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Surface characterization of corn stalk superfine powder studied by FTIR and XRD

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ABSTRACT

Corn stalk superfine powder was ground by a special designed machine. The physical–chemical properties of corn stalk powders with particle sizes of >300, 300-150, 150-74, 74-37 and <15 μm were investigated. The particle size distributions of the powders were: d_{90} = 362, 147, 74, 40 and 12 μm. The size of corn stalk powders was smaller, the surface area (from 1.188 to 2.432 m^2/g) and bulk density (from 0.103 to 0.1145 g/ml) were greater. Light microscopy (LM) and scanning electron microscopy (SEM) observations revealed the shape and surface morphology of five types of corn stalk powders. FTIR analysis showed that some position of absorbing peaks was shifted as the powder particle size decreased. X-ray diffraction analyses for corn stalk coarse and superfine powders revealed no evident changes in X-ray pattern. However, the crystallinity, intensity of crystal peaks and crystal size of corn stalk powders with particle sizes from >300 to 300-150 μm dropped, then, as the size of the powders decreased, the crystallinity, intensity of crystal peaks and crystal size increased in some degree.

1. Introduction

Cellulosic biomass is a kind of valuable and abundant renewable biomass resource on earth. Corn stalk is considered as the most abundant biomass resource among the crop-based residues, such as wheat, barley, rice, oats, etc. Generally, the major carbohydrate polymer making up the primary cell walls of corn stalk is lignocellulosics. Pretreatment of lignocellulosics is important for its efficient conversion into low-cost sugar, a promising renewable feedstock for biological conversion to fuels and chemicals, feedstuff and other useful products. The best pretreatment options are those combining both physical and chemical modification with the minimum damage and loss of value via side reactions, and then result in the best substrate for hydrolysis with the least material lost [1,2].Constantly, any biomass utilization process requires the biomass in fine particle size and a freely flowable form, in order to improve the processes efficiently and reduce energy consumption and environmental costs. The surface of biomass superfine powder has the following outstanding characteristics, such as surface effect, mini-size effect, quantum effect and macroquantum channel effect, optical property, magnetic property, mechanical property, chemical and catalytic properties. The mechanical size reduction also increases bulk density, flowability, new surface area, pore size, and hydrolysis reaction rates [3]. It was found that some biomaterials were changed in structure and chemical activation after superfine grinding. Therefore, the handled biomass needs to be at a reduced particle size.

The superfine grinding technology is widely applied in ceramics, electrics materials, chemical and papermaking fields. Nowadays superfine grinding technology has also been applied in biotechnology and biomass materials, but only rarely. Milling of some fiber materials has been reported in the literature [4,5]. It suggested that the superfine grinding was a good way to fractionate bio-materials into easily bio-converted and hydrolyzed part. While very limited information is available on the effect of the superfine grinding on surface characterization of corn stalk powder.

The surface chemistry of corn stalk powder also changes during superfine grinding. Fourier transform infrared (FTIR) spectroscopy is one tool that can be used to determine changes in chemistry at the corn stalk surface during superfine grinding [6]. Peaks that appear on the spectra can be assigned to functional groups present at the corn stalk surface. X-ray diffraction (XRD) has also been found to characterize the crystallinity of corn stalk powder [7].

In this study, corn stalk powders with different size were manufactured. The objective of the work was to gain insight into how the surface of corn stalk powder changes during superfine grinding. To accomplish this, we determined surface characteristics of corn stalk powder before and after superfine grinding. Scanning electron micrographs (SEM), FTIR and XRD in conjunction with physical characterization measurements are used to examine. By comparison with corn stalk coarse particles, the corn stalk superfine powder has different structural and physical–mechanical properties.

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2. Materials and methods

2.1. Materials

Corn stalk was taken from the local farmer in Beijing, China. The corn stalks were cut into pieces approximately 3 cm in length for further use. The corn stalk pieces were milled to pass though 6 mm screens. Then the crushing corn stalks were placed in a mechanical drier at 50 °C for 6 h. The water content of crushing corn stalks reached less than 6%. The water content was determined by using AACC method No. 44-19 [8]. The dried corn stalk was milled coarse particles by a disc-mill, which were screened through different sized sieves to separate granulates ($d < 1$ mm) (>300 and 300-150 μm); the superfine powders with the size range of 150-74, 74-37 and <15 μm were obtained in an HMB-701 type micronizer, The planetary rubbing mill (power 0.75 kW) was a vertical batch type mill. Three rubbing rings were vertically equipped with pot holders on the turntable. The inner volume and diameter of the cylindrical shape pot were 300 ml and 400 mm, respectively. The pot was made of wear-resistant zirconia, and the rubbing rings with diameter of 300 mm were also made of the same material. The sample was mainly ground with pressure, collision and abrasion between rubbing rings and inner bottom of pot. The revolution speed of turntable was unfixed at 2500–2800 rpm/min.

