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# Production of sugar alcohols from real biomass by supported platinum catalyst

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ABSTRACT

The influence of lignin and inorganic salts on the catalytic activity was studied in the hydrolytic hydrogenation of real biomass by a supported Pt catalyst. The direct conversion of raw silver grass by Pt/carbon catalyst under $H_2$ pressure produced small amounts of sorbitol (2.8 wt%), xylitol (7.3 wt%), and other sugar alcohols. It has been suggested that lignin reduces the reactivity of cellulose, as lignin exists together with cellulose in the biomass and both compounds are insoluble in water. Moreover, even weak bases drastically change the product distribution with more by-products such as EG and PG. Bases enhance the decomposition of sugar intermediates and sorbitol. The removal of lignin and inorganic salts by alkali-explosion and neutralization raises the contents of cellulose and hemicellulose, thus increasing the yields of sorbitol (13 wt%) and xylitol (14 wt%) in the hydrolytic hydrogenation reactions.



## 1. Introduction

Catalytic conversion of lignocellulosic biomass has attracted great interest for the production of renewable chemicals and fuels, since this abundant material has been largely wasted [1,2]. Furthermore, the use of lignocellulose in chemical industry does not compete with food production, which is contrastive to current biorefinery using starch and molasses. Lignocellulose consists of cellulose, hemicellulose, and lignin, in which cellulose is a polymer of glucose and hemicellulose is a copolymer of various $C_5$ and $C_6$ sugars. Thus, the hydrolytic hydrogenation of the sugar polymers produces hexitols and pentitols (Fig. 1), and these sugar alcohols are practically used as precursors to plastics, surfactants, and medicines as well as low-calorie and non-cariogenic sweeteners [2]. The annual productions of sorbitol and xylitol have already been $6.5 \times 10^5$ and $2–4 \times 10^4$ tons per year, respectively, although the current feedstock of sorbitol is starch. Hence, the hydrolytic hydrogenation of lignocellulosic biomass is an attractive issue for the next-generation biorefinery.

Cellulose conversion by heterogeneous catalysts has been intensively studied in the last several years [2], and it has been known that pure cellulose can be converted into sugar alcohols in good yields in one-pot by various supported metal catalysts under $H_2$ pressure [3–27]. In the mechanism of this reaction, it has been found that the hydrolysis step is promoted by some supported metal catalysts [6,7] in addition to effect of hot-compressed water [28], and the hydrogenation is catalyzed by transition metals. In contrast, only a few reports have addressed the one-pot conversion of raw or less-treated biomass; arabitol [29] and xylitol [30,31] have been synthesized from beet fiber and bleached birch kraft pulp, respectively. Furthermore, influence of various ingredients such as lignin and ionic compounds on this catalytic reaction has not yet been evaluated. Both acid and reduction catalysis can be affected by these components, and hydrolysis rate of cellulose is indeed declined by sulfate ions [32]. In this study, we conducted the conversion of real biomass and crystalline cellulose by a supported Pt catalyst (Pt/BP2000) to evaluate the effects of lignin and salts. Pt/BP2000 is one of the most active and durable catalysts for the conversion of pure cellulose [7]. Silver grass was mainly used as a substrate because this plant survives in cold climate unsuitable to food crops. Furthermore, silver grass moves nutrients such as K and P from the plant body to rhizomes before winter [33], and hence loss of the elements in soil by collecting the plant for biorefinery is small.

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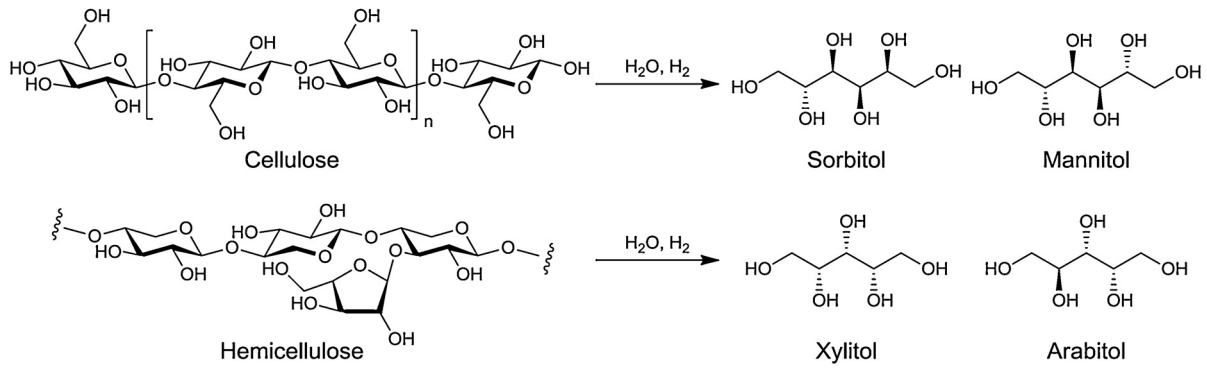


**Fig. 1.** Hydrolytic hydrogenation of cellulose and hemicellulose.

## 2. Materials and methods

### 2.1. Biomass materials

*Silver grass-1* is silver grass (*Miscanthus sinensis*) collected in summer in Kochi, and *silver grass-2* is that mowed in winter in Nakashibetsu (Hokkaido). Other biomass used in this study was Amur silver grass (*Miscanthus sacchariflorus*) sampled in Nakashibetsu (Hokkaido) and wheat straw (*Triticum aestivum*) in Memuro (Hokkaido). These samples were coarsely ground using a cutter mill with a 3 mm screen (Horai MAC-0.75kW). Microcrystalline cellulose (Avicel, 1.02331.0500) was purchased from Merck.

