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An efficient pretreatment for the selectively hydrothermal conversion of corncob into furfural: The combined mixed ball milling and ultrasonic pretreatments

Huiling Li[a,b], Xiaohui Wang[b], Changyu Liu[c], Junli Ren[b,*], Xianhai Zhao[a], Runcang Sun[b], Aimin Wu[a]

[a] Guangdong Key Laboratory for Innovative Development and Utilization of Forest Plant Germplasm, State Key Laboratory for Conservation and Utilization of Subtropical Agro-bioresources, South China Agricultural University, Guangzhou 510642, China
[b] State Key Laboratory of Pulp and Paper Engineering, Plant Micro/nano Fiber Research Center, School of Light Industry and Engineering, South China University of Technology, Guangzhou 510640, China
[c] College of Mathematics and Informatics, South China Agricultural University, Guangzhou 510642, China

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ABSTRACT

A mixed ball milling of corncob and the solid acid catalyst (SO_4^{2-}/SiO_2-Al_2O_3/La^{3+}) followed by the ultrasonic pretreatment has been developed for the selectively catalytic hydrothermal conversion of corncob into furfural. Results showed that the combined mixed ball milling and ultrasonic pretreatment (MU) was an efficient mechanocatalytical approach to destroy the complex structure of corncob, and most of the hemicelluloses could be released from the corncob cell wall during the subsequent hydrothermal reaction. In comparison with the ultrasonic pretreatment, ball milling played a more important role in the deconstruction of corncob and the depolymerization of polysaccharides. The existence of the solid acid catalysts (SO_4^{2-}/SiO_2-Al_2O_3/La^{3+}) during the ball milling and ultrasonic pretreatments had the significant influences on the successful conversion of corncob into furfural due to the solid–solid reaction of the solid acids and the dewaxed corncob during the pretreatment process, which was in favor of the furfural production. A highest furfural yield of 197.76 mg/g could be obtained at 190 °C for 30 min from the MU-pretreated corncob.

1. Introduction

Lignocellulosic biomass is considered as a promising material for the manufacture of energy products, fuels and chemicals to solve the problems derived from the progressive depletion of fossil fuel reserves due to its abundant, inexpensive, eco-friendly and renewable characteristics. Corncob, which is rich in hemicelluloses, possesses a great potential for the production of versatile chemicals, such as furfural (Oh et al., 2013).

The conversion of corncob into furfural is a sequential two-step reaction: the hydrolysis of corncob hemicelluloses into water-soluble pentose (mainly xylose), and the dehydration of pentose into furfural. In comparison with the dehydration process, the hydrolysis of corncob hemicelluloses is the rate-controlling step (Schneider et al., 2016; Yabushita et al., 2014). However, it is hampered by the complexity of the cell wall matrix due to the crystalline domains of cellulose, the structural heterogeneity and the complex cross-linking of cell-wall constituents (French, 2014). Therefore, it is necessary to destroy the recalcitrant nature of corncob firstly by an effective pretreatment method (Dutta et al., 2012; Li et al., 2014b).

A number of pretreatment approaches have been used to improve the accessibility of cellulose and hemicelluloses (Evangelina Vallejos et al., 2015; Ruiz et al., 2013). Among them, dilute acid pretreatment has been intensely investigated as a promising technique for the industry (Garlock et al., 2011). However, several negative impacts such as equipment corrosion and environmental pollution should be concerned. Ball milling is considered as one of the oldest and simplest mechanical techniques to break down the complex structure of lignocellulosic biomass. Nevertheless, severe pretreatment conditions were required to achieve the higher product yield. Therefore, the development of effective and environmental friendly pretreatment strategies is of great sig-

* Corresponding author.
E-mail address: renjunli@scut.edu.cn (J. Ren).

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nificance to the sustainable society (Cai et al., 2014; Romani et al., 2010; Taylor et al., 2015).

The mixed ball milling of biomass feedstock and solid acid catalysts is a desirable approach for the deconstruction of lignocellulosic materials (Schneider et al., 2016; Yabushita et al., 2014). The utilization of solid acids instead of mineral acids can overcome the disadvantages resulting from the dilute acid pretreatment (Li et al., 2015; Ordomsky et al., 2013; Wang et al., 2015). The presence of solid acids during the ball milling process can greatly promote the structure damage of feedstock to yield water-soluble oligosaccharides under solvent-free conditions (Canilha et al., 2012; Kleine et al., 2013; Tabasso et al., 2015). In addition, ultrasonic pretreatment is another commonly used method for the cleavage of glycosidic linkages in polysaccharides (Bussemaker et al., 2013; Sindhu et al., 2013; Tabasso et al., 2015). Therefore, the combined mixed ball milling and ultrasonic pretreatment (MU) can be a highly efficient pretreatment technology in the biorefinery (Schneider et al., 2016; Yabushita et al., 2014). In the present study, a mixed ball milling of corncob and the solid acid catalyst (SO_4^{2-}/SiO_2-Al_2O_3/La^{3+}) followed by the ultrasonic pretreatment was developed for the selectively catalytic hydrothermal conversion of corncob into furfural. The aim of this work was to achieve a high furfural yield from corncob which was pretreated by an efficient and environmental friendly pretreatment approach.

2. Methods

2.1. Materials

Corncob was collected from a farm in Shandong Province (China) and ground into particles with a size of 40–80 mesh by a pulverizer. The obtained particles were dewaxed with a 2:1 (v/v) toluene/ethanol mixture in a soxhlet extractor for 6 h, and then washed with DI water and oven-dried at 55 °C to constant weight. The dewaxing process could reduce the resistance of the recalcitrant nature and benefited the seperation of cell wall constituents in the following experiments. The composition of the dry dewaxed corncob was measured by the established National Renewable Energy Laboratory procedure (NREL/TP-510-42618) with a mass fraction of 37.09% glucose, 31.39% xylose, 2.28% arabinose and 14.47% lignin. Elemental analysis revealed that the dry dewaxed corncob contained 45.35 wt% of C, 48.18 wt% of O, 6.31 wt% of H and 0.16 wt% of N.

