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High gravity enzymatic hydrolysis of hydrothermal and ultrasonic pretreated big bluestem with recycling prehydrolysate water

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ABSTRACT

Enhancing sugar concentration and minimizing water consumption are key objectives for future cellulosic biofuel economics. To achieve those objectives, high-solids loading pretreatment and enzymatic hydrolysis (up to 20%, w/v) were studied. Big bluestem was selected and combined hydrothermal and ultrasonic treatment without chemicals addition was carried out in this study. Optimal high-solids loading pretreatment (16%, w/v) was identified in the ultrasonic reactor at 200 °C for 30 min. High-solids enzymatic hydrolysis (12%, w/v) was inefficient in the laboratory rotary shaker. However, using a horizontal reactor with good mixing is effective for high solids loading (20%, w/v), yielding 75 g/L of glucose. Minimum water to detoxify pretreated biomass while maintaining high sugar yields was 10 mL/g, which reduced by 50% as compared to the conventional washing process for steam-treated wheat straw. Recycling pretreatment liquor to treat the next batch of biomass was proved to be feasible without affecting the sugar yields.

1. Introduction

Biofuel, a sustainable and renewable energy source, has a strong impact to relieve the burden in over-consumption of petroleum-based fuels and chemicals, consequently reducing global carbon dioxide (CO_2) emission and also dependence on foreign oil imports [1,2]. As the global population expands and the production of vehicle around the world increases, the demands to produce transportation fuels increase rapidly. Among numbers of potential alternative fuels, bioethanol is considered as the widest utilized transportation fuels [1,3]. Bioethanol is a renewable alternative fuel derived from various sustainable feedstocks such as sugar-based crops (sugarcane, sweet sorghum, sugar beet, etc.), starch-based crops (wheat, corn, cassava, grain sorghum, etc.), cellulosic biomass (agricultural residues such as corn stover or wheat straw, herbaceous biomass such as switchgrass, big bluestem, miscanthus, woody biomass such as polar, etc.).

Lignocellulosic biomass is considered as a desirable alternative to currently used petroleum-based energy sources due to its abundant availability and no competition with food [4]. Big bluestem (Andropogon gerardii), a dominant warm-season (C4) perennial native grass, consists as much as 80% of the plant biomass in the Midwestern grasslands of North America [5]. Although big bluestem is not commonly considered as a traditional cellulosic biomass such as switchgrass and corn stover, it offers many economic benefits, including more biomass yields, greater ability to grow with low input and increase ecosystem biodiversity [6,7].

The process of converting lignocellulosic biomass to ethanol mainly consists of pretreatment, hydrolysis, fermentation and distillation. Pretreatment is a critical process to break down the recalcitrant structure of cellulosic biomass in order to improve biomass enzymatic digestibility [8,9]. Hydrothermal pretreatment is an eco-friendly process as only water is used as reaction medium without chemicals addition, which is usually processed at relatively high temperatures (140–220 °C) under mild acidic conditions [10,11]. At room temperature, the corresponding pH of water is 7.0. However, as the temperature and pressure of saturated liquid water increases, pH of water decreases until reaching a minimum point of 5.6 at around 250 °C [9]. The concentration of hydronium ions increases as pH of water drops, which enhances the ability to catalyze acid reactions 25 times stronger than at room temperature [9]. During hydrothermal pretreatment, the hydronium ions released by water depolymerizes hemicellulose from plant cell wall to form acetic acids, improving enzymatic accessibility to cellulose and thus enzyme-catalyzed hydrolysis yields of fermentable glucose [10].

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Ultrasonic pretreatment is a mechanical process equipped with heating source, in which biomass structure is disrupted by cavitational bubbles. During ultrasonic pretreatment, microbubbles are developed in local hotspots and then collapsed to release a huge amount of energy which may cause the melting of the crystalline structure of biomass as reactive radicals (•HO and •H) can be formed at the moment of bubble collapse [12]. Compared with other thermochemical conversion technologies, such as acid and alkaline pretreatments, ultrasonic pretreatment is conducted without chemical agents and does not require severe conditions. Another advantage is that ultrasound-treated biomass can be converted into sugar and fermented to ethanol without additional pH adjustment and formation of inhibitors in chemical reactions during pretreatment process.

High-solids loadings (≥15%, w/w) of pretreatment and hydrolysis processes towards lignocellulosic ethanol is superior to lower-solids loading, including concentrated fermentable sugars, potential enhanced ethanol titers and reduced capital and energy costs [13]. This process is environmentally friendly as it minimizes water usage and waste disposal. In order to meet the minimum ethanol concentration (>40 g/L) for industrial distillation process, at least 15% (w/w) solids is required for enzymatic hydrolysis [13–16]. However, high-solid pretreatment and hydrolysis could result in poor mass transfer, increased slurry viscosity and increased inhibitors concentration [17].

