Bioresource Technology 151 (2014) 244–248

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Lignin removal and benzene–alcohol extraction effects on lignin measurements of the hydrothermal pretreated bamboo substrate

X.J. Ma, S.L. Cao, X.F. Yang, L. Lin, L.H. Chen, L.L. Huang *

College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, PR China

HIGHLIGHTS

- The extractives of the pretreated substrate increased with the reaction severity.
- Benzene–alcohol extraction gave rise to a low lignin measurement.
- Tappi standard should be modified.
- Lignin removal was the results of lignin degradation and migration.

ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 21 October 2013
Accepted 23 October 2013
Available online 1 November 2013

Keywords:
Benzene–alcohol extraction (BAE)
Lignin
Pseudo lignin
Hydrothermal pretreatment

ABSTRACT

Lignin content of hydrothermal pretreated bamboo chips was determined by the two methods: TAPPI standard method (222om-06) and TAPPI standard method without benzene–alcohol extraction (BAE). The results showed that including BAE resulted in lower Klason lignin (KL) and acid soluble lignin (ASL) measurements in the prehydrolyzed substrate, that is to say, BAE removed parts of KL and ASL. Therefore, the TAPPI standard method should be modified by omitting the BAE for lignin measurements of pretreated substrate. The following lignin removal analysis suggested that lignin was removed from the bamboo substrate during pretreatment by a combination of degradation reaction and deconstruction; thereafter the pseudo lignin generated in the hydrothermal pretreatment and condensation reaction between the lignin fragments accounted for the later KL increase.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

To alleviate the energy crisis and climate change based on the use of fossil energy, biofuel production from renewable resources has received significant attention (Ragauskas et al., 2006; Clark, 2007). For sustainable development, lignocellulosics (including agricultural residues, forestry wood and energy crops) are regarded as more appropriate feedstock for bioethanol production; lignocellulosic ethanol is also called second-generation bioethanol (Blanca and Juan, 2008). All lignocellulosic materials consist primarily of cellulose, hemicelluloses, and lignin. In a heterogeneous enzymatic reaction, the presence of hemicelluloses and lignin and complex three-dimensional structure (called as recalcitrance) make the cellulose inaccessible to hydrolytic enzymes (Himmel et al., 2007). Pretreatment can remove hemicelluloses/lignin and disrupt the structure of the lignocellulosic material to increase cellulose accessibility to enzymes, and thus improve the hydrolysis and fermentation efficiency. Employing pretreatment before enzymatic hydrolysis is essential in a multi-step process for cellulosic ethanol production. Lignin is a key factor that hinders enzymatic hydrolysis through physical inhibition and adsorption. Lignin is subjected to chemical reaction and physical changes during pretreatment. One of the expected lignin chemical reaction pathways in dilute or hydrothermal pretreatment is the cleavage of β-O-4 linkage (Cao et al., 2012); the cleavage gives rise to a high content of lignin with low molecular weight during hydrothermal pretreatment (Leschinsky et al., 2008a). In addition, polymerization reactions of lignin with itself or with carbohydrate degradation products also occur depending upon the reaction conditions (Leschinsky et al., 2008; Bujanovic et al., 2012). Moreover, as lignin melts, it migrates through the cell wall and forms droplets or coalesces on the biomass surface; this migration and redistribution of lignin has been viewed as an obstacle for enzyme hydrolysis (Bujanovic et al., 2012). Additionally, lignin degradation products in the hydrolysate impede the dissolution of hemicelluloses because of their tendency to form deposits (Leschinsky et al., 2008b). Further, several studies have demonstrated that the Klason lignin (KL) content of dilute acid pretreated biomass was higher than that of the starting material (Mao et al., 2010; Chen et al., 2010; Jung et al., 2010; Sannigrahi et al., 2008). It has been suggested that aromatic materials formed by the combination of carbohydrate

* Corresponding author. Tel.: +86 15959041385; fax: +86 0591 83715175.
E-mail address: fafuhll@163.com (L.L. Huang).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.10.078

and lignin degradation products during acid pretreatment could be responsible for the increase of KL content (Hu et al., 2012). Katahira, Sannnigrahi and Hu verified that dilute acid hydrolysis of holocellulose or cellulose could give rise to an increase of KL measurements of the hydrolyzed substrate and the KL content increased with increasing reaction severity (Sannigrahi et al., 2008; Hu et al., 2012; Katahira et al., 2013). This gain of KL is termed pseudo-lignin and could account for the surprising increase of KL measurements and negatively affect enzymatic hydrolysis. As lignin is an obstacle to the enzymatic saccharification of biomass, accurate determination of lignin content is important to the quantitative analysis of lignin effects.

Generally, the TAPPI standard method is used to determine lignin content of biomass. Briefly, benzene–alcohol extraction is the first step in order to decrease the interference of extractives. Thereafter, extractives-free biomass is depolymerized by hydrolyzing holocellulose with 72% sulfuric acid and followed by hydrolysis of the dissolved polysaccharide in 3% boiling sulfuric acid. The residual solids are considered as acid insoluble or Klason lignin (KL) while the acid soluble lignin (ASL) in the filtrate is determined by UV–visible spectroscopy at 205 nm.

