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ORIGINAL ARTICLE

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Decomposition behavior of woody biomass in water-added supercritical methanol

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Abstract The chemical conversion of Japanese beech (*Fagus crenata* Blume) in water-added supercritical methanol was studied for a wide range of water content using a batch-type reaction vessel to obtain chemicals from lignocellulosics. It was consequently found that addition of water enhanced the decomposition of wood cell wall components; cellulose, hemicelluloses, and lignin. In cases of high water content, however, it resulted in low solubility of lignin-derived products causing an increase in the mass of the residue. The water content was thus optimized to be around 10% (v/v) for the decomposition of wood. Concomitantly, the yields and selectivity of the chemicals from wood could be regulated by the addition of water, especially for the lignin-derived products. As a result, the monomeric compounds of lignin, coniferyl alcohol and sinapyl alcohol, were recovered as their γ-methyl ethers in the presence of water in higher yields than those obtained without addition of water.

Key words Supercritical methanol · Japanese beech · *Fagus crenata* · Lignin · Cellulose

Introduction

In the present state of environmental conditions, including global warming, acid rain, and exhaustion of fossil resources, biomass resources that are renewable, carbon neutral, and remarkably massive in amount on the earth are becoming more important as alternatives to fossil resources. According to our recent survey, about 360 million tonnes of biomass resources are generated annually in Japan, of which 76 million tonnes are unutilized.[1] The latter value is enormous and equivalent to about 11% of the carbon dioxide emitted in 1990 in Japan. Therefore, technologies that can convert biomass resources into valuable liquid fuels and chemicals will be important for mitigating our energy and environmental problems. For the chemical conversion of biomass resources, recently, the use of supercritical fluid has been thought to be attractive due to its unique properties.

Supercritical water (>374°C, >22.1 MPa) has a lower dielectric constant and higher ionic product than those of liquid water at ambient conditions. These values can be continuously varied by regulating temperature and pressure.[2–5] The supercritical (or near-critical) water treatment of cellulose has been studied by various groups to obtain hydrolysis products for a subsequent alcohol fermentation.[6–14] In these cases, although the pyrolysis was found to be depressed by controlling the reaction conditions, hydrolysis products such as glucose were further rapidly decomposed due to the high critical temperature of water.

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. In supercritical methanol, therefore, side reactions caused by pyrolysis are expected to be depressed. In addition, the dielectric constant of liquid methanol at ambient conditions is about 32, which allows moderate solubility for many kinds of polar and electrolytic substances, as well as substances with low polarity. In turn, the dielectric constant lowers to be about 7 at the critical point,[5] which is equivalent to that of typical nonpolar organic solvents, and it can dissolve many kinds of nonpolar organic substances and inorganic gases. Therefore, the use of methanol as a solvent for supercritical fluid treatment is expected to readily dissolve relatively high molecular weight products from cellulose, hemicelluloses, and lignin.

McDonald et al.[15] and Poirier et al.[16] reported good conversion of wood to liquefied products by supercritical methanol treatment. Ishikawa and Saka[17] studied the treatment of cellulose samples including avicel (microcrystalline

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cellulose), cotton linters, and dissolving pulp, and reported that the cellulose could be decomposed by methanolysis to produce methyl glucosides. Minami and Saka[18] also studied the treatment of hardwood and softwood and reported that all cell wall components of wood, cellulose, hemicelluloses, and lignin, were decomposed and liquefied efficiently in methanol at 350°C/43 MPa. In these cases, however, a prolonged treatment of about 30 min was required for the decomposition of cellulose due to its fine fibrillar and crystalline structures.

In this study, therefore, the water-added supercritical methanol treatment of woody biomass was studied to produce chemicals more efficiently with higher yields. The addition of water to methanol is expected to give high reactivity in the solvolysis caused by the higher ionic product of subcritical water,[2] with the relatively milder conditions of supercritical methanol.

