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Enhanced enzymatic cellulose hydrolysis by subcritical carbon dioxide pretreatment of sugarcane bagasse

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HIGHLIGHTS

- A subcritical CO_2 pretreatment was investigated to improve the glucose yield.
- Liquid fractions and solid residues were thoroughly analyzed.
- The enzymatic hydrolysis was affected by different pretreatment conditions.
- The enhanced digestibilities were confirmed by XRD, FTIR, SEM, and TGA analyses.
- The proposed process can be a contribution to develop a biorefinery.

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ABSTRACT

Most biomass pretreatment processes for sugar production are run at low-solid concentration (<10 wt.%). Subcritical carbon dioxide (CO_2) could provide a more sustainable pretreatment medium while using relative high-solid contents (15 wt.%). The effects of subcritical CO_2 pretreatment of sugarcane bagasse to the solid and glucan recoveries at different pretreatment conditions were investigated. Subsequently, enzymatic hydrolysis at different hydrolysis time was applied to obtain maximal glucose yield, which can be used for ethanol fermentation. The maximum glucose yield in enzyme hydrolyzate reached 38.5 g based on 100 g raw material after 72 h of enzymatic hydrolysis, representing 93.0% glucose in sugarcane bagasse. The enhanced digestibilities of subcritical CO_2 pretreated sugarcane bagasse were due to the removal of hemicellulose, which were confirmed by XRD, FTIR, SEM, and TGA analyses.

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1. Introduction

Global energy inevitable depletion has generated strong interest in the development of more sustainable transportation fuels and renewable carbon-based raw materials, such as those produced from biomass (Dodds and Gross, 2007; Somerville, 2006). Sugarcane bagasse was used for the bioconversion of lignocellulosic biomass to bio-fuels (such as ethanol and biodiesel) due to its availability, abundance, and renewability (Pandey et al., 2000; Rabelo et al., 2009).

The abundant cellulose in sugarcane bagasse could be hydrolyzed to glucose by enzyme for subsequent ethanolic fermentation (Martin et al., 2002). The coexistence of hemicellulose and lignin with cellulose make the enzymatic hydrolysis of cellulose difficult and tedious (Kim and Hong, 2001; Zheng et al., 1998). And a pretreatment process is essentially required to break it down (Cuvilas and Yang, 2012). The pretreatments using acid or base solutions can achieve high reaction rates and significantly improve cellulose hydrolysis but they require corrosion resistant equipment (Sun and Cheng, 2002; Wei et al., 2012). Dilute NaOH treatment of lignocellulosic materials caused disruption of the lignin structure, separation of linkages between lignin and carbohydrates, the digestibility of NaOH-treated hardwood increased with the decrease of lignin content, but they require chemicals which are not friendly to the environment (Esteghlalian et al., 1997). The hot water treatment produces digestible cellulose and needs high energy for operation (Zhang et al., 2013). The cost of ammonia fiber expansion (AFEX) is low, but the degradation and loss of hemicellulose, and the requirement of water to wash pretreated solids resist the development of it (Krishnan et al., 2010). As a consequence, the search for new methods that are less toxic with low-cost are still being actively pursued (Muhammad et al., 2013).

Supercritical CO_2 which has been mostly used as an extraction solvent (Kim and Hong, 2000), is being considered for pretreatment process due to its attractive properties such as nontoxicity, ready

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availability, low-cost consumption. Furthermore, CO_2 has a low critical temperature (31.1 °C) and pressure (7.36 MPa), can form weak acid catalyst with water ($CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$) (Muzafera et al., 2007; Luterbacher et al., 2012), which helps degrade cellulose or/and lignin, increase the accessible surface area of lignocellulose, and improve biomass digestibility at enzymatic hydrolysis stage (Gao et al., 2002; Narayanaswamy et al., 2011). Many of the current efforts are directed at the supercritical CO_2 pretreatment of biomass material. Narayanaswamy et al. (2011) investigated that the largest glucose yield reached 30 g/100 g dry corn stover during enzymatic hydrolysis after supercritical CO_2 pretreatment, which was achieved at 24.1 MPa and 150 °C for 60 min. When the cellulosic materials were treated with supercritical CO_2, the capability of cellulose hydrolysis were enhanced (Schacht et al., 2008). Compared with supercritical CO_2 pretreatment, the demands of apparatus to the subcritical CO_2 process is easy to realize, and the improved glucose yield from sugarcane bagasse with subcritical CO_2 pretreatment (<7.36 MPa) has yet not been reported.

Based on the above viewpoint, subcritical CO_2 pretreatment of sugarcane bagasse was proposed to improve glucose yield during enzymatic hydrolysis. Firstly, the solid yield and glucan recovery under different pretreatment conditions (CO_2 pressure, pretreatment time and temperature) were investigated. Subsequently, enzymatic hydrolysis under different length of time were carried out to evaluate the efficiency of subcritical CO_2 pretreatment process. Furthermore, we also detected the changes of raw material, pretreated, and enzymolysis residue samples (5 MPa CO_2, 100 min time and 180 °C pretreatment temperature) in the crystallinity by X-ray diffraction (XRD), in functional groups by Fourier transform infrared spectroscopy (FTIR), in surface structure by Scanning electron microscopy (SEM), and in thermochemical properties by Thermogravimetric analysis (TGA) to provide a mechanism for subcritical CO_2 pretreatment.

