



Recycling of pre-hydrolysis liquor to improve the concentrations of hemicellulosic saccharides during water pre-hydrolysis of aspen woodchips

Zongquan Li^a, Jungang Jiang^a, Yingjuan Fu^a, Zhaojiang Wang^a, Menghua Qin^{a,b,*}

^a Key Laboratory of Paper Science & Technology of Ministry of Education, Qilu University of Technology, Jinan, Shandong, 250353, China

^b Organic Chemistry Laboratory, Taishan University, Taian, Shandong, 271021, China

ARTICLE INFO

Article history:

Received 1 September 2016

Received in revised form 10 June 2017

Accepted 12 June 2017

Available online 13 June 2017

Keywords:

Aspen

Pre-hydrolysis

Hemicelluloses

PHL recycling

High-molecular-weight hemicelluloses

ABSTRACT

In this study, the pre-hydrolysis liquor (PHL) was recycled during aspen chip water pre-hydrolysis, and the effects of PHL recycling on the extraction and accumulation of the hemicellulosic saccharides especially that with high molecular weight in the PHL were studied. The results showed that the concentration of hemicellulose saccharides in PHL depended on the pre-hydrolysis temperature and PHL recycling times. Compared to the unrecycled PHL, the concentration of hemicellulosic saccharides in PHL increased significantly when recycling PHL once or twice at 170 °C. Furthermore, the amount of high-molecular-weight hemicelluloses (HMHs) in PHL recycled once at 170 °C increased from 2.58 g/L (unrecycled) to 6.18 g/L, but the corresponding average molecular weight of HMHs decreased from 9.2 kDa to 7.6 kDa. The concentration of hemicellulosic saccharides in PHL decreased with PHL recycling time at 180 °C, accompanied by the formation of a significant amount of furfural.

© 2017 Published by Elsevier Ltd.

1. Introduction

In recent years, biorefineries have been attracting much attention due to the shortage of fossil fuels. The concept of a biorefinery has been advanced as the effective separation of lignocellulosic materials for high-value-added production (Van Heiningen, 2006). Hemicelluloses are the most abundant plant polysaccharides (other than cellulose) and are biosynthesized in large quantities by trees and other terrestrial plants (Mikkonen & Tenkanen, 2012). Lignocellulosic materials rich in hemicelluloses have been successfully used for the production of furfural, which for many years, has been an important chemical species. In addition to furfural, xylitol and oligosaccharides such as xylo-oligosaccharides (XOS) and mannan-oligosaccharides (MOS), which have been used in both the food and pharmaceutical industries, are important products from hemicelluloses (Akpınar, Erdogan, Bakir, & Yilmaz, 2010; Mohamad, Kamal, & Mokhtar, 2015; Montarop, Suttipong, Witsanu, & Dietmar, 2016; Rafiqul & Sakinah, 2013). In recent years, many new applications

for hemicelluloses as bio-materials such as hydrogels, surfactants, cosmetics and films have been developed (Damez et al., 2007; Egüés et al., 2014; Mikkonen & Tenkanen, 2012; Sun, Wang, Jing, & Mohanathas, 2013; Zhu Ryberg, Edlund, & Albertsson, 2011). Furthermore, hemicelluloses can also be used as a source of sugar for the production of biofuels, such as bioethanol, by fermentation after hydrolysis (Boucher, Chirat, & Lachenal, 2014; Van Heiningen, 2006).

Water pre-hydrolysis, also called auto-hydrolysis and hydrothermal treatment, has been considered as an effective process for the extraction of hemicelluloses (Song, Pranovich, Sumerskiy, & Holmbom, 2008; Yoon, Macewan, & Van Heiningen, 2008). Pre-hydrolysis is promising because no chemicals other than water or steam are needed in this step, thus making it an environmentally friendly technology (Garrote, Dóminguez, & Parajó, 1999). Additionally, pre-hydrolysis is an important step for removal of hemicelluloses in the kraft-based dissolved pulp production process.

