



Effect of the addition of calcium hydroxide on the hydrothermal–mechanochemical treatment of *Eucalyptus*



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HIGHLIGHTS

- Ca(OH)₂ enhanced cleavage of ester bonds between lignin and hemicellulose.
- Glucose yield was increased up to 90% with two-thirds lignin remaining.
- Specific surface area of substrate increased efficiently by milling with Ca(OH)₂.

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ABSTRACT

The effect of Ca(OH)₂ addition on optimization of hydrothermal–mechanochemical pretreatment, which combines hydrothermal and milling treatments, was examined. The highest glucose yield of 90% was achieved in the ball-milled specimen previously treated at 170 °C in the presence of 20% Ca(OH)₂ per substrate weight. The specific surface area of the substrate was closely correlated with glucose yield, and a larger specific surface area was obtained when treating the specimen at 170 °C in the presence of Ca(OH)₂ compared to treatment at 170 °C without Ca(OH)₂. Although the Ca(OH)₂-treated specimen was relatively unaffected by delignification, the cleavage of the ester bonds between lignin and hemicellulose was confirmed by FT-IR. This suggests that Ca(OH)₂ weakens the substrate structure by loosening the bonds between lignin and hemicellulose as the mechanism to increase the specific surface area regardless of the high lignin content, facilitating the fibrillation of fibers with mechanical milling.

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1. Introduction

Cellulose is the largest accumulated biomass in the natural world, and it is a bioresource that is anticipated to become a candidate to replace conventional fossil fuels without competing with sugar or starch. We aimed to produce cellulose fibers or nanofibers efficiently from woody biomass used as a raw material, and to expand the application of such fibers. One of our efforts involved bioethanol production. Cellulosic bioethanol production requires a pretreatment process in order to increase the reactivity of the cellulolytic enzymes by decomposing the strong structure of lignocellulosic biomass. We have adopted the wet-milling process (mechanochemical treatment) using a ball mill or a grinder, and we demonstrated that this pretreatment process leads to the effective fibrillation of wood fibers and improves enzyme reactivity (Endo, 2010). This method is compatible with hydrothermal treat-

ment, improving the efficiency of wet-milling and helping to achieve high saccharification at lower enzyme loading via boiling at relatively low temperatures below 200 °C to soften the substrate in advance (Inoue et al., 2008). In a previous article, we examined the addition of NaOH to the hydrothermal–mechanochemical treatment, and we observed that the enzymatic saccharification improved by 50% for the specimen treated in the presence of NaOH compared to when it was processed with hydrothermal–mechanochemical treatment alone (Ishiguro and Endo, 2014). While this result showed that the addition of NaOH improves the efficiency of hydrothermal–mechanochemical treatment, herein we will report the results of an investigation of Ca(OH)₂. As with sodium hydroxide and ammonium hydroxide, Ca(OH)₂ is an alkali used for the pretreatment of various types of biomass. However, it is less expensive than these chemicals, generates smaller environmental loads, and is an alkali that is relatively easy to use with the established recovery process (Mosier et al., 2005). Moreover, since cellulose crystallinity is also maintained with the dilute alkaline treatment and the wet-milling process, the products generated

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after pretreatment are expected to be applicable not only as a raw material to produce bioethanol but also as lignocellulosic composite materials exhibiting the functionality of cellulose. Therefore, we believe that the optimization of the hydrothermal–mechanochemical treatment would also play a significant role in optimizing the production of cellulose nanofibers.

2. Methods

2.1. Materials

Wood chips (~3 cm, with bark) from *Eucalyptus globulus* trees about 10 years old, were used as the raw material. Accellerase DUET (Genencor, CA, USA), a cellulase cocktail derived from *Trichoderma reesei*, was used for enzymatic saccharification. Both were provided by Oji Holdings Co., Tokyo, Japan. Calcium hydroxide (lime) was purchased from Wako Chemicals, Japan.

