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Associating cooking additives with sodium hydroxide to pretreat bamboo residues for improving the enzymatic saccharification and monosaccharides production

Caoxing Huang [a], Juan He [a], Yan Wang [b], Douyong Min [b], Qiang Yong [a,*]

[a] College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China
[b] College of Light Industry Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

HIGHLIGHTS

- Three pretreatments for sugars production were evaluated.
- Alkali pretreatment was effective for bamboo saccharification.
- Alkali pretreatment with cooking additive facilitated sugars releasing.

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ABSTRACT

Cooking additive pulping technique is used in kraft mill to increase delignification degree and pulp yield. In this work, cooking additives were firstly applied in the sodium hydroxide pretreatment for improving the bioconversion of bamboo residues to monosaccharides. Meanwhile, steam explosion and sulfuric acid pretreatments were also carried out on the sample to compare their impacts on monosaccharides production. Results indicated that associating anthraquinone with sodium hydroxide pretreatment showed the best performance in improving the original carbohydrates recovery, delignification, enzymatic saccharification, and monosaccharides production. After consecutive pretreatment and enzymatic saccharification process, 347.49 g, 307.48 g, 142.93 g, and 87.15 g of monosaccharides were released from 1000 g dry bamboo residues pretreated by sodium hydroxide associating with anthraquinone, sodium hydroxide, steam explosion and sulfuric acid, respectively. The results suggested that associating cooking additive with sodium hydroxide is an effective pretreatment for bamboo residues to enhance enzymatic saccharification for monosaccharides production.

1. Introduction

Lignocellulosic biomass, containing high polymeric carbohydrates, are regarded as renewable resources to obtain hexose and pentose for the production of bio-ethanol or bio-based chemicals (Herrera, 2004; Gusakov et al., 2007; Barr et al., 2012). Technically, bio-based products are usually produced from the sugar platform, which can be creased by monomeric sugars hydrolyzed from cellulose and hemicellulose (Barr et al., 2012). For decades, lignocellulose-based agriculture and forestry residues, such as sugarcane bagasse, wheat straw, and corn stover, have been extensively investigated to obtain the monosaccharides (glucose and xylose) (Jorgensen et al., 2007; Huang et al., 2015). Bamboo is an economic forest and covers an area of 3.19 million hm^2 in China. In bamboo utilization industry, fractions of bamboo green, bamboo yellow, bamboo node, and bamboo branches are discarded due to the weakness in mechanical properties, generating approximately 46 million tons processing residues annually (Chand et al., 2006). However, only a part of these bamboo residues are burned to recover energy in industry. Therefore, efficient utilization of bamboo residues is an ideal choice for bio-based chemical production and reducing the risk of pollution.

In the cell wall of lignocellulosic biomass, cellulose is high-crystalline and associates with the hemicellulose and lignin, which are the major obstacles restricting for enzymes converting the polysaccharides into monosaccharides (Chen et al., 2011; Rahikainen et al., 2011). Therefore, an effective pretreatment is required to destroy the recalcitrant structure of lignocellulosic biomass and reduce the cellulose crystallinity for increasing the

* Corresponding author. Tel./fax: +86 25 85427797.
E-mail addresses: swhx@njfu.com.cn, szxapy@163.com (Q. Yong).

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accessibility of cellulase to the cellulose (Mosier et al., 2005; Barr et al., 2012). For decades, the pretreatments of dilute sulfuric acid, steam explosion and sodium hydroxide have been investigated extensively. The dilute sulfuric acid pretreatment can degrade the hemicellulose, generating more pore for increasing accessibility portion of the biomass. Mosier et al. (2005) reported that high dilute sulfuric acid charge and high temperature can effectively degrade the hemicellulose and improve the enzymatic hydrolysis efficiency significantly. Steam explosion pretreatment has shown effective performance in degrading the lignin and hemicellulose, leading to an excellent enzymatic hydrolysis efficiency (Chen et al., 2014). Sodium hydroxide pretreatment can successfully disrupt the ester bonds between lignin and carbohydrates, resulting in the exposure of carbohydrates to enzymes (Li et al., 2010; Sambusiti et al., 2013). Meanwhile, alkali pretreatment provides the effective delignification and chemical swelling of the fibrous cellulose, which are the beneficial factors for achieving an excellent enzymatic saccharification efficiency (Zhao et al., 2009). Therefore, these pretreatments have been recognized as the effective methods to enhance the enzymatic digestibility of lignocellulosic biomass.

Technically, an ideal pretreatment is able not only to produce a readily digestible substrate with low content of lignin, but also to recover the maximum amount of available sugars in feedstocks (Li et al., 2014). Due to the random alkali degradation and the peel reaction, a significant amount of carbohydrates are degraded during the alkali pretreatment process (Gu et al., 2012). Hence, an alkali-based pretreatment with maximizing the remained carbohydrates while minimizing the remained lignin in pretreated sample is considered as a potential method for monosaccharides production. In paper-making industry, cooking additives, such as sodium polysulphide (PS), anthraquinone (AQ) and borohydrate, have shown excellent performance in improving the degree of delignification and keeping as much carbohydrates as possible in the pretreated samples (Jameel et al., 1995; Copur and Tozluoglu, 2008). Although cooking additives have been extensively applied in paper-making industry for decades, applying these additives in the alkali pretreatment for the bioconversion of lignocellulosic biomass has not previously been reported.

