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Effect of steam explosion pretreatment with ultra-high temperature and pressure on effective utilization of softwood biomass

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ABSTRACT

Effective utilization process of not only cellulose but also lignin contained in softwood biomass into useful fuel and materials was developed using steam explosion with ultra-high temperature and pressure steam, extraction and various conversion methods. The conversion of softwood biomass into useful materials was studied for the effective utilization of its components such as cellulose, water soluble material, methanol soluble lignin, and Klason lignin. The cellulose, water soluble material, methanol soluble lignin, and Klason lignin were converted into useful fuel and materials, i.e. ethanol, antioxidant material, lignin epoxy resin, and activated carbon, respectively. 49.6 g of glucose or 17.4 g of ethanol was obtained from 100 g of steam-exploded product treated at a steam pressure of 45 atm and 3 min. Water soluble material had a comparatively high antioxidant activity and methanol soluble lignin was converted into a cured epoxy resin with heat-resisting property for solder demanded in the electronic material field.

1. Introduction

Steam explosion method has been recognized as one of the most effective pretreatments for delignification of wood biomass [1–3]. This method seems to be very effective for hardwoods [4], but ineffective for softwoods that contain a comparatively large amount of condensed-type lignin [5]. In recent years the pretreatment using SO_2-catalyzed steam explosion has been attempted for increasing the delignification effect of softwood materials, i.e. Douglas-fir (*Pseudotsuga menziesii var. menziesii*), lodgepole pine (*Dendroctonus ponderosae*), spruce (*Picea abies*), etc. [6–9]. Though SO_2-catalyzed steam explosion is useful for softwood pretreatment, it may be not an environmentally friendly method because of SO_2 usage. Therefore, in this work the steam explosion with only ultra-high temperature and pressure steam, i.e. up to 281 °C and 67 atm, that are significantly higher than the conventional steam explosion (200–245 °C and 15–35 atm), was applied for not only the pretreatment of softwood biomass but also the environmental protection.

On the other hand wood biomass is a natural renewable resource that can be converted into useful materials and energy [10,11]. The amount of carbon contained in wood waste biomass annually emitted into the environment in Japan is approximately 30% of the carbon consumed in the production of a variety of petrochemicals from oil. The development of industrial techniques for converting not only cellulose but also lignin contained in wood biomass into useful materials and products completely without generating pollutants such as waste gas, wastewater, and solid waste materials is desired for global environmental protection.

This investigation aims to develop the total conversion process structural components of softwood biomass into useful fuel and materials using Japanese cedar. The structural components, i.e. cellulose, water soluble material, methanol soluble lignin, and Klason lignin, in the softwood biomass treated by the steam explosion were converted into various useful materials.

2. Methods

2.1. Samples

Softwood biomass, Japanese cedar (*Cryptomeria japonica*) C material, that consisted of 48% sapwood, 48% heartwood, and 4% bark was chopped into wood chips (2–4 cm in length and 1–3 cm in width) and then treated by various steam explosional conditions for delignification. In Japan a large amount of C material, i.e. a surplus and thinning material, is unused and discharged from forest areas every year, so it is desired strongly to develop the effective utilization method of C material.

2.2. Steam explosion apparatus

For the steam explosion with ultra-high temperature and pressure, the steam explosion apparatus having a batch pilot unit

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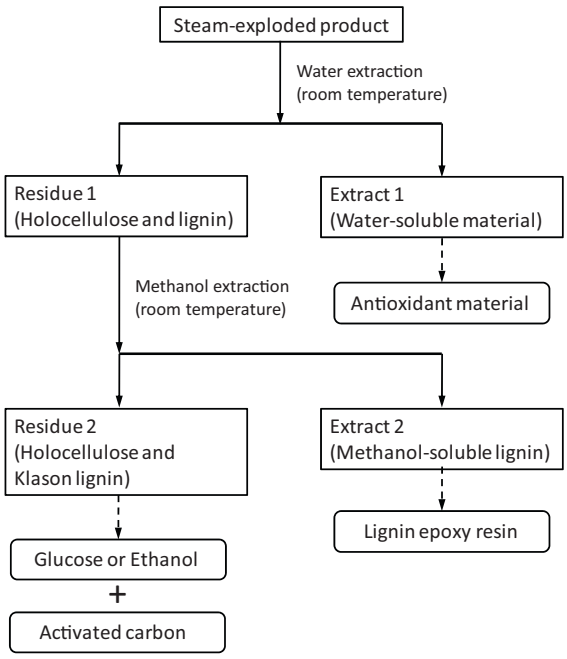

Fig. 1. Extraction, separation, and utilization of each component of steam-exploded product.

equipped with a 2 l of high-pressure reactor (Steam explosion apparatus NK-2L, Japan Chemical Engineering and Machinery Co. Ltd., Osaka, Japan) was used in this work. The highest pressure and temperature are 67 atm and 281 °C, respectively, and they are the highest values of steam explosion in the world. 200 g of wood chips was introduced into the reactor and exposed to the saturated steam. After the exposure to the saturated steam for a steaming time of 1–10 min, a ball valve at the bottom of the reactor was suddenly opened to bring the reactor rapidly to atmospheric pressure. The product containing liquid–solid materials was obtained as the steam-exploded sample in the receiver.

