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Hemicellulose decomposition and saccharides production from various plant biomass by sulfonated allophane catalyst

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ABSTRACT

Typical biomass in Japan (bamboo, Japanese cedar and rice straw) were decomposed by using sulfonated allophane catalyst and hemicellulose in bamboo was preferentially decomposed to xylose. The maximum xylose yield was 40.9% (on the base of hemicellulose) in the reaction at 150 °C for 4.0 h. Mannose and xylose were mainly produced from Japanese cedar and arabinose was mainly produced from rice straw.
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1. Introduction

Currently environmental problems such as global warming and dwindling energy resources are becoming increasingly critical issues. Utilization of biomass, especially inedible lignocellulosic biomass is highly desirable for the construction of sustainable society [1].

Hydrolysis of polysaccharide such as cellulose in biomass is the crucial process for utilizing biomass such as ethanol fuels or chemicals. This process is performed by using hydrolysis with mineral acids [2], enzymes [3], or high pressure compressed water [4]. However, these processes have some drawbacks such as usage of highly corrosive mineral acid, difficulty in reaction control of long conversion time, cost of enzyme and severe reaction condition of high pressure compressed water.

Recently, utilizations of solid catalysts for cellulose conversion have been eagerly investigated [5–8]. Solid catalysts are thought to be more beneficial than homogeneous catalysts such as mineral acids because of facile catalyst separation. High surface area, high amount of hydroxyl group on the surface and high stability are thought to be important elements for surface modification to solid acid catalyst. Mesoporous silicas are materials which meet these requirements. They have much hydroxyl groups on their surfaces (e.g. MCM-41 $5.3 \pm 0.5\,nm^{-2}$) [9] and they can be chemically bonded to sulfone groups easily [10]. They are used as catalysts for saccharide hydrolysis such as sucrose and starch [11].

Allophane, an amorphous aluminosilicate [12–14], has high surface area (ca. $300\,m^2\,g^{-1}$) and high amount of surface hydroxyl group ($8.6 \pm 1.9\,nm^{-2}$), which is higher than various mesoporous silicas. Therefore, it is very suitable material for various chemical modifications of functional groups.

Herein, we report the selective production of saccharides by hydrolysis of bamboo, Japanese cedar and rice straw, which are typical Japanese biomass resources, using various solid acid catalysts. We found that hemicellulose in bamboo was preferentially decomposed and xylose is mainly produced, while xylose and mannose are mainly produced from Japanese cedar and arabinose is mainly produced from rice straw.

2. Experimental

2.1. Biomass materials

The biomass used in these experiments are bamboo (*Phyllostachys pubescens*), Japanese cedar (*Cryptomeria japonica*) and rice straw. Bamboo and Japanese cedar were obtained from Chiba Industrial Technology Research Institute. Rice straw was obtained from Chiba Prefectural Agriculture and Forestry Research Center.

These were ground with a centrifugal mill (Type ZM-1, Retsch) and screened with a 0.177 mm (80 mesh) sieve and dried at 105 °C

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Table 1
Chemical components of biomass used.

Component	Bamboo (wt%)	Japanese cedar (wt%)	Rice straw (wt%)
Cellulose	43.5	45.6	42.7
Hemicellulose	26.6	18.3	22.9
Lignin	26.4	33.3	12.6
Extractives	0.9	2.2	7.9
Ash	2.6	0.6	13.9

for 3.0 h. Rice straw was extracted with water using the method of the literature [15] before the experiment because extractives contained free monosaccharides. Chemical components of these biomass are shown in Table 1.

2.2. Catalysts

The catalysts used were Ap-PS (sulfonated allophane), sulfated zirconia [16], H-ZSM-5 (zeolite) and diluted sulfuric acid (0.006 M). Ap-PS was prepared as follows: propane-1,3-sultone (0.31 g, 2.5 mmol, Tokyo-kasei) and 1.0 g of allophane (Secado P-1 200 mesh, Shinagawa Chemicals Co. Ltd.) were refluxed in toluene for 48 h and dried. Sulfated zirconia and H-ZSM-5 were obtained from Catalysis Society of Japan as reference catalyst JRC-SZ-1 and JRC-Z5-90H, respectively. Characterization data of these catalysts are shown in Table 2.

2.3. Analyses of chemical components of biomass

Chemical components of the biomass used were analyzed according to the methods in the literature [15] except hemicellulose contents are calculated by subtracting the cellulose, lignin, extractive and ash contents from whole.

2.4. Decomposition of biomass using solid catalyst

Hydrothermal decomposition of biomass was carried out as follows. Biomass powder (0.1 g), catalyst (0.05 g) and water (5.0 ml) in a high pressure glass tube (volume 20 ml) with PTFE screw cap in an oil bath were stirred by magnetic stirrer for a specific time at a specific temperature. At certain intervals, the glass tube was cooled at room temperature and about 200 μl was sampled for analyses.

