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Production of xylo-sugars from corncob by oxalic acid-assisted ball milling and microwave-induced hydrothermal treatments

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ABSTRACT

A feasible approach for the production of xylose and xylooligomer from corncob was developed using oxalic acid-assisted ball milling, followed by the microwave-induced hydrothermal treatment. Parameters such as milling time, the amount of oxalic acid, hydrothermal treatment time and temperature were evaluated. Results showed that most of hemicelluloses in the cell wall could be released and degraded into xylose and xylooligomer after ball milling for 60 min in the presence of trace oxalic acid and then treated by the hydrothermal treatment under microwave. The maximum yield of xylo-sugars (xylose and xylooligomer) was 86.10% under the ball milling pretreatment of corncob for 60 min with 15-mM oxalic acid and followed by the hydrothermal treatment at 130 °C for 30 min. Under this optimal treatment condition given, the production of by-products such as acetic acid and furfural was limited.

1. Introduction

As the major source of energy and chemicals, fossil fuels have caused negative effects on the global climate and environmental issues. The use of renewable feedstocks, in particular lignocellulosic materials, is a promising option as the substitute of fossil fuels with economic and environment characteristics (Kamm et al., 2005). Recently, lignocellulosic biomass, such as wood and agricultural residues, has been widely employed to produce chemicals and materials (Li et al., 2015; Wang et al., 2015). Lignocellulosic biomass mainly is composed of cellulose, hemicelluloses and lignin, and each component has specific properties destined for different uses. As the second most abundant polymer in lignocellulose, hemicelluloses have received increased attentions for obtaining diverse products (Zhang et al., 2014). Among agricultural residues, corncob is the important by-product of the corn processing industry. About 25–35% of corncob is xylan-type hemicelluloses, which are rich in xylose (Ruiz et al., 2013). Therefore, corncob can serve as a potential source for the production of pentose by chemical and mechanical processing.

Due to the rigid and compact structure of the plant cell walls, lignocellulosic biomass is recalcitrant to degradation (Zhao et al., 2012). Thus, an effective pretreatment technology is crucial to reduce the recalcitrance of lignocellulosic biomass and separate them into cellulose, hemicelluloses and lignin for the economic use (Huber and Corma, 2007). In the past several decades, different pretreatment technologies have been developed. Among them, the dilute acid pretreatment is regarded as a suitable and conventional technology for the industry. During in this pretreatment process, hemicelluloses can be released from lignocellulosic biomass and be further degraded into xylose and other products (Garlock et al., 2011; Mosier et al., 2005). However, for the utilization of mineral acids in the dilute acid pretreatment, several negative impacts should be concerned, such as byproducts and the equipment corrosion. For this reason, organic acids such as oxalic acids and maleic acids were developed for the direct acid hydrolysis of lignocellulosic materials into sugar products (Kootstra et al., 2009; Lee et al., 2009). Oxalic acid has attractive chemical and practical features, such as controlled stepwise acidity, biodegradability, and convenient handling and storage with limited corrosive behavior (vom Stein et al., 2011). Compared to mineral acids such as sulfuric acid, oxalic acid exhibits two pK_a values, which may impart more efficient hydrolysis of the substrate over a range of temperature and pH values (Lee and Jeffries, 2011). Previous studies showed that

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oxalic acid could hydrolyze β-(1,4)-bonds more selectively than sulfuric acid (Lu and Mosier, 2007). Under mild conditions, oxalic acid can selectively depolymerize the amorphous hemicelluloses regions and effectively avoid the cellulose degradation (Lee et al., 2010). Hence, oxalic acid may be applicable to remove hemicelluloses from lignocellulose biomass.

As a typical physical pretreatment approach, ball milling can increase the accessible surface area and pore size, decrease the crystallinity and the polymerization degrees of cellulose (Lin et al., 2010; Inoue et al., 2008). It can be used to promote the enzymatic hydrolysis or biodegradability of lignocellulosic waste materials (Taherzadeh and Karimi, 2008). Ball milling involves high energy costs. Therefore, it was suggested to use a combination of ball milling with enzymatic hydrolysis or hydrothermal pretreatment to decrease the energy costs (Inoue et al., 2008; Lin et al., 2010).

In the last decade, microwave heating technology is an important and rapid developing technology in green chemistry. The microwave technique can be used under high pressure and temperature conditions and provides fast and uniform heating for chemical transformations (Yemiş and Mazza, 2011). In this study, a tiny amount of saturated oxalic acid solution (10 mM, 15 mM and 20 mM, based on the hydrolysate) was applied in the period of corncob ball milling process, and then microwave-assisted hydrothermal treatment was followed. The main objective of our work was to achieve the hydrolysate containing high xylo-sugars (xylose and xylooligomer) content by the optimization of the reaction conditions. Xylo-sugars in the hydrolysates could be further converted into furfural or xylitol by the catalysis process or biofuel production through C5 sugars fermentation. The solid residues (mainly cellulose and lignin) could be used as the raw materials to produce bioethanol, biomaterials or other chemicals.