Because of the complex chemical reactions and physical changes that lignin undergoes during pretreatment, it is doubtful that the TAPPI standard (222om-06) is applicable for lignin determination of pretreated substrate. Thus, a systematic hydrothermal pretreatment of bamboo chips was performed. The TAPPI standard (222om-06) and TAPPI standard without benzene–alcohol extraction (BAE) were used to determine the lignin content (KL and ASL) and the differences between the two methods were explored by quantitative analysis of the lignin measurements. In addition, lignin removal was thoroughly analyzed by combination of substrate, hydrolysate liquor and precipitate.

2. Methods

2.1. Materials

Bamboo chips (*Dendrocalamopsis oldhami*) were provided by a forest center (Fujian province, China, 2011). The bamboo chips with size of $(40 \pm 2) \times (15 \pm 1) \times 5$ mm were selected as the starting materials.

2.2. Pretreatment experiments

18 experiments were carried out in an oil-bathed digester which equipped with 10 cooking pots. The reactions were carried out at 160 to 180 °C with the liquor/solid ratio 3:1 (180 g bamboo chips) for times up to 180 min. The cooking pots were put into the oil-bathed digester starting the reaction when the oil temperature reached the target temperature; the cooking pots started to rotate while the rotate button was switched on. The schematic diagram of the digester was shown in Fig. 1. At the end of the reaction, the cooking pots were taken out and cooled in cold water. The solids and hydrolysate were separated by filtration with 80 mesh bags. The lignin content of the solid substrate was analyzed while the filtrate was subjected to TEM analysis.

2.3. Holocellulose separation and hydrolysis

Holocellulose was obtained from bamboo powder following the procedure described by Cao et al. (2012). The extractives-free powder was subjected to oxidation reactions for removing lignin. Holocellulose pretreatment was conducted in the oil-bathed 25 mL hydrothermal reactor at 170 °C for up to 240 min.

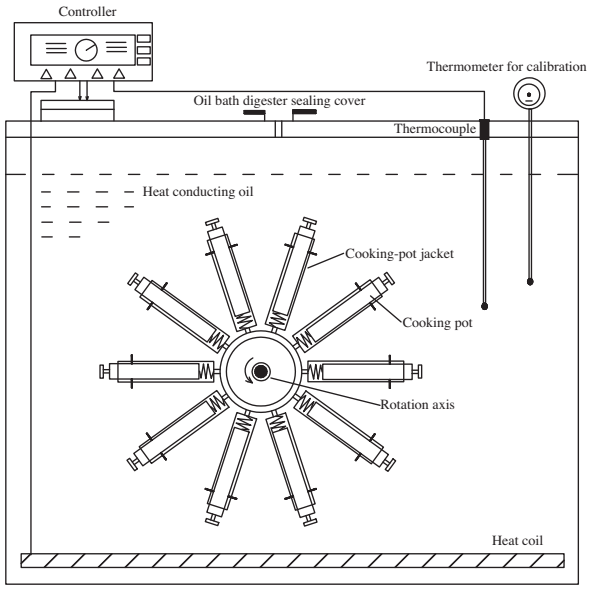

Fig. 1. Schematic diagram of prehydrolysis apparatus.

2.4. Analytical methods

The yields of pretreatment were determined by the weight and moisture content of the starting bamboo chips and treated bamboo chips.

The extractives of benzene–95% alcohol (2:1) extraction were determined by TAPPI standard method T264 cm-97.

KL content was determined by TAPPI standard 222om-06 and the TAPPI standard method without BAE. In order to compare the changes of KL removal, KL values were based on the original material, i.e., the KL measurements were calculated by multiplying KL measurements of the pretreated substrate with the pretreatment yield. ASL in the filtrate was determined by UV–visible spectroscopy at 205 nm. Multiple measurements (3–4 runs) were conducted for all characterization techniques, and a mean value was reported. The error margin of the KL and ASL measurements was ±0.1% to ±0.4% and ±0.03% to ±0.07%, respectively.

The pretreatment hydrolysate liquor was dripped onto a copper mesh and vacuum dried for about 24 h. Images of the colloid particles in hydrolysate liquor were taken with a Transmission Electron MicroscopeTEM (JEM1010, Japan).

Bamboo and pretreated bamboo powder was characterized by solid state cross-polarization magic angle spinning (CPMAS) ^{13}C NMR (Advance III500, Bruker, Switzerland) operating at a frequency of 125.75 MHz.

Field Emission Scanning Electron Microscope (FE-SEM, FEI Nova NANOSEM 230, operated at an accelerating voltage of 15 kV) was used to characterize the morphology of the holocellulose and pretreated holocellulose samples.

3. Results and discussion

3.1. BAE effects on lignin measurements

From Fig. 2, the KL and ASL determined by the TAPPI standard method showed that the KL decreased gradually at the initial stage and then showed an increase in the later stage ($\geqslant$170 °C). In contrast, ASL decreased first and then plateaued at extended pretreatment times. Furthermore, the KL and ASL content determined by TAPPI standard method was 10–35% and 15–75% lower than that determined without BAE. Increasing reaction severity increased

Download English Version:

https://daneshyari.com/en/article/7079753

Download Persian Version:

https://daneshyari.com/article/7079753

Daneshyari.com