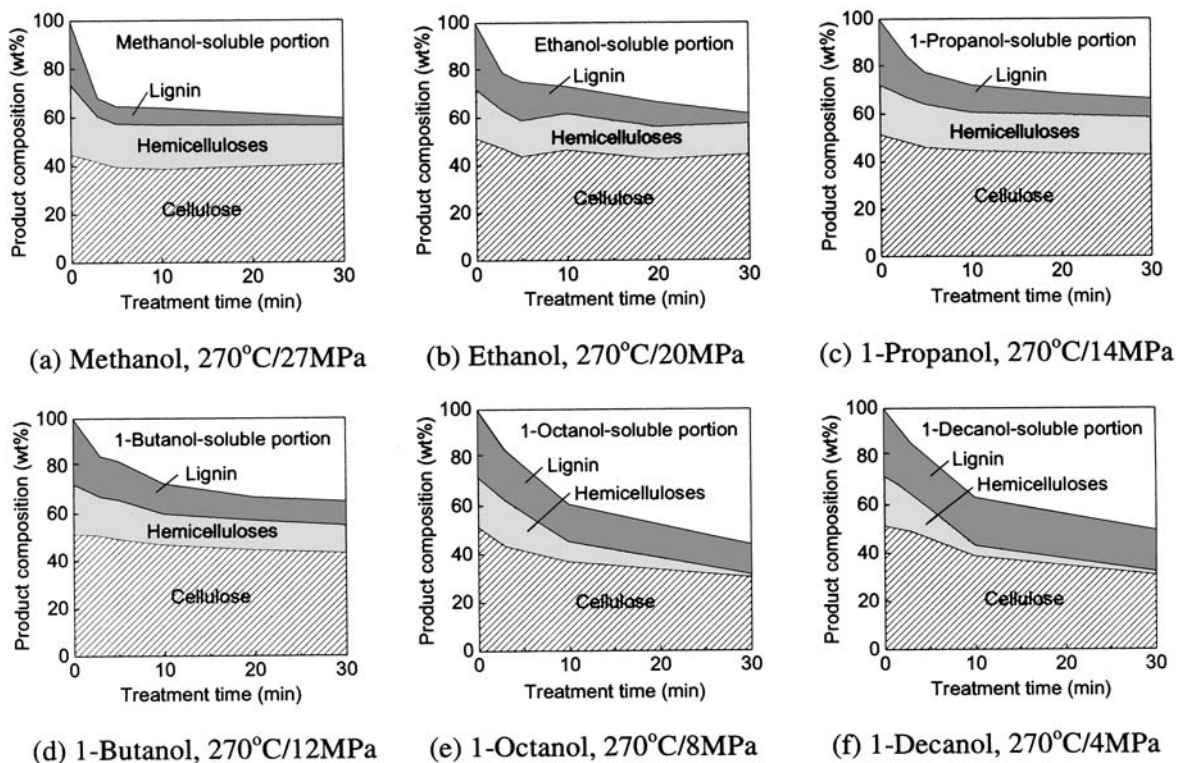
Fig. 2a–f. Chemical composition in the alcohol-insoluble residue after treatment with various sub/supercritical alcohols at 270°C. **a** Methanol, 27 MPa; **b** ethanol, 20 MPa; **c** 1-propanol, 14 MPa; **d** 1-butanol, 12 MPa; **e** 1-octanol, 8 MPa; **f** 1-decanol, 4 MPa
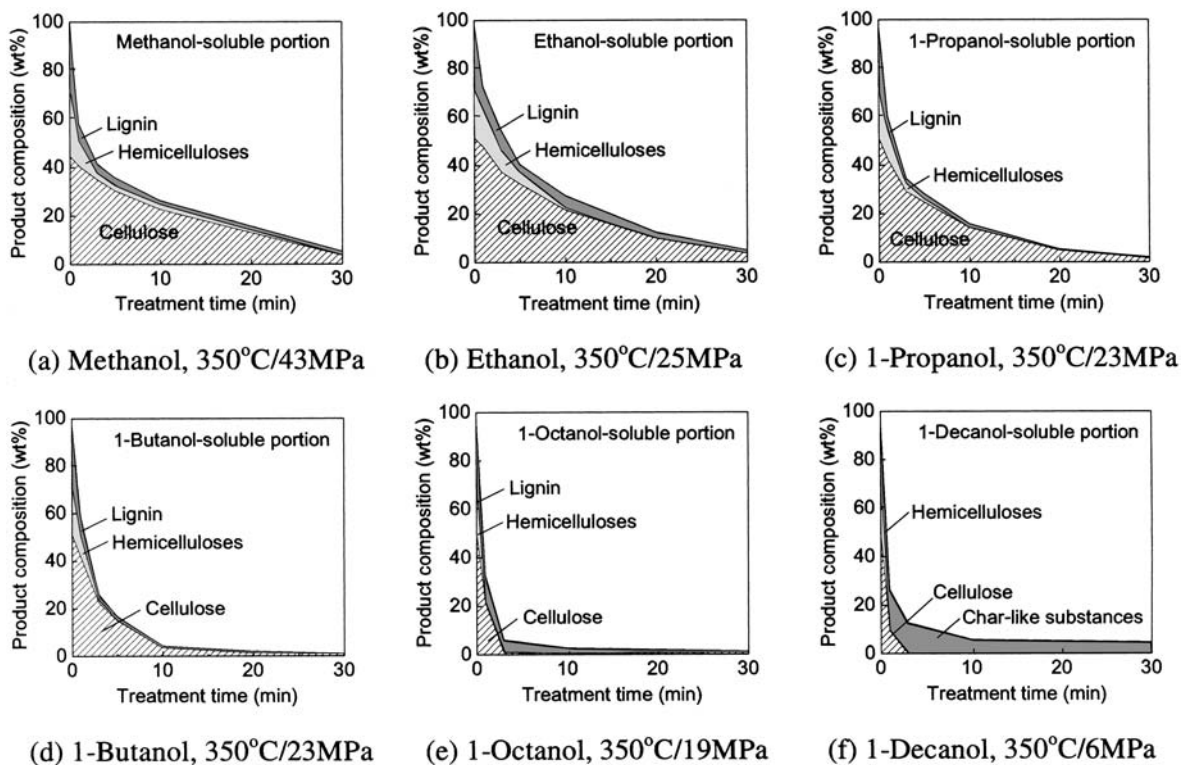

