Carbohydrate Polymers 136 (2016) 203–209

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

# Effect of structural characteristics of corncob hemicelluloses fractionated by graded ethanol precipitation on furfural production

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ARTICLE INFO

*Article history:*
Received 3 July 2015
Received in revised form
12 September 2015
Accepted 12 September 2015
Available online 16 September 2015

*Keywords:*
Corncob
Water-soluble polysaccharides
Alkali-soluble hemicelluloses
Graded ethanol precipitation
Furfural

ABSTRACT

In the present study, a graded ethanol precipitation technique was employed to obtain hemicelluloses from the alkali-extracted corncob liquid. The relationship between the structural characteristics of alkali-soluble corncob hemicelluloses and the production of furfural was investigated by a heterogeneous process in a biphasic system. Results showed that alkali-soluble corncob hemicelluloses mainly consisted of glucuronoarabinoxylans and L-arabino-(4-*O*-methylglucurono)-D-xylans, and the drying way had less influence on the sugar composition, molecular weights and the functional groups of hemicelluloses obtained by the different ethanol concentration precipitation except for the thermal property, the amorphous structure and the ability for the furfural production. Furthermore, alkali-soluble corncob hemicelluloses with higher xylose content, lower branch degree, higher polydispersity and crystallinity contributed to the furfural production. A highest furfural yield of 45.41% with the xylose conversion efficiency of 99.06% and the furfural selectivity of 45.84% was obtained from the oven-dried hemicelluloses precipitated at the 30% (v/v) ethanol concentration.



## 1. Introduction

Concerns regarding the progressive depletion of fossil fuel resource, together with the necessity of limiting the growing $CO_2$ emissions, have spurred on the research for developing carbon-neutral alternative from non-fossil carbon energy sources (Bond, Alonso, Wang, West, & Dumesic, 2010; Li et al., 2014a,b; Nitsos, Matis, & Triantafyllidis, 2013). Lignocellulosic biomass is considered as the only sufficiently prevalent sustainable resource for the conversion into renewable liquid transportation fuels and chemicals (Cai, Nagane, Kumar, & Wyman, 2014; Knez, Markocic, Hrncic, Ravber, & Skerget, 2015; Lynd, Cushman, Nichols, & Wyman, 1991).

Hemicelluloses, which rank second to cellulose in plant cell walls, are heterogeneous polymers mainly containing xylose, arabinose, galactose, mannose, 4-*O*-methyl-D-glucuronic acid and so on (Binder, Blank, Cefali, & Raines, 2010; Girio et al., 2010; Li et al., 2013; Peng, Peng, Bian, Xu, & Sun, 2011). Despite their abundance, the utilization of hemicelluloses is relatively limited on an industrial scale due to their complex and heterogeneous structure. Therefore, developing ideal techniques to obtain more homogeneous hemicellulosic fractions from lignocellulosic biomass is of great significance for the efficient conversion of hemicelluloses to high-value added chemicals.

Several fractionation processes, such as the stepwise addition of ammonium sulfate, ethanol and potassium iodine–iodine as well as ion-exchange chromatography with DEAE column, have already been brought forward in achieving homogeneous hemicelluloses from biomass raw materials (Izydorczyk, Macri, & MacGregor, 1998; Peng et al., 2010a,b; Schooneveld-Bergmans, Beldman, & Voragen, 1999). Among them, the graded ethanol precipitation technique is considered as a unique and convenient approach to selectively yield arabinoxylan with different branching patterns from gramineous and hardwood lignocellulosic biomass (Dervilly, Saulnier, Roger, & Thibault, 2000).

