Bioresource Technology 150 (2013) 321–327

Contents lists available at ScienceDirect

Bioresource Technology

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

Alkaline hydrogen peroxide pretreatment of softwood: Hemicellulose degradation pathways

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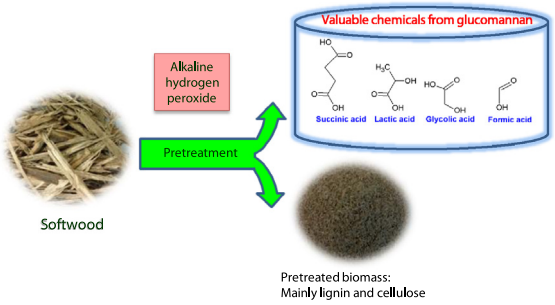
HIGHLIGHTS

- Alkaline H_2O_2 pretreatment (AHP) of softwood led to valuable hemicellulose products.
- A significant amount of lactic and succinic acids can be produced from glucomannan.
- Glucomannan to organic acids conversion pathways were elucidated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 August 2013
Received in revised form 1 October 2013
Accepted 6 October 2013
Available online 12 October 2013

Keywords:
Alkaline hydrogen peroxide
Softwood
Glucomannan
Carboxylic acids
Endwise depolymerization

ABSTRACT

This study investigated softwood hemicelluloses degradation pathways during alkaline hydrogen peroxide (AHP) pretreatment of Douglas fir. It was found that glucomannan is much more susceptible to alkaline pretreatment than xylan. Organic acids, including lactic, succinic, glycolic and formic acid are the predominant products from glucomannan degradation. At low treatment temperature (90 °C), a small amount of formic acid is produced from glucomannan, whereas glucomannan degradation to lactic acid and succinic acid becomes the main reactions at 140 °C and 180 °C. The addition of H_2O_2 during alkaline pretreatment of D. fir led to a significant removal of lignin, which subsequently facilitated glucomannan solubilization. However, H_2O_2 has little direct effect on the glucomannan degradation reaction. The main degradation pathways involved in glucomannan conversion to organics acids are elucidated. The results from this study demonstrate the potential to optimize pretreatment conditions to maximize the value of biomass hemicellulose.

1. Introduction

The structural and chemical recalcitrance of plant biomass presents a major challenge to the development of an economically viable process to convert biomass to biofuels and bioproducts. A variety of pretreatment technologies have been developed to disintegrate biomass and facilitate downstream processing of its components (i.e. cellulose, hemicellulose, lignin) by biological and chemical means to produce biofuels and biochemicals (Larsson et al., 1999; Mosier et al., 2005; Pan et al., 2004; Wyman et al., 2005).

Softwood is recognized as the most recalcitrant biomass feedstock to deconstruction to produce sugars for biofuels conversion. Acid or SO_2 catalyzed steam explosion and organosolv pretreatments have been employed (Del Rio et al., 2012; Kumar et al., 2012; Singhania et al., 2011), both facing limitations. During acidic treatment conditions, hemicelluloses are prone to degradation to furfural and hydroxymethylfurfural (HMF) (Nitsos et al., 2013) which show significant inhibitory effect to downstream enzymatic hydrolysis and fermentation processes (Palmqvist and Hahn-Hägerdal, 2000). During organosolv treatment, complete solvent recovery has been a critical issue to the process economy (Zhu and Pan, 2010).

Compared to hardwood and agricultural biomass, softwood has higher lignin content and more frequent carbon–carbon linkages

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http://dx.doi.org/10.1016/j.biortech.2013.10.020

within lignin macromolecules. Alkaline treatment of softwood has been shown to facilitate lignin removal and swell biomass substrate. Several recent studies have investigated the use of alkaline hydrogen peroxide (AHP) for pretreatment of biomass feedstock. The AHP pretreatment of corn stover and hybrid polar led to glucan hydrolysabilities up to 95% and 97%, respectively (Banerjee et al., 2011, 2012; Gupta and Lee, 2010). A comprehensive investigation of AHP pretreatment of softwood has not been reported.

During biomass pretreatment, not only the integrity of the biomass physical structure is disrupted, but a significant amount of biomass components, mainly hemicelluloses, are also dissolved in the pretreatment solution and collected as the water soluble fraction (WSF). Pretreatment optimization has been mostly focused on improving solid substrate yield and its hydrolysability. Little effort has been made to obtain a detailed understanding of the degradation pathways of hemicellulose during pretreatment process. The objective of this project is to determine the potential of alkaline hydrogen peroxide for efficient softwood pretreatment. As the first part of a series studies to investigate the potential of AHP pretreatment of softwood for fuel and chemicals production, this paper elucidated the softwood hemicelluloses degradation pathways during the pretreatment and discussed potential means of converting softwood hemicelluloses to value chemicals.

2. Methods

2.1. Chemical composition of Douglas fir

Douglas fir (*Pseudotsuga menziesii*) wood chips collected from Washington State were used in this study. The chemical composition of D. fir was determined following the standard procedures (Hames et al., 2008; Sluiter et al., 2011). The glucomannan contents of D. fir samples were estimated based on this composition using an average value of mannose to glucose units of 3:1 on glucomannan (Fengel and Wegener, 1984; Hames, 2009). Cellulose content was then obtained by subtracting glucan presented in glucomannan from the total glucan. The hemicellulose content was calculated based on the total weight of O-acetyl-galactoglucomannan and arabino-4-O-methylglucuronoxylan (Fengel and Wegener, 1984).

