Turnitin Originality Report

Food Chemistry 203 (2016) 158–164 by Suryadi Ismadji

From paper 2 (Hippo-hippo 02)

Processed on 16-Feb-2018 06:31 WIB
ID: 916683690
Word Count: 6931

Similarity Index	Similarity by Source	
7%	Internet Sources:	6%
	Publications:	6%
	Student Papers:	4%

sources:

1 1% match (Internet from 23-Nov-2017)
https://opus4.kobv.de/opus4-fau/frontdoor/deliver/index/docId/8955/file/AngelaLopezPinarDissertation.pdf

2 1% match (Internet from 05-Sep-2013)
http://rsce2012.its.ac.id/search.php

3 < 1% match (Internet from 31-Jul-2014)
http://www.cropbio.or.kr/index.php?mid=ContentofPast&category=126&page=2&document_srl=10000000003311

4 < 1% match (publications)
T. Adeniyi Afolabi. "Functional and tableting properties of acetylated and oxidised finger millet (Eleusine coracana) starch", Starch - Stärke, 04/2012

5 < 1% match (publications)
Zhu, Dawei, Hongcheng Zhang, Baowei Guo, Ke Xu, Qigen Dai, Cunxu Wei, Guisheng Zhou, and Zhongyang Huo. "Physicochemical properties of indica-japonica hybrid rice starch from Chinese varieties", Food Hydrocolloids, 2017.

6 < 1% match (Internet from 15-Jul-2015)
http://elibrary.trf.or.th/Projectfile2554/RTA5180006/RTA5180006_full.pdf

7 < 1% match (Internet from 29-Aug-2017)
http://www.cavs.msstate.edu/publications/docs/2016/05/14914Phase-field_simulation_of_austenite_growth_behavior_Insights.pdf

8 < 1% match (Internet from 23-Feb-2017)
https://www.deepdyve.com/search?author=Ahsan%2C+Sitti+Faika

9 < 1% match (Internet from 14-Nov-2010)
http://www.agro.ku.ac.th/file/dep_research/262/KC4506065.pdf

10 < 1% match (publications)
Li, Wenhao, Guiling Wu, Qingui Luo, Hao Jiang, Jianmei Zheng, Shaohui Ouyang, and Guoquan Zhang. "Effects of removal of surface proteins on physicochemical and structural properties of A- and B-starch isolated from normal and waxy wheat", Journal of Food Science and Technology, 2016.

11 < 1% match (Internet from 27-Jun-2017)
https://mie-u.repo.nii.ac.jp/index.php?action=pages_view_main&active_action=repository_action_common_download&attribute_id=17&block_id=21&file_no=1&item_id=10835&ite

12 < 1% match (publications)
Sandhu, K.S.. "Some properties of corn starches II: Physicochemical, gelatinization, retrogradation, pasting and gel textural properties", Food Chemistry, 2007

13 < 1% match (publications)
Shifeng Yu. "Physicochemical Properties of Starch and Flour from Different Rice Cultivars", Food and Bioprocess Technology, 02/27/2010

14 < 1% match (student papers from 12-Apr-2016)
Submitted to Chapman University on 2016-04-12

15 < 1% match (Internet from 06-Sep-2017)

http://internationalscienceindex.org/publications/10006032/physical-properties-and-resistant-starch-content-of-rice-flour-residues-hydrolyzed-by-%CE%B1-amylase

16 < 1% match (publications)
Chagam Koteswara Reddy, Lalmuan Kimi, Sundaramoorthy Haripriya, Nayoung Kang, "Effects of Polishing on Proximate Composition, Physico- Chemical Characteristics, Mineral Composition and Antioxidant Properties of Pigmented Rice", Rice Science, 2017

17 < 1% match (student papers from 26-Aug-2013)
Submitted to Universiti Sains Malaysia on 2013-08-26

18 < 1% match (Internet from 21-Dec-2017)
http://repository.its.ac.id/44003/1/A%20new%20approach%20in%20maximizing%20and%20direct%20utilization%20of%20whole%20jatropha

