Bioresource Technology 196 (2015) 426–430

Contents lists available at ScienceDirect

Bioresource Technology

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

Separation and purification of hemicellulose-derived saccharides from wood hydrolysate by combined process

Xiaojun Wang [a], Jingshun Zhuang [a], Jungang Jiang [a], Yingjuan Fu [a], Menghua Qin [a,b], Zhaojiang Wang [a,c,*]

[a] Key Laboratory of Paper Science & Technology, Qilu University of Technology, Jinan 250353, China
[b] Laboratory of Organic Chemistry, Taishan University, Taian 271021, China
[c] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510641, China

HIGHLIGHTS

- Process was developed to separate hemicellulose-derived saccharides from wood hydrolysate.
- Mixed bed ion exchange resin was effective to remove lignin-derived phenolic impurities.
- Non-saccharides compounds was removed selectively by a combined process.
- Xylooligosaccharides accounted 28% for the total purified saccharides.

ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form 17 July 2015
Accepted 18 July 2015
Available online 4 August 2015

Keywords:
Hemicellulose
Hydrolysis
Lignin
Purification
Saccharide

ABSTRACT

Prehydrolysis of wood biomass prior to kraft cooking provides a stream containing hemicellulose-derived saccharides (HDSs) but also undesired non-saccharide compounds (NSCs) that were resulted from lignin depolymerization and carbohydrate degradation. In this study, a combined process consisting of lime treatment, resin adsorption, and gel filtration was developed to separate HDSs from NSCs. The macro-lignin impurities that accounted for 32.2% of NSCs were removed by lime treatment at 1.2% dosage with negligible HDSs loss. The majority of NSCs, lignin-derived phenolics, were eliminated by mixed bed ion exchange resin, elevating NSCs removal to 94.0%. The remaining NSCs, furfural and hydroxymethylfurfural, were excluded from HDSs by gel filtration. Chemical composition analysis showed that xylooligosaccharides (XOS) with the degree of depolymerization from 2 to 6 accounted for 28% of the total purified HDSs.

1. Introduction

The prehydrolysis of wood prior to kraft cooking has been deemed as a significant facet for the biorefinery of forest biomass. Prehydrolysis using water or mineral acid can solubilize the majority of hemicellulose and result prehydrolysis liquor (PHL) containing large quantities of hemicellulose derived saccharides (HDSs), e.g., xylose and its oligomers for hardwood (Cara et al., 2012; Mohammad, 2008). After prehydrolysis, the solid can still be processed into dissolving-grade pulp.

HDSs in PHL are promising raw material for multiple products, such as xylitol (Vallejos et al., 2015), ethanol (Oliveira et al., 2014; Santos et al., 2012), rheology control agents (Shi et al., 2011), food additives (Barreteau et al., 2006; Nabarlatz et al., 2007), packaging films (Al Manasrah et al., 2012), furfural (Buranov and Mazza, 2010) and noncarcinogenic sweetener (Mohammad, 2008). Over the years there has been much speculation concerning recovery and utilization of HDSs. However, the presence of non-saccharide compounds (NSCs) that are derived from lignin depolymerization and carbohydrate degradation hampers the separation and utilization of HDSs. To obtain HDSs with improved purity, NSCs have to be removed specifically and selectively (Chen et al., 2014).

Many methods had been reported to remove lignin-derived NSCs, such as ethanol extraction (Liu et al., 2011), polymer precipitation (Yasarla and Ramarao, 2012), membrane filtration, and gel chromatography (Moniz et al., 2014). Ultra and nanofiltration are

* Corresponding author at: Key Laboratory of Paper Science & Technology, Qilu University of Technology, Jinan 250353, China. Tel.: +86 531 89631168; fax: +86 531 89631117.
E-mail addresses: qmh@qlu.edu.cn (M. Qin), wzj@qlu.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.biortech.2015.07.064
0960-8524/

widely used for the elimination of lignin-derived NSCs because of its advantages, like low energy requirements and easy modification of the critical operational variables (Pinelo et al., 2009), but very susceptible to fouling problem (Koivula et al., 2013). The study of Shen et al. (2011b) showed that lignin removal was elevated significantly by the addition of polydiallyldimethylammonium chloride (*p*-DADMAC) to lime-treated PHL, which was ascribed to the simultaneous adsorption of *p*-DADMAC to lime mud. Numerous studies suggest that single treatment can hardly achieve the complete removal of NCSs. Therefore, an effective combined process is needed.

To upgrade the prehydrolysis-kraft based dissolving production process into a biorefinery platform, HDSs in PHL should be recovered specifically as value-added products. In this work, a combined process consisting of lime treatment, mixed bed ion exchange resin and gel filtration was proposed for the separation and purification of HDSs. The chemical structures and properties of the NSCs removed in each step were investigated to explain the treatment selectivity towards NSCs. Further, oligosaccharides content in the purified HDSs was determined to provide basic information for wood biorefinery.