Materials and methods

Water-added supercritical methanol treatment

As woody biomass sample, wood flour of Japanese beech (*Fagus crenata* Blume) having passed 80 mesh (280 μm) was subjected to water-added supercritical methanol treatment. High performance liquid chromatography (HPLC)-grade methanol and distilled water were used as solvents. The treatment was conducted using a batch-type supercritical fluid biomass conversion system.[17,19]

To start the treatment, approximately 4.9 ml of methanol and water mixture was placed with 150 mg of beech wood flour in a 5-ml reaction vessel. The percentage of water (v/v) [water/(water + methanol)] ranged from 0% to 100%. The reaction vessel was then immersed in a molten tin bath preheated to 270°C or 350°C. Typical time courses of the temperature and pressure in the vessel are shown in previous work.[12,17]

After the treatment time, which ranged between 1 and 30 min, the reaction mixture was filtered with a 0.2-μm membrane filter to separate water/methanol-soluble portion from the residue. The residues included hydrophobic oily substances, especially in cases with high water content, in a manner similar to that observed in the supercritical water treatment of wood.[14] Therefore, the water/methanol-insoluble residue was washed with 10 ml of methanol to recover the oily substances as the methanol-soluble portion and the remaining residue was referred to as methanol-insoluble residue. The masses of each portion were weighed after drying.

Analytical methods

The water/methanol-soluble and methanol-soluble portions were directly analyzed by HPLC carried out with a Shimadzu LC-10A system under the following conditions: (1) column, STR ODS-II; flow rate, 1.0 ml/min; eluent, CH_3OH/H_2O 20/80 → 100/0 (0 → 60 min); detector, ultraviolet light (UV, λ = 280 nm); temperature, 40°C; (2) column, Ultron PS-80P; flow rate, 0.8 ml/min; eluent, H_2O; detector, refractive index detector (RID); temperature, 80°C. Gel permeation chromatography (GPC) was also carried out for the water/methanol-soluble and methanol-soluble portions with the same system under the following conditions: column, Shodex KF-801 connected with KF-802, KF-802.5, and KF-803 in series; flow rate, 0.6 ml/min; eluent, tetrahydrofuran (THF); detector, UV (280 nm) and RID; temperature, 50°C.

For the methanol-insoluble residue, the Klason lignin content and acid-soluble lignin were determined according to the described method.[20] In addition, the amounts of constituent monosaccharides from the methanol-insoluble residue were determined by HPLC analysis of the clear filtrate from the acid hydrolyzates in the Klason lignin determination under the conditions mentioned above. The cellulose and hemicelluloses contents in the methanol-insoluble residue were then estimated based on the amounts of glucose and other monosaccharides, respectively.

Results and discussion

Decomposition behavior of wood in water-added supercritical methanol

Figure 1 shows the changes in each fraction from beech wood as a function of water content as treated at 350°C for 5 min. In the presence of water, decomposition and liquefaction of wood proceeded efficiently and the methanol-insoluble residue was less than that found without water

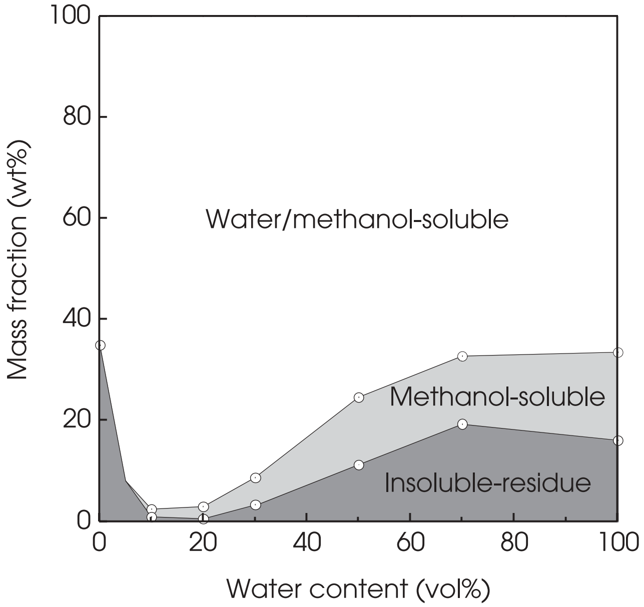


Fig. 1. Changes in the mass fraction of water/methanol-soluble portion, methanol-soluble portion, and methanol-insoluble residue from beech wood treated in water-added supercritical methanol with various water contents at 350°C for 5 min