Fig. 3a–f. Chemical composition in the alcohol-insoluble residue after treatment with various sub/supercritical alcohols at 350°C. **a** Methanol, 43 MPa; **b** ethanol, 25 MPa; **c** 1-propanol, 23 MPa; **d** 1-butanol, 23 MPa; **e** 1-octanol, 19 MPa; **f** 1-decanol, 6 MPa
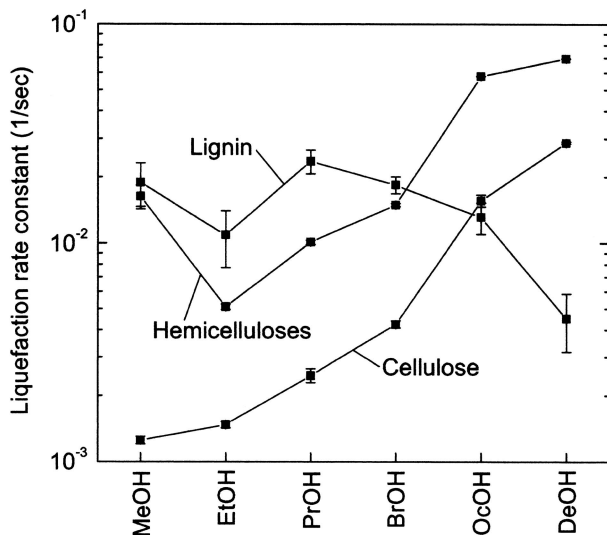
Fig. 4. Liquefaction rate constants of wood cell-wall components in the various sub/supercritical alcohols at 350°C
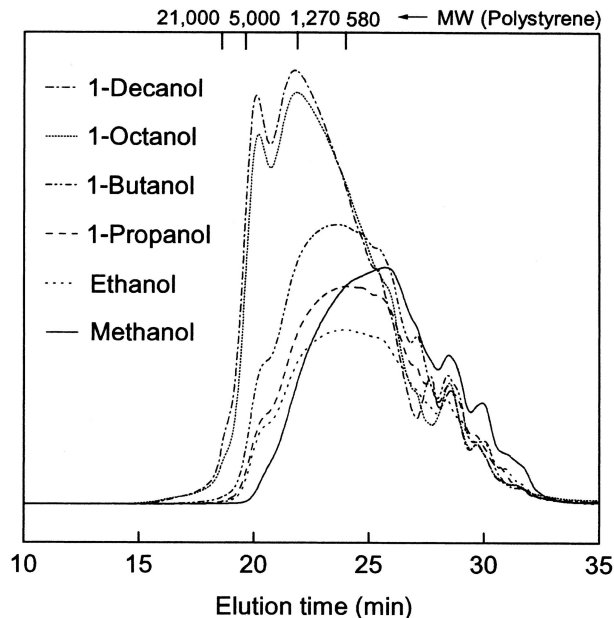

