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Quantitative approaches for illustrating correlations among the mechanical fragmentation scales, crystallinity and enzymatic hydrolysis glucose yield of rice straw

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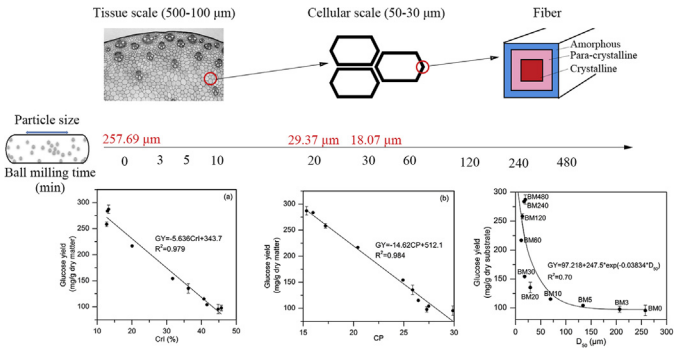
HIGHLIGHTS

- Increase of glucose yield is limited with reduction of particle size at tissue scale.
- Crystallinity significantly changed with particle size decreased to cellar scale.
- Significant correlations among particle size, crystalline property and glucose yield.
- Quantitative analysis for particle size, crystalline property and glucose yield.

GRAPHICAL ABSTRACT



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ABSTRACT

Mechanical fragmentation is an important pretreatment in the biomass biotransformation process. Mechanical fragmentation at the tissue scale significantly reduced the particle size of rice straw but did not significantly change its crystalline properties; the increase in the glucose yield was limited from 28.75% (95.55 mg/g substrate) to 35.29% (115.28 mg/g substrate). Mechanical fragmentation at the cellular scale destroyed the cell wall structure and reduced its crystalline properties. Thus, the glucose yield also showed a significant increase from 35.29% (115.28 mg/g substrate) to 81.71% (287.07 mg/g of substrate). The quantitative equations among the particle size, crystalline properties and glucose yield (mg/g substrate) are as follows: CrI = 44.14 × [1−exp(−0.03658 × D_{50})] and CP = (8.403 × logD_{50}−24.18 36)/(1−4.225/D_{50}^0.5); GY = −5.636CrI + 343.7 and GY = −14.62CP + 512.1; and GY = 97.218 + 247.5 × exp(−0.03824 × D_{50}). The quantitative correlations among the mechanical fragmentation scales and crystalline properties can determine the effect and mechanism of mechanical fragmentation on biomass and can further promote the construction of a cost-competitive biotransformation process for biomass.

1. Introduction

The lack of fossil fuels and the concern over global climate change have led to a demand for alternative energy (Himmel et al., 2007). The biotransformation of lignocellulosic biomass to fuels has attracted increased attention due to its many advantages, such as high annual yield, environmental friendliness and low cost

Abbreviations: D_{50}, median particle size; CrI, cellulose crystallinity index; GY, glucose yield; XRD, X-ray diffraction analysis.

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(Deng et al., 2016; Hideno et al., 2009; Ribeiro et al., 2015; Xu et al., 2012b).

Lignocellulosic biomass is composed of macromolecular polymers, primarily consisting of cellulose, hemicellulose and lignin (Hewetson et al., 2016). Cellulose is composed of D-glucose linked by β-1,4 glycosidic bonds that contain crystalline and amorphous areas. Hemicellulose consists of different polymers, such as xylose and hexoses. Hemicellulose also serves as the connection between lignin and cellulose. Lignin is an amorphous heteropolymer that contains three different linkages of p-coumaryl, coniferyl and sinapyl alcohol (Barakat et al., 2015; Hideno et al., 2009). The complex structure formed by cellulose, hemicellulose and lignin has restricted the conversion efficiency from lignocellulosic biomass to biofuels (Ding et al., 2012). Thus, the pretreatment of lignocellulosic biomass has become an essential procedure. However, acid pretreatment, alkali pretreatment and other chemical pretreatments often change the composition of lignocellulosic biomass and produce environmentally harmful substances (Barakat and Rouau, 2014; Castro et al., 2011; Sun and Cheng, 2005; Xu et al., 2012a; Zhang et al., 2016).

Mechanical fragmentation pretreatment can reduce the particle size, destroy the supramolecular structures of cellulose, hemicellulose and lignin and overcome the internal binding of the lignocellulosic biomass. In addition, mechanical fragmentation can be used to pretreat biomass on a large scale without any effluent production, in contrast to chemical pretreatment (Barakat et al., 2013; da Silva et al., 2010; Licari et al., 2016; Silva et al., 2012). Previous studies have concluded that different scales of mechanical pretreatment have different effects on the physicochemical properties and enzymatic hydrolysis of lignocellulosic biomass (Barakat et al., 2015; Ji et al., 2016; Yang et al., 2014). These studies about the effects of sole mechanical fragmentation pretreatment on lignocellulosic biomass have only provided a qualitative description. Despite quantitative correlations of particle size or cellulose crystallinity and enzymatic hydrolysis has been discussed in some studies (Agarwal et al., 2012; Kim and Holtzapple, 2006), these research combined mechanical size reduction pretreatment with thermo/chemical pretreatment (such as delignification process) which can change lignocellulosic biomass in multiaspect, such as cellulose crystallinity and chemical composition, leading to the simple models in these studies lack of accuracy. Meanwhile, the quantitative correlation analysis based on different mechanical fragmentation scales have been rarely reported. Quantitative approaches for illustrating correlations among the particle size, crystallinity and enzymatic hydrolysis based on sole mechanical size reduction pretreatment can determine the impact and mechanism of mechanical fragmentation on biomass and can further promote the construction of a cost-competitive bioconversion process for biomass.

Rice straw is a major lignocellulosic biomass, accounting for 731 Tg/yr worldwide (average for 1997–2001), which is mostly generated in Asia (Park et al., 2014). Therefore, rice straw were determined as the preferential lignocellulosic biomass for fuel ethanol production in Asia. In this study, 10 rice straw samples with different particle sizes were characterized using multiple approaches, and then, the samples hydrolyzed by cellulase to quantify the correlations among mechanical fragmentation scale, crystalline properties and enzymatic hydrolysis glucose yield.

2. Materials and methods

2.1. Raw materials

Rice straw was collected from Hubei Province (China) in 2014. The moisture of rice straw is 5.84%. The carbohydrates and lignin of rice straw were determined using the NREL/TP-50-42618 method (Sluiter et al., 2008). The chemical composition of rice straw (on a dry weight basis) was 37.65% glucan, 19.10% xylan, 3.69% arabinan, 17.34% lignin, 13.38% ash and 8.84% others.

2.2. Preparation of rice straw samples with different particle sizes

Raw rice straw was first cut into 3- to 5-cm-long pieces using a hay cutter and then coarsely milled using an RT-34 milling machine (Hongquan Pharmaceutical Machinery Ltd., Hong Kong, China) with the final sample passing through a 1.00-mm screen, denoted as BM0.

An ultrafine vibration ball mill CJM-SY-B (Qinghuangdao Taiji Ring Nano Ltd., Heibei, China) was used to produce different particle size samples by mixing BM0 and ZrO_2 balls (6–10 mm diameter) in a volume ratio of 1:2 for 3, 5, 10, 20, 30, 60, 120, 240 and 480 min. The samples obtained by different milling times are denoted as BM3, BM5, BM10, BM20, BM30, BM60, BM120, BM240 and BM480, respectively. A cooling circulating water system was used to control the milling process below 20 °C.

2.3. Particle size distribution and SEM of rice straw

A laser diffraction particle analyzer, the Mastersizer3000 (Malvern Instruments Ltd., United Kingdom), was used to measure the particle size distribution of rice straw. Rice straw powders expand when dispersed in water, leading to larger particles; therefore, rice straw powders were dispersed in air in this study.

D_{10}, D_{50} (median particle size), and D_{90} were determined using particle size distribution curves, which represent the 10th, 50th and 90th percentiles of the total volume, respectively. The span was calculated as $(D_{90}-D_{10})/D_{50}$, which was a representative parameter to evaluate the overall heterogeneity of the particle size of rice straw powders (Silva et al., 2012). Each sample was measured in duplicate.

Rice straw samples were dried at 105 °C for 4 h and then sputtered with Platinum for 2 min using an E-1010 Iron Sputtering system (Hitachi, Japan). SEM images of rice straw samples were characterized with an S-3400N scanning electron microscope (Hitachi, Japan) at 5.00 kV.

2.4. Crystalline properties of rice straw

2.4.1. X-ray diffraction analysis (XRD)

Rice straw powder was compacted and then measured using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu Kα radiation at 40 kV and 40 mA. The scanning range of 2θ was from 5° to 40° at a rate of 2°/min in 0.02° increments. The cellulose crystallinity index can be determined from XRD curves using Eq. (1) according to the method in a previous study (Segal et al., 1959). Each sample was measured in duplicate.

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

I_{002} is the maximum intensity of the 002 peak at approximately $2\theta = 22.5°$; I_{am} is the amorphous intensity at approximately $2\theta = 18°$.

2.4.2. Solid-state CP/MAS ^{13}C NMR

The crystalline phase amount could be measured using solid-state ^{13}C NMR (Vaidya et al., 2016). Solid-state CP/MAS ^{13}C NMR measurements were recorded at 100 MHz on an Avance DPX400 spectrometer with a 4-mm CP/MAS probe (Bruker, Germany). Data were collected with a 3-ms cross-polarization contact time and a 30-ms acquisition time with a 2-s repeat interval. The total acquisition time was 56 min, and each sample was measured in dupli-