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Environmentally friendly pretreatment of plant biomass by planetary and attrition milling

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HIGHLIGHTS

- Planetary and attrition milling both reduced loss of biomass during treatment.
- Planetary milling significantly lowered the crystallinity index of the rice straw.
- Both milling processes gave monosaccharide yields of about 0.4 g-sugar/g-biomass.
- Milling significantly lowered the generation of phenolics from the lignin.

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ABSTRACT

This study evaluated the use of planetary and attrition milling as pretreatment processes for lignocellulosic biomass using rice straw. Planetary milling reduced the rice straw crystallinity from 0.48 to 0.11. Since the samples could be milled and enzymatically treated using the same media, loss of the biomass due to washing was effectively eliminated. In contrast, conventional sodium hydroxide and soaking in aqueous ammonia (SAA) processes showed a loss of 34.2% and 14.8%, respectively. Furthermore, milling produced significantly lower concentrations of soluble phenolics than the alkali treatments. Using a bioluminescent bioreporter strain that is sensitive to these phenolics, neither of the milled samples elicited a response while the sodium hydroxide and SAA samples led to a 25.8 and 4.7 -fold induction, respectively. Although planetary milling produced more reducing sugars than attrition milling before saccharification, both had similar monosaccharide yields, i.e., 0.38 and 0.34 g/g-biomass, respectively, when 40 g/l rice straw was treated.

1. Introduction

Producing fuels, such as ethanol and butanol, from renewable biomass is of strategic importance to developing alternative energy sources. Biomass-based fuels offer many advantages over petroleum-based fuels, such as their renewability, sustainability, and common availability, as well as their reduction of greenhouse gas (GHG) emissions and biodegradability (Demirbas, 2009). The current biomasses utilized for biofuel production are sugars, starch-based crops, lignocelluloses and microalgae. Among these, lignocellulosic biomass is viewed as the most suitable for biofuel production since it is both a cheap and abundant non-food material (Chandra et al., 2012).

Lignocellulosic biomass is composed of three major components – cellulose, hemicelluloses and lignin. According to its dry weight, this biomass contains 50–80% carbohydrates, primarily in the form of cellulose and hemicellulose, which serve as structural components of the plant cell wall. Due to its highly crystalline structure, cellulose is recalcitrant to enzymatic saccharification. Furthermore, lignin, a polymer of phenylpropane units, forms a three-dimensional network inside the cell wall and adheres to the polysaccharides. These complex structures found within lignocellulosic biomasses contribute to lower biofuel production efficiencies by blocking enzymatic binding, hydrolysis and release of the sugar monomers.

Hence, pretreatment of lignocellulosic biomass is one of the key steps required in biofuel production. Pretreatment processes usually aim to increase the biomass' internal surface area by decreasing the degree of polymerization and crystallinity, separating the structural linkages between lignin and carbohydrates and disrupting the lignin structure. To date several methods have been utilized for pre-treating lignocellulosic biomasses and include both chemical and physical methodologies.

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It is well known that pretreatment of the plant biomass with an acid solubilizes the hemicelluloses and makes the cellulose better accessible (Zhang et al., 2007). This process can use either concentrated or dilute acids to break the rigid lignocellulosic structure within the biomass. Dilute sulfuric acid (Du et al., 2010; Pingali et al., 2010) has most often been used but other acids have also been shown effective, including hydrochloric acid (HCl) (Goldstein et al., 1983), phosphoric acid (H_3PO_4) (Marzialetti et al., 2008) and nitric acid (HNO_3) (Xiao and Clarkson, 1997).

Alkaline pretreatment is one of the more popular methods for lignocellulosic biomass and causes the degradation of ester and glycosidic side chains, resulting in structural changes in the lignin as well as swelling and decrystallization of the cellulose (Cheng et al., 2010; McIntosh and Vancov, 2010). It uses bases such as sodium, potassium, calcium and ammonium hydroxide. The use of dilute $Ca(OH)_2$ was shown to be excellent at reducing the lignin content within the biomass, with a removal efficiency of 87.5% (Kim and Holtzapple, 2005). A soaking in aqueous ammonia (SAA) method is also widely used to enhance sugar production (Kim et al., 2008). While these pretreatment methods improve saccharification, they require a high energy input due to the elevated temperatures used and lead to the conversion of the sugars and lignin into inhibitory compounds, such as furfural or ferulic acid (Lee et al., 2012). Furthermore, the biomass samples should be neutralized after the chemical pretreatment, which requires a lot of water and produces a large amount of waste salts (Brodeur et al., 2011). Both of these also interrupt the subsequent saccharification and fermentation processes while some of the fermentable biomass and sugars is lost during the washing steps to remove these salts.

