Industrial Crops and Products 94 (2016) 117–121

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Short communication

A perspective on lignin effects on hemicelluloses dissolution for bamboo pretreatment

Xiaojuan Ma[a,b,*], Xin Zheng[a], Haiyang Yang[a], Hui Wu[a], Shilin Cao[a,c], Lihui Chen[a], Liulian Huang[a,*]

[a] College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China
[b] Key Laboratory of Pulp and Paper Science & Technology of Ministry of Education of China, Qilu University of Technology, Jinan, 250353, China
[c] State Key Lab of Pulp and Paper Engineering, South China University of Technology,Guangzhou, 510640, China

ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form 13 August 2016
Accepted 13 August 2016

Keyword:
Hydrothermal pretreatment
Hemicelluloses release
Lignin
Bamboo

ABSTRACT

To further explore the factors that resist hemicelluloses degradation and release, the chemical composition and molecular weight (MW) in both the interior and exterior portions of the hydrothermally pretreated bamboo substrates were characterized. The chemical composition analysis showed that pretreatment made the lignin tend to accumulate on the exterior surface of the bamboo chips; and therefore gave rise to a large difference of lignin content between exterior and interior. Along with the degradation of hemicelluloses, the difference of hemicelluloses content in both the exterior and interior part became small. On the contrary, the hemicelluloses from the both exterior and interior portions had an invariable MW in the early stage of pretreatment; whereas, the difference of hemicelluloses MW between the exterior and interior part increased with the pretreatment continue, indicating low MW of hemicelluloses in the interior portion. Long time pretreatment promoted increasingly lignin covering on the surface of the chips; the lignin coatings might act as a hydrophobic layer blocking the access of the degraded hemicelluloses.

1. Introduction

Pretreatment is a primary method to reduce the recalcitrance of lignocellulosic biomass to make the cellulose more accessible to enzymes in the bioconversion processes for ethanol production (Alvira et al., 2010; Carvalho et al., 2015). During the process, the solubilization of hemicelluloses and structure changes of lignin and cellulose result in increased specific surface area and pore size of the fiber cell wall, such that appreciable amounts of enzyme have access to cellulose microfibrils (Foston and Ragauskas, 2010).

Prior to the pretreatment, size reduction of the biomass is usually required to improve enzyme accessibility to speed up the process and to achieve a greater glucose yield (Zhu et al., 2009; Hosseini et al., 2010). However, the size reduction, before the chemical pretreatment is energy- intensive; in contrast, a post size-reduction approach process was reported with significant reduce of the energy consumption (Zhu and Pan, 2010). Unfortunately, it has been reported chip size negatively affected hemicelluloses sugar recovery and enzymatic cellulose saccharification efficiency; more severe pretreatment was required to get same yield with larger size of the biomass (Hosseini et al., 2010).

During the hydrothermal pretreatment, hydronium ions from generated compounds, such as acetic acid, uronic acid and phenolic acid, catalyze the hydrolysis of hemicelluloses (Vallejos et al., 2015). In a batch system, hemicelluloses release limits to a certain level whether hydrothermal or dilute acid pretreatment were applied; instead, employing countercurrent flow of liquid and solids or flow of water through the solids, could recover virtually theoretical yields of hemicelluloses. Adding dilute sulfuric acid could increase the rate of xylan removal in both batch and flow-through system (Yang and Wyman, 2004). Actually, several factors, including initial pH, temperature, and holding time and types of additives, should be taken more seriously to affect hemicelluloses release. Among these factors, temperature and acid level were actually the key factors that could control rate of hemicelluloses degradation, solubilization and even the reaction selectivity.

In addition to reaction conditions, other factors should be considered. As mentioned before, the chips size (thickness) affected hemicelluloses removal substantially; besides, the difference between the concentration in solid and bulk liquor, the viscosity of the solution and the molecular size of the hemicelluloses degradation products were also related to the total

* Corresponding authors.
E-mail addresses: 1212juanjuan@163.com (X. Ma), fafuhll@163.com (L. Huang).

http://dx.doi.org/10.1016/j.indcrop.2016.08.025
0926-6690/

hemicelluloses removal (Liu and Wyman, 2004; Rissanen et al., 2014).

With the help of the heated medium, lignin becomes fluid, coalesce within cell wall layers and cracks by hydrophobic forces. The fluid lignin has the potential to move throughout the cell wall matrix; while the hydrostatic pressures within the cell wall eventually force a portion of the lignin to the exterior surface, potentially blocking further access to cell wall components (Selig et al., 2007). The deep study found that extensive lignin migration might block the hemicelluloses degradation and solubilization (Ma et al., 2013a). As a consequence, characters of the biomass including of surface morphology and substrate pore structure also acts as important factors.

It was showed hemicelluloses removal could only reach to a limited level although hemicelluloses degraded continuously and even with a low MW (molecular weight). The comprehensive study the correlations between hemicelluloses release and lignin behavior is highly desirable. Upon these focus, hemicelluloses isolated from different positions were targeted as starting materials and the MW level were determined.