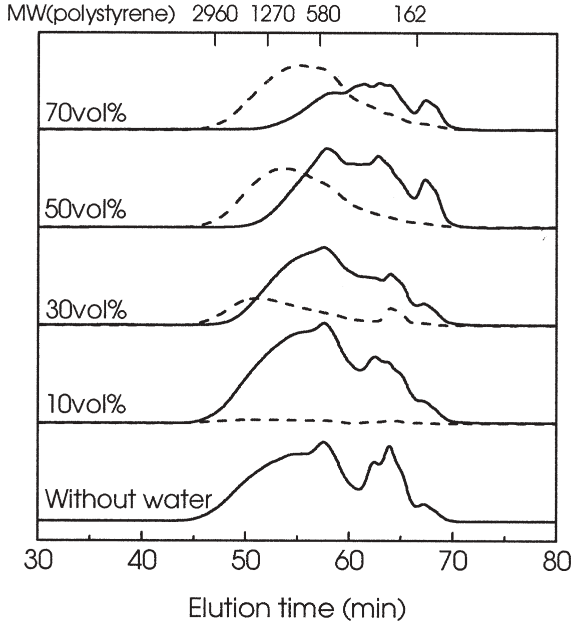


Fig. 2. Gel permeation chromatograms of the water/methanol-soluble portion (*solid lines*) and methanol-soluble portion (*dotted lines*) from beech wood treated in water-added supercritical methanol with various water contents at 350°C for 5 min. Ultraviolet detection (λ = 280 nm)

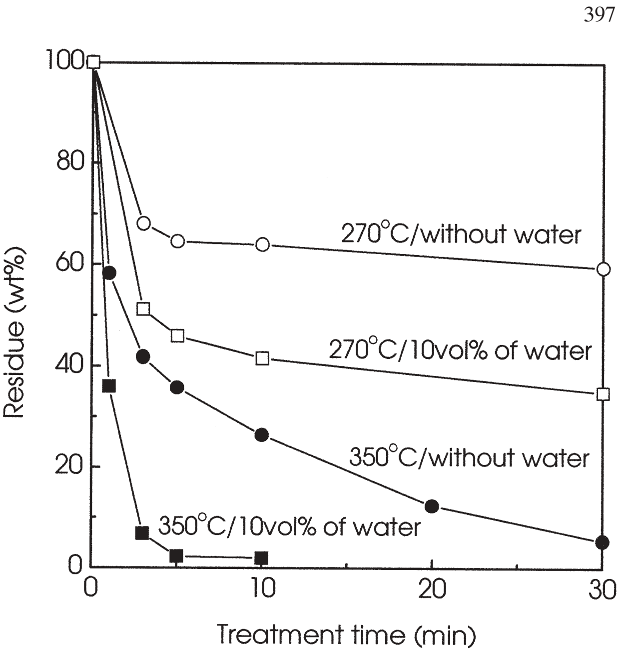


Fig. 3. Changes in the amount of residue of beech wood treated in water-added supercritical methanol under various conditions

(0% v/v). The amount of residue decreased with increasing water content and a minimum residue mass fraction was obtained at around 10% (v/v) water content. In turn, however, the amounts of both the methanol-soluble portion and the methanol-insoluble residue increased gradually as the water content was further increased. According to the study of the supercritical water treatment of wood,[14] the methanol-soluble portion mainly consists of lignin-derived products. Similarly, the methanol-soluble portion obtained in this study was always found to contain only lignin-derived products by HPLC analysis.

Figure 2 shows the molecular weight distributions of the water/methanol-soluble portion and methanol-soluble portion by GPC analysis. In the case without water, the distribution of the water/methanol-soluble portion ranged from about 3000 to less than 162 based on the polystyrene molecular weight standard. With an increase in water content, however, a part of higher molecular weight material in the water/methanol-soluble portion decreased gradually and transferred to the methanol-soluble portion. This result indicates that the increase in the amount of methanol-soluble portion shown in Fig. 1 is caused by the decrease in solubility of the lignin-derived products due to the high polarity of water. Concomitantly, the mass increase of the methanol-insoluble residue is likely to originate from high molecular weight oily substances from lignin being unable to diffuse into the mixture of methanol and water.

Eventually, the optimum water content was found to be around 10% (v/v) for the decomposition and liquefaction of woody biomass at 270°C and 350°C. In the work that followed, therefore, water content was set at 10%. In this case, the amount of the methanol-soluble portion was very small, as shown in Fig. 1, and it was assumed to be negligible.

