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Decomposition behavior of cellulose in supercritical water, subcritical water, and their combined treatments

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Abstract A comparative study on decomposition of cellulose between supercritical water (400°C, 40MPa) and subcritical water (280°C, 40MPa) treatments was made to elucidate the difference in their decomposition behavior. Consequently, the supercritical water treatment was found to be more suitable for obtaining high yields of hydrolyzed products. However, cellulose was found to be more liable to fragment under supercritical water treatment, resulting in a decrease in the yield of hydrolyzed products. On the contrary, cellulose was found to be liable to more dehydration in the subcritical water treatment. Based on these results, we have proposed the combined process of short supercritical water treatment followed by subcritical water treatment so as to inhibit fragmentation. Consequently, this combined treatment was able to effectively control the reaction condition, and to increase the yield of hydrolyzed products.

Key words Cellulose · Chemical conversion · Saccharides · Subcritical water · Supercritical water

Introduction

The conversion of biomass into energy and chemicals has gained considerable attention in recent years because of depletion of fossil fuel resources. Minami and Saka^{1,2} reported that total quantities of biomass annually generated and available in Japan are about 370 million and 77 million tons, respectively. Efficient utilization of these resources must be an obligatory subject of our future, and that of lignocellulosics is particularly important because these materials are abundant and do not compete with food resources.

For the conversion of lignocellulosics into energy and chemicals, saccharification of cellulose and hemicellulose followed by fermentation is one of the methods to obtain ethanol which can be used not only as a useful chemical but also as liquid fuel. The two major methods for hydrolysis of lignocellulosics are by the use of acid^{3,4} and enzyme.⁵ Apart from these approaches, subcritical and supercritical water (>374°C, >22.1MPa) treatments have also been investigated.^{6–14}

Bobleter⁶ proposed the hydrothermal treatment with subcritical water of lignocellulosics without using any catalyst. Recently, Sasaki et al.¹⁰ conducted supercritical water treatment of cellulose, and found that cellulose can be converted to water-soluble saccharides more effectively in supercritical water than in subcritical water. In addition, Sasaki et al.¹⁵ and Antal et al.¹⁶ conducted research on a decomposition mechanism of saccharides in subcritical and supercritical water. It was found that the main reactions of saccharides involve hydrolysis, dehydration, and fragmentation.

We also reported that lignocellulosics can be separated to carbohydrate-derived and lignin-derived products by supercritical water treatment.¹⁷ The former, which mainly consists of polysaccharides, oligosaccharides, monosaccharides, and their decomposed products, are an appropriate source of ethanol fermentation,^{12,14,18} while the latter, which mainly consists of monomeric and oligomeric lignin-derived products, may be useful as alternatives to aromatic chemicals from fossil fuel resources.^{13,19} Therefore, we proposed the ethanol-producing process from lignocellulosics using supercritical water technology followed by fermentation.^{20–22} To realize this process, the treatment conditions must be improved and optimized to produce a high yield of fermentable sugars. Thus, optimization of these reactions has been attempted by developing various treatment systems with appropriate treatment time, temperature, and pressure.

The treatment system can be broadly categorized into batch-type and flow-type systems.²³ Batch-type systems are not flexible enough to control treatment time, temperature, and pressure, and excessive decomposition of hydrolyzed

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products from cellulose inevitably takes place. On the other hand, a flow-type system can flexibly regulate these treatment conditions, and can hydrolyze cellulose without excessive decomposition.¹⁴ However, this system is not enough to regulate the decomposition pathway of cellulose in supercritical and subcritical water. Because the properties of supercritical water and subcritical water can be regulated by their temperature, pressure, and density,^{24,25} it is important to select the pressure and temperature for controlling the decomposition pathway of cellulose.

In this study, we developed an instrument with a flow-type system so as to compare decomposition behaviors of cellulose in supercritical water, subcritical water, and their combined treatments, to increase the yield of water-soluble saccharides.

Materials and methods

Samples and chemicals

Microcrystalline cellulose (Avicel PH-101, Asahi Kasei) was used as a sample. Distilled water were used in high performance liquid chromatography (HPLC) grade, while other chemicals were of reagent grade, and were used without purification.

Treatment system

Figure 1 shows the modified flow-type system that can conduct subcritical, supercritical, and their combined treatments of cellulose. This system can be divided into a slurry-pumping section, a solvent-pumping section, a short reaction tube (19 mm in length, 4 mm in inner diameter), a long reaction tube (7000 mm in length, 5 mm in inner diameter), and a cooling system. Both reaction tubes were made of hastelloy C-276. For the slurry-pumping section, the slurried cellulose in water (4.0% w/w) was routinely stirred by the circulating pump to prevent the sample

from precipitating. The sample was injected into the short reaction tube pressurized by the slurry injector up to an appropriate pressure, and was mixed with the supercritical water or subcritical water provided by the solvent-pumping section.