Fig. 5. Gel permeation chromatograms of the various alcohol-soluble portions after treatment at 350°C for 30 min (column, Shodex KF-801 connected with KF-802; eluent, tetrahydrofuran; detector, ultraviolet light detector (UV, λ = 280 nm); flow rate, 0.6 ml/min; temperature, 50°C)

the efficiency for wood liquefaction changes depending on the kind of alcohol used, it should relate to solubility of the decomposed products with alcohol. It is, thus, suggested that the alcohol with the longer alkyl chain exhibits a faster wood conversion to liquefied products, due to its liquefaction of the higher molecular weight products.

Chemicals from lignin and cellulose

For the determination of lignin-derived products, HPLC analysis was carried out using a reversed-phase column and UV light detector. Therefore, observed peaks were considered to be mainly lignin-derived peaks because ordinary cellulose-derived products could not absorb the UV light except for 5-hydroxymethylfurfural (5-HMF) and furfural. Figure 6 shows the HPLC chromatograms of various alcohol-soluble portions as treated at 270°C. The products observed at the retention times of 16.7 and 17.2 min were identified to be coniferyl alcohol (CA) and sinapyl alcohol (SA), respectively, after comparing them with authentic samples. They appeared at the first stage of the reaction in any alcohol-soluble portion. In the case of methanol, other peaks were also observed at 28.6 and 29.0 min, which were identified to be SA γ-methyl ether and CA γ-methyl ether by ^{1}H-NMR analysis, respectively. In a similar manner, their γ-alkyl ethers were also found for the respective alcohols used. In turn, other peaks observed at retention times of 36.9 and 37.4 min were increased in intensity. These newly formed products were identified to be 2,6-dimethoxy-4-(1-propenyl)phenol and isoeugenol by comparison with authentic samples.

Based on these lines of evidence, the degradation pathway of lignin in various supercritical alcohols was proposed as follows; lignin can be depolymerized to the lower molecular weight products by cleavage of ether linkages,[14,16] and then dissolved in alcohol. However, lignin rich in condensed linkages cannot be depolymerized sufficiently to

liquefy in alcohol and it is recovered in the alcohol-insoluble residue.[15,16] Part of the products liquefied is depolymerized into monomeric units of lignin such as CA, SA, and their γ-alkyl ethers, which are further converted to other products as mentioned above.

On the other hand, Fig. 7 shows the HPLC chromatograms of the methanol-soluble and ethanol-soluble portions as treated at 350°C for 30 min. The analyses were carried out using a column exclusively for saccharides (Ultron PS-80P) so that observed peaks were considered to be mainly cellulose-derived signals. The compounds observed at retention times of 9.6, 10.1, 10.9, 11.7, and 21.9 min were identified to be methyl-β-D-glucoside (Me-β-glu), ethyl-β-D-glucoside (Et-β-glu), methyl-α-D-glucoside (Me-α-glu), ethyl-α-D-glucoside (Et-α-glu), and levoglucosan (LG), respectively, by comparison with authentic samples. Although products in other alcohol-soluble portions remained unclear, it is suggested that alkyl-α, β-D-glucosides were generated by alcoholysis of cellulose in supercritical alcohol. Furthermore, 5-HMF and furfural, which were considered to be alkyl-α, β-D-glucoside-derived compounds, were found in all alcohol-soluble portions as mentioned previously (Fig. 6).

