

Evaluating the production of monosaccharides and xylooligosaccharides from the pre-hydrolysis liquor of kraft pulping process by acid and enzymatic hydrolysis



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ARTICLE INFO

Keywords:

Pre-hydrolysis liquor
Acid hydrolysis
Enzymatic hydrolysis
Monosaccharides
Xylooligosaccharides

ABSTRACT

Pre-hydrolysis liquor (PHL) from the kraft-based dissolving pulp process contains large amounts of hemicelluloses and their degradation products, which makes it a promising candidate for the production of xylose or xylooligosaccharides (XOS). However, it is usually treated as wastewater of the pulp and paper industries. In this study, both acid hydrolysis and enzymatic hydrolysis were applied to prepare xylose and XOS from the PHL, which contained 47.80 g/L of sugars and 14.10 g/L of lignins. Results showed that an optimal xylose yield (30.10 g/L) was obtained at 120 °C for 0.5 h with 4% aqueous sulfuric acid, while the maximum XOS yield (11.63 g/L) was achieved with 0.3% aqueous sulfuric acid at 120 °C for 2.0 h. For the enzymatic hydrolysis, the highest XOS yield of 15.65 g/L was obtained under the optimal condition (60 IU/L PHL, 50 °C, 6 h), and the XOS were mainly composed of xylobiose and xylotriose.

1. Introduction

Pre-hydrolysis is an essential process for producing kraft-based dissolving pulp. During the pre-hydrolysis process, large amounts of hemicelluloses and partial lignin are degraded and dissolved into the pre-hydrolysis liquor (PHL). The PHL contains various saccharides (including polysaccharides, oligosaccharides, and monosaccharides) and partial lignin fractions with low molecular weights, which is usually treated as wastewater of the pulp and paper industries. Generally, the PHL is mostly concentrated with the black liquid from the cooking process and burned in the recovery boiler. However, the concentration of the degraded hemicelluloses and lignin in the PHL is much lower than that of the black liquid, and the heat value of the hemicelluloses (7400 BTU/1b) is also obviously lower than that of the lignin (11,300 BTU/1b for softwood, 10,600 BTU/1b for hardwood) (Adams, 1997; Farhat et al., 2017). This disposal route not only increases the energy consumption of the enterprise but also causes the huge waste of the hemicelluloses from the PHL. Therefore, a rational utilization of the PHL is required.

Xylose is a valuable industrial resource, which can be extensively applied in the production of diabetic sweetener, xylitol and other useful chemicals (Wang et al., 2017). Moreover, with the increasing market demand, xylose can also be used as precursors in biochemical synthesis

for pharmaceutical and food industry (Sainio et al., 2013; Yedro et al., 2017). Given the importance of xylose, the production of xylose from various feedstocks has been explored by dilute acid hydrolysis. Zhang et al. (2015) reported that the xylooligomers-rich liquor produced from corn stover was further hydrolyzed with dilute sulfuric acid to prepare xylose. Results showed that the application of 0.75% H₂SO₄ at 110 °C for 180 min or 0.50% H₂SO₄ at 110 °C for 240 min could almost convert 100% of the oligomers into xylose. Lau et al. (2014) found that the optimum hydrolysis conditions for the depolymerization of birchwood xylan oligomers were obtained at temperatures between 120 and 130 °C and acid concentrations between 0.6 and 1.0 v/v%, where the maximum carbohydrate monomers yields and the minimum degradation products were achieved. Thamsee et al. (2017) used fruit bunches as raw materials to prepare xylose, and an optimal xylose yield of 57.50% was obtained under 4.78% of sulfuric acid concentration.

Xylooligosaccharides (XOS) are oligosaccharides containing two to ten xylose units linked by β-1,4 bonds (de Oliveira et al., 2018; Romero-Fernández et al., 2018). XOS exhibit large variety physicochemical features such as low caloric values, resistance to heat, and stability in acidic conditions. Furthermore, XOS can improve the calcium absorption, reduce the cholesterol, promote the growth of probiotics, lower the risk of colon cancer, etc., which make them very useful food and pharmaceutical additives (Li et al., 2012). Therefore, the production of

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XOS has attracted considerable attention (Aachary and Prapulla, 2011; Lin et al., 2017; Samanta et al., 2016; Zhang et al., 2017). Currently, various methods, such as chemical processing, enzymatic hydrolysis or a combination of both, have been applied to produce XOS from different biomass materials (Aachary and Prapulla, 2011). Lin et al. (2017) reported that an optimized XOS yield of 39.31% from beechwood xylan in the presence of organic acids (oxalic acid, maleic acid, citric acid etc.) catalysts was obtained at 126 °C for 8 min. Similarly, Zhang et al. (2017) found that 139.8 g of XOS could be obtained from 1000 g of oven dried raw corncob under the catalysis of acetic acid. Samanta et al. (2016) used xylan extracted from corn husk as feedstock for XOS production, and results showed that a maximum xylobiose concentration of 1.9 mg/ml was achieved at 44 °C for 17.5 h by enzymatic hydrolysis.

Previous works showed that the PHL was mainly composed of saccharides (~80%), lignin (~6%), and some small molecules such as acetic acid (Liu et al., 2011). Especially, the contents of the saccharides accounted for the overwhelming majority of the PHL components. Furthermore, xylan and xylose are the major saccharides in the PHL, which makes it a promising candidate for xylose or XOS production. However, only few studies investigated the production of xylose and XOS from the PHL of kraft pulping process. Generally, the chemical hydrolysis process for XOS production is low cost and easy to execute, while relatively mild reaction conditions are required for the enzymatic hydrolysis process without special equipment requirements (Chapla et al., 2012). In this work, the production of xylose and XOS from the PHL was comparatively investigated by acid and enzymatic hydrolysis. For the acid hydrolysis, the effects of sulfuric acid concentration, hydrolysis temperature, and reaction time on the yields of xylose and XOS were explored. The influences of enzyme dosage and incubation time on the yield of XOS were also studied for the enzymatic hydrolysis process.

