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Enhanced enzymatic hydrolysis of rapeseed straw by popping pretreatment for bioethanol production

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ABSTRACT

The objective of this study was to find a pretreatment process that enhances enzymatic conversion of biomass to sugars. Rapeseed straw was pretreated by two processes: a wet process involving wet milling plus a popping treatment, and a dry process involving popping plus dry milling. The effects of the pretreatments were studied both in terms of structural and compositional changes and change in susceptibility to enzymatic hydrolysis. After application of the wet and dry processes, the amounts of cellulose and xylose in the straw were 37–38% and 14–15%, respectively, compared to 31% and 12% in untreated counterparts. In enzymatic hydrolysis performance, the wet process presented the best glucose yield, with a 93.1% conversion, while the dry process yielded 69.6%, and the un-pretreated process yielded <20%. Electron microscopic studies of the straw also showed a relative increase in susceptibility to enzymatic hydrolysis with pretreatment.

1. Introduction

Crude oil is a major resource that has been drawn on to meet increased energy demands (Greene et al., 2004). However, high oil prices and public concerns over greenhouse gas emissions have spurred interest in finding alternative fuel sources that could replace or alleviate demand for crude oil, particularly for automotive liquid fuels (Keshwani and Cheng, 2009).

Lignocellulosic biomass, defined as all natural vegetable and tree matter containing carbohydrate compounds as main components, has great potential as an annually renewable energy resource and has attracted much interest as a raw material for the production of bioethanol (Alvira et al., 2009; Kumar et al., 2009). Production of bioethanol from lignocellulosic biomass is a well-known process by which sugars are fermented into ethanol using yeast. However, lignocellulosic biomass is made of sugar polymers, which are not as easily saccharified and fermented (Chandra et al., 2007; Wi et al., 2009). Processes used to produce ethanol efficiently from biomass include (i) pretreatment to make the biomass readily hydrolyzable, (ii) enzymatic hydrolysis to convert cellulose and hemicelluloses components to their sugar monomers, and (iii) fermentation of sugar monomers to ethanol.

Enzymatic saccharification is considered a more promising technology than other saccharification methods. While biomass pretreatment is not required for acid-catalyzed saccharification, this method still has some disadvantages in terms of cost competitiveness and environmental impacts. To provide efficient enzymatic degradation of lignocellulose, the cellulosic fibers of the raw material must be rendered accessible to the enzymes. The efficiency and effectiveness of cell wall saccharification are affected by many factors, including feedstock characteristics, pretreatment technology, and hydrolysis conditions such as use of enzyme mixtures and type (Mansfield et al., 1999). To achieve the highest saccharification rate with a given feedstock, a pretreatment must render the fiber readily degraded by the enzymes, recognizing that pretreatment must overcome the main factors governing the ease of lignocellulose breakdown to fermentable monosaccharides, namely, pore size (Chandra et al., 2007), cellulose crystallinity (Chang and Holtzapple, 2000), and lignin removal (Mansfield et al., 1999).

Various substrate pretreatment processes have been used to alter the structure of cellulose biomass, including biological, physical, and chemical processes or a combination of these processes (Sun and Cheng, 2002). Diverse pretreatment methods have been reported for various biomasses, making these biomasses potentially useful for industrial applications. Many methods have

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reported high sugar yields, above 90% of the theoretical yield for lignocellulosic biomasses such as woods, grasses, and corn (Díaz et al., 2010; Kim and Holtzapple, 2006; Kim et al., 2006; Liu and Wyman, 2005; Liu et al., 2009; Pérez et al., 2008; Teymouri et al., 2004; Wang et al., 2010).

Biological pretreatment utilizes wood-degrading fungi to modify the chemical composition of lignocellulosic biomass, but requires careful control of growth conditions and large amounts of space (Taniguchi et al., 2005; Zhang et al., 2007). Physical pretreatment, such as hammer and ball milling, can procure smaller feedstock particles that are more amenable to enzymatic hydrolysis. However, neither of these pretreatment methods is considered commercially attractive at present. In chemical pretreatment, the pulping process is already used commercially and is more effective for biomass containing low lignin, but chemical processes in general significantly solubilize hemicelluloses and have high negative environmental impact compared to biological and physical pretreatments (Alvira et al., 2009).

Rapeseed straw, an agricultural waste product and a bio-oil extracted substrate, is a lignocellulosic material that is abundant and inexpensive in European and Asian countries (Karaosmanoglu et al., 1999). Previously studied chemical pretreatments of straw include a high-pressure and hot water pretreatment (Díaz et al., 2010), a phosphoric acid-acetone pretreatment (Li et al., 2009), and a dilute sulfuric acid pretreatment (Jeong et al., 2010; Lu et al., 2009). However, existing chemical methods are both expensive and environmentally undesirable because of solvent recycling issues and corrosion and pollution from waste. Conversely, biological and physical pretreatments are more environmentally friendly as they do not require solvents and use chemicals with little or no generation of hazardous waste.

