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Production of glutinous rice flour from broken rice via ultrasonic assisted extraction of amylose

Yohana Dwi Setyawati [a], Sitti Faika Ahsan [a], Lu Ki Ong [a], Felycia Edi Soetaredjo [b], Suryadi Ismadji [b,*], Yi-Hsu Ju [a,*]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec. 4 Keelung Rd., Taipei 10607, Taiwan
[b] Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia

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ABSTRACT

In this study, a modified aqueous leaching method by complex formation of amylose with glycerol was employed for reducing the amylose content of starch in broken white rice to less than 2%, so that the resulting starch can be classified to that of glutinous rice flour. By employing ultrasonication in alkaline condition, extraction of amylose could be performed by washing at lower temperature in shorter time compared to the existing aqueous leaching method. The effects of glycerol concentration, alkali concentration, ultrasonication and treatment time on the amylose content of the treated starch were systematically investigated. Under optimum condition, amylose content of broken white rice starch can be reduced from 27.27% to 1.43% with a yield of 80.42%. The changes in the physicochemical properties of the rice flour before and after treatment were studied.

1. Introduction

Glutinous rice or sticky rice is a type of rice which has sticky texture after being cooked. This rice type contains a very small content of amylose (1.0–2.3%) in its starch (Wani et al., 2012). Glutinous rice flour is excellent for many applications in food products such as thickening agent for white sauces, gravies, puddings and waxy rice dumpling (Ding, Wang, Zhang, Shi, & Wang, 2015; Prasad, Anil, Singh, & Sinha, 2013). The wide application of this flour has raised the demand of glutinous rice flour in the market. Despite its high value in food processing industry, the productivity of this flour seems to be low and in some countries, such as Thailand, glutinous rice price was significantly high in the past years (Titapiwatanakun, 2012; Zhu et al., 2000).

Non-waxy rice or white rice is more popularly known as one of the staple foods in the world and is predicted to increase 40% in demand by 2030 (Khush, 2005). This type of rice commonly contains 12.2% to 28.6% amylose in its starch (Wani et al., 2012). During rice milling, some rice grains break and become the major byproduct known as broken rice. This byproduct is often mixed with bran and ground rice husk to become cattle feed (Shih, Champagne, Daigle, & Zarins, 1999). As the rice production and demand for polished white rice increase, the amount of broken rice produced worldwide also increases.

Due to higher price of glutinous rice flour in the market, there is an incentive to develop a method to obtain rice flour with similar characteristic to glutinous-rice flour from the under-utilized broken rice. Since an amylose content less than 2% is the only criterion for a rice to be classified as sticky rice, extracting of amylose from the starch of white rice is one way to turn white rice flour into glutinous rice flour. The existing techniques to selectively extract amylose from starch, especially for structural analysis purpose, include aqueous dispersion followed by selective precipitation and aqueous leaching (Doblado-Maldonado, Gomand, Goderis, & Delcour, 2015; Pigman & Wolfrom, 1945). There are several disadvantages in the first method such as long gelatinization time, requirement of an elaborate procedure of starch dispersion under controlled pH in an autoclave and the necessity to use a large amount of water. While aqueous leaching method offers easier and non-destructive approach, slow extraction may occur as the process is based on diffusional mass transfer (Doblado-Maldonado et al., 2015).

During aqueous leaching, the diffusion rate of amylose is affected by external factor (operating condition) and internal factor (structure of solid matrix). By manipulating operating condition and disruption of solid matrix, diffusion resistance of amylose

* Corresponding authors.
E-mail addresses: suryadiismadji@yahoo.com (S. Ismadji), yhju@mail.ntust.edu.tw (Y.-H. Ju).

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can be reduced. In this method, in addition to low starch/water concentration, high temperature and long processing time were required to obtain high amylose removal and yield. Better molecular mobility by introducing organic molecules as plasticizer without affecting starch crystalline structure has been successfully performed by heating starch in 85 wt.% aqueous solution of glycerol, n-butanol, pentasol, cellosolve or dioxane prior to the extraction step (Montgomery & Senti, 1958). However, two to three subsequent extraction steps with very low starch/water concentration (2 wt.%) in nearly boiling water were required to completely extract amylose.

Ultrasonication has been acknowledged as a diffusion-enhancer unit process in food processing (Knorr, Zenker, Heinz, & Lee, 2004). In this study, the mechanical force of ultrasonic wave was harnessed to erode the diffusion barrier such as protein on the surface of starch granule, create a cavity in the dense solid matrix and induce chain scission on polysaccharide matrices so that amylose could diffuse out more easily under lower processing temperature. The effect of glycerol concentration was investigated with the aim to produce rice flour with similar amylose content to that of glutinous rice flour. Alkalinity, ultrasonication and processing time were found to affect amylose removal. Physicochemical properties of the treated rice flour starch, including proximate composition, pasting properties, morphology, crystallinity structure, swelling power and solubility, thermal decomposition and gelatinization properties were further analyzed.

