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Assessment of integrated process based on hydrothermal and alkaline treatments for enzymatic saccharification of sweet sorghum stems

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HIGHLIGHTS

- Integrated biorefinery based on hydrothermal and alkaline treatments was developed.
- Intensified hemicellulosic degradation led to increased cellulose saccharification.
- Optimum case was obtained at 170 °C for 0.5 h and subsequent 2% NaOH treatment.
- The removal of lignin facilitates enzymatic saccharification of substrate.

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ABSTRACT

In this study, sweet sorghum stem was subjected to hydrothermal pretreatment (HTP) and alkaline post-treatment to enhance its saccharification ratio by reducing its recalcitrance. The results showed that the HTP (110–210 °C, 0.5–2.0 h) significantly degraded hemicelluloses, and the pretreatment at the temperature higher than 190 °C led to the partial degradation of the cellulose. As compared to the sole HTP, the integrated process removed most of lignin and hemicelluloses, which incurred a higher cellulose saccharification ratio. Under an optimum condition evaluated (HTP at 170 °C for 0.5 h and subsequent 2% NaOH treatment), 77.5% saccharification ratio was achieved, which was 1.8, 2.0 and 5.5 times as compared to the only HTP pretreated substrates, alkaline treated substrates alone and the raw material without pretreatment, respectively. Clearly, the integrated process can be considered as a promising approach to achieve an efficient conversion of lignocellulose to fermentable glucose.

1. Introduction

The rampant use of petroleum products increases carbon dioxide emissions associated with climate change. Against this background, production and use of energy resources including renewable lignocellulosic biomass assumes a high priority to ensure global energy security (Fargione et al., 2008). Biofuels produced from lignocellulosic biomass has taken a lead position as a viable option to petroleum-derived fuels. Among them, high productivity sweet sorghum could be the best option mainly owing to richness in carbohydrate content, drought and high-temperature stress tolerance (Rao et al., 2013). Unfortunately, lignocellulosic biomass is recalcitrance to enzymatic and microbial deconstruction due to the rigid and compact structure of plant cell walls (Himmel et al., 2007). The recalcitrance of biomass is mainly constructed by its chemical compositions that build a dimensional and irregular network as a protective bulwark (Zhao et al., 2012). This recalcitrance greatly limits the cellulose saccharification of lignocelluloses. Therefore, pretreatment is generally required as the first step for improving the cellulose saccharification of lignocelluloses.

The primary objective of pretreatment is to reduce biomass recalcitrance by changing the cellular structure so that the polysaccharides (mainly cellulose) locked in the intricacy of plant cell walls can become more accessible and amenable to enzymatic saccharification (Mosier et al., 2005). Numerous pretreatment approaches including physical, chemical, physic-chemical, and biological pretreatments have been applied to reduce recalcitrance and enhance enzymatic saccharification of lignocelluloses. Dependent on the pretreatment factors, several key factors of lignocelluloses are altered and believed to impact the recalcitrance of the pretreated substrates including the resulting substrates ingredients, surface morphology, content of lignin and hemicelluloses, and cellulose crystallinity and degree of polymerization (Pu et al., 2013; Zhu and Pan, 2010).

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Hydrothermal pretreatment (HTP) has been considered to be a promising pretreatment technology that can improve sugar release performance of biomass. HTP, also called autohydrolysis or hot water pretreatment, is an economical and eco-friendly technology because the pretreatment only uses water as a reaction medium without additional chemicals and has a lower cost of construction materials (Liu, 2010). HTP is usually implemented at a relatively high temperature which comes about largely from the release of organic acids from biomass compositions (mainly hemicelluloses) at the elevated temperature (Pu et al., 2013). These acids can effectively accelerate sugar release from lignocelluloses. In other words, HTP mainly causes solubilization of hemicelluloses as well as structural variations of lignin, which in turn contribute to the reduction of biomass recalcitrance. Some important chemicals such as oligosaccharides and furfural can be produced by the HTP process (Romaní et al., 2010). Furthermore, some integrated biorefinery technologies based on liquid hot water and H_2SO_4-catalysis were also developed (Lu et al., 2012). These technologies cause structural variations of lignin and cellulose as well as solubilization of hemicelluloses, which in turn contribute to the reduction of biomass recalcitrance. However, the delignification in this process was performed under acidic conditions, and the delignification process was limited. Although HTP process is a promising technology for lignocelluloses, some limitations, such as only partial degradation of hemicelluloses and destruction of lignin-hemicelluloses matrix as well as some inhibitors will impede the enzymatic saccharification of the pretreated substrate. To obtain a higher yield of glucose by enzymatic hydrolysis of the pretreated substrates, the lignin and residual hemicelluloses should be removed as far as possible before enzymatic hydrolysis. Consequently, a further treatment needs to be performed to remove lignin and the residual hemicelluloses from the pretreated substrates. It has been reported that alkaline treatment is the most widely used approach for the effective removal of hemicelluloses and lignin from biomass, especially for gramineous plants (Sun et al., 1995). In this work, aqueous sodium hydroxide was used to treat the hydrothermally pretreated sorghum. The reason for this is that among various alkali regents, sodium hydroxide exhibits the most significant effect on degrading lignin and improving subsequent fermentation yields (Lawther et al., 1996). The sodium hydroxide solution could swell plant cell wall and disrupt lignin structure, reduce the degree of polymerization and crystallinity of cellulose, as well as increase the surface area of cellulose (Taherzadeh and Karimi, 2008).