19 < 1% match (publications)
Shujun, W.. "Studies on the physicochemical, morphological, thermal and crystalline properties of starches separated from different Dioscorea opposita cultivars", Food Chemistry, 2006

20 < 1% match (publications)
Kasim, N.S.. "Recovery of @c-oryzanol from biodiesel residue", Journal of the Chinese Institute of Chemical Engineers, 200705

paper text:

14**Food Chemistry 203 (2016)** 158–164 **Contents lists available at ScienceDirect Food Chemistry journal homepage: www.elsevier.com/locate/foodchem**

8**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,

2**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**

7**article info Article history: Received 3** August **2015 Received in revised form 21 January 2016 Accepted** 9 February **2016 Available online** 10 **February 2016 Keywords:**

Amylopectin Amylose Broken rice Glutinous rice flour Glycerol Ultrasonication 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 concen- tration, ultrasonication and treatment time on the amylose content of the treated starch were systemat- ically 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 **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 con- tent of amylose (1.0–2.3%) in its starch (Wani et al., 2012). Gluti- nous 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 mar- ket. Despite its high value in food processing industry, the produc- tivity 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 con- tains 12.2% to 28.6% amylose in its starch (Wani et al., 2012). Dur- ing 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, ⇑ Corresponding authors.

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

1**http://dx.doi.org/10.1016/j.foodchem.2016.** 02.068 **0308-8146/Ó 2016 Elsevier Ltd. All rights reserved.**

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 bro- ken 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 disad- vantages 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 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 molecu- lar mobility by introducing organic molecules as plasticizer with- out affecting starch crystalline structure has been successfully performed by heating starch in 85 wt.% aqueous solution of glyc- erol, n-butanol, pentasol, cellosolve or dioxane prior to the extrac- tion step (Montgomery & Senti, 1958). However, two to three subsequent extraction steps with very low starch/water concentra- tion (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 har- nessed 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 gluti- nous rice flour. Alkalinity, ultrasonication and processing time were found to affect amylose removal.

5**Physicochemical properties of** the treated **rice flour starch,**

including proximate composition, pasting properties, morphology, crystallinity structure,

5**swelling power and solubility, thermal** decomposition **and** gelatinization **properties were**

further analyzed.

20**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), HNO3 (63%, May and Baker, UK), H2SO4 (98%, Scharlau, Spain), crystalline phenol (99%, Wako, Japan) and NaNO3 (99%, Acros Organics, USA). Liquid a-amylase from Bacillus licheniformis (500 U/mg protein, 10 mg protein/mL, Sigma Aldrich, USA) and amyloglucosidase from Aspergillus niger (P300 U/mL, Sigma Aldrich, USA) were diluted in acetate buffer (pH 5, 0.2 M) to obtain the stock solutions of 450 U/mL a-amylase and 5.25 U/mL amy- loglucosidase, respectively. Anhydrous NaCH3COO (P99%, Nacalai Tesque, Japan) and glacial acetic acid (P99%, Scharlau, Spain) were utilized for making the buffer. Standard for glucose analysis was anhydrous a-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 pullu- lan 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

> 11**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 HNO3 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 lm). 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 NaNO3 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

> 11**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

> 6**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

> 10**°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 col- lected for analysis of total sugar. The retained residue was hydro- lyzed using 4 mL of 450 U/mL a-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% H2SO4 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 Official method 923.03 and AOAC Official method 920.39, respectively. 2.8. Physical properties analysis Physical properties of the rice flours investigated in this study include microscopic appearance, starch crystallinity, gelatinization properties, solubility in water, swelling power, and pasting proper- ties. In taking electron microscopy image of rice flour sample, about 2 mg of the sample was applied onto a double-sided tape attached to a specimen stub. The starch granules were then evenly distributed on the surface of the tape and coated with gold. SEM micrographs were obtained with a JEOL SEM (JSM-6390LV) at an accelerating voltage of 20 kV. The crystalline structure of rice flour samples were analyzed by using a Bruker D2 Phaser X-ray Diffrac- tometer