Figure 3 shows the changes in the methanol-insoluble residues as a function of the treatment time. At 270°C and without water, the residue remained constant after 5 min of treatment and about 65% of the residue was recovered after 30 min. Even though in the presence water the residue was less than that in the case without water, the methanol-insoluble residue also remained constant after 5 min of treatment. Regarding the cell wall components, Fig. 4 shows the changes in the chemical composition of cellulose, hemicelluloses, and lignin in the methanol-insoluble residue treated at 270°C without water and with 10% water. It was found that the lignin treated with 10% water was liquefied to a greater extent than that without water. A more apparent trend was observed in the conversion of hemicelluloses. In the case without water, 16% (w/w) of hemicelluloses remained in the residue even after treatment for 30 min, whereas, with 10% water, the hemicelluloses disappeared completely after 30 min. In this way, the addition of a small amount of water enhanced the decomposition of lignin and hemicelluloses, which should be caused by the solvolytic character of subcritical water. On the other hand, however, cellulose was not decomposed under the given condition in both cases. This observed difference between hemicelluloses and cellulose possibly originates from the differences in their molecular structures; hemicelluloses are in amorphous form, whereas cellulose is in crystalline form. Therefore, hemicelluloses are more accessible to molecules of methanol and water than cellulose.

At 350°C, however, more than 90% (w/w) of wood was eventually liquefied in both cases as shown in Fig. 3. This result indicates that the cellulose in wood decomposes efficiently in water/methanol at such a high temperature. As

Fig. 4. Product composition from beech wood treated in supercritical methanol at 270°C **a** without water and **b** with 10% (v/v) water

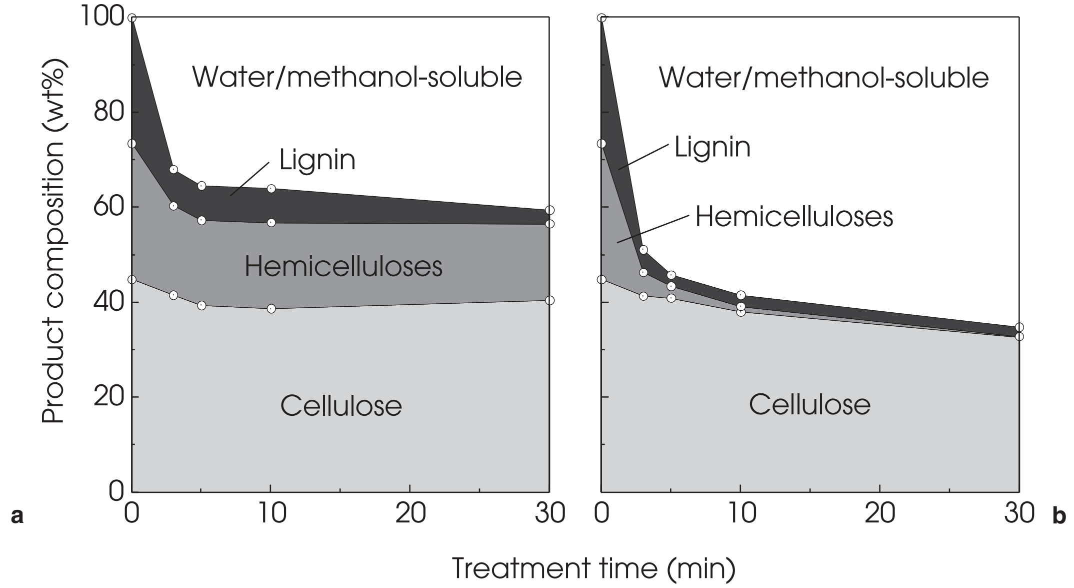
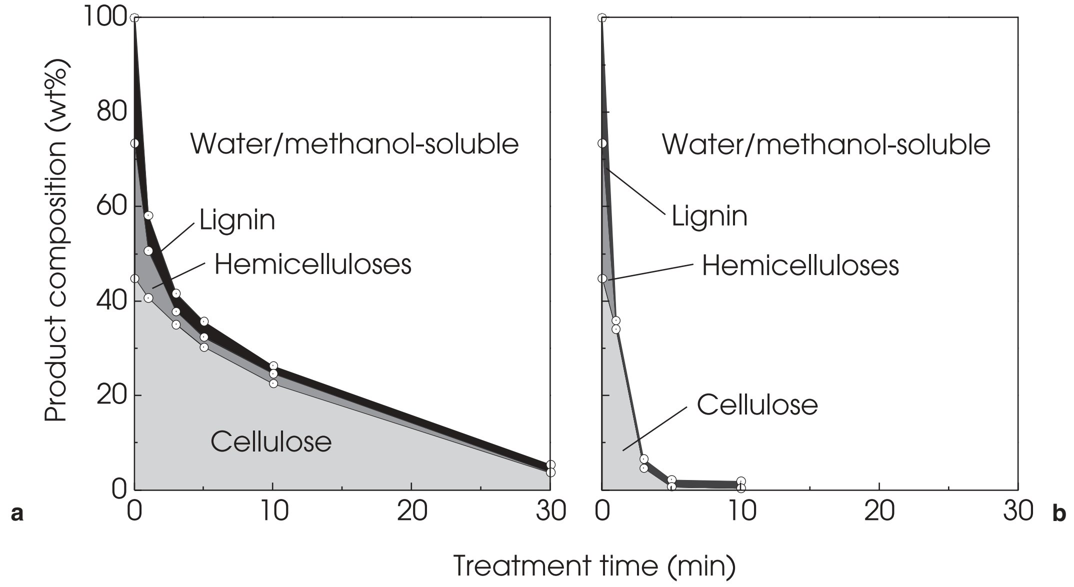