Na_2SiO_3 (AR, ≥99%), NH_4OH (AR, 25%–28%), $AlCl_3{\cdot}6H_2O$ (AR, ≥97%) and $La(NO_3)_3{\cdot}6H_2O$ (AR, ≥99%) were purchased from Kermel Co. Ltd. (Tianjin, China). Standard reagents of furfural (≥99.0%, HPLC), glucose (≥99.0%, HPLC), xylose (≥99.0%, HPLC), arabinose (≥98.0%, HPLC), formic acid (50.0%, HPLC) and acetic acid (≥99.0%, HPLC) were purchased from Sigma-Aldrich. Xylobiose (X2, ≥95.0%, HPLC) and xylotriose (X3, ≥95.0%, HPLC) were purchased from WAKO (Japan). Xylotetraose (X4, ≥95.0%, HPLC), xylopentaose (X5, ≥90.0%, HPLC) and xylohexaose (X6, ≥90.0%, HPLC) were obtained from Megazyme (Ireland). All reagents were used without any purification.

2.2. Catalyst preparation

Solid acid catalysts SO_4^{2-}/SiO_2-Al_2O_3/La^{3+} (SSAL) were prepared by the co-precipitation and impregnation methods according to our previous studies (Li et al., 2014c, 2014d). Na_2SiO_3 (50 g) and $AlCl_3{\cdot}6H_2O$ (42.50 g) were dissolved in ultrapure water (500 mL), followed by the addition of $La(NO_3)_3{\cdot}6H_2O$ (2.01 g). The pH of the solution was adjusted to the range of 9–10 with concentrated ammonia. The washed powder was dried at 110 °C for 24 h, and then impregnated with 1.0-M H_2SO_4 for 6 h at the proportion of 15 mL/g. The solid products were dried at 110 °C for 12 h and calcined at 450 °C for 4 h to get the target catalyst.

2.3. The pretreatment and conversion of corncob

Mechanical pretreatment referred to the pretreatments without solid acid catalysts, such as ball milling pretreatment, ultrasonic pretreatment and the combined ball milling and ultrasonic pretreatments. Mechanocatalytical pretreatment indicated to the mechanical pretreatment with solid acids, such as mixed ball milling of corncob and solid acids, and the combined mixed ball milling and ultrasonic pretreatments. The mechanocatalytical pretreatment of corncob was conducted in a planetary ball mill (QM-3SP04, Nanjing Nanda Instrument Plant, China) and an ultrasonic cleaners (KQ-300DE, Kunshan Ultrasonic Instrument Co. Ltd., China). SSAL was used as the solid acid catalyst. In briefly, a mixture of the dewaxed corncob (2.0 g) and solid acid catalysts (0.02 g) was milled for 6 h at 400 rpm. The milled mixtures were added into the ultrapure water (40 mL), and then ultrasound for 30 min. Experiments for the catalytic hydrothermal conversion of the pretreated corncob into furfural were carried out in a 100-mL high-pressure batch reactor (SLM-100, Shenlang Co. Ltd., Beijing, China) equipped with a stainless steel pressure vessel (reactor), electric furnace, temperature controller, stirring equipment, pressure meter and air valve. The reactor was heated up to the desired temperature within a certain time period with a magnetic agitator operating at 600 rpm. Zero time was recorded when the temperature reached to the setting point. After the reaction, the reactor was cooled quickly to room temperature with flowing water. Products were filtrated to get the liquid and solid fractions. Each experiment was repeated twice under the same conditions to ensure the reproducibility of the results. Liquid products were denoted as A-B-C, where A is the capital letter of the pretreatment method (U for ultrasonic, B for ball milling, M for mixed ball milling), B is the hydrothermal reaction temperature (°C), and C refers to the hydrothermal reaction time (min).

2.4. Product analysis

2.4.1. Liquid product analysis

Furfural, formic acid, acetic acid, glucose, xylose and arabinose were detected by the high performance liquid chromatography (HPLC, Waters 2414, America) coupled with a refractive index detector (RID) and a Bio-rad Aminex HPX-87H (300 × 7.8 mm) column. 5 mM of H_2SO_4 was employed as the eluent with a flow rate of 0.5 mL/min at 50 °C. Xylooligosaccharides (X2, X3, X4, X5 and X6) in the hydrolysates were measured by HPLC (Waters 2414, America) equipped with a Bio-rad Aminex HPX-42A (300 × 7.8 mm) column and a refractive index detector. DI water was employed as the mobile phase with a flow rate of 0.3 mL/min at 70 °C. Calibration curves were established for the quantitative calculation. The product yields were defined as milligram from per gram (mg/g) of dry dewaxed corncob.

2.4.2. Solid product analysis

The composition of the solid residues was detected by the high-performance anion-exchange chromatography (HPAEC, Dionex ICS-3000, Sunnyvale, America) coupled with a Carbopac™ PA-20 column (4 × 250 mm, Dionex, America). Detailed procedure was illustrated in the Ref. (Sluiter et al., 2007). Briefly, solid residues (300 mg) was hydrolyzed by 72% H_2SO_4 (3.0 mL) at 30 °C for 1 h. The hydrolysate was diluted with water (84 mL), followed by autoclaving at 121 °C for 1 h. Experiments were duplicated to decrease the errors. Calibration curves were performed with a standard solution of glucose, xylose, arabinose, galactose and glucuronic acid, respectively.