



Improvement of the enzymatic hydrolysis of furfural residues by pretreatment with combined green liquor and hydrogen peroxide



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HIGHLIGHTS

- Green liquor coupled with peroxide (GL–H₂O₂) removed lignin effectively.
- Glucose yield was greatly improved after GL–H₂O₂ pretreatment.
- The loading of H₂O₂ can be decreased by adding ethylenediaminetetraacetic acid.
- Combined pretreatment removes the lignin and reduces the cellulase–lignin binding.
- The carbonyl from lignin plays an important role in cellulase binding.

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ABSTRACT

A potential commercial pretreatment for furfural residues (FRs) was investigated by using a combination of green liquor and hydrogen peroxide (GL–H₂O₂). The results showed that 56.2% of lignin removal was achieved when the sample was treated with 0.6 g H₂O₂/g-DS (dry substrate) and 6 mL GL/g-DS at 80 °C for 3 h. After 96 h hydrolysis with 18 FPU/g–cellulose for cellulase, 27 CBU/g–cellulose for β-glucosidase, the glucose yield increased from 71.2% to 83.6%. Ethylenediaminetetraacetic acid was used to reduce the degradation of H₂O₂, the glucose yield increased to 90.4% after the addition of 1% (w/w). The untreated FRs could bind more easily to cellulase than pretreated FRs could. The structural changes on the surface of sample were characterized by X-ray photoelectron spectroscopy. The results indicated that the surface lignin could be effectively removed during pretreatment, thereby decreasing the enzyme–lignin binding activity. Moreover, the carbonyl from lignin plays an important role in cellulase binding.

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1. Introduction

The utilization of biomass for transport fuels, chemicals, and materials is increasing because of the shortage of fossil fuels and the need to reduce greenhouse gas emissions. The conversion of fermentable sugars is a critical process for producing bioethanol and chemicals (Kemppainen et al., 2012; Ragauskas et al., 2006; Tang et al., 2011). The typical process of converting lignocellulosic biomass to fermentable sugars (especially glucose) is enzymatic hydrolysis. Many biomass resources such as agricultural residues, hardwood, and softwood have been used to produce biofuels. In particular, agricultural residues are becoming attractive biomass materials, since they are the most abundant renewable resources (FAO, 2010). Furfural residue (FR) is an industrial byproduct that

is produced during the production of furfural from corncobs. Corncobs are heated at high temperature (170–185 °C) under acidic conditions (5–8% dilute sulfuric acid) to hydrolyze arabinoxylans (hemicelluloses) into xylose, after which the xylose are converted into furfural by further dehydration reaction. The cellulose and lignin present in cobs are relatively stable under these conditions, so the waste residues are composed mainly of cellulose and lignin, with about 45% of the component being cellulose (Bu et al., 2012). However, most of FRs is burned as waste, which not only increases the release of greenhouse gases but also results in loss of a valuable biomass resource. Therefore, it would be worthwhile to retain such cellulose-rich wastes for the production of bioethanol.

Researches have demonstrated that the presence of lignin in biomass substrates could inhibit enzymatic hydrolysis (Kumar et al., 2012; Yu et al., 2011; Berlin et al., 2006). Specifically, lignin modified by a dilute acid at high temperature led to better enzyme–lignin binding (Nakagame et al., 2010). The intensified interaction between the lignin and enzyme would reduce the activity of

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cellulase for cellulose through destroying the folded structure of the enzyme protein (Rahikainen et al., 2011). Therefore, a pretreatment to separate the lignin from the substrate is a promising approach to increase the enzymatic digestibility of cellulose. Different pretreatment methods including chemical (acid, alkali, ozone, alkaline peroxide), physical (comminution, hydrothermolysis), and physicochemical (steam explosion, ammonia fiber explosion) techniques have been developed for lignocellulosic waste pretreatment (Karagöz et al., 2012; García-Cubero et al., 2009; Wang et al., 2009; Antoni et al., 2007; Asada et al., 2011). Among the pretreatment methods, steam explosion, dilute acid, alkaline, and oxidative pretreatment methods have been widely employed for improving enzymatic hydrolysis. Compared with oxidative pretreatment, alkaline delignification is not an effective method to remove lignin from FRs owing to the condensed structure of lignin (Bu et al., 2011). The literature has reported that peroxides are effective agents for dissolving lignin and improving the conversion of agriculture residues to sugars in enzymatic hydrolysis processes (Saha and Cotta, 2006, 2007, 2010). In particular, alkaline hydrogen peroxide pretreatment could effectively degrade the acidic lignin from FRs (Xing et al., 2012).

After alkaline hydrogen peroxide pretreatment, the black liquor is obtained from the substrate washing. It consists of various organic components (such as low-molecular-weight lignin) and some inorganic compounds originating from the cooking chemicals and reaction product, such as sodium hydroxide and sodium carbonate. The high-valued utilization of that waste liquor is in recovering the organic and inorganic compounds. Pulp mills have been successfully making use of the black liquor (Lennholm and Blomqvist, 2003). First, the black liquor is evaporated until 90% of water is removed. Subsequently, the concentrated liquor is burned to recover the heat. In the sodium hydroxide pulping method, the sodium compound is obtained as sodium carbonate and sodium hydroxide after burning the organic compounds. The sodium carbonate and sodium hydroxide exit the recovery boiler in melted form and are dissolved in water, thus forming green liquor (GL).