2.5. Analyses of saccharides in biomass extracts

The analyses of saccharides in bamboo extracts were carried out by high performance liquid chromatography (HPLC) with refractive index detection (RI). Details of HPLC instruments and conditions are as follows: column, Shodex KS-801 + KS-802 (8.0 mm ID × 300 mm × 2 in series); detector, Hitachi L-3300 RI; pump, Hitachi L-6000; column oven, Hitachi L-5030; autosampler, Hitachi AS-2000; eluent, distilled water; flow rate, 0.5 ml/min; column temperature, 80 °C; injection volume, 10 μl. The analyses of saccharide in Japanese cedar and rice straw extracts were carried out by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). Instruments and conditions are as follows: instrument, Dionex DX-500; column, Dionex CarboPac PA1 (4 mm × 250 mm); detector, Hewlett–Packard 1049A electrochemical detector; column temperature, 25 °C; injection volume, 25 μl; eluent, 22.5 mM NaOH; flow rate, 1.0 ml/min.

Yields of xylose, arabinose, mannose and galactose are calculated based on hemicellulose in the original biomass. Glucose yields are estimated on the bases of cellulose in the original biomass except for Japanese cedar, in which glucose yield is calculated based on hemicellulose as it contains glucose in glucomannan chain.

Table 3
Decomposition of bamboo powder and yields of xylose and glucose during the reaction at 150 °C for 4.0 h.

Catalyst	Yield[a] (wt%)	
	Xylose	Glucose
Ap-PS	40.9	0.6
Allophane	Trace	Trace
Blank	Trace	Trace

[a] Percentages of xylose and glucose yield are shown on the bases of hemicellulose and cellulose in the original biomass, respectively.

3. Results and discussion

3.1. Decomposition of bamboo biomass using Ap-PS

Table 3 shows the decomposition of bamboo powder and the yields of xylose and glucose during the reaction at 150 °C for 4.0 h using Ap-PS catalyst, allophane (without sulfo group) and blank (without catalyst).

When Ap-PS was used, 40.9 wt% of hemicellulose in the bamboo powder was liberated in aqueous phase as xylose, whereas very little glucose was detected (0.6 wt%). This result indicates that xylan in bamboo hemicellulose was selectively hydrolyzed and very little cellulose was decomposed. Traces of xylose and glucose were produced during the reaction using allophane and in blank. This result indicates that the sulfo groups on catalyst surface are effective for the decomposition of hemicellulose.

3.2. Decomposition of bamboo biomass using various catalysts

Fig. 1(a) shows the time courses of xylose formation during the reaction at 150 °C by using various catalysts. Ap-PS showed the highest activity among the solid catalysts. However, it did not reach the yield of dilute sulfuric acid (0.006 M), whose acid concentration is equivalent to the surface acid amount of Ap-PS. Hydrolysis of hemicellulose by sulfuric acid must be proceeded more rapidly than that of Ap-PS due to its homogeneous system.

Fig. 1(b) shows the time courses of glucose at the same condition. Glucose yield was very low at all catalysts less than 2.0 wt% even after 6.0 h.

Xylose yields by all catalysts except for H-ZSM-5 decreased after 4.0 h. This indicates that xylose was successively converted to smaller molecules such as furfural and organic acids such as formic acid as similarly observed by Oefner et al. [18].

Table 2
Characterization data of catalysts used in these experiments.

	Allophane	Ap-PS	Sulfated ZrO_2 (JRC-SZ-1)	H-ZSM-5 (JRC-Z5-90H)
BET surface area (m^2/g)	300[a]	114	67[b]	>300[c]
Acid amount (mmol/g)	0.5[d]	1.2[d]	0.11[b]	0.28[c]

[a] From the catalogue data of Shinagawa Chemicals Co. Ltd.
[b] From Ref. [16].
[c] From Ref. [17].
[d] Titrated by NaOH solution.

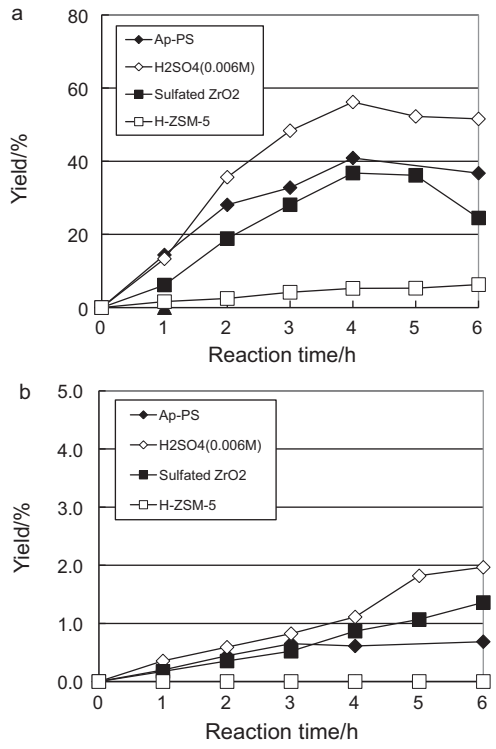

Fig. 1. Yields of xylose (a) and glucose (b) during the reaction of bamboo by using various catalysts at 150 °C.

