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Effects of water content on ball milling pretreatment and the enzymatic digestibility of corn stover

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A B S T R A C T

Lignocellulosic biomass pretreatment is a key step to determine the efficacy of biofuel production because of the recalcitrance of lignocellulosic feedstock. The effects of various water inputs, i.e., 0, 25, 100, and 400% (w/w), on the ball milling pretreatment of corn stover and enzymatic hydrolysis were studied under two milling temperatures (80 °C and 100 °C) and three milling times (10, 20, and 30 min). Ball milling reduced corn stover particle size and disrupted the rigid cell wall matrix. As milling time increased, corn stover size decreased remarkably. Changes in corn stover were analyzed using size distribution graphs and geometric mean diameter with respect to milling temperature and time. Milling with 0% (w/w) water resulted in the rapid grinding of corn stover. The highest glucose yield (66.96%) was obtained after milling at 80 °C for 30 min with no water. The corn stovers milled with 0% or 25% (w/w) water showed higher glucose yields when milled at 80 °C than at 100 °C, while the samples milled with 100% or 400% (w/w) water showed higher glucose yields at 100 °C. Finally, several ball milling conditions were proposed to construct a combinational pretreatment process based on the study results. These results provide a basis for minimizing water use during lignocellulosic biofuel production and improving sustainability.

Introduction

Biofuels, such as bioethanol or biobutanol, have received increasing attention owing to the challenges associated with declining fossil resources and increasing greenhouse gas emissions. The use of biomass to produce fuel is important for the development of sustainable sources of energy, since biomass availability is relatively stable over time (Gomez et al., 2008). There is considerable interest in lignocellulosic biofuel because of the potential for improved sustainability and carbon dioxide fixation as well as the lack of conflict with food resources (Balan, 2014). Lignocellulosic sources include agricultural residues, dedicated energy grasses, forestry residues, and so on. Lignocellulosic biofuel technology involves a pretreatment process, followed by enzymatic saccharification, after which the fermentable sugars undergo fermentation to produce biofuel. The pretreatment and enzymatic hydrolysis steps are the key determinants of the overall economic feasibility of the process owing to the recalcitrance of lignocellulosic feedstock.

A nexus approach is emerging to address the challenge of biofuel development because sustainability is an important issue for the realization of the UN Sustainable Development Goals (Shastri, 2017; Wolfe et al., 2016). As transport is shifting from fossil fuel use to the use of fuel mixtures with a larger fraction of biofuels, such as bioethanol and biodiesel, the global biofuel water footprint is expected to increase more than tenfold from 2005 to 2030 (Gerbens-Leenes et al., 2012). The global blue water footprint for biofuel would occupy 5.5% of the total blue water for humans by 2030. Biomass cultivation is the most water-intensive step in biofuel production processes (Dominguez-Faus et al., 2009). The water quantity used for the biorefining process is modest compared to that used for the biomass cultivation step, but it cannot be ignored. Biorefinery for corn-based biofuel production in the US uses the equivalent of the water used by 5000 people in 1 year (NRC, 2007). Lignocellulosic biorefineries require 2.9 times more water than corn biorefineries for ethanol production (Nikolakopoulos and Kokossis, 2017). The water footprint of lignocellulosic biofuel is considerably smaller than the water footprint of corn-based biofuel. However, this can be explained by the assignment of the water footprint of lignocellulosic biomass, such as rice husks, to

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the main product, e.g., rice (Chiu et al., 2015; Mathioudakis et al., 2017). If only bioconversion processes are considered, the water consumption of biorefineries in lignocellulosic biofuel production is very large, even when compared to that for corn biorefineries. Water consumption for lignocellulosic biorefineries is 9.8 L/L ethanol (Aden et al., 2007). Considering that the water consumption for thermochemical biofuel and crude oil gasoline production processes are 2 L/L and 2.5 L/L, respectively, technologies are needed to reduce water consumption. The use of large quantities of water necessitates facilities for water treatment and distillation, which may cost up to 29% of the total capital cost (EuropaBio, 2011; NRC, 2007). A water-energy nexus concept should be introduced in lignocellulosic biorefineries to improve sustainability. Water-saving pretreatment that does not require a washing step could be employed. We previously proposed a facile biofuel production process using planetary milling pretreatment (Kwon et al., 2016). This physical pretreatment method does not result in toxic byproducts and does not require washing or detoxification steps, which are beneficial properties for a water-energy nexus approach. For industrial applications, attrition type milling is feasible for lignocellulosic pretreatment because it is amenable to large-scale processes. However, we found that fermentable sugar production is less efficient using attrition milling than planetary milling (Kim et al., 2013). Therefore, attrition type milling requires chemical catalysts to achieve the sufficient conversion of lignocellulosic biomass, and it is important to ensure a lack of toxicity. Chemical catalysts are used as an aqueous solution, which affects grinding efficiency during ball milling.

