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Mechanochemical effects of micronization on enzymatic hydrolysis of corn flour

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Abstract

Corn flour samples with different particle size were prepared by ball milling, and then liquefaction and saccharification of the corn flour samples were carried out by using commercially available α-amylase and glucoamylase, respectively. Mechanochemical effects of micronization on the enzymatic hydrolysis were studied for developing a new technology of low-temperature enzymatic hydrolysis of corn flour.

The commercial corn flour of 273.6 μm could be micronized to 17.5, 15.4, 14.6, 13.3 and 9.8 μm in median diameter by wet-milling for 20 min, 1, 2, 3 and 5 h, respectively. Microscopic observation and X-ray diffractometry revealed the starch crystal structure of corn flour could be destroyed by wet-milling for more than 3 h. All the wet-milled corn flours could be liquefied at 30 °C. The liquefaction rate of corn flour increased with increasing wet-milling time. The glucose yield was 46.8% for the 20 min milled corn flour. It was increased to 83.7% by wet-milling for more than 3 h. The increase of glucose yield corresponded with the destruction of starch crystal structure and the decrease of gelatinization temperature.

Our experimental results indicated that wet-milling had mechanochemical effects, which resulted in a remarkable increase of glucose yield in low-temperature enzymatic hydrolysis of corn flour.

Keywords: Corn; Enzymatic hydrolysis; Micronization; Mechanochemical effect; Biorefine

1. Introduction

Biomass is considered as one of the key renewable resources that possess significant economic potentials and have various social and environmental benefits (Demirbas, 2001; Hall, 1997). Research efforts have been focused on the development of a cost effective technology for commercial production of liquid fuel and chemicals such as ethanol, lactic acid and succinic acid from renewable resources. Corn is a main feedstock in the bio-chemical industry. It is estimated that the energy content of bio-ethanol derived from corn grain is higher than the energy content of ethanol (Shapouri, Duffield, & Wang, 2002).

Hydrolysis is an essential process in the bio-chemical industry using corn flour as raw material. The role of hydrolysis is to convert the starch in corn flour to fermentable sugars. A two-step enzymatic hydrolysis of corn flour includes a liquefaction step and a saccharification step. Corn flour, the ground endosperm, usually contains 75–87% starch and 6–8% protein. In native corn flour, starch granules are surrounded by a continuous phase of protein (Chanvrier, Colonna, Valle, & Lourdin, 2005), which protects the starch granules from the attack of enzymes. Therefore, in order to promoting the hydrolysis of corn starch, it is necessary to destroy the protein network by cooking at a high temperature. The cooking process, however, requires 30–40% of the total energy consumption in the bio-ethanol production, and produces non-fermentable impurities. A number of studies have been carried out to select thermostable and effective enzymes for hydrolysis at a relatively low temperature. However, reports on the development

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of hydrolysis process are rare (Ma, Shi, & Zhang, 2005; Mojovic, Nikolic, Rakin, & Vukasinovic, 2006).

In a previous work, the authors compared the liquefaction rate, the glucose yield in a two-step enzymatic hydrolysis of commercially available and micronized corn flour samples. We found that the activation energy and reaction rate in the liquefaction was decreased, and the glucose yield was increased by micronizing of corn flour (Miao, Wu, Jiang, & Yang, 2007). However, the mechanism of the enzymatic hydrolysis of micronized corn flour was not clarified. The objectives of the present work were, (1) to investigate mechanochemical effects of micronization on the enzymatic hydrolysis of corn flour, and (2) to determine the optimum conditions for micronizing of corn flour.

2. Materials and methods

2.1. Corn flour samples

Commercially available corn flour (Anhui Yanzhifang Food Co., China) was obtained from a supermarket. It had a median diameter of 273.6 μm, and contained 10.5% water, 77.8% starch, 5.2% protein, 4.1% fat and 0.7% ash.