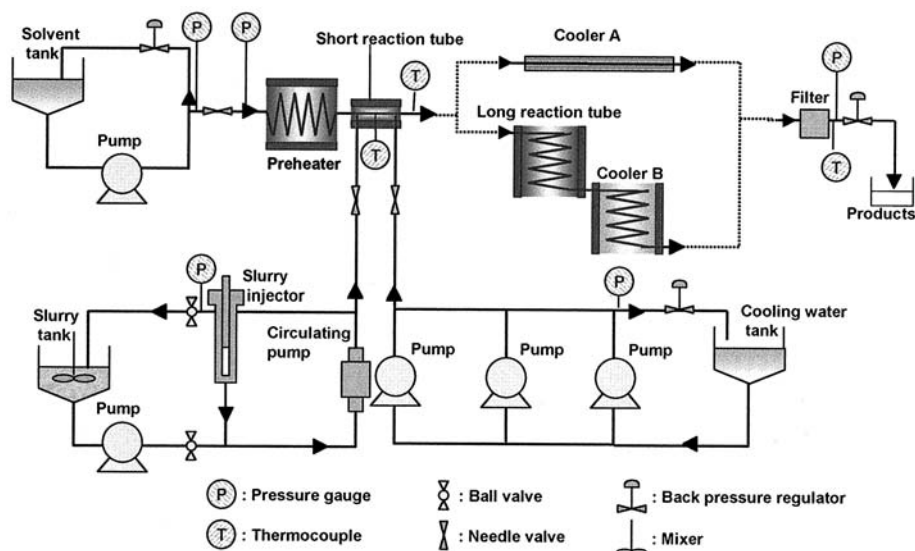
For supercritical water treatment at 400°C and 40 MPa, a five-fold volume excess of cold water was injected into the reactant in supercritical water to quench the reaction. The mixture was further cooled by passing through external cooler A. For subcritical water treatment at 280°C and 40 MPa, cold water was not injected and the reactant was treated further in the long reaction tube. The reactant was, then, cooled by external cooler B. For the combined treatment in supercritical water and subsequent subcritical water, the treatment was conducted first in the short reaction tube. An appropriate volume of cold water was then injected into the reactant to cool the supercritical water to subcritical water conditions. The subsequent subcritical treatment was then carried out in the long reaction tube, and was completed by external cooler B.

Treatments were conducted by injecting slurry (1.0 g cellulose in 25 ml water) to the reaction tube. The treatment time was defined as the residence time of slurried Avicel in the reaction tube, which was calculated from the volume of the reaction tube, the mass flow rate at room temperature, and the density of water at the reaction temperature and pressure.

Fractionation of the treated samples

The treated sample was separated into the supercritical water-soluble portion and supercritical water-insoluble residue by filtration. On standing for 12 h, the precipitates were generated from the former portion due to the change of dielectric constant of water from the supercritical state to the ordinary one. The precipitates were collected by filtration. The treated sample was finally separated into the water-soluble portion, precipitates, and supercritical water-insoluble residue.¹⁴

Fig. 1. Flow-type supercritical water biomass conversion system



Analytical methods

Analysis of the water-soluble portion was carried out by the HPLC (Shimadzu LC10-A) using refractive index detector. The column was an Ultron PS-80P (Shinwa Chem) which has ligand-exchange function. HPLC was operated at 80°C with a water flow rate of 1.0 ml/min.

High-resolution mass spectra (matrix-assisted laser desorption ionization time of flight, MALDI-TOF) were acquired from the Axima-CFR instrument (Shimadzu), operating in the linear mode with an accelerating potential of 20 kV and equipped with a UV pulsed laser (N₂, λ = 337 nm, 200 μ J per shot). The data were acquired by scanning the sample spot manually and averaging 100 laser shots. The samples were prepared by mixing 0.5 μ l of the matrix solution, which was 10 mg/ml of 2,5-dihydroxybenzoic acid, with 0.5 μ l of water-soluble portion directly on the sample slide and allowing the solvent to evaporate under air.