2. Material and methods

2.1. Materials

3-year-old green bamboo (*Dendrocalamopsis oldhami*) was graciously provided by Nanjing Forestry (Zhangzhou, Fujian, China). Prior to chipping, the roots and tips of the bamboo were cut off. The selected sizes of the chips were $(40 \pm 2) \times (20 \pm 2) \times (6 \pm 2)$ mm. For the experiment, the outer and inner skin and knot of the chips were removed with a knife.

The acceptable chips were washed several times for removing the sand and dirt; afterward, the washed chips were air dried for the further experiments, the moisture of the chips was about 10.2%.

2.2. Hydrothermal pretreatment

Pretreatment experiments were carried out in an oil-bathed digester, in which 10 canisters were equipped on a shaft that could rotate in the digester. The temperature of pretreatment was controlled at 170 °C by adjusting temperature of glycerinum; while the liquor/solid ratio was kept at 3:1. When the temperature of the glycerinum reached to the target temperature, the canisters filled with bamboo chips were put into the digester and fixed onto the shaft; the reaction time was set at 10, 30, 60 and 90 min, respectively. After finishing the pretreatment reaction, the solid substrate was collected by filtering the contents with a plastic bag (200 meshes). The solid substrate was washed with deionized water for removal of residual soluble species. Yield of pretreatment was determined by the weight ratio between pretreated substrate and raw material.

2.3. Samples preparation

The pretreated bamboo chips were sliced by a sharp knife; briefly, the chips were split into 3 parts along the thickness direction. The central parts of the chips were denoted as interior while the left 2 parts were collected as exterior.

2.4. Analytical procedures

The determination procedures of the hemicelluloses and cellulose content of the solid residue (pretreated substrate) were following the method of the literature (Wei et al., 2015; Ma et al., 2013b). Klason lignin content was determined by the Tappi standard method without benzene alcohol extraction. Fig. 1 shows the diagram of α-cellulose and hemicelluloses isolation from starting

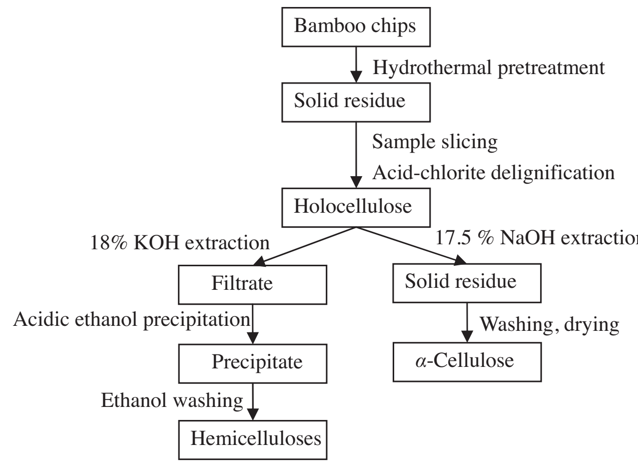

Fig. 1. Diagram of hemicelluloses and cellulose isolation.

material and pretreated solid residue (Ma et al., 2013b; Ma et al., 2014); afterward, DP (degree of polymerization) of cellulose was determined according to the method ISO 5351/2012; while the MW (molecular weight) of hemicelluloses was analyzed by GPC (Gel Permeation Chromatography) techniques. The detailed procedure was presented in the literature (Ma et al., 2014). All the compositional measurements were performed on four replicates per samples, the figures were calculated based on the starting materials; whereas the GPC experiments were performed in duplicate and the average value was reported.

3. Results and discussion

3.1. Hemicelluloses and lignin content of exterior and interior part

Fig. 2a shows the hemicelluloses contents of the exterior and interior portions of the treated chips. It can be found that the hemicelluloses content decreased with the pretreatment time; however, higher hemicelluloses content was observed on the exterior portion than that in the interior. During the pretreatment, hydronium ions, with a typical size of 0.4 nm, penetrate into the bamboo pores to hydrolyze the glycosidic bonds of hemicelluloses molecules. In such a case, some soluble hemicelluloses are formed in the pores and one portion of them transfers out to the bulk liquor by diffusion within the pores of the chips and convection outside the chips. Mittal et al. (2009) have found that pore-space mass-transfer coefficients were an order of magnitude higher than the liquid-phase mass-transfer coefficients; in this case, once the hemicelluloses oligomers were formed in the interior of the biomass pores, they could diffuse outward to the water phase. In addition, the hemicelluloses solubility increases drastically with temperature, particularly when the temperature was above 100 °C (Zhang et al., 2010). It was anticipated that some of the degraded hemicelluloses fragments were soluble at the high temperature 170 °C, and could diffuse into the bulk liquor. After the pretreatment finished, parts of the soluble species precipitated out and built up onto the surface of the chips due to the sharp drop of solubility caused by reactor cooling. Combining these effects, it can be concluded that high hemicelluloses appeared on the exterior surface of the bamboo chips. Jung et al. (2010) reported that after dilute acid pretreatment of poplar wood chips, the xylan concentration was about 30% higher on the surface of the wood chips than the average of the wood chips, while bulk carbohydrate analysis showed that the relative concentration of xylose decreased 10 times in comparison with untreated poplar wood.