The commercial corn flour was dry-milled for 5 h and wet-milled for 20 min, 1, 2, 3 and 5 h respectively, by a planet-type ball mill (XQM-4 L, Nanjing Kexi Institute of Experimental Instruments, China) with a rotate speed of 500 rpm. In the wet-milling, the weight ratio of corn flour to water was 1:3. The particle size distribution of corn flour samples was measured with a particle size analyzer (2000, Malvern, UK). The 5 h dry-milled corn flour had a median diameter of 28.9 μm, and the 20 min, 1, 2, 3 and 5 h wet-milled corn flours had a median diameter of 17.5, 15.4, 14.6, 13.3, 9.8 μm, respectively. Fig. 1 shows the particle size distribution of commercial, 5 h dry-milled and 3 h wet-milled corn flours.

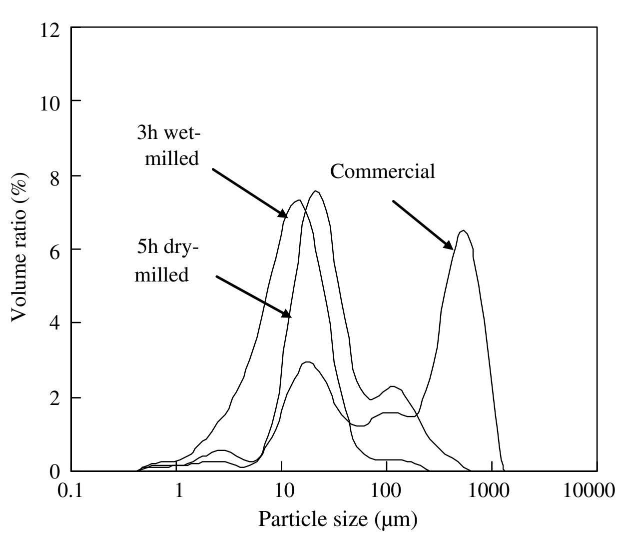

Fig. 1. Particle size distribution of commercial, 5 h dry-milled and 3 h wet-milled corn flours.

2.2. Measurement of gelatinization temperature

A microscope equipped with a heating table (XP-203, Nanjing Donglilai Optics Co., China) was used to observe the granule shape and Maltan cross of the corn flours, under general and polarized light condition, respectively. Suspension of each corn flour was prepared with deionized water. A drop of the suspension was sandwiched by two flat glass slides, and heated by the heating table at a rate of 2.6 °C/min. The clearance between the two flat glass slides was sealed up with edible salad oil to prevent the suspension from evaporation. The temperature at which 2% of the particles with Maltan cross disappeared was defined as initial gelatinization temperature, and the temperature at which 98% disappeared was defined as final gelatinization temperature (Liu, 2003; Xiang, Tian, & Li, 2006). Images of granule shape and Maltan cross were recorded by a color CCD camera (TK-C921EC, Victor Company of Japan Limited) and a personal computer (M4600, Lenovo).

2.3. X-ray diffractometry

The X-ray diffraction pattern of a corn flour sample also reveals the presence and characteristics of the crystal structure of its starch granules (Wang, Yu, Gao, et al., 2007). X-ray diffractometry of the commercial, 5 h dry-milled and 3 h wet-milled corn flours were performed by an X-ray diffractometer (ARL X'TRA, Thermo Electron Corporation, USA). The 3 h wet-milled corn flour was air-dried under the room condition before the analysis. Each corn flour sample was packed tightly in a square plastic cell (20 × 20 mm). The samples were exposed to the X-ray beam from an X-ray generator running at 45 kV and 35 mA. The scanning regions of the diffraction angle 2θ were 5–80°.

2.4. Enzymatic hydrolysis

A two-step enzymatic hydrolysis method including liquefaction and saccharification was applied to the wet-milled corn flours.

In the liquefaction step, a wet-milled corn flour sample equivalent to 60 g dry matter was mixed with 540 ml deionized water in a 1000 ml three-meatus flask. The pH of the mixture was adjusted to 6.0–6.5 by 5% H_2SO_4 solution and 1% NaOH solution. A commercially available α-amylase (Wuxi Saide Bio-technology Co.), which had an optimum temperature of 70 °C and pH of 6.0–6.5, was added to the mixture at a ratio of 10 U/g. The liquefaction was performed at 30 °C on a thermostated water bath with an electric motor-driven stirrer. Reducing sugar content of the mixture was analyzed with the DNS method (Miller, 1959; Mojovic et al., 2006; Yu & Zhang, 1991) and expressed by dextrose equivalent: