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Microwave assisted alkaline pretreatment to enhance enzymatic saccharification of catalpa sawdust

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HIGHLIGHTS

- Catalpa sawdust was pretreated by microwave to enhance biofuel yield.
- Hemicellulose and lignin were solubilized after microwave-alkali pretreatment.
- Reducing sugar yield increased by 682.15% after microwave-$Ca(OH)_2$ pretreatment.
- Catalpa sawdust with microwave-$Ca(OH)_2$ pretreatment is promising for enzymolysis.

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ABSTRACT

Catalpa sawdust, a promising biofuel production biomass, was pretreated by microwave-water, -NaOH, and -$Ca(OH)_2$ to enhance enzymatic digestibility. After 48 h enzymatic hydrolysis, microwave-$Ca(OH)_2$ pretreated sample showed the highest reducing sugar yield. The content of hemicellulose and lignin in catalpa sawdust decreased after microwave-alkali pretreatment. SEM observation showed that the catalpa sawdust surface with microwave-$Ca(OH)_2$ pretreatment suffered the most serious erosion. Crystallinity index of catalpa sawdust increased after all three kinds of pretreatment. The optimum conditions of microwave-$Ca(OH)_2$ pretreatment were particle size of 40 mesh, $Ca(OH)_2$ dosage of 2.25% (w/v), microwave power of 400 W, pretreatment time of 6 min, enzyme loading of 175 FPU/g, and hydrolysis time of 96 h, and the reducing sugar yield of microwave-$Ca(OH)_2$ pretreated catalpa sawdust reached 402.73 mg/g, which increased by 682.15% compared with that of raw catalpa sawdust. The catalpa sawdust with microwave-$Ca(OH)_2$ pretreatment is promising for biofuel production with great potential.

1. Introduction

With the inevitable depletion of fossil fuels and negative environmental effects caused by burning fossil fuels, more attention has been focused on biofuel production from lignocellulosic biomass (César et al., 2015). There were many sources of lignocellulosic biomass for biofuels production, such as forestry, agriculture, and municipal wastes (Ho et al., 2014). The statistics from Liu and Shen (2007) showed that more than a third of a log is turned into wastes in the process of wood processing. In China, 37 million cubic meter forestry wastes are generated from forestry industry each year (Xin et al., 2014). Catalpa is a common commercial wood and catalpa sawdust is an abundant forestry waste. Our previous work has shown that the catalpa sawdust had great potential as raw material for biofuel production (Jin et al., 2015).

Enzymatic saccharification from lignocellulosic biomass to yield fermentable sugar is a crucial step for biofuel production (Krishania et al., 2013). Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. In general, it is difficult for enzymes to hydrolyze cellulose from the tight cellulose-hemicellulose-lignin network (Himmel, 2008). Therefore, a large number of pretreatment methods have been developed for efficient enzymatic hydrolysis. These methods include mechanical pretreatment, steam explosion, ammonia fiber explosion, hot water treatment, alkali or acid pretreatment, microwave assisted pretreatment (MAP), supercritical CO_2 treatment, and biological pretreatment (Behera et al., 2014; Kudakasseril Kurian et al.,

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2013; Moretti et al., 2014; Tian et al., 2014; Zhu et al., 2016). The aim of these pretreatment methods is basically to remove the hemicellulose or lignin, change the cellulose crystallinity, and expand the accessible surface area of lignocellulosic biomass (Ma et al., 2009). In order to achieve these aims, most pretreatment methods require heating at high temperature. However, conventional heating methods (e.g. air bath heating, water bath heating, oil bath heating, and oven heating) caused massive energy consumption. On the contrast, microwave heating is more energy-efficient and operation-easy than the conventional heating methods (Binod et al., 2012).

Microwave creates heat by direct interaction between a heated object and an applied electromagnetic field (Diaz et al., 2015). Therefore, the heating efficiency is higher than the conventional conduction/convection heating. Hu and Wen (2008) employed microwave-water to pretreat switchgrass, and the total sugar yield was 53% higher than that with the conventional heating pretreatment. Ooshima et al. (1984) pretreated rice straw and bagasse by microwave with water, and the accessibility of biomaterials for enzymatic hydrolysis was markedly enhanced. Zhu et al. (2006) pretreated wheat straw with microwave-alkali and presented higher hydrolysis efficiency than the conventional heating samples. Lin et al. (2015) pretreated water hyacinth with microwave-alkali, and the enzymatic digestibility and H_2/CH_4 production was improved.