Sulfated zirconia (JRC-SZ-1) also showed high activity. However, the pH of the supernatant solution in the reactor became from 4.30 to 2.40 after the reaction at 150 °C for 4.0 h. This result indicates significant leaching of sulfate groups which would cause its lower activity than Ap-PS.

For Ap-PS, the pH of the supernatant became 3.62 from 4.40 during the reaction at 150 °C after 6.0 h. This indicates that the decomposition of bamboo biomass occurred at relatively high pH. From these results, the decomposition of hemicellulose can be proceeded under relatively high pH region in the case of Ap-PS. The little pH changes of Ap-PS indicate that the leaching of the sulfo group during the reaction is relatively low and the reusability of Ap-PS is promising.

Although H-ZSM-5 (JRC-Z5-90H) showed high decomposition rate (55.6 wt%), it exhibited low xylose yield. It is thought the decomposition to small molecules other than saccharides was predominant in the case of H-ZSM-5.

3.3. Decomposition of Japanese cedar biomass using Ap-PS

Fig. 2 shows the time courses of various monosaccharide yields from Japanese cedar by using Ap-PS as a catalyst at 150 °C. Five monosaccharides (xylose, mannose, glucose, galactose and arabinose) were detected in the products.

Because hemicellulose in softwood such as Japanese cedar contains galactoglucomannan and arabinoglucuronoxylan chains in its structure [19]. The formation of these five monosaccharides was observed and these yields of saccharides were fairly lower than those of bamboo. As shown in Table 1, hemicellulose content of Japanese cedar is lower than that of bamboo. In addition, its hemicellulose contains glucomannan chain as well as xylan chain whereas hemicellulose in bamboo includes exclusively xylan chain. Moreover, high content of lignin in Japanese cedar (33.3%) causes the robust structure of the feedstock due to the chemically linked complexes derived from lignin and hemicellulose [20]. Low content of xylose unit and the robust structure composed of lignin and hemicellulose could give low yields of saccharides.

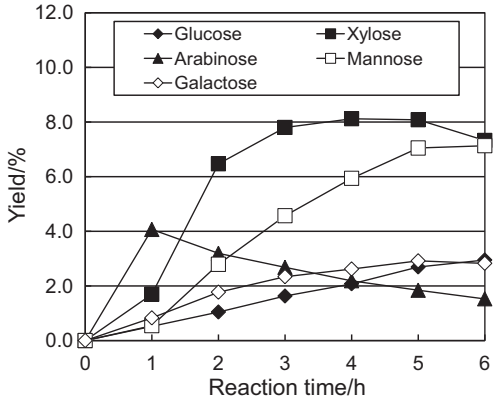

Fig. 2. Changes of various monosaccharide yields during the reaction of Japanese cedar at 150 °C using Ap-PS.

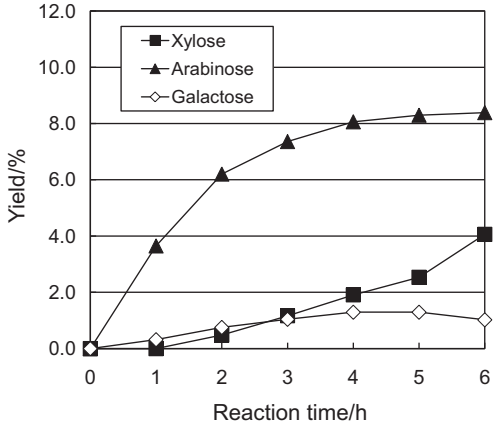

Fig. 3. Changes of various monosaccharide yields during the reaction of rice straw at 150 °C using Ap-PS.

3.4. Decomposition of rice straw biomass using Ap-PS

Fig. 3 shows the time courses of various monosaccharide yields from by using rice straw by using Ap-PS as a catalyst at 150 °C. Three monosaccharides (arabinose, xylose and galactose) were generated during the reaction. Arabinose was mainly produced during the reaction for 6.0 h. Though xylose yield gradually increased, the production rate was extremely slower than that of bamboo and production of glucose was very low (0.5 wt% on cellulose base at 6.0 h). Thus, cellulose decomposition hardly occurred in this condition.

This difference seems to be accounted for extremely high contents of ash (13.9 wt%) which is mainly composed of silica and may be resistant to decomposition of rice straw. Indeed, Chen et al. indicated the negative effect of silica component in enzymatic hydrolysis of rice straw [21].

4. Conclusions

In these experiments, we have shown that the xylose can be selectively produced from the bamboo by using Ap-PS. We have also shown that xylose and mannose are mainly produced from Japanese cedar and arabinose is mainly produced from rice straw by using our Ap-PS catalyst. From these results, we believe that our solid acid catalyst process has promising potential to separate beneficial chemicals from biomass without harmful acidic liquid medium.

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