Pre-hydrolysis of lignocellulosic materials has been widely investigated, including the kinetics and mass transfer during extraction, the effects of pre-hydrolysis conditions on the release of hemicelluloses, and the properties of extracted hemicelluloses. The pre-hydrolysis temperature was suspected as the most critical parameter for the extraction and conversion of hemicelluloses (Leppanen et al., 2011; Li, Saeed, Jahan, Ni, & van Heiningen,

* Corresponding author at: Organic Chemistry Laboratory, Taishan University, Taian, Shandong, 271021, China.

E-mail addresses: pplizongquan@163.com (Z. Li), jiangjungang1991@163.com (J. Jiang), fyingjuan@163.com (Y. Fu), wzj820415@126.com (Z. Wang), qmh@qlu.edu.cn (M. Qin).

2010; Song et al., 2008). It was found that only small amounts of hemicelluloses were extracted below 160 °C, and the yield of carbohydrates extracted using hot water increased substantially as the pre-hydrolysis temperature increased to 170 °C or higher (Leppanen et al., 2011; Li et al., 2010). High temperatures (>200 °C) can result in near total dissolution of woody biomass, but the amount of hemicelluloses present in the pre-hydrolysis liquor (PHL) decreases rapidly with the temperature due to the conversion of hemicelluloses to furfural and other byproducts (Li et al., 2010; Liu et al., 2012). The choice of the pre-hydrolysis temperature should be based on the end use of the isolated hemicelluloses. For isolating hemicelluloses with high molar mass, 170–180 °C is the most promising temperature range because at this temperature, a sufficiently high yield can be obtained without extensive degradation of the extracted polysaccharides (Leppanen et al., 2011; Song et al., 2008). In general, the levels of non-cellulosic carbohydrates start to decrease when the pre-hydrolysis times are too long or the temperature is too high (Rissanen, Grénman, Willför, Murzin, & Salmi, 2014).

Given the rapid development of the biorefinery industry, pulp mills tend to convert to biorefinery mills. In recent years, fast-growing aspen has been widely planted in North China and used as the raw material for pulp and paper production (Xu et al., 2010). The main hemicellulose in aspen is xylan, and the hemicelluloses can be extracted and used in novel industrial applications. The applications of extracted hemicellulosic saccharides with high molecular weight as bio-materials such as hydrogels and films are believed as promising applications of hemicelluloses (Mikkonen & Tenkanen, 2012; Egüés et al., 2014; Ferrari, Ranucci, Edlund, & Albertsson, 2015). The extraction of hemicelluloses by pre-hydrolysis prior to pulping is one of the most effective processes for woody biomass biorefinery (Garrote et al., 1999; Mao, Genco, van Heiningen & Pendse, 2008). During the separation and application of the hemicellulosic saccharides or byproducts in PHL, the high concentration of components in PHL will benefit from their separation or application, both in economic and effluent discharge. In the present work, PHL of aspen chips was recycled for pre-hydrolysis, and the effects of PHL recycling on the extraction and accumulation of the hemicellulosic saccharides especially that high molecular weight at various temperature were studied, and the degradation and conversion of extracted hemicelluloses during PHL recycling was also discussed.

2. Experimental

2.1. Materials

Aspen woodchips were obtained from the Huatai Group, a pulp and paper mill in Shandong Province, China. The average size of woodchips was approximately 33.0 mm × 42.0 mm × 3.6 mm. The aspen woodchips contained 42.10 ± 0.62% glucan, 15.91 ± 0.30% xylan, 1.92 ± 0.11% mannan, 0.62 ± 0.03% araban, 0.55 ± 0.03% galactosan as determined by the standard methods published by the National Renewable Energy Laboratory (Sluiter et al., 2008a), and they also contained 20.50 ± 0.32% Klason lignin (acid insoluble lignin), 2.62 ± 0.15% acid-soluble lignin and 0.67 ± 0.03% ash as determined by TAPPI T 223, TAPPI T 222 and TAPPI UM 250, respectively. The composition content was their weight percent to the oven-dried woodchips.