As far as we know, the MAP of hard wood sawdust has little been reported before. The objective of this study is to evaluate the characteristics and efficiency of catalpa sawdust MAP. The catalpa sawdust was pretreated by microwave with water, NaOH, and $Ca(OH)_2$. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and FT-IR spectra analysis were used to determine the change of physicochemical characteristics of catalpa sawdust after MAP pretreatments. Reducing sugars yield by enzymatic hydrolysis was used to evaluate the pretreatment efficiency. The operating conditions of enzymatic hydrolysis (cellulase loading and hydrolysis time) and MAP (particle size, $Ca(OH)_2$ dosage, microwave power and pretreatment time) were optimized.

2. Material and methods

2.1. Raw materials

Catalpa sawdust used in this study was collected from a furniture factory located in Beijing, China. It was air-dried for two weeks and screened with sieve shakers. The sample was placed in sealed plastic bags and stored in a desiccator at room temperature.

2.2. MAP pretreatment

MAP pretreatment was carried out using a domestic microwave oven (Samsung, S7A73) with an operating frequency of 2450 MHz. The power of microwave oven was set at 200, 400, and 600 W. Distilled water and two kinds of alkali solution, NaOH and $Ca(OH)_2$, were used for the MAP of catalpa sawdust. The catalpa sawdust of 5.0 g was immersed in 100 ml water or 0.75% (w/v) alkali solution. The suspension was subjected to microwave pretreatment for a certain time. After MAP pretreatment, the sample was cooled to room temperature, and the solid residues were recovered by filtration with a vacuum pump. The solid residues were thoroughly washed with distilled water to a neutral pH, then dried at 105 ± 3 °C for a minimum of 4 h. The dried solid sample was used for enzymatic hydrolysis, compositional analysis, and structure test.

2.3. Enzymatic hydrolysis

The enzymatic hydrolysis of sample was carried out using commercial cellulase from *Aspergillus niger* (powder, $\geqslant$0.3 units/mg solid), purchased from Sigma–Aldrich Co. LLC. The sample of 0.5 g was incubated with enzyme of 25 Filter Paper Unit (FPU)/g biomass in stoppered conical flasks. The conical flasks were shook at 50 °C for 48 h in a shaking water bath (100 r/min). The supernatant was taken at certain time interval for the determination of reducing sugar yield. All experiments were carried out three times, and the given data were the mean values.

2.4. Analysis methods

The chemical composition of raw and pretreated catalpa sawdust was analyzed by a fiber analyzer (A200i, Ankom, USA) (Vogel et al., 1999). Reducing sugar was measured by 2,5 dinitrosalicylic acid method (Miller, 1959). The crystallinity of catalpa sawdust samples was examined by XRD measurement with an X-ray diffractometer (D8 Advance, Bruker, Germany). The samples were scanned and the intensities were recorded in 2θ range from 5° to 40° with a step of 0.2°. Crystallinity index (CrI) of cellulose was calculated according to Eq. (1) (Segal et al., 1959):

$$CrI = \left(\frac{I_{002} - I_{amorphous}}{I_{002}}\right) \times 100\% \tag{1}$$

where I_{002} is the maximum diffraction intensity of crystalline structure ($2\theta = 22.6°$), and $I_{amorphous}$ is the diffraction intensity of amorphous fraction ($2\theta = 18.0°$). The functional group change of catalpa sawdust sample was recorded from 4000 to 400 cm^{-1} by a FTIR spectrometer (VERTEX 70, Bruker, Germany).

3. Results and discussion

3.1. Chemical composition change of catalpa sawdust

Lignin and hemicellulose are crucial barriers to efficient enzymatic hydrolysis of lignocellulosic biomass (Kumar et al., 2009a). Therefore, one aim of pretreatment is to solubilize the lignin and hemicellulose as much as possible from the lignocellulosic biomass. The composition of catalpa sawdust before and after MAP was analyzed and the cellulose, hemicellulose, and lignin contents are shown in Table 1. The raw catalpa sawdust contained of 50.87% cellulose, which was higher than many raw materials of biofuels production (Jin et al., 2016). Higher cellulose content of raw materials was in favour of fermentable sugar production (Jung et al., 2013). After the microwave-water pretreatment, the cellulose, hemicellulose and lignin content all slightly increased. Diaz et al. (2015) demonstrated that these three compositions of rice straw were all increased after microwave-water pretreatment. The possible reason was that the microwave-water pretreatment only slightly dissolved other compositions rather than the cellulose, hemicellulose and lignin. On the other hand, after microwave-alkali pretreatment, the hemicellulose and lignin contents were both decreased due to their solubilization. This phenomenon might lead to a higher enzymatic hydrolysis.

Table 1
Chemical composition of samples.

Sample	Chemical composition (%)			
	Cellulose	Hemicellulose	Lignin	Others
Control	50.87	17.21	18.95	12.97
Microwave-water	51.62	17.34	19.03	12.01
Microwave-NaOH	55.78	15.82	17.09	11.31
Microwave-$Ca(OH)_2$	56.28	14.71	16.77	12.24