Therefore, in this study, we investigated the characteristics and enzyme hydrolysis process for corn stover particles when water was added during attrition milling. Changes in corn stover size and enzyme digestibility were investigated with respect to the quantity of water and milling temperature. The temperature is an important parameter, since most chemical pretreatments are performed at high temperatures. To reduce wastewater production and easily recycle the chemical solvent, the quantity of water input should be minimized (Park et al., 2017). This study provides insight into the optimal conditions for ball milling pretreatment before chemical pretreatment, and may facilitate the development of efficient physico-chemical combinational pretreatment processes.

Materials and methods

Preparation of raw materials

Corn stover was harvested in Shandong province, China and was kindly supplied by CJ Cheil Jedang. The composition of the corn stover was 34.8 wt% glucan, 17.6 wt% xylan, 1.7 wt% arabinan, 3.1 wt% manan, 2.1 wt% galactan, 15.9 wt% lignin, and 0.6 wt% ash. The corn stover was ground and particles of <5 mm were obtained to improve the reproducibility of results. The corn stover naturally contained 11% water in ambient conditions.

Attrition milling pretreatment

The attrition type mill device used in this study has been developed for lignocellulosic biomass pretreatment (Korea pulverizing machinery Co., LTD, Incheon, Korea). It has a 2.4-L inner jar where a steel ball (Φ = 10 mm) crushes the corn stover particles. The attrition mill device was equipped with a heater that can increase the temperature inside the jar up to 200 °C. The attrition mill device has a pin type impeller to circulate the steel balls. According to a previous study (Kim et al., 2013), 70% of the total volume of the jar was filled with corn stover and grinding balls (equal volumes). The remaining space was kept empty for effective grinding. The rotating impeller was set at 300 rpm. The temperatures were controlled depending on the pretreatment conditions.

Analytical methods

The particle size distribution of pretreated corn stover was analyzed using a particle size distribution analyzer (LA-950 V2; Horiba, Kyoto, Japan). The microscopic images of corn stover were obtained by a scanning electron microscope (JSM-6700F; JEOL, Tokyo, Japan). To obtain SEM images, corn stover particles were coated with Pt on a Cressington Scientific Instruments 108 Auto Sputter Coater (Cranberry Twp., PA, USA). The efficiency of pretreatment was determined by glucose production. Commercial cellulase (Cellic CTec3; Novozymes, Bagsværd, Denmark) was added at 15 FPU/g dry biomass to a pretreated corn stover slurry (2% solids, w/v) with 50 mM sodium acetate (pH 4.8). The mixture was incubated at 50 °C for 72 h with agitation using a rotator (JEIO Tech, Daejeon, Korea) set to 200 rpm. Glucose production was measured by the Glucose Test Method (Merck, Darmstadt, Germany). The color change in the strip was converted to a glucose concentration using a Reflectometer. The enzymatic digestibility was expressed as the glucose yield, as calculated using Eq. (1):

$$\text{Glucose yield } (\%) = [\text{Glucose produced after enzyme hydrolysis}/(\text{Glucan in corn stover} \times 1.11)] \times 100 \qquad (1)$$

Results and discussion

Physical changes

Fig. 1 shows SEM images of unpretreated and pretreated corn stovers. After milling, corn stover was reduced to small fragments and the cell wall matrix was disrupted (Fig. 1). As shown in the comparison between Fig. 1(a) and (b), the rigid surface of corn stover was broken after milling. Collisions by the grinding ball caused structural changes. The corn stover absorbed water and swelled up. It has been reported that hot water pretreatment changes the dissolution of hemicellulose, results in the partial removal and relocation of lignin, and limits the deconstruction of cellulose in severe conditions, e.g., >150 °C (Grénman et al., 2011; Nitsos et al., 2016). In the study conditions, lignin could migrate, coalesce, and even be redeposited from the solution onto biomass as the temperature cooled, contributing to the increased biomass recalcitrance. In this study, a mild temperature was used for pretreatment. Therefore, ball milling did not cause significant chemical changes.

Milling pretreatment was performed using two temperatures and four water inputs. For each condition, milling was performed for 10, 20, and 30 min. As the milling time increased, the sizes of corn stover particles decreased remarkably. As an example, Fig. 2 presents the distribution of pretreated corn stover sizes when milled with 400% (w/w) water with respect to milling time. After 10 min of milling, the largest size peak was found around 600 μm. However, the peak shifted to 80 μm after only 20 min of milling. At 20 min, the shoulder peak was detected around 200 μm but it disappeared after milling for an additional 10 min (Fig. 2). These results indicated that the corn stover of around 200 μm was ground to smaller sizes.

Table 1 presents the mean sizes of corn stover after milling at 80 °C and 100 °C. At 10 min of milling, the corn stover milled with 0, 100, and 400% (w/w) water showed smaller mean diameters of corn stover when compared to the sample milled with 25% water. The samples milled with 0 and 25% (w/w) water had higher standard deviation (Table 1). The data obtained from particle size analyzer also showed relatively broad peaks on the samples milled

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