2.2. Hydrothermal–mechanochemical treatment with Ca(OH)₂

We added 0, 0.15, 0.3, and 0.6 g of Ca(OH)₂ (0, 5, 10, and 20 wt% of substrate, respectively) to 3 g of *Eucalyptus* wood chips that were less than 3 mm in size. Distilled water was added for a total weight of 43 g, and then the chips were immersed in the solution overnight. Hydrothermal treatment was performed with autoclaving for 1 h at 130, 150 (STP-3050VP; ALP, Japan), and 170 °C (Model 4565; Parr, IL, USA). The specimens obtained after the hydrothermal treatment were then directly processed in a wet ball mill for 120 min (Pulverisette 7 premium line; Fritch, Germany). The specimens were transferred to 80 mL zirconia pots and milled at room temperatures for 120 min at 450 rpm using 30 zirconia balls with a diameter of 10 mm, and washed with distilled water (by centrifugation and decantation) until they became neutral. After replacing the distilled water with *t*-butyl alcohol, the specimens were freeze-dried for one week.

2.3. Analysis of pretreated substrate

The amount of woody components in the freeze-dried pretreated substrate was measured. Klason lignin and sugar content were quantified with 72 wt% sulfuric acid hydrolysis in accordance with the previously described method (Sluiter et al., 2012).

The specific surface area of the pretreated substrate was determined from the Brunauer–Emmett–Teller plot of nitrogen gas adsorption (Brunauer et al., 1938) with the measuring device BELSORP-max (Bel Japan, Japan).

Fourier-transform infrared (FT-IR) analysis was conducted based on the attenuated total reflectance (ATR) method using an FT-IR spectrophotometer (Spectrum GX; PerkinElmer, MA, USA). A range from 600 to 4000 m⁻¹ of the absorption spectrum was recorded every 4 cm⁻¹ and the average value of the 128 measurements was used for the analysis.

The crystallinity index was measured using an X-ray diffractometer (RINT-TTR III, Rigaku, Japan). Nickel-filtered Cu K α radiation ($\lambda = 0.1542$ nm) was used at 50 kV and 300 mA. The diffraction intensity was obtained in the range of $2\theta = 2^\circ$ to 60° , at 0.02° intervals, at a rate of $2^\circ/\text{min}$.

2.4. Enzymatic saccharification

Enzymatic saccharification was performed at 50 °C for 48 h with a 25 mL reaction solution that contained 75 mg of pretreated substrate, a cellulase preparation (12 FPU per gram of substrate), and a 0.1 M acetic acid buffer solution (pH 5.0). From the reaction solution, 0.5 mL was periodically collected. Then, the liberated sugar content was measured quantitatively by processing the supernatants centrifuged at 1×10^4 g for 5 min using high-performance liquid chromatography (LC-2000 Plus series, Jasco, Japan). Aminex HPX-78P columns (Bio-Rad, CA, USA) were used as a separation column, and the measurement was conducted at 80 °C with a flow rate of 0.6 mL/min. Enzymatic digestibility was represented as the glucose yield, which was calculated using the following equation:

$$\text{Glucose yield (\%)} = \frac{[\text{weight of glucose liberated by enzymatic hydrolysis (mg)}]}{[\text{weight of maximum glucose obtained by sulfuric acid hydrolysis (mg)}]} \times 100.$$

3. Results and discussion

3.1. Changes in the composition of components in the Ca(OH)₂-treated substrate and enzymatic saccharification

Table 1 shows the composition of woody components in the *Eucalyptus* specimens after the hydrothermal–mechanochemical

Table 1
Quantities of lignocellulosic components of *Eucalyptus* remaining after hydrothermal–mechanochemical treatment with Ca(OH)₂, and glucose yields from enzymatic saccharification.

	Treatment temperature (°C)	Glucose yields after 48 h (%)	Cellulose content (%)	Lignin content (%)	Hemicellulose content (%)
0% Ca(OH) ₂	25	2.2	34.0	33.3	18.2
	130	3.4	32.7	34.6	18.2
	150	60.7	31.1	27.3	12.6
	170	64.0	30.0	24.9	6.8
5% Ca(OH) ₂	25	10.7	33.8	28.9	19.0
	130	7.1	28.1	26.1	15.1
	150	31.0	33.1	27.8	16.8
	170	71.0	32.4	25.0	12.2
10% Ca(OH) ₂	25	40.3	33.1	24.8	16.2
	130	28.3	26.1	23.0	12.7
	150	28.3	30.9	25.2	13.9
	170	79.4	32.2	24.7	13.1
20% Ca(OH) ₂	25	67.1	32.0	24.3	14.1
	130	75.2	31.6	24.5	13.1
	150	83.5	31.7	23.0	12.3
	170	90.2	30.0	21.7	11.3

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