According to the decomposition pathway of avicel proposed by Ishikawa and Saka,[13] methanolysis of cellulose in supercritical methanol resulted in methylated cellotriose and methylated cellobiose, which are converted to methyl-α-D-glucoside and methyl-β-D-glucoside. Subsequently, these products were anomerized each other, and as the treatment was prolonged, they were decomposed further to other products, such as LG, 5-HMF, and furfural. For other alcohols, similar pathways should be given for cellulose decomposition.
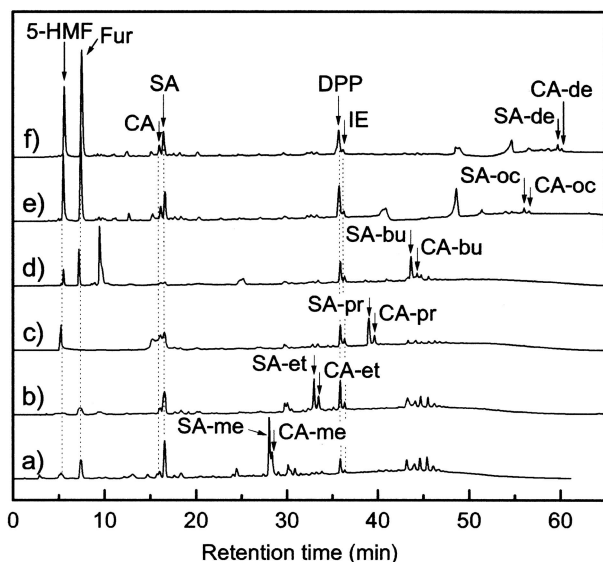
Fig. 6. High-performance liquid chromatography (HPLC) chromatograms of the alcohol-soluble portions after treatment with methanol (**a**), ethanol (**b**), 1-propanol (**c**), 1-butanol (**d**), 1-octanol (**e**), and 1-decanol (**f**) at 270°C for 30 min. Column, STR ODS-II; eluent, CH₃OH/H₂O, 20/80–100/0 (0–60 min; detector, UV(280 nm); flow rate, 1.0 ml/min; temperature, 40°C; *CA*, coniferyl alcohol; *SA*, sinapyl alcohol; *CA-me*, coniferyl alcohol γ-methyl ether; *5-HMF*, 5-hydroxymethylfurfural; *Fur*, furfural; *DPP*, 2,6-dimethoxy-4-(1-propenyl) phenol; *IE*, isoeugenol; other abbreviations are for the respective γ-alkyl ethers
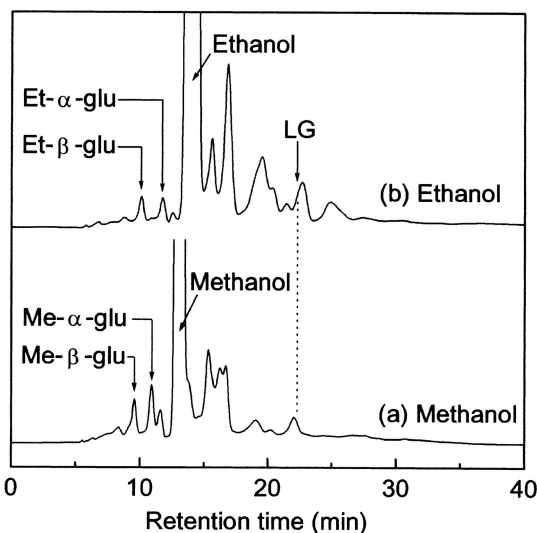

Fig. 7. HPLC chromatograms of methanol-soluble (**a**) and ethanol-soluble (**b**) portions after treatment at 350°C for 30 min. Column, Ultron PS-80P; eluent, H₂O; detector, refractive index detector; flow rate, 0.8 ml/min; temperature, 80°C. *LG*, levoglucosan

Conclusions

The chemical conversion of beech wood in various supercritical alcohols was studied using a batch-type reaction vessel. At 350°C, all three cell wall components of wood were decomposed effectively in all cases and over 90% of the wood was successfully liquefied. Among the

alcohols used in this study, 1-octanol gave the fastest conversion of wood into liquefied products, achieving about 95% conversion only by 3 min of treatment. For the lignin-derived products, the main monomeric products were identified to be CA, SA, and their γ-alkyl ethers, while for the cellulose-derived products, the α and β alkyl-D-glucosides, LG, furfural, and 5-HMF were identified in each alcohol-soluble portion.

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