High gravity enzymatic hydrolysis of high-solids pretreated lignocellulosic biomass envisions great potential in improving the process economics through enhanced fermentable sugars and ethanol yields [18]. Unfortunately, limited data are available for high loading pretreatment and enzymatic hydrolysis of lignocellulosic biomass. The objective of this research was to study the effect of high-solids loading pretreatment and enzymatic hydrolysis on sugar yields. Combined hydrothermal and ultrasonic treatment was used in this study. Furthermore, this study explored possibility of minimizing water usage and waste water disposal, including reduced water consumption for detoxification after pretreatment and recycling pretreatment liquor to treat next batch of biomass.

2. Materials and methods

2.1. Materials

Big bluestem, is a dominant warm-season (C4) perennial native grass planted mostly in the Midwestern grasslands of North America. One big bluestem ecotype (Fults population) which was harvested in Carbondale, IL in 2013 was used for this study. After grinding into <1 mm particle size with a cutting mill (SM 2000, Retsch Inc. Newton, PA, U.S.), the sample with <7% moisture content was sealed in a plastic bag and stored at room temperature. The chemical composition of big bluestem was determined according to the National Renewable Energy Laboratory (NREL) procedure as shown in Table 1. In the NREL procedure, samples were first subject to sulfuric acid (72%) treatment for 60 min at 30 °C and then hydrolyzed by dilute acid (4%) at 121 °C for another 60 min. After acid hydrolysis, carbohydrate including cellulose and hemicellulose was converted monosaccharide, which was measured by high-performance liquid chromatography (HPLC). Lignin consists of acid insoluble and acid soluble lignin. Acid insoluble lignin was weighed from the solid after oven heating overnight at 105 °C (the weight of acid insoluble lignin and ash) and then at 575 °C for at least 6 h to measure the ash content. All chemicals used for this research were purchased from Sigma Chemical Co. (St. Louis, MO).

Table 1
Chemical composition of untreated and treated biomass used in this experiment.

Composition	Untreated big bluestem (%, db)	Treated big bluestem (%, db)[a]
Cellulose	36.6 ± 0.51	58.6 ± 0.65
Hemicellulose	30.6 ± 0.56	5.8 ± 0.58
Lignin	18.2 ± 0.6	31.2 ± 0.43
Ash	4.64 ± 0.78	0.8 ± 0.81

[a] (The pretreatment condition was 200 °C and 30 min residence time). Values are means ± SD (standard deviation).

2.2. Hydrothermal and ultrasound pretreatment

The primary objective of pretreatment is to increase cell wall porosity and accessibility of plant cell wall surfaces to cellulolytic enzymes. Hydrothermal and ultrasonic pretreatment was carried out in a laboratory ultrasonic reactor (Ultrasonic High-Pressure Chemical Reactor, Columbia International). The stainless steel reactor has a total volume of 200 mL and is heated by an electric heater. The recommended maximum input volume is 150 mL as some space is left for slurry expansion. After weighted biomass samples were introduced into the reactor and the target temperature was set, the reactor was heated at a rate of round 4 °C min^{-1}. At the time of reaction temperature reached the target temperature, it was set as Time 0, so Time 30 min means after the reaction temperature reached the target temperature and maintained at this temperature for 30 min. Based on preliminary experimental results, reaction temperature ranged from 180 °C to 200 °C were able to achieve high fermentable sugar yields, thus, the reaction temperature from 180 °C to 200 °C was used for this study. Ultrasound treatment was applied based on determined process conditions and the ultrasonic pattern was set at 5 s on and then 5 s off. After the treatment was complete, the ultrasonic reactor was removed from the electric heater and placed into room temperature water to cool down to 50 °C within 5 min. The slurry was vacuum filtered using Whatman Paper (No. 4). Water insoluble solid was washed thoroughly with water and collected for composition analysis and enzymatic hydrolysis to evaluate the pretreatment effect. Distilled water was used to wash the pretreated solids after pretreatment. The pretreated solids was not dried as drying will destroy the open pores generated by the pretreatment process and consequently result in lower sugar yields.

2.3. Enzymatic saccharification

Enzymatic saccharification of pretreated biomass to evaluate the pretreatment effect was carried out at 4% solid loadings (grams dry weight per 100 mL) in 50 mM sodium acetate buffer solution (pH 5) with addition of 0.2 g/L to prevent microbial contamination. An enzyme complex, Accellerase 1500 is an enzyme complex including cellulose and β-glucosidase [Endoglucanase activity: 2200–2800 CMCU/g (1 CMCU unit of activity liberates 1 l mol of reducing sugars, expressed as glucose equivalents) in 1 min under specific assay conditions of 50 °C and pH 4.8]. Accellerase 1500, was generously provided by DuPont Industrial Biosciences (Rochester, NY, U.S.) and applied to this study at the recommended dosage (0.5 mL/g cellulose) [19]. Flasks were incubated at 50 °C in a rotary shaker (Model I2400, New Brunswick Scientific Inc. Edison, NJ, U.S.) with the speed of 140 rpm. Supernatants were extracted after 72-hr enzymatic hydrolysis to analyze sugar concentration by HPLC. All reactions were performed in duplicate. Glucose yield was calculated as follows: