Bioresource Technology 206 (2016) 225–230

Contents lists available at ScienceDirect

Bioresource Technology

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

Separation of hemicellulose-derived saccharides from wood hydrolysate by lime and ion exchange resin

Xiaojun Wang [a], Jingshun Zhuang [a], Yingjuan Fu [a], Guoyu Tian [a], Zhaojiang Wang [a,*], Menghua Qin [b]

[a] Key Laboratory of Paper Science & Technology, Qilu University of Technology, Jinan 250353, China
[b] Laboratory of Organic Chemistry, Taishan University, Taian 271021, China

HIGHLIGHTS

- Non-saccharide organic compounds (NSOC) were selectively removed from wood hydrolysate.
- Lime treatment and neutralization achieved 44.2% removal of colloidal NSOC.
- 75% saccharides were recovery with 95% purity after mixed bed ion exchange.
- Macroporous resin showed triple exchange capacity compared to gel resin.

ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form 27 January 2016
Accepted 28 January 2016
Available online 3 February 2016

Keywords:
Hemicellulose
Hydrolysis
Lignin
Purification
Saccharide

ABSTRACT

A combined process of lime treatment and mixed bed ion exchange was proposed to separate hemicellulose-derived saccharides (HDS) from prehydrolysis liquor (PHL) of lignocellulose as value added products. The optimization of lime treatment achieved up to 44.2% removal of non-saccharide organic compounds (NSOC), mainly colloidal substances, with negligible HDS degradation at 0.5% lime level and subsequent neutralization by phosphoric acid. The residual NSOC and calcium ions in lime-treated PHL were eliminated by mixed bed ion exchange. The breakthrough curves of HDS and NSOC showed selective retention toward NSOC, leading to 75% HDS recovery with 95% purity at 17 bed volumes of exchange capacity. In addition, macroporous resin showed higher exchange capacity than gel resin as indicated by the triple processing volume. The remarkable selectivity of the combined process suggested the feasibility for HDS separation from PHL.

1. Introduction

The energy crisis, greenhouse effect and the increasing interest in value-added production has led to the comprehensive utilization of wood biomass in a biorefinery platform (Al Manasrah et al., 2012; Shen et al., 2011b; Wang et al., 2014). Lignocelluloses are the most renewable and abundant raw material consisting of cellulose, hemicellulose and lignin (Carvalho et al., 2006; Maas et al., 2008). The prehydrolysis of wood prior to kraft cooking can solubilize fractions of hemicellulose and lignin, resulting in prehydrolysis liquor (PHL) rich in hemicellulose-derived saccharides (HDS), primarily oligomeric and monomeric saccharides, as well as lignin degradation products (Wang et al., 2015). The residual wood solid of hydrolysis still can be applied to dissolving-grade pulp. The whole process fits well with the concept of biorefinery.

The main problem associated with the utilization of HDS from PHL is the presence of non-saccharide organic compounds (NSOC) that are released or generated from the raw material during the hydrolysis. It is well known that NSOC includes furfural, hydroxymethylfurfural (HMF) and organic acid deriving from the depolymerization of hemicellulose, polyaromatic compounds rooting in the degradation of lignin. If these by-products from prehydrolysis of biomass can be recovered economically and effectively, they have many industrial applications (Wang et al., 2014).

To reduce the impact on the downstream products of HDS, considerable efforts have been focused on the elimination of NSOC prior to the utilization of HDS, comprising chemical, physical, and biological methods, including evaporation (Villarreal et al., 2006), overliming (Larsson et al., 1999; Shen et al., 2011a), membrane extraction (Grzenia et al., 2012), solvent extraction (Cruz et al., 1999; Frazer and McCaskey, 1989; Vázquez et al., 2005), polymers, e.g. chitosan (Saeed et al., 2011a), poly ethylene imine (PEI), poly-diallyl dimethyl ammonium chloride (*p*-DADMAC), and cationic poly acrylamide (CPAM) (Wang et al., 2015d), surface

---

* Corresponding author. Tel.: +86 531 89631168; fax: +86 531 89631117.
E-mail address: wzj@qlu.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.biortech.2016.01.107

active materials, e.g. activated carbon (Alves et al., 1998; In, 2001; Liu et al., 2012; Montané et al., 2006; Sainio et al., 2011), and ion-exchange resins (De Carvalho et al., 2004; Nilvebrant et al., 2001). The specific elimination of NSOC is crucial to maximize the recovery of HDS. However, most of these reported separation methods are non-selective toward NSOC. Yasarla and Ramarao (2012) demonstrated that *p*-DADMAC-induced precipitation was not specific to lignin because the loss of total sugars from 37.91 to 23.97 g/L was as significant as the removal of lignin from 5.547 to 1.645 g/L. The results from Koivula et al. (2013) showed that absorption by polystyrene–divinylbenzene and polyacrylate adsorbents was non-selective between lignin and the carbohydrates in wood hydrolysate. Absorption by activated carbon was not specific to NSOC as suggested by great loss of oligosaccharides (Montané et al., 2006; Shen et al., 2012). Our previous study showed lime treatment, a traditional method applied in sugarcane juice clarification, is effective and specific in elimination of colloidal NSOC from PHL (Wang et al., 2015c). In addition, our study also demonstrated the remarkable selectivity of ion exchange toward ionizable impurities in PHL from lignin depolymerization (Wang et al., 2015). In this context, the combination of lime treatment and ion exchange is considered to be worthy of further study for effective and selective HDS separation from NSOC.