Results and discussion

Yield of the fractionated portions

Table 1 shows the yield of the fractionated portions of cellulose as treated in supercritical water, subcritical water, and their combined treatments. For the supercritical water treatment at 400°C and 40 MPa for longer than 0.1 s, cellulose was decomposed and converted to the supercritical water-soluble portion in a yield of over 90%. The supercritical water-soluble portions treated for 0.1, 0.2, and 0.3 s generated 49.0%, 41.7%, and 6.1% of precipitates, respectively. It has already been found that these precipitates are polysaccharides which can be soluble in supercritical water but are insoluble in ordinary water.^{14,26} It was also found that the degree of polymerization (DP) of the pre-

cipitates was widely distributed between 13 and 100.¹⁴ For the subcritical water treatment at 280°C and 40 MPa, however, 17.3% of subcritical water-insoluble residue still remained even if the treatment time was prolonged to 240 s, and no precipitates were found from the subcritical water-soluble portion. These lines of evidence suggest that not only the reaction rate but also the decomposition mechanism of cellulose are different between conditions in supercritical water and subcritical water.

For the combined treatment with 0.1 s supercritical water treatment and subsequent subcritical water treatment for 15, 30, or 45 s, cellulose was completely decomposed and converted to the subcritical water-soluble portion. However, in supercritical water alone, only the 0.1-s treatment resulted in supercritical water-insoluble residue (9.8%). In subcritical water alone, cellulose was incompletely decomposed, and the precipitates from the subcritical water-soluble portion were depressed in quantity as compared with the case of 0.1-s supercritical water treatment. The combined treatment for 45.1 s could convert the cellulose to the water-soluble portion without producing any precipitate. This result suggests that the polysaccharides, which are produced by 0.1-s supercritical water treatment, are further decomposed by subsequent subcritical water treatment.

Characterization of oligosaccharides

To ascertain the decomposition behavior in detail, MALDI-TOFMS analysis of the water-soluble portion was conducted. Figure 2 shows MALDI-TOFMS spectra of the water-soluble portions from cellulose treated in supercritical, subcritical water, and by their combined treatments. The oligosaccharides with DP up to 12 (cellododecaose) were observed in the 0.1-s supercritical water treatment. On the other hand, in subcritical water treatment, the oligosaccharides with DP of up to 7 were observed, which was smaller than those in the supercritical

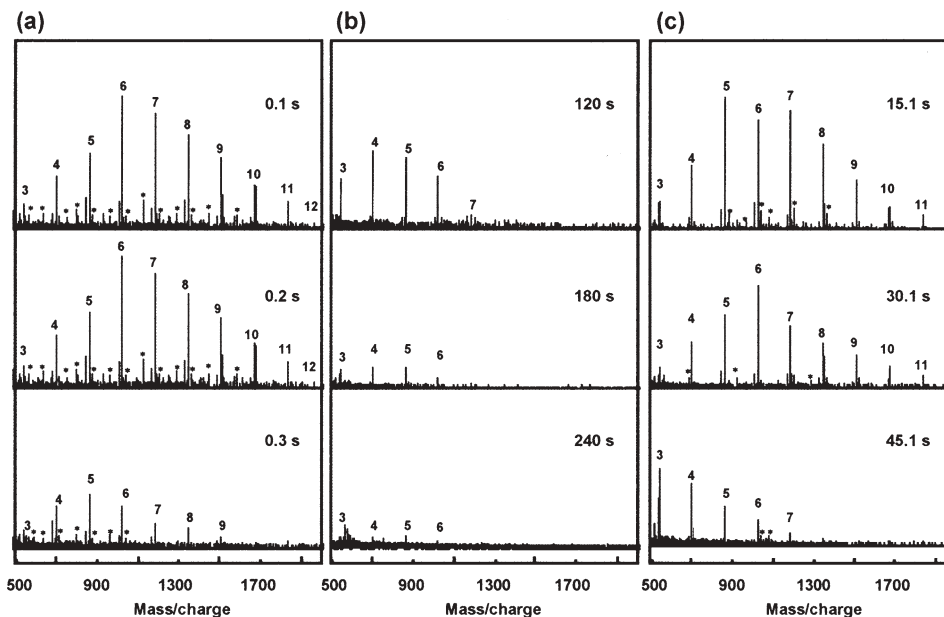
Table 1. Yield of fractionated portions of cellulose as treated in supercritical water, subcritical water, and their combined treatments

Treatment	Time (s)	Yield (%)		
		Supercritical/subcritical water-soluble	Precipitates	Supercritical/subcritical water-insoluble
		Water-soluble ^a		
Supercritical water (400°C, 40 MPa)	0.1	41.2	49.0	9.8
	0.2	58.3	41.7	0.0
	0.3	93.9	6.1	0.0
Subcritical water (280°C, 40 MPa)	120.0	49.5	0.0	50.5
	180.0	58.7	0.0	41.3
	240.0	82.7	0.0	17.3
Combined ^b (400°C, 40 MPa and 280°C, 40 MPa)	15.1	81.9	18.1	0.0
	30.1	88.9	11.1	0.0
	45.1	100.0	0.0	0.0