Fig. 5. Product composition from beech wood treated in supercritical methanol at 350° **a** without water and **b** with 10% (v/v) water



shown in Fig. 5, cellulose was liquefied efficiently in water/methanol at 350°C. Moreover, in the presence of water, the cellulose was completely liquefied after 5 min of treatment, while more than 30 min of treatment was required in the case without water. This implies that the crystalline structure of cellulose can be relaxed at such a high temperature, and once that occurs, the water also enhances the decomposition of cellulose. For lignin, however, about 1.5% (w/w) of the residue on the original wood basis remained constant after 3 min of treatment in both cases as observed in Fig. 5. In our previous study, the remaining lignin was characterized to be rich in condensed structures of linkages, such as aryl–aryl linkages, which are stable in supercritical methanol.[18,21,22]

Chemicals from wood in water/methanol-soluble portion

Lignin-derived products

According to the proposed degradation pathway of lignin in supercritical methanol,[18] lignin can be decomposed to low molecular weight products by cleavage of ether linkages, and the products lower than about 3000 in molecular weight can be liquefied in methanol. After prolonged treatment, part of the liquefied products is further depolymerized into coniferyl alcohol (CA) and sinapyl alcohol (SA), which are the monomeric units of guaiacyl and syringyl lignin, respectively. These are then converted to their γ-methyl ethers (CA-γ and SA-γ) and further decomposed to isoeugenol (IE) and 2,6-dimethoxy-4-(1-propenyl)phenol (DPP), respectively.

Table 1. Yields of lignin-derived products from beech wood treated under various conditions in water-added supercritical methanol

Reaction condition	Yield (wt% on lignin)					
	Guaiacyl lignin			Syringyl lignin		
	CA	CA-γ	IE	SA	SA-γ	DPP
Without water						
270°C/3 min	2.9	1.8	0.0	12.9	6.0	0.0
5 min	2.3	3.7	0.14	9.1	11.4	0.67
10 min	1.2	5.8	0.18	10.0	12.5	1.2
30 min	0.76	2.5	0.58	7.8	10.5	3.5
350°C/1 min	1.8	2.59	1.6	17.2	8.2	4.7
3 min	0.0	0.47	1.8	1.7	1.7	15.3
5 min	0.0	0.27	1.7	0.34	0.27	14.8
10 min	0.0	0.0	2.3	0.25	0.0	14.8
With 10% water						
270°C/3 min	1.3	5.8	1.1	4.1	28.5	3.8
5 min	1.4	4.7	1.5	3.1	22.0	6.1
10 min	0.61	2.5	1.6	3.0	8.5	8.1
30 min	0.0	0.0	2.2	0.0	0.0	11.2
350°C/1 min	0.0	1.1	2.4	0.0	3.5	12.9
3 min	0.0	0.0	2.9	0.0	0.0	15.1
5 min	0.0	0.0	3.8	0.0	0.0	14.4
10 min	0.0	0.0	1.6	0.0	0.0	7.1

CA, coniferyl alcohol; CA-γ, coniferyl alcohol γ-methyl ether; IE, isoeugenol; SA, sinapyl alcohol; SA-γ, sinapyl alcohol γ-methyl ether; DPP, 2,6-dimethoxy-4-(1-propenyl)phenol