As one of the most important agricultural residues, corncob represents a great potential as a raw material for the production of high-value added chemicals, fuels and other industrial products. Due to the high hemicelluloses content and high energy density, corncob is considered as one of the suitable feedstock for the production of furfural through the hydrolysis–dehydration reaction, which serves as a versatile intermediate for the

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http://dx.doi.org/10.1016/j.carbpol.2015.09.045
0144-8617/

synthesis of a multitude of important non-petroleum derived chemicals (Carrasquillo-Flores, Käldström, Schüth, Dumesic, & Rinaldi, 2013; Li et al., 2014a,b; Wang, Ren, Li, Deng, & Sun, 2015; Xing, Qi, & Huber, 2011). It is believed that the hydrolysis and dehydration rates of hemicelluloses are partially determined by the hemicellulosic structure (Dutta, De, Saha, & Alam, 2012). However, it is still unclear for the relationship between the structural characteristics and the hydrolysis–dehydration rate of hemicelluloses.

In the present work, a selective precipitation with the graded ethanol technique was employed to obtain more homogeneous hemicellulosic fractions from the alkali-soluble hemicelluloses liquid, which was achieved by the alkaline extraction of corncob. Detailed chemical composition and structural characteristics of the obtained polymers were measured by high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR), thermal gravity analysis (TG), X-ray diffraction (XRD), $^{1}$H and $^{13}$C nuclear magnetic resonance (NMR) spectra. Furthermore, the relationship between their structural features and the furfural production was also investigated by the heterogeneous catalysis in a biphasic system. This highly efficient catalytic system was brought forward by our research group (Li, Ren, Zhong, Sun, & Liang, 2015), and tin-loaded montmorillonite (Sn-MMT) as a catalyst was used in a biphasic system with a 2-*sec*-butylphenol (SBP) as the organic extracting layer and dimethyl sulfoxide (DMSO) as the co-solvent in contact with an aqueous phase saturated with NaCl (SBP/NaCl-DMSO).

## 2. Experimental

### 2.1. Materials

Corncob was obtained from Shandong Province, China. Prior to the experiments, corncob was smashed into small pieces and then sieved to 20–80 meshes. The obtained corncob was dewaxed with a 2:1 (v/v) toluene/ethanol mixture in a soxhlet extractor for 6 h. The dewaxed solid was washed with water and then oven-dried at 60 °C for 24 h. The biomass composition of the extracted corncob was determined by the standard analytical procedure of the National Renewable Energy Laboratory (NREL/TP-510–42618) with a resulting composition 37.09 wt% of glucose, 31.39 wt% of xylose, 2.28 wt% of arabinose and 14.47 wt% of lignin. Standard reagents were of HPLC grade and purchased from Sigma–Aldrich. Other chemicals used were of analytic grade and obtained from Aladdin-Reagent (Shanghai, China).

### 2.2. Isolation of water-soluble polysaccharides and alkali-soluble hemicellulosic fractions from corncob

The dewaxed corncob was firstly treated by water with a solid to liquid ratio of 1:25 (g/mL) at 75 °C for 20 min under microwave irradiation (400 W, XH-300UL, Beijing Xiang-Hu Science and Technology Development Reagent Co., Ltd., China) at atmospheric pressure. After the reaction, the filtrates were concentrated under reduced pressure, then mixed with four volumes of 95% ethanol, and followed by standing at 4 °C overnight to precipitate the water-soluble polysaccharides (WSP). The collected WSP was washed with acid ethanol (70%, pH 5.5), and then freeze-dried. The water-insoluble residue was treated with the 2% $H_2O_2$ (pH 11.5) solution at 50 °C for 14 h with a solid to liquid ratio of 1:25 (g/mL). The extracted liquid was neutralized to pH 5.5 with 6 M HCl and then concentrated under reduced pressure. The obtained liquid was sequentially fractionated by graded precipitations at different ethanol concentrations of 15%, 30%, 45% and 60% (v/v), respectively, corresponding to four subfractions assigned to $H_{15}$, $H_{30}$, $H_{45}$ and $H_{60}$. Furthermore, these four subfractions were washed with acid ethanol (70%, pH 5.5). Each of them was divided into two parts, and dried by oven and freeze drier, respectively. Oven-dried hemicellulosic fractions were designated as $HO_{15}$, $HO_{30}$, $HO_{45}$ and $HO_{60}$, respectively. Freeze-dried hemicellulosic fractions were labeled as $HF_{15}$, $HF_{30}$, $HF_{45}$ and $HF_{60}$, respectively. Schematic illustration for the fractionation of WSP and alkali-soluble hemicelluloses from corncob is illustrated in Fig. 1.