2.2. Experimental design for the alkaline hydrogen peroxide pretreatment

Alkaline hydrogen peroxide pretreatments of D. fir were carried out at a temperature of 180 °C, reaction times between 0 and 60 min, peroxide loadings of 0–10% wt (g_{H2O2}/g_{wood}) and a solid to liquid ratio of 1/10. The pH was adjusted to 11.6 by using sodium carbonate as buffer (toward pH 10.6) and sodium hydroxide toward a final pH of 11.6. After pretreatment, the solid fraction (water insoluble solids, WIS) and water soluble fraction (WSF) were separated and collected by filtration. Alkaline hydrogen peroxide pretreatment of Konjac glucomannan (20 g/l, Megazyme P-GLCML, Megazyme, Ireland) were carried out at temperatures of 90 °C, 140 °C and 180 °C, reaction times between 0 and 60 min and a hydrogen peroxide loading of 4% wt (g_{H2O2}/g_{wood}). Reaction time was started after the samples reached the desired temperature. Thus, the temperature ramps were 3.2 min for 90 °C, 4.3 min for 140 °C and 5.1 min for 180 °C.

2.3. Analysis of generated water soluble compounds

Concentration of sugars (cellobiose, glucose, fructose, xylose, galactose, arabinose and mannose) and sugar degradation compounds (glyceraldehyde, glycolic acid, lactic acid, formic acid, acetic acid, succinic acid, 2-hydroxybutyric acid, maleic acid, levulinic acid, furfural, HMF, erythrose, pyruvaldehyde, dihydroxyacetone and gluconic acid) in the water soluble fractions (WSF) were analyzed and quantified by HPLC using an Aminex HPX-87P column for sugars and HPX-87H for degradation compounds following the NREL procedure (Sluiter et al., 2008). All chemicals were obtained from Sigma–Aldrich.

2.4. Analysis of water insoluble solid (WIS) and dissolved oligomers

After pretreatment, the remaining solids (WIS) were washed and analyzed for extractives, lignin and carbohydrate contents following NREL standard procedures (Sluiter et al., 2011). To determine the amount of oligomeric sugars in the WSF, a secondary hydrolysis was performed. The pH of the WSF samples was first adjusted to pH 1.5 with sulfuric acid and then subjected to autoclave hydrolysis at 121 °C for 1 h (Sluiter et al., 2008). The ensuing monomeric sugars were analyzed by HPLC following procedure in Section 2.3.

3. Results and discussion

3.1. The effect of AHP pretreatment conditions on hemicellulose removal and degradation

The chemical composition of Douglas (D.) fir was analyzed. Glucan represents 48.0% (48.0 ± 0.9%) of the total dry weight. The amount of mannan (11.4 ± 0.8%) is significantly higher than those of xylan (2.7 ± 0.1%), galactan (2.2 ± 0.1%) and arabinan (0.5 ± 0.0%) in this sample. This D. fir sample contains 27.7% lignin (27.2 ± 0.8% acid insoluble lignin plus 0.5 ± 0.0% acid soluble lignin), and 2.6% acetic acid (2.6 ± 0.2%). It has been shown that O-acetyl-galactoglucomannan (glucomannan) is the most predominant type of D. fir hemicellulose followed by arabino-4-O-methylglucuronoxylan (arabinoxylan), and a ratio of 1:3 between glucose and mannose units is typical found in the softwood glucomannan backbone (Fengel and Wegener, 1984; Hames, 2009). Based on this information, the amount of O-acetyl-galactoglucomannan in D. fir was estimated to be about 20.1%. The amount of arabino-4-O-methylglucuronoxylan was estimated based on xylan and arabinose content to be about 3.2%. Therefore the total hemicellulose content of D. fir was 23.3% (23.3 ± 1.2%). The D. fir cellulose content (44.2 ± 0.9%) was then calculated by subtracting the total glucan by those presented in glucomannan.

In the preliminary studies, AHP pretreatment of D. fir were first conducted at three temperatures; 90 °C, 140 °C and 180 °C. Pretreatments at 90 °C and 140 °C led to little hemicellulose and lignin removal and produced a substrate with a low

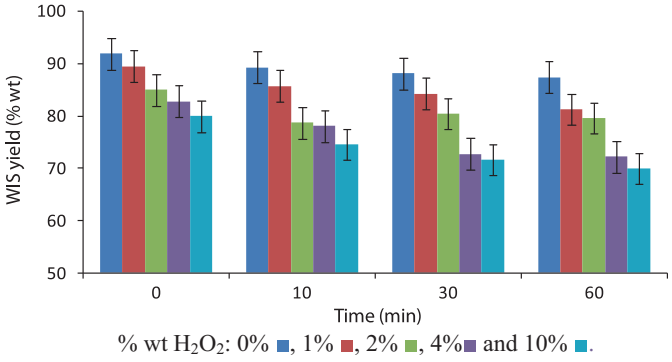

Fig. 1. The WIS yield as a function of AHP pretreatment time at different H_2O_2 loading.