^aThis portion was estimated by subtracting the yields of precipitates plus supercritical water-insoluble residue or subcritical water-insoluble residue from the total

^bSupercritical water treatment (0.1 s) and subsequent subcritical water treatment for 15, 30, or 45 s

Fig. 2. MALDI-TOFMS spectra of water-soluble portions from cellulose as treated in **a** supercritical water, **b** subcritical water, and **c** their combined treatments. The *numbers* and *asterisks* correspond to the degrees of polymerization of oligosaccharides and the fragmented products of their reducing end groups, respectively



water treatment. In addition, the above-mentioned precipitates, which were in a DP range of 13 to 100, were not produced by subcritical water treatment (Table 1). These lines of evidence suggest that internal cleavage of glucosidic bonds in cellulose macromolecules takes place more frequently in the supercritical water. Such a reaction in supercritical water must be caused by cleavage of hydrogen bonds²⁷ in cellulose macromolecules, and provides a great advantage to yield the hydrolyzed products such as polysaccharides and oligosaccharides.

It is known that the reducing ends of oligosaccharides are fragmented to erythrose and glycolaldehyde in supercritical water.^{14,15,28} These fragmented products were found in the water-soluble portion after supercritical water treatment, as depicted by the asterisks in Fig. 2. However, these products were not detected in the subcritical water treatment. Therefore, the fragmentation reaction barely occurred in subcritical water.

The oligosaccharides in the combined treatment were similar in DP but were less fragmented in their reducing ends, compared with the supercritical water treatment alone. It is, therefore, suggested that the combined treatment can convert cellulose to the hydrolyzed products internally just as in the supercritical water treatment but without introducing fragmented oligosaccharides.

We have proposed that the hydrolyzed products produced by supercritical water treatment of lignocellulosics are further hydrolyzed to monosaccharides by dilute sulfuric acid or cellulase and are available for ethanol fermentation.²⁰⁻²² However, cellulase activity, particularly exo-type-cellulase, would possibly be inhibited by the fragmented reducing end groups in oligosaccharides. Therefore in oligosaccharides, the combined treatment in which the fragmentation reaction can be avoided, may be appropriate for the subsequent saccharification of oligosaccharides using the enzyme.

Yield of products in water-soluble portions

The water-soluble portions were analyzed by HPLC to identify the products and determine their yields. The same products were observed in the water-soluble portions for all treatment conditions; hydrolyzed products of cellulose were oligosaccharides, glucose, and fructose, while dehydrated products of monosaccharides were levoglucosan, 5-hydroxymethyl furfural (5-HMF), and furfural, and fragmented products were erythrose, methylglyoxal, glycolaldehyde, and dihydroxy acetone.¹⁴ Besides these products, organic acids, such as pyruvic acid, glycolic acid, lactic acid, acrylic acid, acetic acid, and formic acid, were included (shown as *others* in Table 2).²²

Table 2 shows the yield of products in the water-soluble portions from cellulose as treated in supercritical water, subcritical water, and by their combined treatments. The yields of hydrolyzed products in the supercritical water treatment were higher than the subcritical water treatment. This may be due to the short reaction time which can keep these hydrolyzed products without further decomposition. The result is consistent with the previous reports that showed that the hydrolysis rate of cellulose becomes larger than the decomposition rate of its hydrolyzed products around the critical point of water (374°C, 22.1 MPa).^{10,29}

However, the yields of fragmented products from supercritical water treatment were much higher than those from the subcritical water treatment in spite of its short reaction time. On the contrary, the yields of dehydrated products in the supercritical water treatment were much lower than those in the subcritical water treatment. These results indicate that the excessive decomposition of hydrolyzed products in supercritical water and subcritical water is mainly caused by fragmentation and dehydration, respectively. In addition, there was no difference in the yield of monosaccharides (glucose and fructose) between the

Table 2. Yield of products in water-soluble portions from cellulose as treated in supercritical water, subcritical water and their combined treatments

