



Research paper

Co-production of oligosaccharides and fermentable sugar from wheat straw by hydrothermal pretreatment combined with alkaline ethanol extraction

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ABSTRACT

Co-production of high value-added oligosaccharides and fermentable sugar from wheat straw is very attractive. In this study, hydrothermal pretreatment combined with alkaline ethanol extraction was developed to pretreat wheat straw for the production of both oligosaccharides and fermentable sugar. The major products in the hydrolysate and the enzymatic digestibility of the remaining residue were evaluated. Results showed that xylo-oligosaccharides (XOS) and gluco-oligosaccharides (GluOS) were the major products in the hydrolysate, and a maximum XOS yield of 61.69 g/kg wheat straw was achieved as the wheat straw was hydrothermally pretreated at 180 °C for 0.5 h. The HSQC results revealed that the degraded product in the hydrolysate was mainly (1 → 4)-β-D-xylan attached with α-D-arabinose, 4-O-methyl-D-glucuronic acids, and/or acetyl group. Additionally, the enzymatic hydrolysis rate of the cellulose-rich fractions obtained from the combined treatment process was enhanced 1.5 and 3.5 times, respectively, than that of the hydrothermally pretreated and raw wheat straw.

1. Introduction

The increasing consumption of fossil fuels has induced serious environmental consequences. Against this background, the production of biofuels from renewable lignocellulosic biomass has been explored worldwide to reduce fossil fuel use (Monlau et al., 2015). Wheat straw is considered as a suitable raw material for biofuels production, owing to its characteristics like high-sugar-content, low cost, availability, and renewability (Saini et al., 2015). However, the inherent complex architectural structure of lignocellulosic material forms strong native recalcitrance and blocks its enzymatic hydrolysis (Zhang et al., 2016). Thus, an efficient pretreatment is generally required to remove lignin and hemicelluloses from the lignocelluloses and improve the enzymatic digestibility of cellulose (Rodríguez-Zúñiga et al., 2015).

For the past decades, various pretreatment methods including chemical, physical, biological, and physical-chemical approaches have been developed for the production of fermentable sugar from lignocellulosic materials. Among these pretreatment methods, hydrothermal pretreatment (HTP) is an attractive pretreatment technology for lignocellulosic materials since equipment corrosion and chemical recycling can be effectively eliminated (Zhao et al., 2016). Meanwhile, the auto-hydrolysis of hemicelluloses and cleavage of the lignin-carbohydrates complex (LCC) bonds occurred during the HTP process are conducive to improve the removal of lignin from the lignocellulosic

materials and further accelerate the enzymatic hydrolysis of cellulose (Silva et al., 2013). Additionally, HTP can also effectively convert hemicelluloses into soluble sugars, xylo-oligosaccharides (XOS), or furfural depending on the HTP conditions. Among these products, XOS show great potential in pharmaceuticals, feed formulations, food-related applications, and agricultural purposes (Carvalho et al., 2013). Up to now, various methods have been applied to produce oligosaccharides, such as dilute acid treatment and enzymatic hydrolysis (Eggeman and Elander, 2005). However, due to the strong corrosion of acid, relatively higher equipment costs and subsequent effluent disposal are always required for the dilute acid treatment. Additionally, enzymatic hydrolysis shows high selectivity for oligosaccharide production, but which could not be directly used to treat raw materials because of the natural resistance of lignocellulose. HTP has significant advantages for the production of oligosaccharides, including low-capital cost, high efficiency, no chemical requirement. Nevertheless, in the process of HTP, the degradation and redeposition of lignin usually occurs, which will continue to impede the enzymatic digestibility of substrate (Silveira et al., 2016). To further improve the accessibility of cellulose to the enzymes, post-treatment should also be introduced to remove the lignin from HTP residues. Previous studies reported that alkali treatment showed high efficiency in extracting lignin from gramineous plants, and the extracted lignin could be further utilized as feedstock for many value-added products, such as resins, dispersants, polyols,

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phenols, etc. (Li et al., 2014; Xu et al., 2012). Meanwhile, alkali treatment could disrupt the lignin structure and swell the cellulose fibers, resulting in the enhancement of enzymatic digestibility (Bali et al., 2015; Li et al., 2015). Furthermore, previous literatures reported that lignin had high solubility in organic solution, such as methanol, ethanol, acetone, etc. (Jääskeläinen et al., 2017). The lignin extracted by organic solvent would retain relatively high activity (Sun et al., 2012). Therefore, hydrothermal pretreatment combined with alkaline ethanol extraction was developed to pretreat wheat straw for the production of both oligosaccharides and fermentable sugar.

In present study, hydrothermal pretreatment combined with alkaline ethanol extraction was applied to convert wheat straw hemicelluloses into saccharides and prepare easily hydrolysable wheat straw cellulose for enzymatic hydrolysis. The monosaccharides, oligosaccharides, and polysaccharides in the hydrolysate were analyzed by using high-performance anion exchange liquid chromatography (HAPEC), high-performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR). The cellulose-rich residues for enzymatic hydrolysis were further investigated using chemical composition analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR).