One simple process that was used on occasion is the physical pretreatment of the biomass, which involves size reduction by chipping, grinding or milling of the biomass materials. These methods make the sugars more accessible to cellulase enzymes for saccharification. However, due to the low efficiency in the past when performed solely, physical pretreatment has often been done in conjunction with chemical pretreatments, such as with dilute H_2SO_4 treatment (Zhao et al., 2006). Recently, a combination of a wet process involving milling plus a popping treatment was applied to enhance enzymatic conversion of rapeseed straw to sugars (Wi et al., 2011). This process involved both a soaking step in tap water for 1 day as well as elevated temperatures of up to 220 °C.

Here, we propose the use of planetary and attrition mill-based pretreatments as efficient and environmentally-friendly methods as they neither use chemicals nor lead to the production of the saccharification and fermentation inhibitors seen in other studies. As such, this method could be subsequently followed by saccharification and fermentation processes without changing the buffer or washing of the biomass, which prevents its loss.

Planetary mill uses artificial gravity to apply to the grinding medium by using a centrifugal force field while conventional ball mill utilizes solely gravity as applying force. In planetary mill, the grinding jar rotates around its own axis in a direction opposite to the direction of support plate rotation, which causes a non-uniform field of centripetal acceleration. Therefore, the balls in planetary mill have notably higher impact energies. Attrition milling, on the other hand, consists of a chamber holding a rotating stirrer. Attrition milling leads to the abrasion of particles by intensive, shear and friction stresses between the agitated grinding balls. The biomass inside the chamber is comminuted in the media solution by abrasion through the action of the stirrer and the chamber wall. Both mills offer a fast and efficient fine grinding alongside a simple operational protocol (Shinohara et al., 1999).

Rice straw was selected as a model biomass to verify the capabilities of the proposed method as it is the largest single feedstock among the current lignocellulosic biomasses being used (Karimi et al., 2006).

2. Methods

2.1. Materials

Rice straw grown and harvested in Gyeongbuk, Rep. Korea in 2011 was used in this study. The rice straw was roughly cut using a home blender and air-dried at 60 °C for 1 day. Mono and disaccharide standards (i.e., glucose, cellobiose, xylose, galactose and mannose), 3,5-dinitrosalicylic acid, sodium azide and sodium acetate trihydrate were purchased from Sigma–Aldrich (USA). The cellulase cocktail was purchased from Worthington Biochemical Co (USA).

2.2. Planetary and attrition mills pretreatment

Planetary milling was performed using a Pulverisette 5 (Fritsch, Germany). Various amounts of air dried rice straw were added to a zirconium jar containing 90 ml of 50 mM sodium acetate buffer (pH 5.0) with 0.02% sodium azide and an equal volume of 5 mm diameter zirconia balls. The mixture was briefly stirred using a glass bar for 10 min and then placed within the planetary mill device. The jar containing the mixture was rotated at a velocity of 300 rpm for 8 h. The same protocol was used for the attrition milling pretreatment except that the mill was an ATM-6407-1B (Dea Wha Tech Co. Ltd, Rep. Korea).

2.3. Chemical pretreatments

For comparison, two chemical pretreatments, sodium hydroxide and soaking in aqueous ammonia (SAA) treatments, were also performed according to previous reports (Kim et al., 2008; Xu et al., 2010). Dried rice straw was dissolved in 1 w/v% of sodium hydroxide at a solid/liquid ratio of 1:10 and incubated at 121 °C for 15 min. For SAA pretreatment, dried rice straw was incubated in 15 wt.% of ammonia at a solid/liquid ratio of 1:6 at 60 °C for 12 h. After the chemical pretreatment, the solids of the slurry were recovered by filtration using 0.2 μm filter paper and washed with deionized water to remove the excess chemicals and adjust the pH to 7.0.

2.4. Enzymatic hydrolysis

Enzymatic hydrolysis of the cellulose was performed according to a modified method based on that recommended by the National Renewable Energy Laboratory, USA (NREL, 2008). Briefly, after pretreatment, a cellulase cocktail (Worthington Biochemical Co., USA) was added to the rice straw slurry to a concentration of 3*g* cellulase/l and incubated at 50 °C for 72 h with agitation using a rotator (JEIO TECH, Rep. Korea) set to 200 rpm.

2.5. Characterization of the samples

The untreated rice straw was coated with Pt on a Cressington Scientific Instruments 108 Auto Sputter Coater (Cranberry Tep., PA, USA). For the pretreated rice straw, the sample was first dried in a freeze-dryer (Ilshin Lab Co. Ltd, Rep. Korea) and then coated. The morphology of each of the coated samples was investigated using a Scanning Electron Microscope (JSM-6700F, JEOL, Tokyo, Japan). The accelerating voltage for the SEM images was 15 kV.

The crystallinity of the rice straw was determined using X-ray diffraction (XRD, Rigaku D/max-RB powder diffractometer, Tokyo, Japan) with Cu κα radiation (λ = 1.542 Å). Samples were scanned over the range of 2θ = 10–90° at a rate of 2°/min. The crystallinity index was calculated using the following equation:

$$\text{Crystallinity Index}(\%) = \{(I_{2\theta=22.5^\circ} - I_{2\theta=18.7^\circ})/(I_{2\theta=22.5^\circ})\} \times 100$$