Classification Product name	Yield (%)								
	Supercritical water			Subcritical water			Combined ^a		
	0.1 s	0.2 s	0.3 s	120s	180s	240s	15.1 s	30.1 s	45.1 s
Hydrolyzed									
Oligosaccharides	28.8	28.8	32.2	8.8	8.8	5.6	42.9	55.4	16.5
Glucose	1.9	9.4	10.5	4.5	8.3	14.8	6.6	9.5	29.2
Fructose	0.0	3.6	4.0	1.4	2.4	2.3	1.7	1.9	6.4
(Subtotal)	(30.7)	(41.8)	(46.7)	(14.7)	(19.5)	(22.7)	(51.2)	(66.8)	(52.1)
Dehydrated									
Levogluconan	0.0	1.6	1.8	0.3	0.6	1.1	0.8	0.4	2.4
5-HMF	0.0	0.1	0.1	1.9	3.7	11.9	0.6	1.0	7.3
Furfural	0.7	0.3	0.3	0.2	0.8	1.7	0.2	0.3	1.0
(Subtotal)	(0.7)	(2.0)	(2.2)	(2.4)	(5.1)	(14.7)	(1.6)	(1.7)	(10.7)
Fragmented									
Erythrose	0.0	0.4	0.4	0.0	0.0	0.4	0.0	0.0	0.2
Methylglyoxal	0.9	1.5	1.8	0.0	0.3	0.8	2.9	3.0	4.2
Glycolaldehyde	3.9	8.9	9.6	0.6	1.6	2.7	2.0	2.8	4.6
Dihydroxy acetone	0.0	0.4	0.5	0.0	0.0	0.0	0.0	0.0	0.7
(Subtotal)	(4.8)	(11.2)	(12.3)	(0.6)	(1.9)	(3.9)	(4.9)	(5.8)	(9.7)
Others ^b	5.0	3.3	32.7	31.8	32.2	41.4	24.2	14.5	27.5
Total	41.2	58.3	93.9	49.5	58.7	82.7	81.9	88.8	100.0

5-HMF, 5-hydroxymethyl furfural

^aSupercritical water treatment (0.1 s) and subsequent subcritical water treatment for 15, 30, or 45 s^bOthers were estimated by subtracting the yields of all identified products listed from the total**Table 3.** The density, ionic product, and dielectric constant of supercritical water and subcritical water in this study

Treatment	Temperature (°C)	Pressure (MPa)	Density (g/cm ³)	Ionic product ^a log K_w (mol ² /l ²)	Dielectric constant ^b
Supercritical water	400	40	0.5	-12.8	9.6
Subcritical water	280	40	0.8	-10.9	25.2

^aIonic product estimated according to reference 31^bDielectric constant estimated according to reference 32

supercritical water and the subcritical water treatments, suggesting that the subcritical water treatment is enough to hydrolyze water-soluble oligosaccharides to monosaccharides. Goto et al.³⁰ and Sasaki et al.¹⁵ reported that fragmentation of glucose and cellobiose in hot compressed water becomes predominant at higher temperatures, while dehydration becomes significant at lower temperatures. Our finding in this study is consistent with their reports.

Table 3 shows the density, ionic product, and dielectric constant of supercritical water and subcritical water applied in this study. The density of the supercritical water is lower than that of the subcritical water. Similarly, the ionic product and dielectric constant of the supercritical water are smaller.^{31,32} These differences in the properties of water must contribute to the difference in the reaction between supercritical water and subcritical water treatments.

In the combined treatment, the yield of hydrolyzed products was successfully increased as compared with that of the supercritical water treatment or the subcritical water treatment alone, and reached 66.8% for 30.1-s treatments. The yields of the fragmented products for 15.1-s, 30.1-s, and 45.1-s treatments were 4.9%, 5.8%, and 9.7%, respectively.

These results were lower than that in supercritical water treatment for 0.3 s. The yields of dehydrated products for 15.1-s, 30.1-s, and 45.1-s treatments were 1.6%, 1.7%, and 10.7%, respectively. These yields were also lower than that for the 240-s treatment in subcritical water. Thus, the combined treatment can successfully increase the yield of hydrolyzed products.

Such an increase in yield of hydrolyzed products can be predicted as follows: cellulose is hydrolyzed to polysaccharides and oligosaccharides by the supercritical water treatment for 0.1 s. The polysaccharides and oligosaccharides must be soluble in supercritical water but the former of these must be insoluble in ordinary water. These products are further hydrolyzed in the subsequent subcritical water to water-soluble oligosaccharides and monosaccharides without introducing fragmented products. This means that in case of the combined treatment, the first stage of the supercritical water treatment may permit a near-homogeneous reaction field for hydrolysis of polysaccharides to the subsequent subcritical water treatment. It seems evident because of the difficulty in controlling hydrolysis in the extremely short supercritical water treatment.

Therefore, it is concluded that the combined treatment is effective to control the excessive fragmentation and dehydration in cellulose decomposition in supercritical water.

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