GL pretreatment as a method of the alkaline pretreatment process to produce biofuels has been recently developed (Jin et al., 2010; Gu et al., 2012). It tends to selectively remove lignin and leave both the hemicellulose and cellulose fractions in the pulp, as a result of the moderate alkaline condition (Wu et al., 2012). Therefore, the GL pretreatment keeps as much polysaccharides as possible in the substrate for enzymatic hydrolysis. In addition, GL pretreatment has potential commercial applications in the future owing to the chemicals being recovered efficiently during pretreatment (Gonzalez et al., 2011). GL from Kraft pulp mills (Kraft-GL) is composed mainly of sodium carbonate and sodium sulfide. The gas containing the sulfur would be discharged into the air during pretreatment, however; thus, the problem of atmospheric pollution needs to be attended to during Kraft-GL pretreatment. In order to protect the environment, the soda pulping method became an alternative in some mills in China. Thus, the high-value utilization of GL from soda pulp mills has attracted more interest in China. In our previous study, alkaline hydrogen peroxide was used for the pretreatment of FRs, and the results showed that the lignin in FRs could be effectively degraded. In this paper, FRs were pretreated with a combination of the green liquor and hydrogen peroxide (GL-H₂O₂). However, the H₂O₂ could be ineffectively decomposed by metal irons in alkaline hydrogen peroxide pretreatment (Cullis and Mansfield, 2010). In order to reduce the degradation of H₂O₂, the ethylenediaminetetraacetic acid was used in this study. The aim of this study was to estimate the effect of GL-H₂O₂ pretreatment on the chemical compositions and enzymatic hydrolysis of FRs. Simultaneously, the surface characterizations of untreated and pretreated FRs were compared.

2. Methods

2.1. Raw material

The FRs were kindly provided by Chunlei Furfural Corporation (Hebei, China). The furfural production process was that corncobs were heated at 170–185 °C for 3 h under solid to liquid ratio of 2.5:1 with 6% dilute sulfuric acid. The initial pH value of the residues was 2–3. They were immersed in fresh water for 24 h and then rinsed until a neutral pH was reached. The residues were screened with 40 meshes after being dried at 50 °C for 12 h. The FRs filtered through the 40 meshes were collected as the experimental samples. The average contents of cellulose, lignin and ash were 45.9%, 45.3% and 5.2%, respectively.

The GL was supplied by Chenming Group (Shandong, China). It was precipitated overnight and the supernatant was obtained for use. The contents of sodium hydroxide and sodium carbonate were tested according to TAPPI T6424 cm-00 (TAPPI, 1994a). The determination of the calcium and iron contents in the GL was done according to TAPPI T266 om-2 (TAPPI, 1994b). The composition of GL can be seen in Table 1.

2.2. Pretreatment with combined green liquor and hydrogen peroxide

The pretreatment was carried out in pressure bottles with screw caps (Synthware Co., Ltd). For each experiment, the FRs were slurried in water (3.3%, w/v) containing the desired amounts of GL and H₂O₂ (30%, Sinopharm Chemical reagent Beijing Co., Ltd).

Three different variables were evaluated: (1) loading of GL (2–8 mL GL/g-DS (dry substrate)), (2) H₂O₂ consumption (0.1–0.6 g H₂O₂/g-DS), and (3) stabilizers of ethylenediaminetetraacetic acid (EDTA, 98%, Sinopharm Chemical reagent Beijing Co., Ltd). The pretreatment was conducted in a water bath for 3 h at 60 and 80 °C, with shaking at 100 rpm. At the end of the pretreatment, the insoluble residues were collected by filtration with quantitative paper and washed with distilled water (20:1 of water to solid, v/w) until the pH was neutral. Some of the washed samples were dried in an oven at 105 °C for 6 h to evaluate the yield. The rest, without drying, were stored at 4 °C before performing the enzymatic hydrolysis.

2.3. Enzymatic hydrolysis

The pretreated FRs were further submitted to enzymatic hydrolysis, which was performed for 96 h at 47 °C and pH 4.8. The reaction was carried out with a substrate consistency of 2.5% (w/v), using a shaking incubator at 150 rpm. The filter paper activity of cellulase (Celluclast 1.5 L, Sigma Co., St. Louis, MO, USA) was 67 FPU/mL, and the cellobiase activity of Novozyme 188 (Sigma Co.) was 175 CBU/mL. The enzyme loading for substrate was 18 FPU/g-cellulose for cellulase and 27 CBU/g-cellulose for β-glucosidase. The hydrolysis of FRs without pretreatment was performed as a control. Samples derived from the hydrolysis process were withdrawn and centrifuged at 10,000g for 5 min. Then, the supernatants were filtered through 0.2 μm filters and diluted properly for further sugar analysis. The hydrolysis yield was

Table 1
Chemical composition of green liquor.

	Component	Content, g/L
Green liquor	Na ₂ CO ₃	75.20 ± 0.2
	NaOH	23.04 ± 0.25
	Fe	1.14 ± 0.08
	Ca	0.39 ± 0.03

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