Using a new approach, we have successfully developed a popping pretreatment method that gives very high glucose yield from rapeseed straw treated with commercial enzymes. This method employs a reactor that requires a short thermal reaction time without using chemicals.

2. Methods

2.1. Substrates

Rapeseed straw was obtained from a field in Mooan, South Korea, after being harvested for oil and air dried at ambient temperature to equilibrium moisture content. The dried rapeseed straw was then cut into approximately 2 cm lengths and stored for pretreatment.

2.2. Popping pretreatment of rapeseed straw

Fig. 1 illustrates the overall pretreatment of rapeseed straw applied in this work. For the dry process, 100 g (dry weight, DW) of rapeseed straw was soaked in tap water for 1 day at room temperature and administered the popping pretreatment. Popping pretreatment was performed in a laboratory-scale cast iron cylindrical reactor with a total volume of 3 L, a gas heater, a hatch, and a mechanical rotator (Fig. 2). The reactor was heated at a rate of between 15 and 20 °C min^{-1}. When the temperature and pressure inside the reactor reached 22 °C and 21 kg $f\,cm^{-1}$, respectively, the sample was rapidly exposed to one atmospheric pressure through a hatch attached to the reactor. After the popping pretreatment, popped samples were ground for size reduction (particle size: 251–422 μm) in a Willy mill fitted with stainless steel blades. For the wet process, 100 g (DW) of rapeseed straw were fiberized in a single rotating disk atmospheric refiner and dehydrated in a centrifugal dehydrator (moisture content: 70–75%). Popping pretreatment was then conducted under the same conditions as described above.

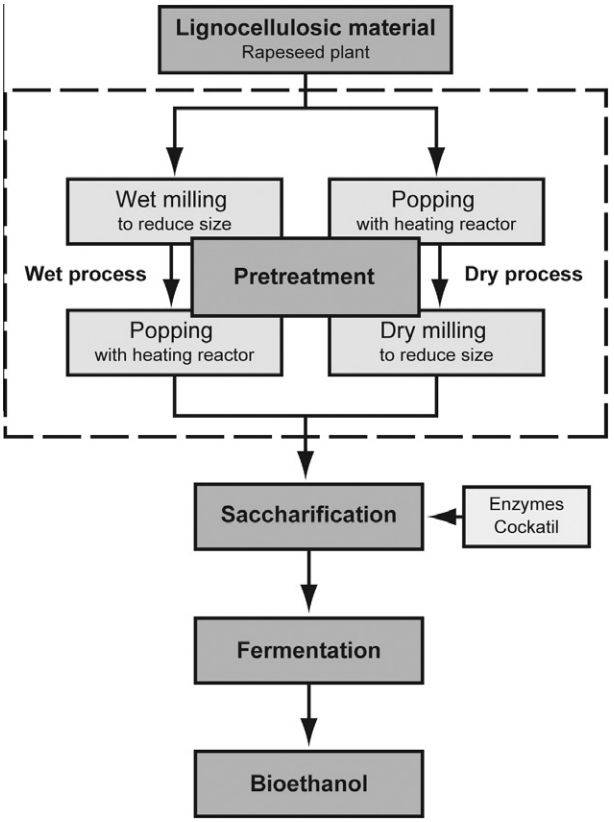

Fig. 1. Schematic diagram of pretreatment process.

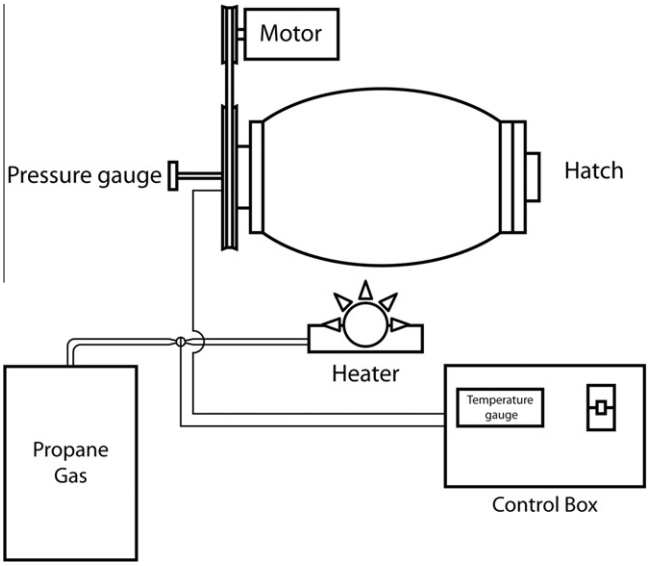

Fig. 2. Diagram of laboratory-scale popping machine.

2.3. Enzyme assays

The commercial enzymes used for this study were cellulose (C8546, Sigma-Aldrich, St Louis, MO, USA) from *Trichoderma reesei* and xylanase (X2753, Sigma) from *Thermomyces lanuginosus* produced by submerged fermentation of a genetically modified *Aspergillus oryzae* microorganism.