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Coproduction of xylose, lignosulfonate and ethanol from wheat straw

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HIGHLIGHTS

- Novel process to coproduce xylose, lignosulfonate and ethanol from wheat straw.
- Recover xylose from the hydrolyzate of acid treatment with 86.4% yield.
- Directly recover sulfomethylation treatment liquor containing 5.5% lignosulfonate.
- Enzymatic hydrolysis of the treated wheat straw to fermentable sugars with 91% yield.
- Fermentation of the obtained fermentable sugars to ethanol with 87.8% yield.

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ABSTRACT

A novel integrated process to coproduce xylose, lignosulfonate and ethanol from wheat straw was investigated. Firstly, wheat straw was treated by dilute sulfuric acid and xylose was recovered from its hydrolyzate. Its optimal conditions were 1.0 wt% sulfuric acid, 10% (w/v) wheat straw loading, 100 °C, and 2 h. Then the acid treated wheat straw was treated by sulfomethylation reagent and its hydrolyzate containing lignosulfonate was directly recovered. Its optimal conditions were 150 °C, 15% (w/v) acid treated wheat straw loading, and 5 h. Finally, the two-step treated wheat straw was converted to ethanol through enzymatic hydrolysis and microbial fermentation. Under optimal conditions, 1 kg wheat straw could produce 0.225 kg xylose with 95% purity, 4.16 kg hydrolyzate of sulfomethylation treatment containing 5.5% lignosulfonate, 0.183 kg ethanol and 0.05 kg lignin residue. Compared to present technology, this process is a potential economically profitable wheat straw biorefinery.

1. Introduction

Wheat straw (WS) is produced worldwide as a byproduct of wheat cultivation. Its annual output is estimated about 850 million tons. Its effective utilization has drawn much attention from researchers and farmers because its traditional uses, such as animal feed, feedstock for paper industry and organic fertilizer tend to be limited based on modern views of animal breeding practice and a growing interest in environmental problems (Curreli et al., 2002; Zhu et al., 2006a; Feng et al., 2014). Many efforts have been made to extend its uses and increase its added value (Zhu et al., 2006b; Talebnia et al., 2010; Wildschut et al., 2013). Use of it as construction and packing material, raw material for handcraft, burning it for electricity and conversion of it to biofuels and bio-based chemicals are some of these efforts (Zhou and Mei, 2000; Talebnia et al., 2010; Giuntoli et al., 2013; Ioelovich, 2015). Among them, the most promising is to convert it to ethanol, which is not only a versatile chemical and organical solvent, but also a transport fuel (Saha et al., 2005, 2015; Zhu et al., 2006b; Talebnia et al., 2010; Wildschut et al., 2013). Although extensive research has been carried out on ethanol production from WS, the high production cost still prevents its commercialization based on current technology (Talebnia et al., 2010). Therefore, it is of great importance in improving the present technology and decreasing its cost. The WS biorefinery is an effective way to achieve this goal by fully utilizing its components and coproducing high value-added chemicals (Deswarte et al., 2007; Cheng and Zhu, 2009; Huijen et al., 2012).

Production of ethanol from WS is generally consists of three subprocesses: pretreatment, enzymatic hydrolysis and ethanol fermentation. The WS is mainly composed of cellulose, hemicellulose and lignin. The complex structure of lignin and hemicellulose and cellulose in WS limits its effective enzymatic hydrolysis. In order to improve its enzymatic hydrolysis efficiency, WS must be pretreated before its hydrolysis. Numerous studies on WS pretreatment

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have been done during the past several decades, such as steam explosion treatment (Liu and Hui, 2014), liquid hot water treatment (Shao and Lynd, 2013), ammonium explosion treatment (Toquero and Bolado, 2014), acid treatment (AT) (Saha et al., 2005; Chen et al., 2014; Feng et al., 2014), alkaline treatment (Zhu et al., 2006a,b), sulfomethylation treatment (ST) (Gu et al., 2013; Jin et al., 2013) and ionic liquid treatment (Qing et al., 2014). Among these WS pretreatments, AT is one of the most widely used and efficient pretreatment methods, which can increase its porosity for enzyme to access by hydrolyzing its hemicellulose and partly removing its lignin, thus improving its enzymatic hydrolysis efficiency (Feng et al., 2014). Currently, the typical ethanol production process based on AT is enzymatic hydrolysis of acid treated WS to obtain fermentable sugars for ethanol fermentation, burning the residue after enzymatic hydrolysis of acid treated WS, which mainly contains lignin, for electricity and recovery of the AT hydrolyzate, which mainly contains xylose, for ethanol production (Ekman et al., 2013). In order to decrease ethanol production cost from WS and fully utilize its components, this process needs to be improved at least from three aspects. Firstly, the acid treated WS still has high lignin content, which has a negative effect on its enzymatic hydrolysis (Li et al., 2014). Secondly, lignin has not been effectively utilized by burning it for electricity. Finally, because the AT hydrolyzate contains some inhibitor of ethanol fermentation, such as phenolics, HMF, furfural and other organic acid, and the commonly used ethanol fermentation strains in industry cannot effectively utilize xylose, there are still some technical difficulties in recovering AT hydrolyzate for ethanol production in a commercial scale (Anuj et al., 2011). Recent researches on ST indicate that it can effectively remove lignin from lignocellulosic biomass and its hydrolyzate containing lignosulfonate can be recovered as a cement water reducer (Gu et al., 2013; Jin et al., 2013). There are also some reports on AT that the xylose in its hydrolyzate can be recovered and used as feedstock for xylitol production, which has huge market demand (Curreli et al., 2002; Franceschin et al., 2011). Compared to ethanol production by recovering AT hydrolyzate, recovery of xylose from AT hydrolyzate as feedstock for xylitol production is much more economically profitable (Franceschin et al., 2011). Therefore, it is possible that ST of acid treated WS further improves its enzymatic hydrolysis and recovers its hydrolyzate containing lignosulfonate as a cement water reducer. Moreover, xylose in AT hydrolyzate can be recovered and used as feedstock for xylitol production. The objective of this work is to establish a WS biorefinery to decrease its ethanol production cost by fully utilizing its components and coproducing high value- added products. In this work, a novel integrated process to coproduce xylose, lignosulfonate and ethanol from WS was investigated, which includes AT of WS to remove hemicellulose and recover xylose as feedstock for xylitol production, ST of the acid treated WS to remove lignin and recover its hydrolyzate containing lignosulfonate as a cement water reducer, enzymatic hydrolysis of the two-step treated WS to obtain fermentable sugars, and fermentation of the obtained fermentable sugars to produce ethanol. The AT and ST conditions were optimized based on pretreatment effectiveness and useful chemicals recovery. The enzymatic hydrolysis of the two-step treated WS to fermentable sugars and the suitability of the obtained fermentable sugars for ethanol production were explored, and a brief comparison between our process and the current typical ethanol production process from WS was also made.