In the present study, a combined process of lime treatment and mixed bed ion exchange was proposed based on the consideration that the elimination of colloidal NSOC can enhance the mass transfer of ion exchange. Optimal conditions of lime treatment were explored. At the same time, the adsorption capacity of macroporous type ion exchange resin was compared to gel type ion exchange resin.

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. Resin 101 × 7 and 201 × 7 are conventional gel type resins with sulfonic acid and quaternary ammonium as the functional groups, respectively, built on a styrene and divinylbenzene matrix. Strong acid cation exchange resin D001 and strong base anion exchange resin D201 are macroporous resin with sulfonic acid and quaternary ammonium as the functional group, respectively, built on a styrene and divinylbenzene matrix (see Table 1 for details about ion exchange resins employed in this work).

Table 2
Chemical compositions PHL (g/L).

HDS	Monosaccharides	
	Arabinose	0.52
	Galactose	0.37
	Glucose	0.16
	Xylose	2.15
	Mannose	0.26
	Oligosaccharides	
	Arabino-oligomers	0.12
	Galacto-oligomers	0.37
	Gluco-oligomers	0.82
	Xylo-oligomers	7.28
	Manno-oligomers	1.04
NSOC	Lignin depolymerization products	
	Soluble lignin[*]	8.77
	p-hydroxybenzoic acid	0.95
	Vanillin	0.10
	Syringaldehyde	0.17
	Guaiacol	0.02
	Carbohydrate degradation products	
	Formic acid	4.31
	Acetic acid	2.91
	Levulinic acid	0.08
	Furfural	1.31
	HMF	0.11
	Ash	0.34
	Total dissolved solid	20.91

[*] Determined by a spectroscopic method at UV 240 nm according to technical report NREL/TP-510-42618.

2.2. Prehydrolysis of wood and PHL preparation

PHL was prepared using a circulation type laboratory pulping digester with a reaction vessel in 20 L size (Greenwood Instruments, LLC. Canada). Prehydrolysis of 1.0 kg wood chips of *Populus* × *euramericana* ‘Neva’ was conducted at 170 °C for one hour with wood to water ratio of 1:6 (w/w). At the end of prehydrolysis, PHL was collected at the reaction temperature of 170 °C from a drain valve which was connected to a condenser. The chemical compositions of PHL were listed in Table 2. HDS in PHL consisted of oligosaccharides and monosaccharides with a total concentration of 13.08 g/L. NSOC consisted of a variety of organics resulted from lignin depolymerization and carbohydrates degradation.

2.3. Separation and purification

Lime treatment was conducted at 25 °C as described in a previous study (Wang et al., 2014). Aliquots of 50 mL of PHL were placed

Table 1
Details about ion exchange resins D001, D201, 001, 101 × 7 and 201 × 7.

	D001	D201	101 × 7	201 × 7
Constructure type	Macroporous	Macroporous	Gel	Gel
Ion exchange type	SACE[a]	SBAE[b]	SACE	SBAE
Functional groups	Sulfonic acid	Quaternary ammonium	Sulfonic acid	Quaternary ammonium
Polymer matrix	S-DVB[c]	S-DVB	S-DVB	S-DVB
TEC[d] on mass basis (mmol/g)	⩾4.35	⩾3.7	⩾4.5	⩾3.6
TEC on volume basis (mmol/mL)	⩾1.8	⩾1.2	⩾1.9	⩾1.4
Particle size (mm)	0.315 ~ 1.25	0.315 ~ 1.25	0.315 ~ 1.25	0.315 ~ 1.25
Water content (%)	45 ~ 55	50 ~ 60	45 ~ 50	50 ~ 60
Bulk density (g/mL)	0.75 ~ 0.85	0.68 ~ 0.74	0.77 ~ 0.87	0.66 ~ 0.75
Specific gravity (g/mL)	1.25 ~ 1.28	1.06 ~ 1.1	1.25 ~ 1.29	1.07 ~ 1.1

[a] Strong acid cation exchange.
[b] Strong base anion exchange.
[c] Styrene divinyl benzene copolymer.
[d] Total exchange capacity.