2. Methods

2.1. Materials

The fast-growing aspen species, *Populus* × *euramericana* 'Neva', was selected in the present study because it is widely used in dissolving pulp mills through prehydrolysis kraft process in North China. Poplar wood chips were prepared from debarked wood logs harvested from the southwest region of Shandong province, China. The sodium acetate was of analytical-reagent grade from Sigma–Aldrich, Inc. Sodium hydroxide and calcium oxide were purchased from Tianjin Damao Chemical Reagent Factory. Strong base anion exchange resin 201 × 7 and strong acid cation exchange resin 001 × 7 were provided by Huizhu Resin co., Ltd, Shanghai, China. Resin 201 × 7 (type I) and 001 × 7 are conventional gel type resin with quaternary ammonium and sulfonic acid as the functional group, respectively, built on a styrene and divinylbenzene matrix. Xylose and xylooligosaccharides (XOS) that were purchased from Megzyme Ireland with degree of Polymerization (DP) from 2 to 6 were used as standard for high performance anion exchange chromatography with pulsed amperometric detector (HPAEC–PAD) to get DP profile of saccharides in PHL. Xylose, XOS and polluan (6.2, 10, 21.7, 48.8 and 113 kDa) from American Polymer Standards Corporation were used as standard for the calibration of gel filtration chromatography.

2.2. Prehydrolysis of wood and PHL preparation

Prehydrolysis of wood chips was carried out in a 23 L pulp digester, using 1.0 kg of oven-dried poplar wood chips. Prehydrolysis was performed at 170 °C with water to wood ratio of 6:1. The heating time was 60 min and the time at 170 °C was 60 min. At the end of prehydrolysis, the digester was cooled, depressurized and the reaction mixture was withdrawn. PHL was collected for the determination of chemical compositions and the results were listed in Table 1.

2.3. Separation and purification

Lime treatment was conducted at 25 °C as described in a previous study (Wang et al., 2014). Lime milk was added gradually to a beaker filling with 500 mL PHL. Once pH 11 was attained, carbonatation reaction was applied to stabilize pH by bubbling carbon dioxide and feeding lime at the same time. When the lime dosage reached 1.2% (based on the weight of PHL), the solution was filtered through 0.45 μm membrane.

Table 1
The chemical compositions of the PHL (g/L).

HDSs						NCSs	
Monomers			Oligomers				
Arabinose	0.32	16.6[a]	Arabinose	0.62	3.4[b]	Lignin	7.12
Galactose	0.21	10.9[a]	Galactose	1.06	5.8[b]	Acetic acid	4.10
Glucose	0.45	23.3[a]	Glucose	4.95	27.3[b]	Furfural	1.64
Xylose	0.87	45.1[a]	Xylose	8.91	49.1[b]	HMF[c]	0.25
Mannose	0.08	4.1[a]	Mannose	2.62	14.4[b]		
Total	1.93		Total	18.17		Total	13.11

[a] % based upon total monomers.
[b] % based upon total oligomers.
[c] Hydroxymethylfurfural.

PHL after lime treatment flowed through a mixed bed ion-exchange column (10 mm inner diameter × 200 mm length) packed with strong acid cation exchange 001 × 7 and strong base anion exchange resin 201 × 7 to eliminate the remaining NSCs and calcium salt. The column had wire mesh plates at both ends to prevent the entrainment of resin particles and was operated in up flow mode to reduce channeling. The solution was fed at 20 mL/h with a pump (Pharmacia Biotech P-500) for 3 h. Outlet stream of 60 mL throughout the resin treatment were collected for the following gel filtration.

Gel filtration was carried out by using a HPLC system (Shimadzu LC-20T) equipped with a gel column (Shodex OH pac SB-803 HQ, 8 × 300 mm, 6 μm) packed with polyhydroxymethacrylate, a UV/Vis detector at 270 nm and a refractive index detector (RID). PHL after resin treatment with a volume of 20 μL was injected into the gel column. Pure water was used as eluent at 1.0 mL/min and 30 °C. Purified HDSs were obtained by collecting fraction of gel filtration according to UV/Vis and RID signals.

2.4. Analytical methods

The lignin content was measured according to a spectrometric method at wavelength of 275 nm (TAPPI UM-250). The content of lignin-derived phenolic compounds was determined by Folin–Ciocalteu's assay (Blainski et al., 2013) using *p*-hydroxybenzoic acid as standard. HDSs were measured by an indirect method based on quantitative acid hydrolysis of the liquid sample with 4% w/w of H_2SO_4 at 120 °C for 60 min according to NREL technical report (Sluiter et al., 2006). HDSs were expressed as monosaccharides (MS) which were determined by high performance anion exchange chromatography with pulsed amperometric detector (HPAEC–PAD) as described in previous studies (Wang et al., 2013). All samples were analyzed in duplicates.

The DP profile of HDSs was determined by a HPAEC–PAD system in a similar way to MS determination, but using different column (CarboPac PA100 and a guard) and elution program. Elution program for DP profile of HDSs was 50–450 mM NaOAc in 100 mM NaOH from 0 to 40 min at a flow rate of 1.0 mL/min and 25 °C. The column was reconditioned using 100 mM NaOH for 15 min after each analysis.

3. Results and discussion

3.1. Elimination of NSCs by lime treatment and mixed bed ion exchange resin

PHL has a pH of 3.8 due to the presence of acetic acid produced from the cleavage of acetyl groups in hardwood hemicellulose.