Table 1 shows the yields of lignin-derived compounds on the basis of the original lignin. At 270°C and without water, CA, SA, and their γ-methyl ethers were relatively stable during the treatment so that the yields of IE and DPP were low. Therefore, CA, SA, and their γ-methyl ethers were obtained in a total yield of about 25%–30% (w/w) on lignin basis, although each yield of them was not high. On the other hand, in the presence of water, the decomposition of lignin proceeded efficiently and CA and SA were quickly converted so that their γ-methyl ethers were obtained in yields that were higher than those without water. As a result, 28.5% (w/w) of SA-γ was recovered after treatment for 3 min. However, prolonged treatment resulted in further conversion of the γ-methyl ethers to IE and DPP. At 350°C, the rapid conversion to IE and DPP was found in both cases so that about 3% (w/w) and 15% (w/w) of IE and DPP were obtained, respectively. In this way, it was found that the addition of water could regulate the yields and selectivity of the compounds produced from lignin during the supercritical methanol treatment of wood. The yield of 28.5% (w/w) of sinapyl alcohol γ-methyl ether was nearly the same as that of syringaldehyde from the alkaline nitrobenzene oxidation of wood.[23]

Cellulose-derived products

According to the decomposition pathway of cellulose that was proposed previously,[17] methanolysis of cellulose in supercritical methanol results in methylated cello-oligosaccharides, such as methylated cellotriose and cellobiose, which are converted to methyl β-D-glucoside (MG-β) and methyl α-D-glucoside (MG-α). Subsequently, these were anomerized and as the treatment was prolonged, these were further decomposed to other products, such as levoglucosan (LG) and 5-hydroxymethylfurfural (5-HMF).

Table 2 shows the yields of cellulose-derived compounds on the basis of the original cellulose. At 350°C and with no added water, methyl glucosides were about 15% (w/w) of the total yield after 30 min of treatment but were not produced in the first stage of the reaction. Furthermore, in case with water, although the methyl glucosides were further decomposed to other products, such as 5-HMF, they were also produced in short reaction times. In this way, the addition of water could also regulate the yields of the compounds produced from cellulose, as well as lignin. At 350°C and with 5% water, 6.1% (w/w) of MG-β and 9.9% (w/w) of MG-α were found after treatment for 5 min, and these values were slightly higher than those found in the case without water.

Conclusions

The decomposition behavior of wood during water-added supercritical methanol treatment was studied to obtain chemicals from lignocellulosics. It was found that the addition of water enhanced the decomposition of cellulose, hemicelluloses, and lignin even though higher water content resulted in lower solubility of the high molecular weight products from lignin, causing an increase in the yield of the methanol-insoluble residue. The optimum water content for the conversion of woody biomass to the liquefied

Table 2. Yields of cellulose-derived products from beech wood treated under various conditions in water-added supercritical methanol

Reaction condition	Yield (wt% on cellulose)				
	MG-β	MG-α	LG	5-HMF	Fur
Without water					
350°C/5 min	Trace	Trace	Trace	0.46	0.32
10 min	1.6	3.2	7.6	0.47	0.31
20 min	3.7	6.6	5.4	0.37	0.21
30 min	5.4	9.0	5.0	0.57	0.27
With 10% water					
350°C/1 min	0.89	2.8	0.0	0.83	0.26
3 min	3.0	3.8	2.8	1.5	0.28
5 min	1.6	1.8	2.4	0.72	0.20
10 min	0.0	0.0	0.0	0.08	0.20

MG-β, methyl β-D-glucoside; MG-α, methyl α-D-glucoside; LG, levoglucosan; 5-HMF, 5-hydroxymethyfurfural; Fur, furfural

products was found to be around 10% (v/v). As a result, at 350°C, more than 95% (w/w) of beech wood was decomposed in water/methanol mixture after treatment for 5 min. In addition, yields and the selectivity of chemicals from both cellulose and lignin could be regulated by the addition of water. Overall, by the treatment with water-added supercritical methanol, chemicals such as coniferyl alcohol γ-methyl ether, sinapyl alcohol γ-methyl ether, and methyl glucosides could be obtained rather efficiently. Sinapyl alcohol γ-methyl ether was recovered in a high yield of 28.5% (w/w) on lignin.

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