Carbohydrate Polymers 141 (2016) 238–243

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Hemicellulose isolation, characterization, and the production of xylo-oligosaccharides from the wastewater of a viscose fiber mill

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A R T I C L E I N F O

Article history:
Received 11 September 2015
Received in revised form 7 December 2015
Accepted 8 January 2016
Available online 12 January 2016

Keywords:
Xylo-oligosaccharides (XOS)
Hemicellulose
Structural features
Isolation
Xylanase
Viscose fiber

A B S T R A C T

Viscose fiber mills generate a lot of wastewater enriched with hemicelluloses. The structure of the hemicellulose in the wastewater was characterized and the hemicellulose was isolated to produce xylo-oligosaccharides (XOS). It was confirmed that the hemicellulose was mainly 4-*O*-methylglucuronoxylan with a small amount of glucomannan and xyloglucan. The 4-*O*-methylglucuronoxylan was completely de-acetylated and linear with a few 4-*O*-methyl glucuronic acid attached. After purified by the acid precipitation and washing, the hemicellulose was pretreated by dilute acid, and then subjected to xylanase hydrolysis. After the dilute H_2SO_4 pretreatment at pH 2.6 and 150 °C for 30 min and the followed xylanase hydrolysis (65 IU/g xylan), the total XOS yield was improved from 0.215 to 0.578 g/g xylan. The percentage of XOS in the final sugar product was 68.9%. These results demonstrated the potential economical and environmental benefits of the process to utilize the byproducts from viscose fiber mills.

1. Introduction

Xylooligosaccharides (XOS) are oligosaccharides containing two to ten xylose molecules linked by β 1–4 bonds. Considered as non-digestible oligosaccharides (NDOs), XOSs can be used as dietary sweeteners in low-calorie diet foods. Furthermore, because XOSs can stimulate beneficial microorganisms in gut, they are considered to have prebiotic effects which could improve bowel functions and have other health benefits (Carvalho, Neto, Da Silva, & Pastore, 2013). As substitutes for antibiotics in feed, XOSs have a huge market potential and economic benefits (Carvalho et al., 2013).

Nowadays, XOS are mainly produced from xylan-rich lignocellulosic material by the method of acid or enzymatic hydrolysis. The most applied acid in acid hydrolysis was H_2SO_4 (Akpinar, Erdogan, & Bostanci, 2009; Otieno & Ahring, 2012; Samanta et al., 2012). And the yields of XOS by acid hydrolysis were highly dependent on the acid concentration, processing time and temperature. These conditions needed to be controlled strictly to avoid the further degradation of XOS into xylose and other byproducts such as furfural and hydroxymethylfurfural (HMF). Compared to acid hydrolysis, enzymatic hydrolysis is mild and environmentally friendly. To achieve a higher XOS yield, the enzymatic complex should have a low activity of β-xylosidases to avoid the generation of xylose. Also, some enzymes which can remove the side groups on the xylan backbone could improve hydrolysis of xylan. Regarding to the substrate, the starting materials are usually pretreated to extract xylan or make the xylan more digestible to acid or enzyme. The most widely used methods for pretreatments are autohydrolysis (Moure, Gullon, Dominguez, & Parajo, 2006; Sabiha-Hanim, Noor, & Rosma, 2011), acid (Aachary & Prapulla, 2009; Yang, Xu, Wang, & Yang, 2005) or alkaline (Aachary & Prapulla, 2009; Brienzo, Carvalho, & Milagres, 2010) pre-hydrolysis.

Most of the resources for XOS production studied to date have been the wastes from agriculture and forestry, such as corn cob (Aachary & Prapulla, 2009; Chapla, Pandit, & Shah, 2012; Nabarlatz, Ebringerova, & Montane, 2007; Parajo, Garrote, Cruz, & Dominguez, 2004), sugarcane bagasse (Brienzo et al., 2010; Jayapal et al., 2013; Otieno & Ahring, 2012; Sun, Sun, & Tomkinson, 2004) and rice husk (Gullon et al., 2008; Parajo et al., 2004). In addition, there are a lot of hemicelluloses generated during the alkaline steeping of

Abbreviations: XOS, xylo-oligosaccharides; NDO, non-digestible oligosaccharide; HMF, hydroxymethylfurfural; NREL, National Renewable Energy Laboratory; GPC, gel permeation chromatography; DMF, *N*,*N*-dimethylformamide; DMAc, *N*,*N*-dimethylacetamide; HSQC, heteronuclear single quantum correlation; DEPTQ, distortionless enhancement by polarization transfer including the detection of Quaternary nuclei; AQ, acquired time; NS, scanning time; *Mw*, weight-average; *Mn*, number-average; DP, degree of polymerization.

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http://dx.doi.org/10.1016/j.carbpol.2016.01.022
0144-8617/

Table 1
The neutral sugar composition of the hemicellulose in the wastewater from a viscose fiber mill.

Composition	Xylan	Glucan	Mannan	acetyl	MeGluA[b]	Lignin	Oligosaccharide[c] and monosaccharide
Concentration (g/L)	79.58	7.23	0.44	n.d.[a]	Trace	1.04	n.d.

[a] Not detected.
[b] 4-*O*-methyl glucuronic acid.
[c] Degree of polymerization ≤10.

Table 2
The average molecular weight of the hemicellulose before and after acid pretreatment.

Sample	Molecular weight		Polydispersity indice (*Mw*/*Mn*)	Degree of substitution (DS)	Degree of polymerisation (DP)[a]
	Weight-average (*Mw*)	Number-average (*Mn*)			
Untreated	15,910	11920	1.33	0.86	86
Treated	15,570	5723	2.72	1.22	75

[a] DP = *Mw*/(132 + 61 × DS).