2.3. Extraction, separation, and utilization of components

The amounts of the components, i.e. water soluble material, methanol soluble lignin, cellulose, and Klason lignin, in the wood chips treated by various steam explosional conditions were measured by the procedure according to Wayman's extraction method [12] as shown in Fig. 1. 5 g of dry steam-exploded sample was added to 100 ml of distilled water and extracted for 24 h at room temperature. The solid and liquid materials were separated by filtration, and the filtrate, i.e. Extract 1 (water soluble material), was recovered from the liquid, then concentrated, dried, and weighed. Residue 1 was extracted at room temperature for 24 h in a Soxhlet extractor with 150 ml methanol to dissolve Extract 2 (methanol soluble lignin), a low molecular weight lignin. After concentration and drying of the extract, the methanol soluble lignin was weighed. Residue 2 from the methanol extraction consisted of cellulose and Klason lignin, a high molecular weight lignin. Furthermore, Extract 1 was tested as an antioxidant material and Extract 2 was used as a raw material for the synthesis of lignin epoxy resin. Residue 2 was used as not only a substrate of enzymatic saccharification and simultaneous saccharification and fermentation for producing glucose and ethanol but also a raw material for carbonization.

2.4. Antioxidant activity

Antioxidant activity of polyphenols contained in Extract 1 (water soluble material) was measured according to Liegeois's method [13]. In this experiment trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, a water soluble derivative of vitamin E) was used as a compared material.

2.5. Epoxy resin synthesis

Extract 2 (methanol soluble lignin) was used as a sample for resinification. Though a high temperature such as 80 °C can obtain a large amount of extracted lignin, this lignin has a high molecular weight (weight-average molecular weight (Mw), about 1600) and is not suitable for the synthesis of strength resin. Therefore, Extract 2 that was extracted at room temperature (Mw, about 1200) was used in this work. The epoxy reaction was conducted in two stage epoxy reactions using epichlorohydrin, TBAB (tetrabutyl ammonium bromide), and 50 wt% NaOH [14]. In order to remove the excess of epichlorohydrin, the reprecipitation with isopropyl alcohol was carried out, and then the epoxidized lignin, i.e. lignin epoxy resin, was obtained. The 2E4MZ-CN (1-cyanoethyl-2-ethyl-4-methylimidazole) or Extract 2 was used as a curing reagent of epoxidized lignin. The temperature of thermal cracking was measured using an exothermic curve (heating rate of 5 °C/min) under the atmosphere of nitrogen (200 ml/min), using a differential scanning calorimeter (DSC-50, Shimadzu Co. Ltd., Kyoto, Japan). α-Alumina was used as a primary standard substance.

2.6. Enzymatic saccharification

The enzymatic saccharification of Residue 2 (cellulose and Klason lignin) was carried out using a cellulolytic enzyme, which was performed in 110 ml sample tubes at an initial sample concentration of 2% (w/v) in 10 ml of 100 mM sodium acetate buffer pH 5.0 and using enzyme (Meicelase, Meiji Seika Co. Ltd., *Trichoderma viride*, 224 FPU/g; β-glucosidase activity, 264 IU/g) loading of 20 FPU/g sample. The enzymatic reaction was carried out in a reciprocating water bath shaker at 140 strokes/min for 72 h at 45 °C because this enzyme shows the highest activity at 45–50 °C. The supernatant was centrifuged and removed the solid residue for sugar content.

2.7. Simultaneous saccharification and fermentation (SSF)

Saccharomyces cerevisiae AM 12, a heat-tolerant yeast, was obtained from *Bio Academia* Co. Ltd., Japan, and used for ethanol production [15]. It was incubated on potato dextrose agar plates at 30 °C and then stored in the refrigerator at 4 °C. Pure yeast culture from an agar plate was added to 10 ml L-tubes containing 5 ml of sterile medium. The medium compositions were as follows: 10 g/l glucose, 1 g/l yeast extract, 0.1 g/l KH_2PO_4, 0.1 g/l $MgSO_4{\cdot}7H_2O$ and 0.1 g/l $(NH_4)_2SO_4$ [16]. This preculture was incubated at 30 °C for 24 h using a seesaw incubator at 60 rpm. Residue 2 (cellulose and Klason lignin) with various initial concentrations were put into 200 ml Erlenmeyer flasks, and then autoclaved for 20 min at 121 °C. Then, the sterilized nutrient solution, the enzyme and the sodium acetate buffer were added. The composition of the nutrient solution and enzyme loading in the fermentation medium were adjusted as follows: 2 g/l yeast extract, 0.05 g/l $MgSO_4{\cdot}7H_2O$, 1 g/l $(NH_4)_2HPO_4$ [16], 20 FPU/g sample and 100 mM of sodium acetate buffer at pH 5.0. After the previously precultured yeast suspension was centrifuged and the supernatant was removed, the suspended yeast by sterilized water was inoculated and the mixture was incubated in a rotary shaker at 40 °C at 100 rpm because this yeast can produce ethanol from glucose at temperatures as high as 40 °C.