2. Methods

2.1. Raw material

Sugarcane bagasse were supplied by a company located in Guangdong, China and cut with a laboratory mill (XuLang Machinery, Guangzhou, China) to a particle size <1 mm. Then the samples were air-dried for further use. The chemical composition of the raw material (on a dry weight basis) was 37.2 ± 1.1% glucan, 24.6 ± 0.1% xylan, 1.5 ± 0.2% arabinan, 0.6 ± 0.1% galactan, 22.6 ± 0.9% acid-insoluble lignin (AIL), 2.2 ± 0.2% acid-soluble lignin (ASL) and 4.6 ± 0.6% ash.

CO_2 was purchased from Guangzhou Junduo Gases Co. (Guangzhou, China) and was purified to 99.9% purity using an activated carbon column.

2.2. Subcritical CO_2 pretreatment

Subcritical CO_2 pretreatment was carried out in a stirred 1L Parr reactor. The pretreatment were performed at various pressures (0–7 MPa), time periods (20–100 min), and temperatures (140–180 °C) with the 15% (w/v) solid to liquid ratio. Forty-five grams of dry sugarcane bagasse and 300 mL of de-ionized water were added to the reactor. Then a certain amount of CO_2 was loaded into the reactor to reach the given pressure though a pressure regulator. The agitation was set at 300 rpm to mix biomass with CO_2 during the reacting process. When the reaction process was finished, the reactor was immediately cooled down by cooling water (until below 40 °C). Then the pressure was released instantaneously using a quick release ball valve. The pretreated solution was then separated by filtration. The solid yield and glucan content in the pretreated solids were analyzed. Then the solid fraction was stored in refrigerator for further enzymatic hydrolysis.

2.3. Enzymatic hydrolysis

The enzymatic hydrolysis was then performed in 500 mL flasks using 0.05 mol/L acetic acid sodium acetate buffer (pH 4.8) and 2% dry matter (w/w) at 50 °C on an shaker at 150 rpm for 6 h, 12 h, 24 h, 48 h and 72 h. Cellulase was purchased from Genencor (Shanghai, China), with a filter paper activity of 20 FPU/mL. The cellulase enzymes were added at the loading of 20 FPU/g dry substrate for all hydrolysis experiments. At the same time, two drops of acetic ether were added to inhibit microbial contamination or growth. After the enzymatic hydrolysis process was completed, glucose in enzyme hydrolyzate were analyzed by IC system.

2.4. Characterization

2.4.1. Analysis methods

The chemical composition of sugarcane bagasse and pretreated solids were determined using the standard provided by the National Renewable Energies Laboratory in USA (Sluiter et al., 2006). All liquid products from the enzyme hydrolysate were diluted appropriately with the de-ionized water and then filtered using a 0.22 um filter. The concentration of glucose was quantitatively analyzed at 30 °C by IC system (Dionex ICS-3000) with a CarboPac PA20 column.

2.4.2. Crystallinity measurements

The crystallinity of untreated, pretreated solid and enzymatic residue (5 MPa CO_2, 100 min time and 180 °C pretreatment temperature) were determined by X-ray diffraction using a Bruker D8-ADVANCE (German) with Ni-filtered and Cu radiation (k = 0.15418 nm). The scattering angle (2θ) was from 10 to 60° in steps of 0.04° at time intervals of 0.2 s. The crystalline index (CrI) was determined based on the formula by Segal et al. (1959) as follows.

$$\mathrm{CrI} = [(I_{002} - I_{\mathrm{am}})/I_{002}] \times 100\%$$

in which I_{002} is the scattered intensity at the main peak around 22.5°; where I_{am} is the scattered intensity due to the amorphous portion evaluated as the minimum intensity between the main and secondary (the broad peak at 18.0°) peaks.

2.4.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was recorded from a FT-IR spectrophotometer (Tensor 27, Bruker, Germany). The samples (KBr pellets) for analyses were prepared by mixing 2 mg material powder with 200 mg KBr. Thirty-two scans were taken from 4000 to 400 cm^{-1}.

2.4.4. Scanning Electron Microscopy (SEM) analysis

Scanning electron microscopy (SEM) of the three samples was carried out with a HITACHI S-3700N (Japan) instrument at 10 kV. Each sample was sputter-coated with gold for 180 s prior to the observation. All observations were utilized at 2000× magnification.

2.4.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a TA Q500 instrument (America). Dynamic TG scans were conducted in a temperature ranging from 30 to 700 °C at a heating rate of 10 °C/min. The experiments were carried out under 25 ml/min nitrogen atmosphere. About 5–7 mg samples were used.

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