In this work, the monosaccharides (glucose and xylose) were obtained from bamboo residues after consecutive pretreatments and enzymatic saccharification process, which were pretreated by sulfuric acid, steam explosion and sodium hydroxide. Furthermore, cooking additives of sodium borohydride ($NaBH_4$), sodium polysulphide (PS) and anthraquinone (AQ) were firstly applied in the sodium hydroxide pretreatment, with the goal of improving the monosaccharides production from the pretreated samples after enzymatic saccharification.

2. Methods

2.1. Materials

The residues used in this study were from the stems of older moso bamboo (*Phyllostachys heterocycla*) provided by the He Qi Cang Bamboo Processing Factory in Fujian, China. The primary chemical components of moso bamboo residues used in this work were as follows (%, dry weight basis): 39.21% glucan, 17.30% xylan, and 32.80% lignin. Cellulase (No. C2730, with an activity of 117 FPU/g) and β-glucosidase (No. NZ188, with an activity of 504 IU/g) were purchased from Sigma–Aldrich Inc. (USA).

2.2. Pretreatment

2.2.1. Dilute sulfuric acid pretreatment

Dilute sulfuric acid pretreatment was carried out in a 1 L cooking pot in an oil bath at 120 °C, 140 °C, and 160 °C for 60 min. 100 g of dry bamboo residues were put into the pot with certain volume of sulfuric acid solution. The sulfuric acid charge was varied in the range of 1–4% (w/v) and the ratio of solid to liquid was 1:10. The pretreated solids were washed with distilled water (with a dry mass-to-water ratio of 1:50) to neutrality. The resulting samples were stored at 4 °C for subsequent experiments.

To elucidate the effect of acid pretreatment severity on carbohydrate recovery and delignification, the combined severity (CS) factor was used to characterization according to Chum et al. (1990), calculating as following equation:

$$R_0 = t \cdot \exp[(T_H - T_R)/14.75]$$

$$\mathrm{CS} = \log R_0 - \mathrm{pH}$$

where R_0 is severity factor, t is reaction time (min), T_H is the target temperature in pretreatment (°C), T_R is a reference temperature, and pH is the measured pH in initial cooking liquor.

2.2.2. Steam explosion pretreatment

Steam explosion pretreatment was carried out in a batch pilot equipped with a 1 L reaction vessel. 100 g dry bamboo residues were packed into the reactor and maintained at the temperature of 180 °C, 200 °C and 220 °C for 10 min. After exposure at the designated condition, the bottom valve was opened to reduce the pressure to obtain the pretreated samples. The steam-exploded solids were washed with distilled water (with a dry mass-to-water ratio of 1:50) to neutrality. The resulting samples were stored at 4 °C for subsequent experiments.

2.2.3. Sodium hydroxide (NaOH) pretreatment

Dry bamboo residues (100 g) were put into a 1 L cooking reactor with an oil bath. The pretreatment was performed at 120 °C, 140 °C and 160 °C for 60 min. The charge of NaOH was varied in the range of 2–10% (w/w) and the ratio of solid to liquid was 1:6. The pretreated solids were washed with distilled water (with a dry mass-to-water ratio of 1:50) to neutrality. The resulting samples were stored at 4 °C for subsequent experiments.

2.2.4. Sodium hydroxide pretreatment with cooking additives

Before pretreatment, the cooking additive was added with sodium hydroxide (8%, w/w) into 1 L cooking reactor, charging with 100 g dry bamboo residues. The charges of $NaBH_4$, PS, and AQ were 1–5% (w/w), 0.5–2.5% (w/w), and 0.03–0.15% (w/w), respectively. The pretreatments were maintained at 160 °C for 60 min. The pretreated solids were washed with distilled water (with a dry mass-to-water ratio of 1:50) to neutrality. The resulting samples were stored at 4 °C for subsequent experiments.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis experiment (50 mL) was performed at a substrate loading of 5% (w/v) and with an enzyme cocktail of 20 FPU/g-glucan cellulase and 3 IU/g-glucan β-glucosidase. The experiments were performed in a 150 mL Erlenmeyer flask at 50 °C using 50 mmol citrate buffer (pH4.8) with shaking at 150 rpm for 48 h. Aliquots were withdrawn and centrifuged for 10 min at 4000 rpm, the supernatants were subsequently filtered through a 0.22 μm syringe filter and analyzed for monosaccharides.

2.4. Analysis methods

The chemical components of bamboo residues and pretreated samples were determined based on the procedure developed by the National Renewable Energy Laboratory for analyzing biomass materials.