2. Methods

All experiments were performed three times, and the data reported were expressed as the mean values ± standard deviation.

2.1. Materials and chemicals

Raw WS was obtained from a local farmer in Badong, Hubei province, China. Before any pretreatment, it was cut to nominally 1–2 cm lengths and then air dried for further treatment. Its main composition was moisture 10.8 ± 0.2%, cellulose 40.6 ± 0.5%, lignin 18.2 ± 0.4%, and hemicellulose 24.8 ± 0.5%. The Cellulase (Onozuka R-10) and β-glucosidase (Novozyme 188) were purchased from Sigma–Aldrich (St. Louis, MO). The cellulase activity of Onazuka R-10 was 10 FPU mg^{-1}, and β-glucosidase activity of Novozyme 188 was 500 CBU ml^{-1}. All other chemicals were of reagent grade and purchased from Wuhan Chemicals & Reagent Corp., China.

2.2. Acid treatment and xylose recovery

Twenty grams of WS and 180 mL given concentration sulfuric acid were added to a three-necked flask with reflux and kept it boiling for times ranging from 15 min to 2 h. The AT residues (acid treated WS) were collected, dried at 65 °C and weighed. Then they were cut to 10–20 mesh for their composition analysis and subsequent ST or enzymatic hydrolysis. The AT hydrolyzate was reused for AT of WS after adjusting its volume to 180 mL with fresh given concentration sulfuric acid. After the AT hydrolyzate was recycled to certain times, it was used to recover xylose. The xylose recovery and purification from the AT hydrolyzate were carried out as described by Curreli et al. (2002). Firstly, the obtained AT hydrolyzate was autoclaved for 1.5 h at 121 °C, to allow complete hydrolysis of the oligosaccharide fragments, then filtered through a filter paper, and decolourised with activated charcoal. The solution was adjusted to pH 7 with calcium hydroxide and centrifuged. The clear supernatant was desalted through an ion-exchange column. The eluate was concentrated by vacuum evaporation in a rotatory evaporator. The addition of ethanol to 50% v/v allowed precipitation of xylose as a white crystalline paste, which was washed with ethanol and dried at 105 °C for 2 h. The obtained xylose was weighed and its purity was analyzed. The xylose recovery yield was calculated as follows:

$$\text{Xylose yield } (\%) = \text{The recovered xylose} \times 0.88/\text{The total dissolved hemicellulose} \times 100$$

2.3. Sulfomethylation treatment and lignosulfonate recovery

Thirty-five grams of acid treated WS and 200 mL standard sulfomethylation reagent [1% (w/v) sodium hydroxide, 3% (w/v) formaldehyde and 2% (w/v) sodium bisulfite] were added to a 500 mL high pressure reactor and kept it reacting at a given temperature for a certain time. After the reaction, it was cooled to room temperature. The ST residues (two-step treated WS) were collected, dried at 65 °C and weighed. Then they were used for their composition analysis and subsequent enzymatic hydrolysis. The ST hydrolyzate containing lignosulfonate was directly recovered as a cement water reducer without further processing.

2.4. Enzymatic hydrolysis

The typical hydrolysis mixture consisted of 8 g cellulose in the treated WS (9 g two-step treated WS or 13.7 g acid treated WS), Onazuka R-10 12 mg, Novozyme 188 0.5 mL and 100 mL 0.1 M citric acid/sodium citrate buffer (pH 4.8) which was supplemented with antibiotics tetracycline (40 μg mL^{-1}) and cycloheximide (30 μg mL^{-1}) to prevent microbial contamination. The mixture was incubated at 50 °C in a rotary shaker with the vibration frequency of 160 rpm. Samples (1 mL) were taken from the reaction