### 2.2. Pretreatment of biomass

Five pretreatment methods were used in this study [34]; *silver grass-1* was boiled in water at 373 K for 3 h (*silver grass-1W*), treated by the Soxhlet extraction using water for 3 days (*silver grass-1S*), or washed with 10 wt% HCl aq. at 298 K for 3 h (*silver grass-1H*). *Silver grass-2* was immersed in 1.4 wt% NaOH at 298 K for 24 h, and exploded after keeping the temperature at 463 K for 2 min (*silver grass-2A*). *Silver grass-2A* was neutralized with HCl at room temperature to adjust its pH to 3, and washed with water (*silver grass-2AN*). This set of alkali-explosion and neutralization is expressed as AN treatment hereafter, and also used for Amur silver grass and wheat straw (*Amur silver grass-AN* and *wheat straw-AN*, respectively).

### 2.3. Composition analysis of biomass

Elemental analysis of biomass was performed using energy dispersive X-ray spectroscopy (EDX; Shimadzu, EDX-720). The content of each sugar fraction in biomass was analyzed according to the literature (NREL, TP-510-42618 [35]). Biomass (300 mg) was stirred in 72% $H_2SO_4$ aq. (3.0 mL) for 1 h at 303 K. Water of 84 mL was added to the solution, and then agitated at 394 K for 1 h in a high-pressure reactor. The mixture was filtrated and the aqueous phase was analyzed by a high-performance liquid chromatography (HPLC; Shimadzu, LC10-AT*VP*, refractive index detector) equipped with a Shodex Sugar SH-1011 column (ø8 mm × 300 mm, mobile phase: water 0.5 mL $min^{-1}$, 323 K) after neutralizing with $CaCO_3$ to pH 6. The amount of acid-insoluble lignin was determined from the weight difference before and after the combustion of solid residue at 848 K. Crystallinity of biomass was analyzed by X-ray diffraction (XRD; Rigaku, MiniFlex, Cu Kα).

### 2.4. Preparation of catalysts

$Pt(NH_3)_2(NO_2)_2$ nitric acid solution (Tanaka Kikinzoku Kogyo, 138 μmol) was dropped into a mixture of carbon black BP2000 (Cabot, Black Pearls 2000, 2.0 g) and water (20 mL), and the mixture was stirred for 16 h. After drying in vacuo, the solid was treated with $H_2$ (30 mL $min^{-1}$) at 673 K for 2 h. The prepared catalyst is denoted as 1.3 wt% Pt/BP2000.

### 2.5. Hydrolytic hydrogenation of biomass

Biomass (324 mg), Pt/BP2000 catalyst (200 mg, Pt 14 μg-atom), and water (40 mL) were transferred into a stainless steel high-pressure reactor (OM Lab-Tech, MMJ-100), and 5 MPa of $H_2$ was charged at room temperature. The reactor was heated to 463 K and kept at this temperature for 24 h with stirring at 600 rpm. Products were separated by centrifugation and decantation, and water-soluble products were analyzed by HPLC. The columns used in this work were a Phenomenex Rezex RPM-Monosaccharide Pb++ column (ø7.8 mm × 300 mm, mobile phase: water 0.6 mL $min^{-1}$, 343 K) and a Shodex Sugar SH-1011 column (ø8 mm × 300 mm, mobile phase: water 0.5 mL $min^{-1}$, 323 K). Product assignment was also checked by LC/MS (Thermo Fisher Scientific, LCQ-Fleet, APCI). The conversion of cellulose was determined by liquid-phase total organic carbon analysis (TOC; Shimadzu, TOC-V CSN) when we performed the model reactions using pure cellulose and salts. The formation of small amounts of gaseous products was excluded in this estimation.

## 3. Results and discussion

### 3.1. Analysis of treated silver grasses

Elemental compositions of silver grasses were analyzed by EDX as shown in Table 1. Si of 3.7 wt% was detected in *silver grass-1* as gramineous plants use silica for their frameworks (entry 1) [36]. Other ingredients were K (1.0 wt%), Ca (0.14), P (0.13), S (0.09), Fe (0.03), and Cl (0.02). K, P, and Cl were almost completely removed by boiling in water, and the amounts of Si and S decreased by half (*silver grass-1W*, entry 2). However, the contents of Ca and Fe were unchanged. The Soxhlet extraction reduced Ca to 0.03 wt% in addition to the effect of boiling water (*silver grass-1S*, entry 3). The HCl treatment provided a similar result to that of the Soxhlet extraction, but Si remained unchanged at 3.4 wt% (*silver grass-1H*, entry 4). The amounts of K (0.08) and P (0.01) in *silver grass-2*, collected in winter, were significantly lower than those in *silver grass-1* (entry 5) mowed in summer. The AN treatment for *silver grass-2* (entry 6) had a similar effect to that of the Soxhlet extraction (entry 3). It is thus shown that K and P are eliminated completely and the S content is declined in these four treatments.

The NREL/TP-510-42618 method [35] was used to determine the contents of sugar polymers and lignin. *Silver grass-1* had cellulose (34 wt%), hemicellulose (19 wt%), and lignin (26 wt%) (Table 2, entry 7), and the hemicellulose consisted of xylan 16 wt%, arabinan 2.6 wt%, and negligible amounts of other sugar residues. The