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Effect of defatting on acid hydrolysis rate of maize starch with different amylose contents

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ABSTRACT

The effect of defatting on the physiochemical properties and the acid hydrolysis rate of maize starch with different amylose contents was evaluated in this study. The increase in the number of pores and the stripping of starch surface layers were observed after defatting by scanning electron microscopy. X-ray diffraction spectrum showed that the peaks attributing to the amylose–lipid complex disappeared. The relative crystallinity increased by 19% for high-amylose maize starch (HMS) on defatting, while the other tested starches virtually unchanged. Differential scanning calorimetry study indicated an increase in the thermal stability for the defatted starches. Compared with native waxy maize starch, the acid hydrolysis rate of the defatted one increased by 6% after 10 days. For normal maize starch (NMS) and HMS, the higher rate of hydrolysis was observed during the first 5 days. Thereafter, the hydrolysis rate was lower than that of their native counterpart. The increase in susceptibility to acid hydrolysis (in the first 5 days) was mainly attributed to the defective and porous structures formed during defatting process, while the decrease of hydrolysis rate for NMS and HMS samples (after the first 5 days) probably resulted from the increase in the relative crystallinity.

1. Introduction

Acid hydrolysis has been widely used to modify starch granule structure and produce thin boiling starch, which was extensively used in food, textile and paper industries [1]. In these fields, acid-modified starch is prepared with dilute sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) at 25–55 °C for different periods. Two distinct stages were observed in the course of acid hydrolysis of starch as a function of time. The first stage (i) was attributed to a relatively fast hydrolysis of starch, mainly hydrolyzing the amorphous lamellae, while a slow hydrolysis of the crystalline lamellae occurred during the second stage (ii) [2,3]. Due to the two-stage hydrolysis pattern, acid-modified process of starch mainly took 5–15 days [4]. The effects of different factors on the hydrolysis were investigated. The major results showed that the first stage (i) could be affected by granule size, pores on the surface, amylose content, amylopectin content, the mode of distribution of α (1–6) branches between the amorphous and the crystalline regions, and degree of packing of the double helices within the crystallites [4]. However, little attention was attracted to the natural lipids presented in starch granules.

Starch granules usually contained lipids. The content and the composition of these lipids varied in different kinds of plants. It was generally known that the amount of total starch lipids was 0.01–1.46% in cereals [5,6], 0.01–0.87% in legumes [7], and 0.08–0.19% in tuber and roots [6,8,9]. The lipids presented in starch could be classified into three categories, including non-starch lipids, starch surface lipids, and internal starch lipids [10]. Starch lipids presented in free state were connected with starch components, either linking via ionic and hydrogen bonds to hydroxyl groups (non-starch lipids and starch surface lipids) or in the form of amylose–inclusion complexes (starch surface lipids and internal starch lipids) [11,12]. Therefore, it could be deduced that surface lipids and non-starch lipids might prevent the starch granule hydrolyzing by acid at the first hydrolysis stage (i). Lipid-complexd amylose chains showed great resistance to the acid hydrolysis [13,14]. The complexes, formed by internal starch lipids and amylose, hindered the attack of acid on glucosidic bonds, since the glucose unit should change its conformation from chair to half-chair in order to be hydrolyzed [15]. Therefore, it could be hypothesized that defatting treatment could increase the

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Table 1
Removal ratio of starch lipids by the methanol/water extracted method.

Sample	Lipids contents (mg per 100 g starch)		
	Acid hydrolyzed[a] (total lipids)	Solvent extracted[b]	Removal ratio by solvent extracted method (%)
WMS	134 ± 19[c]	125 ± 26	93.3
NMS	523 ± 31	508 ± 23	97.1
HMS	1042 ± 39	1006 ± 31	96.5

[a] Lipids obtained by extraction after acid hydrolysis (24% HCl) of native starches at 70 °C for 30 min.
[b] Lipids obtained by methanol–water (85%, v/v) extraction at 75 °C for 24 h.
[c] Mean ± SD of at least triplicate.

accessibility of acid to the starch granules and increase the degree of acid hydrolysis of starches.

The present study, thus, was designed to determine the effect of defatting on the susceptibility of granular starches to acid hydrolysis. Maize starches with different amylose contents were studied, since the lipids content was related to amylose content or long chain (1 → 4)-α-D-glucan content [16]. This would provide a deeper insight into the effect of defatting on acid hydrolysis rate of starches.

