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Liquid hot water pretreatment of energy grasses and its influence of physico-chemical changes on enzymatic digestibility

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HIGHLIGHTS

- *Pennisetum* hybrid was proved to be a prospective feedstock for cellulosic ethanol production.
- The ratio of syringyl and guaiacyl units of lignin played an important role on the hemicellulose hydrolysis in LHW.
- Branch degree of hemicellulose contributed more on the characterization of xylooligomers degree of polymerization.
- No significant corresponding relationship was observed between increase of ED and changes of CrI, DP and surface area.

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ABSTRACT

Pennisetum hybrid I, II and switchgrass were pretreated with liquid hot water to enhance the release of sugars. The optimum hydrolysis factor for three energy grasses was 5.98, and the total xylose yield was 88.4%, 98.1% and 83.6% for grass I, II and S. It was indicated that the ratio of syringyl and guaiacyl units of lignin played an important role on the hemicellulose hydrolysis in LHW than branch degree, but latter contributed more on the characterization of xylooligomers degree of polymerization. Moreover, the analysis of multi-scale changes of substrate suggested that cellulose crystallinity index and degree of polymerization seemed no direct relationships for increase of enzymatic digestibility. While lignin barrier was the main factor limiting efficiency of sugar release, and *Pennisetum* hybrid with low lignin content and high sugar recovery was proved to be a prospective plant feedstock for cellulosic ethanol production.
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1. Introduction

Lignocellulosic biomass is a prospective renewable resource to produce biofuels and value-added products. Perennial herbaceous energy crops such as *Miscanthus* and *Pennisetum purpureum* have many advantages to exploit them as a feedstock such as its high solar energy conversion and water use efficiency, high raw material yield, high adaptability and strong resilience, high cellulose content and environmentally friendly (McKendry, 2002; McLaughlin et al., 2002). Both the US and EU have supported research on herbaceous energy crops since the mid-1980s, especially switchgrass is considered as the most promising and a model bioenergy crop.

However, taking cellulosic ethanol bio-finery process for example, the native lignocellulosic biomass has limited its accessibility to enzymes and microorganisms due to its complex cell wall structure of cellulose/hemicellulose/lignin. Therefore, how to overcome this recalcitrance efficiently is one of the practical problems in course of biomass energy conversion. Pretreatment operation using physical, chemical and biological methods prior to enzymatic saccharification can get rid of the shields from lignin and hemicellulose to enhance the accessibility of cellulose to enzyme. Based on the type of pretreatment, glucose yields of switchgrass range from 70% to 90%, xylose yields range from 70% to 100%, and ethanol yields range from 72% to 92% of the theoretical maximum (Keshwani and Cheng, 2009). An effective pretreatment not only makes cellulose more accessible to the enzymes but also minimizes the formation of inhibitor to microorganisms.

Liquid hot water (LHW) pretreatment using pressure to maintain water in a liquid state at elevated temperature does not require the addition of chemicals but recover most of pentosans from hemicellulose (Garrote et al., 1999; Yu et al., 2011b). Biomass deconstruction in LHW is catalyzed by hydronium ions

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which generated in situ from water autoionization and acetic acid resulting from acetyl substituents of hemicelluloses, the later having a much higher contribution to the hydrolysis (Heitz et al., 1986). Although many works have been reported in the last decade, most of them focus the reaction condition optimization to maximize the total sugar recovery (Yu et al., 2013b). At present, understanding the reason of enchantment of cellulose accessibility in pretreatment process and role of this accessibility on enzymatic hydrolysis is becoming the new focus. Alvira et al. (2010) pointed that substrate related factors like cellulose crystallinity index (CrI), degree of polymerization (DP) of cellulose, surface area, lignin and hemicellulose content, particle size and cell wall thickness limited the enzymatic hydrolysis. However, what contributes more on the cellulose accessibility is still unclear. In addition, the information from different biomass species such as woody and herbaceous could not support the hydrolysis behaviors of biomass with same provenance.

Pennisetum hybrid, a monocot C4 perennial tropical grass, is a potential resource to biogas production after pretreatment and anaerobic digestion (Li et al., 2012). In this work, two *Pennisetum* hybrid were selected to investigate its recalcitrance to LHW and enzyme. Moreover, potentiality of cellulosic ethanol production was evaluated by the comparison of sugar recovery and enzymatic digestibility (ED) to switchgrass. Furthermore, multi-scale changes of substrate were charactered to deep understanding of mechanisms of ED enhancement.

2. Methods

2.1. Materials

Pennisetum hybrid I, II and switchgrass were grown in Zengcheng District, Guangzhou City, China which were harvested in September, 2014. They were knife milled and screened to 8–18 mesh and dried to constant weight. *Pennisetum* is triploid hybrid crossed by *Pennisetum americanum* Tift23A and elephantgrass (*P. purpureum Schum*) N51, so I and II are phylogenetically close which have same hybridization parents but differ slightly in phenotype, such as II has higher plant height but less tillers. According to the standard Laboratory Analytical Procedures (LAPs) for biomass analysis exploited by the US National Renewable Energy Laboratory (NREL), the chemical composition for grass I, II and S (on a dry weight basis) was 34.5%, 31.7%, 36.9% glucan, 20.1%, 18.7%, 25.1% pentosan with arabinose/xylose ratio of 15.9%, 18.7% and 12.3%, 17.5%, 20.1%, 21.6% acid-insoluble lignin, respectively.

Cellulase (151.7FPU/g) were obtained from Imperial Jade Biotechnology Co., Ltd. China. CCRC and JIM series of monoclonal antibodies were obtained from the Complex Carbohydrate Research Center collection.

2.2. Pretreatment and enzymatic hydrolysis

Details of the LHW pretreatment were described elsewhere (Yu et al., 2013a). The reaction condition was based on 180 °C, 5% (w/v) substrate, 0–60 min. Hydrolysis factor was introduced as follow to reflect the affection of reaction time and temperature on sugar recovery and degradation (Vroom, 1957).

$$H = \int_0^t \exp\left(\ln K_0 - \frac{E}{RT_{(t)}}\right) dt$$

where, t represents the reaction time. $T_{(t)}$ is the reaction temperature as a function of reaction time K_0 is the pre-exponential constant, and $\ln K_0 = \frac{E}{RT}$ when the reaction rate is assumed as 1 at 100 °C. E is the activation energy, 88.8 kJ/mol for hemicellulose hydrolysis, and R is the universal gas constant, 8.314 J/(mol × K).

Enzymatic hydrolysis was performed at 50 °C with an agitation speed of 150 rpm on a rotary shaker for 72 h in 250 ml Erlenmeyer flasks, each containing 100 ml of 0.05 M sodium citrate buffer (pH 4.8) and 5% (w/v) substrate (Yu et al., 2011a). The concentration of glucose and xylose in the samples was measured by HPLC as described below.

2.3. Sugar analysis in the liquid fraction

The quantification of oligomeric sugars were done by Waters HPLC using Shodex sugar KS-802 and KS-801 columns coupled with refractive index detector. The mobile phase was H_2O at a flow rate of 0.6 ml/min, with a column temperature of 85 °C.

The total sugars in the liquid fraction were calculated after a secondary hydrolysis into monomerics with 4% sulfuric acid. Monomeric sugars were quantitatively determined by HPLC using a Shodex sugar SH-1011 column coupled with refractive index detector. The mobile phase was 0.005 M H_2SO_4 at a flow rate of 0.5 ml/min, the column temperature was 50 °C. The yield of total sugars was calculated as the ratio of the total sugars in the liquid fraction per 100 g of potential sugars in the untreated biomass material (Yu et al., 2015).

2.4. Microstructure characteristics

The surface morphology of the three grasses were characterized by scanning electron microscopy (SEM, Hitachi-S4800). Imaging was performed at beam accelerating voltage of 2.0 kV, and images were obtained at magnifications of 250.

The specific surface area and the internal pore distribution of solid materials were analyzed by Brunauer–Emmett–Teller (BET) and aperture Analyzer (SI-MP-10/PoreMaster 33, Quantachrome Instruments, Boynton Beach, FL, USA).

For the immunofluorescence labeling, treated and untreated samples were embedded in 3% agarose, and 8-μm-thick sections were cut using a vibratome (Leica Microsystems). Sections were incubated for 1 h together with monoclonal antibodies (1/20 dilution), and were then washed three times with 0.1 M PBS (Na_2HPO_4/NaH_2PO_4, pH 7.4)/0.5 M NaCl, followed by incubation for 1 h with fluorescein isothiocyanate (FITC)-conjugated antibodies (1/50 dilution, Sigma). Following three further washes, the immunofluorescence was observed at 480 nm with magnifications of 40 using a Zeiss LSM510 confocal microscope (Wu et al., 2009).

2.5. Crystallinity measurement

The CrI of unpretreated and pretreated samples was measured by XRD using a X'Pert Pro MPD generator (PW3040/60, Philips, Holand). The dried samples were scanned in 2^θ range from 5° to 80° using Cu radiation generated at 40 kV and 40 mA. The CrI of cellulose was calculated from the XRD spectra according to the XRD peak height method (Yu et al., 2010).

$$\text{CrI } \% = \frac{I_{\text{crystalline}(002)} - I_{\text{amorphous}}}{I_{\text{crystalline}(002)}} \times 100$$

$I_{\text{crystalline}(002)}$ is the intensity of crystalline regions ($2^\theta = 22.5°$) and $I_{\text{amorphous}}$ means intensity of amorphous regions ($2^\theta = 18.7°$).The ^{13}C CP/MAS-NMR spectra with total suppression of spinning side bands (TOSS) of three grasses were obtained at room temperature on a Bruker AV-400 solid-state NMR spectrometer. Acquisition was performed with a CP pulse sequence using a 1 ms proton 90° pulse of 5.6 μs. The MAS speed was 5 kHz, and the relaxation delay

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