Sweet sorghum as substrate in biorefinery and bioenergy by enzymatic saccharification has been widely investigated. The effect of steam pretreatment on enzymatic saccharification of sweet sorghum had been investigated (Sipos et al., 2009). Li et al. (2010) evaluated the enzymatic saccharification of ammonia fiber expansion pretreated sweet sorghum, and Wu et al. (2011) examined the influence of low temperature alkaline pretreatment on the enzymatic saccharification of sweet sorghum. However, these studies mainly focus on the influence of the pretreatment on the enzymatic saccharification efficiency of sweet sorghum and overlook the underlying value of hemicelluloses and lignin. Therefore, based on biorefinery concept, an integrated process consisting of HTP (i.e., 110–230 °C, 0.5–2.0 h) and mild alkaline post-treatment (2% NaOH at 90 °C for 2.0 h) has been developed to explore sweet sorghum stem (SSS) for the improvement of its enzymatic saccharification in this study. All substrates obtained were characterized by chemical composition, scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and solid state cross-polarization/magic angle spinning ^{13}C nuclearmagnetic resonance (CP/MAS ^{13}C NMR), and their enzymatic saccharification behaviors were also analyzed. Simultaneously, the yield, purity, dissociation mechanisms, structural features, and structural transformations of the hemicelluloses and lignin recovered from the integrated process have been thoroughly investigated (Sun et al., 2014a,b). These results will offer some valuable information in the commercial exploitation of sweet sorghum stem for the large-scale production of bioethanol and bio-based chemicals in future biorefinery industry.

2. Methods

2.1. Raw materials

SSS was obtained from the experimental farm of the North-Western University of Agricultural and Forest Sciences and Technology (Yangling, Shanxi. China). The SSS was first dried in an oven at 60 °C for 24 h and then ground in a mill to obtain a 20–60 mesh fraction. Then the particle was extracted with toluene–ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h to remove extractives (approximate 9.24%) and then dried in an oven at 60 °C for 24 h to serve as control substrate. More details of the materials used in this study are given in a recent literature (Sun et al., 2014a). All chemicals were analytical grade and purchased from Sigma–Aldrich and Megazyme.

2.2. Integrated process

SSS was treated by an integrated process based on HTP and followed by alkaline treatment. The HTP conditions (110, 130, 150 °C for 1.0 h, 170 °C for 0.5, 1.0, 2.0 h, and 190, 210, 230 °C for 0.5 h, respectively) were performed in a 1000 mL stainless steel autoclave (Parr, USA) with a magnetic stirrer at a solid to liquor ratio of 1:10 (g/mL) by a PID controller (Sen Long Instruments Company, Beijing, China). The hydrothermally pretreated substrates were labeled as $H_{110(1.0)}$, $H_{130(1.0)}$, $H_{150(1.0)}$, $H_{170(0.5)}$, $H_{170(1.0)}$, $H_{170(2.0)}$, $H_{190(0.5)}$, $H_{210(0.5)}$, and $H_{230(0.5)}$, respectively, corresponding to the pretreatment at various temperatures and times. Meanwhile, a further treatment was performed with 2% aqueous NaOH at 90 °C for 2 h under a solid to liquid ratio of 1:20 (g/mL) to remove lignin and the residual hemicelluloses from the pretreated substrates. The alkaline post-treated substrates were obtained from the correspondingly hydrothermally pretreated substrates and named as $A_{110(1.0)}$, $A_{130(1.0)}$, $A_{150(1.0)}$, $A_{170(0.5)}$, $A_{170(1.0)}$, $A_{170(2.0)}$, $A_{190(0.5)}$, $A_{210(0.5)}$, and $A_{230(0.5)}$, respectively. The details of integrated process were described in a recent publication (Sun et al., 2014a). As a control, the un-pretreated substrate was also treated under the same alkaline treatment condition and the obtained post-treated substrate labeled as control-A. All prepared (control, hydrothermally pretreated, and combining alkaline post-treated) substrates were used to produce glucose by enzymatic saccharification experiment in the present study.

2.3. Enzymatic saccharification

Enzymatic saccharification experiment was performed on the substrate (2% w/v) in 10 mL 50 mM sodium acetate buffer (pH 4.8) with a 25 mL Erlenmeyer flask at 50 °C in a double-layer shaking incubators (ZWYR-2102C) (Shanghai, China) at 150 rpm for 72 h. Commercial cellulose (15 FPU/g substrate) was purchased from Youtell Biochemical Co. Ltd. (Shanghai, China) and employed for all saccharification experiments. The hydrolyzates were sampled periodically and analyzed by a high-performance anion exchange chromatography (HPAEC) (Dionex, ICS 3000, U.S.) system equipped with an integral amperometric detector and CarboPac PA 100 (4×250 mm, Dionex) analytical column. Separation was obtained using a gradient elution of two solvents at a flow rate of 0.4 mL/min at 30 °C. The gradient elution was performed as