



Selective production of valuable chemicals from biomass by two-step conversion combining pre-oxidation and hydrothermal degradation



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HIGHLIGHTS

- We proposed two-step treatment method to overcome the problem of low selectivity.
- Valuable chemicals were recovered selectively from biomass through proposed method.
- The degradation mechanism of cellulose was discussed.
- New refinery scheme of biomass was proposed.

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ABSTRACT

Biomass is getting notable as a new energy resource to replace fossil resources and to restrain CO₂ emission recently. However, it is obvious that the energy use of biomass is unsuitable for its limit of available amounts. Consequently, we investigated the possibility of new refinery scheme of biomass to utilize biomass as an alternative raw material to fossil resources with suggested two-step treatment method. We oxidized cellulose and biomass with H₂O₂ first and put the residue into hydrothermal condition to obtain some specific chemicals. Through the first oxidation of cellulose, 0.26 g/g-cellulose of organic acid was obtained, and 0.35 g/g-cellulose of oxalic acid was obtained under the catalytic condition. Both cedar and cellulose decreased their crystallinity through the first oxidation and increased their reactivity, we could obtain hydroxymethylfurfural(HMF) from cellulose and biomass through the hydrothermal degradation, 0.11 g/g-cellulose and 0.12 g/g-cedar respectively.

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1. Introduction

The recent growth of economy is rapid and leading to the increase of the annual world energy consumption. We mostly depend on fossil resources for the energy production, which is leading to the drying up of those resources. The CO₂ emission with burning those resources is considered as the problem as well for promoting the global warming. To solve these problems, biomass is getting notable as a new energy resource to replace fossil resources and to restrain CO₂ emission recently. It takes an important role for creating recycling society for its nature of carbon neutrality and sustainability [1–3]. However, as the source of energy, biomass has huge barriers such as the relatively low energy content, seasonality or discrete geographic availability [4]. As an alternative raw material, on the other hand, biomass would be profitable by being converted into valuable chemicals because chemical production requires far lower volumes of biomass to satisfy demand. For example, in 2007, chemical products took only 3%

of the petroleum consumption in the United States [5]. Consequently, the US Department of Energy identified 12 chemicals which should be made from biomass. These chemicals, which could be used as building block chemicals, potentially enable biomass to be main resource of making chemicals which derive from petroleum for now. The important factor for utilizing biomass as an alternative to fossil resources is the choice of material feedstock and target product. Because biomass consists of several components, we should aim not just one but various kinds of products so that we do not waste any of them [6]. In other words, there is a need of proposition of biorefinery scheme that enables to use “wastes” as “byproducts” or “materials”. For example, glycerol used to be recognized as “waste material” for its less value. However, as being the material for propylene glycol, it has established its position as a “low-cost building block material” recently [7]. As with the example, we need to broaden our sights for utilizing biomass and to obtain various kinds of products such as fuels, power, materials and chemicals from biomass not wasting any components through conversion [5]. Although there are some opinions that use of biomass as renewable fuel in agro-industrial field would be profitable for saving fossil resources, converting biomass into

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chemicals is still effective. That is because the residue through the conversion is one of the source of energy, and the products also would be the energy resources through combustion in their final stage of life. In this way, almost same amount of energy as through direct combustion could be extracted from biomass eventually. That means converting biomass into valuable chemicals is profitable in the point of economy and reducing consumption of fossil resources. For converting biomass, many studies using biochemical technology have been done so far [8–10]. For example, we can obtain ethanol or organic acids from biomass by fermentation with high selectivity [11–13]. However, the bioprocess requires high technology of sewage treatment and complicated control of reactor, which leads to a high cost. In addition, it produces sludge which decreases efficiency and causes long reaction time. Considering these disadvantages of biotechnology process, thermal conversion of biomass now should be investigated. Oxidation, among the many reactions on biomass, is disadvantageous for energy recovery since it decreases the low heat of combustion of biomass further. On the contrary, for converting biomass into some valuable chemicals, oxidation would be advantageous since some functional groups containing oxygen in biomass work as active sites. However, in thermochemical process, the problem of low selectivity of final products remains [14,15]. To overcome this problem, we proposed two-step treatment method. The idea of this method is to change the materials into desired precursor under the mild conditions first. Then the modified precursor is degraded under the hydrothermal condition at higher temperature to valuable chemicals. Although a lot of studies about oxidative pretreatment have been done before, most of them are followed by biotechnologies such as enzymatic saccharification or fermentation [16,17]. There are some studies about thermochemical two-step treatment method, but the target products are low molecular weight chemicals breaking the natural structure of biomass [18,19]. Our objective is to obtain valuable chemicals leaving the advantage of natural structure of biomass, such as carbocyclic ring. In this study, we especially focused on the degradation of cellulose, one of the major components of woody biomass. Cellulose is expected to be converted into valuable chemicals for its clear structure unlike the other components of biomass. However, there are some blocking factors for the degradation of cellulose, such as the rigid structure and crystallinity of cellulose or a physical barrier by surrounding components, lignin and hemicellulose [20]. For the degradation of cellulose in biomass, it would be effective to remove the inhibitors like lignin and to break the rigid structure of cellulose through the pretreatment. H_2O_2 is one of the oxidants, which is known to be capable of removing lignin and lowering the crystallinity of cellulose [21,22]. Thus, in this study, we oxidized biomass with H_2O_2 to obtain desired precursor first. Then we degraded obtained precursor to valuable chemicals solving the problem of low selectivity and examined the validity of the proposed method. In summary, we proposed a new refinery scheme of biomass.