XAD-7 resin was purchased from Sigma-Aldrich LLC. *tert*-Butyl methyl ether (MTBE, chromatographically pure) and anhydride ethanol (analytically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

2.2. Methods

2.2.1. Water pre-hydrolysis of woodchips and PHL recycling

The water pre-hydrolysis was carried out in a set of laboratory digesters (Model 2201-6, Greenwood instruments, LLC.). Thirty grams (oven dry basis) of aspen chips and the required amount of water was added in order to reach a 6:1 liquid-to-solid ratio. The digesters were heated from room temperature to the maximum temperature in 60 min and then held at the maximum temperature for 60 min. Six digesters were used at the same pre-hydrolysis conditions at the same time. At the end of the pre-hydrolysis, the digesters were cooled in a water bath, and the extracted mixture was withdrawn and collected as PHL after filtered with filter paper. Then the obtained PHL from the digesters was mixed together and directly recycled for the pre-hydrolysis of the fresh woodchip instead of water, and PHL was recycled three times in the same manner. During the PHL recycling experiments, the amount of PHL obtained after the pre-hydrolysis of the fresh woodchip was less than the liquid added for pre-hydrolysis, therefore, the number of the digesters used for pre-hydrolysis at the same conditions decreased with the increase of the PHL recycling times.

2.2.2. Analysis of PHL

The concentration of the monosaccharide including glucose, arabinose, xylose, mannose and galactose in PHL was determined using an ion chromatography ICS-5000 system (Thermo Fisher Scientific, MA, USA) with a pulsed amperometric detector (PAD), which was controlled by Chromeleon 7.0 SR1 software. A CarboPac PA20 (3 × 150 mm) coupled with a guard column (Dionex, CA, USA) was used. The column and detector temperatures were 30 °C and 25 °C, respectively. The injection volume was 20 µL, and the operating pressure was approximately 17.93 MPa to 20.68 MPa. The mobile phases consisted of 4% 50 mmol/L NaOH and 96% ultrapure water at 0–22 min; 40% 1 mol/L NaCOOCH₃, 20% ultrapure water and 40% 50 mmol/L NaOH at 22–27 min; and 20% ultrapure water and 80% 250 mmol/L NaOH at 28–35 min. The flow velocity was 0.4 mL/min. Saccharides were identified and quantified by comparison with the retention times and the peak area of the standard sample. The unit was able to detect monosaccharides; therefore, for the measurement of the total saccharides content, acid hydrolysis was carried out at 120 °C with 4% (w/w) H₂SO₄ for 60 min, according to the technical report from NREL (Sluiter et al., 2008b). Measuring the saccharides concentration before and after acid hydrolysis determined the mono and total saccharides concentrations, respectively. The content of polysaccharides (including oligosaccharides) in PHL was calculated based on the difference between the total saccharides and monosaccharides concentrations. The saccharides concentration was analyzed in duplicate, and the relative mean deviation of determined results of the samples was less than 5%.

Hemicellulosic saccharides including arabinose, xylose, mannose and galactose were detected, and the corresponding polysaccharides concentration were calculated. The hemicellulosic saccharides concentration in the results were the sum of these saccharides concentration.

The degradation byproducts of carbohydrates in PHL, such as acetic acid, furfural, hydroxymethyl furfural (HMF) and levulinic acid (LA), were analyzed with a Shimadzu Prominence LC-20A HPLC system consisting of a UV-vis detector, CTO-20A column oven and a LC-20AT pump, which was controlled by Shimadzu LC-solution software (Shimadzu International Trading (Shanghai) Co., China). High-performance liquid chromatography (HPLC) was conducted using a Synergi Hydro-RP C18 column (250 mm × 4.6 mm × 4 µm) from Phenomenex Corp. The injector and column temperature was set to 30 °C, and the injection volume was 20 µL. The mobile phases consisted of 10% CH₃OH (solvent A) and 90% H₃PO₄ (0.1% v/v, solvent B).

Download English Version:

<https://daneshyari.com/en/article/5156821>

Download Persian Version:

<https://daneshyari.com/article/5156821>

[Daneshyari.com](https://daneshyari.com)