2. Materials and methods

2.1. Materials

Broken white rice was obtained from a local mill in Taiwan. The broken rice was ground first by a home blender. Particles passed through a 25-mesh stainless steel screen (particle size < 0.71 mm) was then dried in a freeze dryer (−40 °C, 0.05 mbar) for 2 days and stored in an air-tight container at room temperature for later use. The moisture content of broken rice flour was analyzed according to the AOAC 925.09 procedure and was found to be 11.87%. All chemicals were used as received, including ACS grade anhydrous glycerol (J.T. Baker, USA), reagent grade NaOH (Fischer Scientific, UK), HNO_3 (63%, May and Baker, UK), H_2SO_4 (98%, Scharlau, Spain), crystalline phenol (99%, Wako, Japan) and $NaNO_3$ (99%, Acros Organics, USA). Liquid α-amylase from *Bacillus licheniformis* (500 U/mg protein, 10 mg protein/mL, Sigma Aldrich, USA) and amyloglucosidase from *Aspergillus niger* (⩾300 U/mL, Sigma Aldrich, USA) were diluted in acetate buffer (pH 5, 0.2 M) to obtain the stock solutions of 450 U/mL α-amylase and 5.25 U/mL amyloglucosidase, respectively. Anhydrous $NaCH_3COO$ (⩾99%, Nacalai Tesque, Japan) and glacial acetic acid (⩾99%, Scharlau, Spain) were utilized for making the buffer. Standard for glucose analysis was anhydrous α-D(+)-glucose (99 + %, Acros Organics, USA). Ethanol (95%, Echo, Taiwan) and n-hexane (95%, Tedia, USA) were used as the solvents to extract sugar and lipid from rice flour, respectively. Commercialized glutinous rice flour was purchased from a local supermarket and used without any pretreatment. Standard pullulan set with known molecular weights (708,000, 107,000, 21,100 and 6100) was purchased from Showa Denko, Japan.

2.2. Effect of glycerol concentration on amylose leaching

Rice flour sample (0.6 g, dry basis) was placed in a reaction tube and mixed with 2.4 g of various concentrations (25, 50, 70, 75, 77 and 85 wt.%) of glycerol in 1 N NaOH. Solvent and rice flour were mixed using a vortex mixer and then placed in an ultrasonic bath (Lissome LS-300H, 40 kHz, 300 W) at 70 °C for 1 h. The mixture was subsequently mixed every 15 min using a vortex mixer. After 1 h, the sample was centrifuged (2000×*g*, 10 min). The supernatant was removed and the solid residue was washed 3 times each using 15 mL of deionized water to remove glycerol and NaOH. The washed residue was freeze dried for 2 days before analysis.

2.3. Effect of NaOH on amylose leaching

The procedure is exactly the same as in Section 2.2 except 85 wt.% glycerol in 1 N NaOH or in water was used.

2.4. Effect of treatment time on amylose leaching

The procedure is exactly the same as in Section 2.2 except 85 wt.% glycerol in 1 N NaOH was used and the mixture of solvent and rice flour was ultrasonicated for various times (30, 45, 60, 75 and 90 min).

2.5. Effect of ultrasonication on amylose leaching

The procedure is exactly the same as in Section 2.2 except 85 wt.% glycerol in 1 N NaOH was used and either the mixture was put in a ultrasound bath or in a water bath.

2.6. Amylose content quantification by gel permeation chromatography (GPC)

About 100 mg of flour sample was dispersed in 5 mL of 1 N NaOH solution and stirred at 380 rpm overnight. Several drops of 0.5 M HNO_3 were added to neutralize the mixture. The mixture was then transferred into a 50 mL volumetric flask and diluted. The aliquot was first centrifuged (2000×*g*, 10 min) to remove some solid residues. Clear supernatant (20 mL) was taken and filtered to pass a nylon membrane (0.2 μm). The filtered aliquot containing starch was injected into a GPC system, which consists of a series of standard pullulan-calibrated GPC column (Waters Corp., 7.8 × 300 mm, WAT011520, WAT011530, WAT011540 and WAT011545) at 40 °C, an RI detector (Waters 2414) and a binary HPLC pump (Waters 1525). The mobile phase was 0.1 N $NaNO_3$ with a flow rate of 0.8 mL/min. Acquisition time was programmed to 45 min. Amylopectin and amylose were identified based on molecular weight. The amylose content of starch was determined as the ratio of the peak area correlated to amylose to the total peak area.

2.7. Proximate analysis

Total free sugar and starch were determined using the method of Castillo et al. (2000) with a slight modification. Dried ground sample (100 mg) was extracted twice each with 30 mL of 80% v/v aqueous ethanol at 80 °C with constant stirring at 275 rpm for 30 min. After cooled, the solid was separated by centrifugation (1800×*g*, 20 min). The clear supernatant was decanted and collected for analysis of total sugar. The retained residue was hydrolyzed using 4 mL of 450 U/mL α-amylase in a boiling water bath for 30 min. After that, hydrolysis was continued using 4 mL of 5.25 U/mL amyloglucosidase at 55 °C for 16 h. Total free sugar and starch as glucose were analyzed using phenol sulfuric acid method by adding 1 mL of 5% phenol followed by 5 mL of 96% H_2SO_4 into 1 mL of sample solution. UV–vis spectrophotometer measurement of the supernatant was conducted at 490 nm. Blank solution for total free sugar and starch analysis was made by replacing the sample with 1 mL of deionized water. In addition to total free sugar and starch content analysis, the contents of crude fiber, protein, ash, lipid were also analyzed following the AOAC Official method 962.09, AOAC Official method 955.04, AOAC