2. Experimental section

To achieve the hydrothermal degradation effectively, we pretreated cellulose or biomass with H_2O_2 . The experiments were performed by using Swagelok (316 stainless steel) batch reactor with an internal volume of 30 cm³.

2.1. Samples

Crystalline cellulose, amorphous cellulose and biomass were used to examine their oxidative degradation behaviors. To investigate the difference between the kinds of biomass, pulverized cedar

(*cryptomeria japonica*), cypress and beech were chosen. The ultimate analyses of those samples used are listed in Table 1.

2.2. Thermal degradation of cellulose

Crystalline cellulose and amorphous cellulose were oxidized in a batch reactor under the condition of high pressure and high temperature with H_2O_2 . Cellulose concentration was prepared at the range of 0.10–0.37 wt% and H_2O_2 was prepared at 0.001–1.23 wt%. The reactor vessel was put in an oil bath heated to 80–200 °C for 5–150 min as first treatment. Then, the reactor was cooled in a water bath and the products were filtered by suction after the reactions. Filtrates were diluted with pure water by 50 mL and analyzed using gel permeation chromatography (GPC) and ion chromatography. Oxidized cellulose, which was collected as residue, was put in the hydrothermal condition at higher temperature, from 200 to 260 °C, as second treatment. The products were filtered by suction, then filtrates were treated as after first treatment and residues were analyzed using a CHNS analyzer. For comparison, first treatment was conducted under the catalytic condition as well. As the catalyst, $FeSO_4(II)$ was added by 5% of cellulose.

2.3. Thermal degradation of biomass

0.5 g of cedar, 30 g of pure water and 0–1.5 g of H_2O_2 were mixed in a sealed batch reactor and put in an oil bath heated to 200 °C for 60 min as first treatment. The reactor was cooled in a water bath and the products were filtered by suction after the reactions. Filtrates were diluted with pure water by 50 mL and residues were put in the hydrothermal condition at higher temperature, from 200 to 260 °C, as second treatment. The products were filtered by suction, then filtrates were treated as after first treatment and residues were analyzed using a CHNS analyzer. For comparison, first treatment was conducted under the catalytic condition as well. As the catalyst, $FeSO_4$ was added by 5% of biomass. To investigate the difference between the kinds of biomass, the whole process was conducted using cypress and beech instead of cedar as well.

2.4. Analyses of products

Ultimate analysis of the samples was performed using a CHNS elemental analyzer (BEL Japan, Inc., ECS4010). Crystallinity of samples was measured using X-ray diffraction (XRD) (Rigaku Corporation). The GPC was used to estimate the molecular weight distribution of the product solution after oxidation and hydrothermal degradation. The packed column used is Shodex OHpak SB-802.5 (SHOWA DENKO), and an eluent distilled water was supplied at the flow rate of 1.0 mL/min to the high performance liquid chromatography (HPLC) equipped with an refractive index detector (RID) (Shimadzu, RID-10A). For the organic acid analysis, an aqueous solution containing 951 mg/L of p-toluene sulfonic acid, 4185 mg/L of Bis-Tris, and 29 mg/L of ethylenediaminetetraacetic acid was used as the eluent, and it was fed at 0.8 mL/min to the HPLC equipped with a sulfonated polystyrene gel column (Shim-pack SCR-102H) and an electric conductivity detector (Shimadzu,

Table 1
Ultimate analyses of sample used.

	C (wt%)	H (wt%)	O (wt%)	H/C (-)
Crystalline cellulose	42.95	6.20	50.85	0.14
Amorphous cellulose	43.37	6.12	50.52	0.14
Cedar	46.87	4.84	48.28	0.10
Cypress	49.72	6.34	43.93	0.13
Beech	46.35	6.30	47.36	0.14

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