2. Experimental and methods

2.1. Materials

Corncob used in this study was harvested from a farm in Shandong province, China. Before the ball milling pretreatment, corncob was grounded into particles with a size of 40–60 mesh and oven-dried at 60 °C to constant weight. $C_2H_2O_4{\cdot}2H_2O$ (≥99.5%, AR), sulfuric acid (98%, AR) and CH_3CN (≥99.9%, HPLC) were purchased from Tianjin Kermel Co., Ltd. (Tianjin, China). The standard reagents (D-xylose, D-glucose, L-arabinose, furfural, etc.) were supplied by Sigma–Aldrich. All reagents were used without any purification.

2.2. Oxalic acid-assisted ball milling pretreatment

A tiny amount of saturated oxalic acid solution (10 mM, 15 mM and 20 mM, based on the hydrolysate) was dripped into corncob (1.0 g), and mixed. Then the mixture was added to a planetary ball mill machine (QM-3SP04, Nanjing NanDa Instrument Plant Co., Ltd., Nanjing, China). The sample was milled at 400 rpm in 40.0-mL zirconia milling-cup with several 10 mm diameter zirconia balls. Milling was carried out for a particular time (with a cycle of 6-min milling and 6-min pausing) at room temperature. The ball milling time refers to the actual milling time, excluding the paused time.

2.3. Microwave-induced hydrothermal treatment

Experiments of microwave-assisted hydrothermal treatment were carried out in a 100 mL closed-vessel PTEF (polytetrafluoroethylene) microwave reactor (GAS-800, Beijing Xianghu Science and Technology Development Reagent Co., Ltd., Beijing, China) at 130, 140, and 150 °C within a range of 0–40 min, respectively. The milled sample was suspended in deionized water with a solid to liquor rate of 1:20 ($g \cdot mL^{-1}$). A microwave irradiation (400 W) was applied to heat the suspension to the target temperature with a heating rate of 10 °C min^{-1}. The heating time was not calculated in the reaction time. The pressure of microwave reactor was controlled under 4 M Pa. After the reaction was over, the reactor was cooled down in an ice bath. The hydrolysates and solid fractions were separated by centrifugal filtration. The solid residue was washed with hot water for several times and dried for the characteristic analysis. All liquid samples were filtered with 0.22 μm syringe filter prior to analysis. All experiments were duplicated under the same conditions and took the average to ensure the reproducibility and accuracy of results.

2.4. Analysis of liquid and solid products

2.4.1. Analysis of liquid products

Sugars (xylose, glucose and arabinose) were measured by a high-performance liquid chromatography (HPLC) equipped with a Waters 1515 pump, an aminex column HPX-87H (BIO-RAD) and Waters 2412 Refractive Index Detector. The mobile phase was 5-mM H_2SO_4 at a flow rate of 0.5 mL/min, and the column oven temperature was maintained at 50 °C. Furfural was determined by HPLC with C18 column (Waters). A solution of acetonitrile/water (15/85, v/v) was used as the mobile phase at a flow rate of 1 mL/min, and the column oven temperature was maintained at 30 °C. In order to measure xylooligomer, the hydrolysates were subjected to quantitative post-hydrolysis (with 4% sulphuric acid at 121 °C for 60 min), and then analyzed by HPLC. Compared with the hydrolysates obtained from microwave-assisted hydrothermal treatment, the xylooligomer concentration was measured by the increase in xylose concentration caused by posthydrolysis (Garrote et al., 2001).

Xylan recovery in treated solid and yields of xylose and xylooligomer were expressed as follows:

$$\text{Xylanrecovery}(\%) = \frac{\text{xylaninpretreatedsolid(g)}}{\text{xylaninuntreatedsolid(g)}} \times 100\% \quad (1)$$

$$\text{Xyloseyield}(\%) = \frac{\text{xyloseinhydrolysate(g)}}{\text{xylaninuntreatedsolid(g)}} \times \frac{132}{150} \times 100\% \quad (2)$$

$$\text{Xylooligomeryield}\,(\%) = \frac{\text{Xylooligomerinhydrolysate}\,(g)}{\text{Xylaninuntreatedsolid}\,(g)} \times 100\% \quad (3)$$

Xylose is converted to xylan equivalent by multiplying the ratio of the molecular weight of xylos to xylan (132/150).

2.4.2. Analysis of solid products

Carbohydrates and lignin in corncob before and after treated were determined by National Renewable Energy Laboratory's (NREL) Laboratory Analytical Procedures (Sluiter et al., 2007). The BET surface area of samples was measured by N_2 adsorption using a Micromeritics ASAP 2010 instrument at 77 K and calculated from the adsorption data in the relative pressure ranging from 0.05 to 0.30. X-ray diffraction (XRD) patterns of samples were tested on a Bruker diffractometer with Cu Kα radiation. The tube voltage was 40 kV and the current was 40 mA. The selected 2θ range was 10–40°, scanning at a step of 0.02°. According to the method of Segal et al. (1959), the crystallinity index (CrI) was calculated by:

$$\text{Cr}I = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100 \quad (4)$$

where I_{002} is the peak intensity on the 002 lattice plane, and I_{am} is the peak intensity of amorphous zone diffraction intensity of $2\theta = 20.9°$.

The ^{13}C NMR spectra of samples were obtained on a Bruker BioSpin GmbH solid NMR spectrometer operating at room temperature using a combination of cross-polarization (CP). The