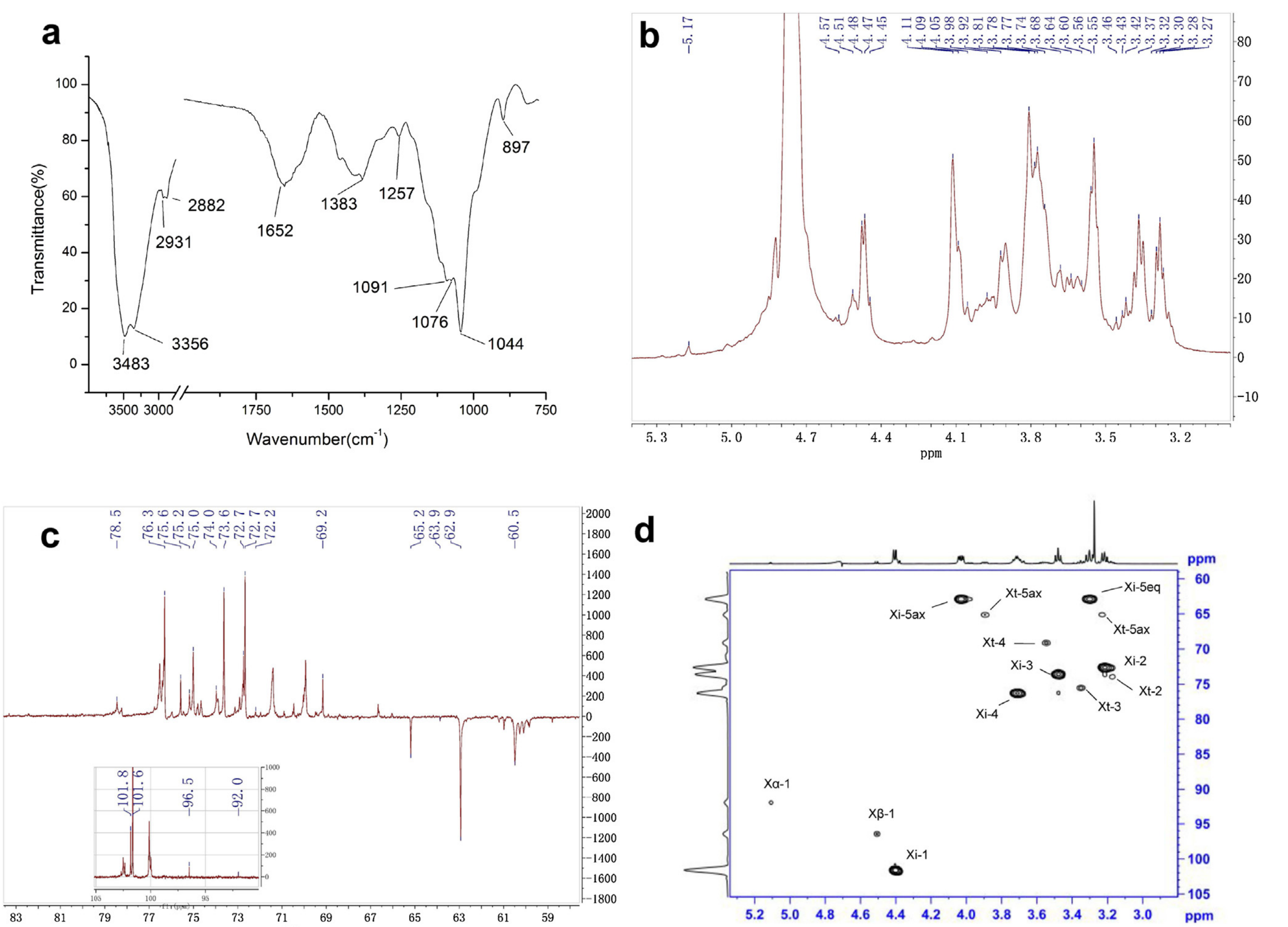

Fig. 1. FT-IR spectra (a) of the hemicellulose isolated by ethanol precipitate from waste water of a viscose fiber mill; ^{1}H NMR (b), ^{13}C DEPT-NMR (c) and HSQC (d) spectra of the acid hydrolysis fragment of the hemicellulose from the wastewater of a viscose fiber mill.

dissolving pulp in viscose fiber industry. Many researches for determining the compounds in the press lye after the alkaline steeping of dissolving pulp in viscose production have been reported (Croon, Jonsen, & Olofsson, 1968; Ivanova, Kipershlak, Pakshver, Usov, & Pevzner, 1986; Liftinger et al., 2015; Mozdyniewicz, Schild, & Sixta, 2014). However, structure analysis of the xylan in the press lye has not been exploited. And the hemicellulose is hard to be utilized in an economical and practical way because it associates with too much alkali and other compounds. Nowadays, with an industrial membrane treatment, most alkali in the press lye could be recycled, and a lot of wastewater enriched with insoluble hemicellulose was generated. Thus, it is of critical importance to make better use of the wastewater from viscose production. The fully utilization of the hemicelluloses for production of XOS can not only solve the proper disposal of the waste, but also provide additional income for the viscose factory. Therefore, the aim of this study was to (1) comprehensively characterize the hemicellulose in the wastewater of a viscose fiber mill, and (2) prepare XOS from the hemicellulose derived from the viscose fiber mill wastewater.