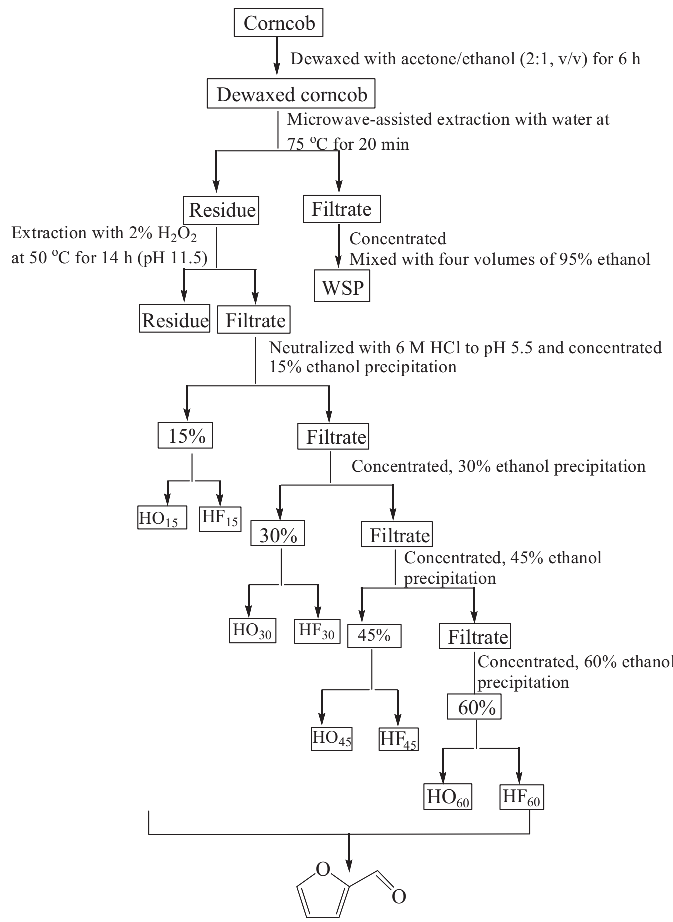


**Fig. 1.** Scheme for the fractionation of water-soluble polysaccharides and alkali-soluble hemicelluloses from corncob by the graded ethanol precipitation.

### 2.3. Chemical and spectroscopic characteristics of water-soluble polysaccharides and alkali-soluble hemicellulosic fractions

The classical iodine test was performed to verify the presence of starch in the WSP and the precipitated hemicellulosic fractions. High-performance anion-exchange chromatography (HPAEC, Dionex ICS-3000, Sunnyvale, America) coupled with a Carbopac$^{TM}$ PA-20 column (4 mm × 250 mm, Dionex, America) was used to analyze the monomeric sugars and uronic acids liberated by the hydrolysis of WSP and alkali-soluble hemicellulosic fractions according to the NREL methods. Due to the hardness of the oven-dried hemicelluloses samples, ball-milling and impregnation were carried out before the acid hydrolysis. Acid-soluble lignin in the hydrolysates of hemicelluloses was measured by ultraviolet spectrograph (UV-1800, Shimadzu, Japan), and the acid-insoluble residue was regarded as the acid-insoluble lignin. Each experiment was repeated twice and the average value was obtained.

The weight-average ($M_w$) and number-average ($M_n$) molecular weights of the hemicellulosic fractions were measured by gel permeation chromatography (GPC) with an Agilent PL aquagel-OH