2. Material and methods

2.1. Material

Poplar was used as raw material for the production of the PHL. The PHL of kraft pulping process was collected from a mill located in Shandong province. The PHL was mainly composed of polysaccharides (38.76 g/L), lignin (14.10 g/L), and xylose (5.74 g/L), while furfural (2.13 g/L), hydroxymethyl furfural (0.85 g/L), and acetic acid (8.25 g/L) were also detected in the PHL. Xylanase (13,800 IU/g) was kindly supplied by Youtell Biochemical Corporation (Shanghai, China). All chemical reagents were analytical grade and used as received.

2.2. Acid hydrolysis

According to the desired target product, different reaction conditions were used to treat the PHL. For the production of xylose, the reaction was conducted in the presence of different sulfuric acid concentrations (1, 3, 4, 5, 9, and 11%) at moderate temperatures (105, 120, and 135 °C) for 0.25, 0.5, 1.0, 1.5, and 2.5 h, respectively. For producing XOS, relatively low acid concentrations (0.1, 0.2, 0.3, 1.0, and 3.0%) were applied under the same reaction temperatures and periods as xylose production. Upon the completion of the treatment, the reactant was cooled to room temperature and filtered for further analysis. All experiments were performed in duplicate, and the results were averaged.

2.3. Enzymatic hydrolysis

The pH of the PHL was adjusted to 5.0 with aqueous NaOH solution before enzymatic hydrolysis. Then, the enzymatic hydrolysis of the PHL (20 mL) was performed in a 50 mL Erlenmeyer flask at 50 °C in a double-layer shaking incubators at 150 rpm. Different enzyme dosages (15, 30, 60, and 120 IU/L PHL) were evaluated in the enzymatic hydrolysis experiments. The hydrolyzate was collected at specific time

intervals and analyzed using high-performance anion exchange liquid chromatography (HPAEC).

2.4. Analytical methods

The chemical compositions of the PHL were determined according to National Renewable Energy Laboratory's (NREL) standard analytical procedure (Sluiter et al., 2008). The PHL was also directly freeze-dried to be characterized by two-dimensional nuclear magnetic resonance (2D-NMR). The two-dimensional heteronuclear single-quantum coherence (2D-HSQC) spectrum of the PHL was recorded on a Bruker NMR spectrometer (AVIII, 400 MHz, Germany) according to the previous report (Sun et al., 2013). The contents of monosaccharides in the PHL obtained from the acid hydrolysis were determined using a Dionex ICS-3000 HPAEC system equipped with an AS50 autosampler and a Carbowac PA-20 column (4 × 250 mm, Dionex) (Yang et al., 2011). The content of XOS obtained from the acid and enzymatic hydrolysis was also analyzed by HPAEC according to the procedure described in a previous paper (Bian et al., 2014).

3. Results and discussion

3.1. Compositions of the PHL

Generally, PHL was produced from the pre-hydrolysis of the kraft-based dissolving pulp production process. Hydrothermal pre-hydrolysis was applied to degrade hemicelluloses from the wood chips before the cooking process, which was conducive to the production of the dissolving pulp with high cellulose purity (Li and Pan, 2018). Therefore, large amounts of saccharides (including monosaccharides, oligosaccharides, and polysaccharides) appeared in the PHL (Li et al., 2017; Xu et al., 2018).

The chemical compositions of the obtained PHL are shown in Fig. 1. It could be observed that xylose (5.74 g/L) and galactose (1.83 g/L) were the major monosaccharides in the PHL, while only a small amount of glucose, arabinose, and rhamnose were detected. Moreover, the contents of oligosaccharides and polysaccharides (38.76 g/L) in the PHL accounted for 81% of the total sugars, suggesting that the PHL is a promising source for the production of XOS and/or xylose. Besides saccharides, 14.10 g/L lignin was also observed in the PHL.

To further understand the precise structure of the saccharides in the PHL, 2D-HSQC spectra of the PHL were investigated and are shown in Fig. 2. The peak assignments of the HSQC spectra are illustrated in Table 1 according to previous reports (Chen et al., 2018; Kim and Ralph, 2014; Mansfield et al., 2012).

Two strong correlations observed at 62.9/3.15 and 62.9/3.85 ppm

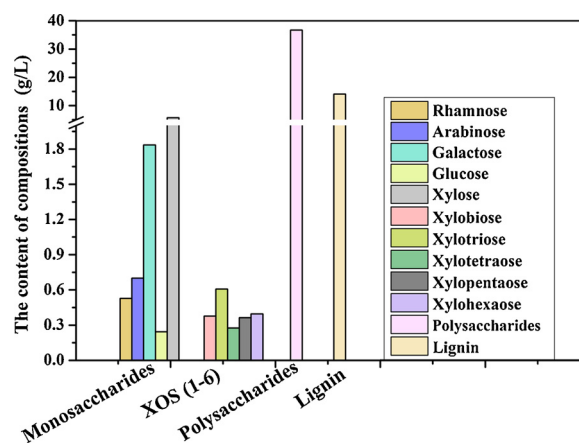


Fig. 1. The composition of the industrially produced pre-hydrolysis liquor (PHL).

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