2. Materials and methods

2.1. Materials

Waxy maize starch (WMS) was kindly donated by Tianjin Tingfung Starch Development Co., Ltd. (Tianjin, China). Normal maize starch (NMS) and high-amylose maize starch (amylomaize V, HMS) were purchased from Puluoxing Starch Co., Ltd. (Hangzhou, China). All other chemicals and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Suzhou, China) and of analytical grade unless otherwise stated. The amylose contents for WMS, NMS, and HMS were 0.5%, 26%, and 62%, respectively.

2.2. Starch defatting

Defatted starches were prepared according to the method of Schoch [17]. Maize starches with different amylose contents were Soxhlet extracted with 85% aqueous methanol at 75 °C for 24 h. The solvent was removed by vacuum evaporation and the starch was air-dried to a constant moisture of ~10%. Lipids content was determined using the method of Jitngarmkusol et al. [18] and calculated on a dry starch basis.

2.3. X-ray diffraction (XRD) pattern and relative crystallinity (RC)

Prior to XRD test, native and defatted starch samples were milled to powers (200 mesh) and hydrated at 75% relative humidity (RH) in a sealed vessel using saturated sodium chloride. Basically, the samples (0.8 g) were pressed into a pellet (10 mm × 25 mm) with hydraulic press. XRD pattern was obtained using a Bruker D8-Advance XRD instrument (Bruker AXS Inc., Karlsruhe, Germany). The diffractograms were collected under the conditions of 40 kV and 30 mA with nickel-filtered Cu-Kα (wavelength 1.5405 Å) radiation. Powdered samples were scanned from 4° to 30° (2θ) with a scanning rate of 4°/min. Each sample was scanned at least in triplicate. The RC (ratio of the crystalline portion to the sum of crystalline and amorphous portions) of the starches and diffraction angle (2θ) of X-ray pattern were analyzed by Jade 5.0 software (Materials Data Inc., CA, USA) and quantitatively estimated using the method of Nara et al. [19].

2.4. Differential scanning calorimetry (DSC)

Thermal analysis of native and defatted maize starches was performed by a DSC7000 instrument (Seiko Instruments Inc., Chiba, Japan). Water (11 μL) was added with a microsyringe to native and defatted starches (3.0 mg) in an aluminum DSC pan. The mixtures were sealed and equilibrate at 4 °C for 24 h. The thermal behaviors of the starch samples were studied by heating samples at a heating rate of 5 °C/min from 20 °C to 120 °C under ultrahigh-purity nitrogen atmosphere. An empty pan was used as a reference. The onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) together with enthalpy change (ΔH) were quantified by the Muse software.

2.5. Field emission scanning electron microscopy (FE-SEM)

FE-SEM was performed using a Hitachi S-4800 (Hitachi, Japan) at an acceleration voltage of 1 kV. The starch samples were placed on aluminum specimen stubs with double-sided adhesive tape and coated with gold for observation.

2.6. Acid hydrolysis of the native and defatted starches

The starches were hydrolyzed with 3.16 M H_2SO_4 at 40 °C (10 g starch per 100 mL acid) for 10 days with constant stirring at the speed of 200 rpm. At different time intervals, aliquots of the reaction mixtures were neutralized and centrifuged (3773 × g). The supernatant liquid was assayed for total carbohydrates [20]. The acid hydrolysis rate was determined by expressing the solubilized carbohydrates as a percentage of the initial dry starch.

2.7. Statistical analysis

Statistical analysis was performed using ORIGIN 7.5 (OriginLab Inc., Hampton, USA). Data were expressed as means ± standard deviations and analyzed by a one-way analysis of variance (ANOVA). A probability $P < 0.05$ was considered significant throughout the study.

3. Results and discussion

3.1. Comparison of lipids content between starches

Starches derived from different origins usually contained quantities of lipids either on the surface of starches or the inner starch granules. In this study, the lipids contents for WMS, NMS, and HMS were 0.13%, 0.52%, and 1.04%, respectively. It can be seen from Table 1, methanol–water (85%, v/v) was a good solvent for defatting, as it resulted in almost complete removal of the starch lipids after 24 h. The lipid contents for maize starches were within the range as reported in the literature [5], and was positively correlated with amylose content. Since amylose dispersed among amylopectin molecules and might be located primarily in the amorphous zones