2.2. Particle size distribution

The particle size distribution of corn stalk particles was determined using laser diffraction according to AFNOR standard NF X11-666 [9]. It was performed with a Mastersizer IP granulometer (Instruments 2000, UK). Diffraction pattern analysis was carried out in air on a stream of dry powder. Determinations were repeated three times. Three measurements were carried out for each corn stalk powder. From the particle size distribution curves obtained, values of $d(10)$, $d(25)$, $d(50)$, $d(75)$ and $d(90)$ representing the size could be determined. $d(10)$, $d(25)$, $d(50)$, $d(75)$ and $d(90)$ indicate that 10%, 25%, 50%, 75% and 90% (by volume and number) of the particles in the sample were smaller. $d(0.5)$ represents the median of the respective distribution. $d(4,3)$ indicates the volume mean diameter of measured particles; $d(3,2)$ indicates the mean surface area of measured particles. The size of particles was reported in the terms of particle diameter ($d(0.9)$ in μm).

2.3. Determination of surface properties

The specific surface area (m^2/g) of the corn stalk particles was determined by measuring the adsorption of nitrogen at 77 K according to the Brunauer–Emmett–Teller (BET) principle [10] and using ASAP 2010 instrument (Micromeritics instrument Co., USA). Moreover, the volume and size of pores of precipitated materials were examined. The measurements were repeated four times after degassing of each sample for 24 h at 40 °C. The reproducibility measured on a reference sample of alumina (alumina CRM 169) on different days was 0.106 ± 0.009 m^2/g, i.e. a variation coefficient of Ca. 8.5%.

2.4. Bulk density

The bulk density (g/ml) was the density including pores and interparticle voids. Five types of corn stalk powders were filled in a 10 ml volumetric flask (W_1) up to the mark and were weighed (W_2) separately. The bulk density of the corn stalk powders was calculated [11] as follows:

$$d_0 = \frac{W_2 - W_1}{10} \quad (1)$$

where W_2 was the total weight of the corn stalk powder and flask, and W_1 was the weight of the flask only. The experiments were repeated five times and the measurement of each sample was repeated three times.

2.5. Scanning electron microscope (SEM)

Morphological characterization of corn stalk particles was performed on images acquired using a scanning electron microscope (SEM), Quanta 200FEG-SEM (FEI Co. Netherlands) at 150 KV accelerated voltage and 10–15 mm working distance. The samples were coated with platinum of 10 nm thicknesses to make the samples conductive.

2.6. Optical microscopy

The shape of the particles was observed using an Olympus SZX-12 optical microscope. A Sony video camera CCD-IRIS/RGB was used to capture the images. The samples were dispersed in methanol, and the micrographs were taken every 10 s to observe the possible effect of oil leaching [12].

2.7. FTIR analysis

The corn stalk powder samples were prepared with potassium bromide (KBr) pellet method [6]. Infrared spectra were measured with a PekinElmer Model GX Fourier transform infrared spectrophotometer (DTGS) at 20 °C and a diamond cell (Golden Gate) and triangular apodization function. For each spectrum 256 interferograms were collected with a resolution of 4 cm^{-1} with 32 scans and a 2 cm^{-1} interval from the 4000 to 400 cm^{-1} region. Five replicated spectra were collected for every sample pressed on the ATR crystal. The background spectrum was obtained against the air.

2.8. X-ray diffraction analysis

Wide-angle X-ray diffraction (WAXD) data were obtained at 20 °C using a Siemens D8 diffractometer equipped with D/MAX-2550VB + 18k. The sample was dispersed onto a stub and placed within the chamber of a Analytical X-Ray B. V. powder X-ray diffractometer (wavelength = 1.54 Å, Cu Kα radiation). Generator intensity was 40 Kv. Generator current was 30 mA. The sample was then scanned from $2\theta = 5$–$50°$ in step of 0.05°. The resultant graphs were printed out on the Roigink graph plotting package and the amorphous background areas were determined by weighing. The degree of crystallinity was then taken as the ratio of the weight of the crystal peaks to the whole area that was crystal peaks plus background [7]. The process was repeated five times for each of the materials.

2.9. Statistical analysis

Analyses of variance using the general linear models were conducted and averaged and reported along with the standard deviation (±S.D.). The differences in mean were calculated using the Duncan's multiple-range tests for means with 95% confidence limit ($p \leq 0.05$). Statistical analysis of the data was done using the SAS software (Version 8.1, SAS Institute Inc. Cary, NC, USA, 2001).

3. Results and discussion

3.1. Particle size distribution (PSD)

The corresponding $d(0.1)$, $d(0.25)$, $d(0.5)$, $d(0.75)$, $d(0.9)$, $d_{(4,3)}$, $d_{(3,2)}$ of the samples are given in Table 1. As fragments decrease in size, fracture resistance as well as tendency to aggregate increase, and particle fineness approaches a limit [13]. Due to