2. Material and methods

2.1. Material

Wheat straw was manually collected from Shaanxi province, China. The dried wheat straw was grounded in a mill to obtain a 40–60 mesh fraction, which was further extracted with toluene–ethanol (2:1, v/v) for 6 h to remove extractives. The powder was oven dried at 60 °C for 16 h for further experiment. The straw consisted of 41.23% cellulose, 27.70% hemicelluloses, 17.99% lignin (16.06% Klason lignin and 1.93% acid-soluble lignin), and 6.90% ash, according to the standard laboratory analytical procedure (NREL) (Sluiter et al., 2008). All chemical reagents were of analytical grade and used without further purification.

2.2. Hydrothermal pretreatment

The hydrothermal reaction was conducted in a 100 mL of batch reactor with a magnetic stirrer at 800 rpm 5.0 g of dewaxed straw and 50 mL of water were mixed in the batch reactor and hydrothermally pretreated at 120, 140, 160, 180 and 200 °C for 0.5 h, respectively. Upon completion of the pretreatment, the reactor was cooled immediately by ice water. The mixture was filtered to separate the residues with Buchner funnel, and the residues were thoroughly washed with deionized water and freeze-dried using a lyophilizer (Thermo Scientific, USA). The solid residues were labeled as R₁₂₀, R₁₄₀, R₁₆₀, R₁₈₀, and R₂₀₀, respectively, according to the HTP temperature. The liquid fractions were collected for further analysis. The hydrolysates recovered at 120, 160 and 200 °C were directly freeze-dried to prepare XOS-rich fractions and noted as L₁₂₀, L₁₆₀ and L₂₀₀, respectively. Fig. 1 shows the schematic diagram of the experimental procedure.

2.3. Alkaline ethanol treatment

The residues obtained from the HTP straw were further treated with 70% ethanol solution containing 1% NaOH at 90 °C for 2 h at a solid to liquid ratio of 1:20 (g/mL), and the corresponding cellulose-rich residues were named as AR₁₂₀, AR₁₄₀, AR₁₆₀, AR₁₈₀, and AR₂₀₀, respectively. As a control, the raw wheat straw material was also extracted under the same alkaline ethanol treatment condition, and the cellulose-rich residue was labeled as AM.

2.4. Characterization of the liquid fractions

The contents of oligosaccharides, monosaccharides and further sugar degraded products in the recovered liquid fractions were extensively explored. In particular, monosaccharides and XOS (DP, 2-6) were determined by HPAEC as described by Sun et al. (2013).

The total concentration of the oligosaccharides (DP > 2) in the liquid fractions was detected by further hydrolyzing the liquid in 4% H₂SO₄ at 121 °C for 1 h. The concentration of oligosaccharides was calculated based on the contents of the monosaccharides in the liquid before and after post-hydrolysis.

The degraded byproducts of the carbohydrate in the liquid fractions such as hydroxymethyl furfural (HMF) were analyzed by HPLC and the XOS-rich fractions (L₁₂₀, L₁₆₀ and L₂₀₀) were dissolved in DMSO-*d*₆ and characterized by HSQC NMR as described earlier (Chen et al., 2016).

2.5. Characterization of the solid fractions

The chemical composition of the pretreated wheat straw was determined according to the standard laboratory analytical procedure (NREL) (Sluiter et al., 2008). The characterization of the solid fractions including Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM) images were described in more detail elsewhere (Park et al., 2010; Chen et al., 2016).

2.6. Enzymatic hydrolysis

Enzymatic hydrolysis of the solid residues was performed at 2% of residue (w/v) in 15 mL of 50 mM sodium acetate buffer (pH 4.8) using a 50 mL of Erlenmeyer flask at 50 °C in a shaking incubator at 150 rpm for 72 h. Commercial cellulase (Cellic[®] CTec2, 100 FPU/mL) was kindly provided by novozymes (Beijing, China) and employed for all saccharification experiments (15 FPU/g residue). The hydrolysates were monitored at specific time intervals and analyzed by a Dionex ICS-3000 HPAEC system on a CarboPac PA-100 analytical column. All experiments were performed in duplicate, and the results were averaged.

3. Results and discussion

3.1. The yield and chemical composition of the pretreated straw

Since hemicelluloses and lignin are the main factors that impede the enzymatic digestibility of biomass, appropriate pretreatments are always required to overcome the recalcitrance of lignocellulose (Wahlström and Suurnäkki, 2015a, 2015b). In this work, a combined process of HTP and alkaline ethanol treatment was used to improve the accessibility of cellulase to wheat straw. The yields of the pretreated residues are illustrated in Table 1. After hydrothermal pretreatment, the yields of the pretreated residues varied from 83.53 to 59.77% as the HTP temperature increased from 120 to 200 °C. After the wheat straw was further treated with alkaline ethanol, the yields of the remaining residues dramatically reduced to 62.51–41.41%.

Results from the chemical composition analysis of the straw showed that the main degraded components during the HTP were hemicelluloses, which gradually decreased with the increasing HTP temperature. When the HTP temperature reached 200 °C, only 0.74% of hemicelluloses were detected in the remaining residue. However, the cellulose content in the residue enhanced from 41.23 to 52.62% as the temperature increased from 120 to 200 °C. The dissolution of hemicelluloses was mainly attributed to the ionization of water and the formation of acetic acid released from the *O*-acetyl group of hemicelluloses under the relatively high reaction temperature (Ibbett et al., 2014; Patel et al., 2016). It was reported that most hemicelluloses could be degraded into water-soluble saccharides and other small molecules during the HTP process (Deng et al., 2015). Additionally, the lignin

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