(XRD) with the X-ray beam operating at 30 kV, 10 mA and ambient temperature. The X-ray generator was run at Cu Ka wave- length (k = 1.5406 Å) with scanning region of diffraction angle (2h) from 5° to 35°. The specific step size and counting time were set at 0.1° and 2 s, respectively. The relative crystallinity of starch in rice flour was calculated from the following equation (Nara and Komiya (1983) using Origin 9.1 (Microbial, Northampton, MA, USA) for peak smoothing and peak integration. Area of crystalline peak Crystallinity ð%Þ ¼ Total area under XRD curve 100% Gelatinization

13**properties of rice flour were analyzed** using **a** Jade **Perkin Elmer Differential Scanning** Calorimetry **(DSC)**

accord- ing to the method described by Yuliana, Huynh, Ho, Truong, and Ju (2012) with slight modification. About 3.5 mg of dry sample was loaded into a 40 lL aluminum pan (TA Instruments, USA). Deion- ized water (9 lL) was added into the pan and the pan was covered. The sample was then kept

12**for 1 h at room temperature before**

anal- ysis. Prior to this measurement, the DSC instrument was calibrated by using indium and an empty aluminum pan was prepared as the reference. During this analysis, the sample-containing pan and ref- erence

17**pan were heated from 30 °C to 100 °C at a rate of 10 °C/min.**

Nitrogen at 50 mL/min was passed through the system. The results obtained by this analysis comprised

19**onset temperature (To), peak temperature (Tp), conclusion temperature (Tc) and enthalpy of gelatinization (DHgel). The**

method of Nadiha, Fazilah, Bhat, and Karim (2010) was employed to determine the swelling power and solubility. About 0.4 g of pre-dried rice flour was weighed and 40 mL of deionized water was added. This mixture was heated at 90 °C

4**for 30 min in a water bath. The** sample **was cooled to room temperature and centrifuged** (2000 g, **15 min). The** wet residue **was** collected **and weighed** to calculate the **swelling power**

by the following equation. Swelling power ðg=gÞ ¼ weight of the wet residue ðgÞ weight of the dry sediment ðgÞ In order to determine the solubility of starch, supernatant obtained from the centrifugation was dried at 110 °C. The dried residue was weighed and percent solubility

6**was calculated using the following equation.** Solubility **ð%Þ**

¼ weight of dried supernatant ðgÞ weight of the dry flour ðgÞ 100 The pasting properties of representative rice flours were mea- sured in triplicate

3**by using a Rapid Visco Analyzer (RVA Model** 4D, **Newport Scientific, Australia).** Rice flour **sample** (3 **g) was mixed with 25** g **of deionized water in an** Al **canister. The** suspen- sion **was**

stirred using constant paddle speed of 160 rpm with heat- ing and cooling program according to AACC Approved Method 61- 02. The measured viscosities during the program were expressed in rapid viscometer unit (RVU) and translated into pasting properties, which comprised pasting temperature (PT), peak time (tp),

9**peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown** viscosity (BDV = **PV–HPV), and set back (SB = CPV–HPV).**

3. Results and discussion Table 1 shows the proximate analysis results (based on dry flour weight) of the original broken rice flour (BRF) and glutinous rice flour (COMM-GRF) used in this study. It is apparent that the most distinct characteristic between BRF and COMM-GRF is the amylose content. The amylose content

in the starch of broken rice flour is 27.27%, which can be categorized as high amylose rice starch (Wani et al., 2012). Although there are variances in the contents of other components, only amylose content of starch may

13**affect the properties of rice flour**

since starch constitutes about 90% of both rice flours. In addition, only amylose can form complex with lipid and protein, which is closely related to the rheological prop- erties of flour (Yu, Ma, Menager, & Sun, 2012). Therefore, the objec- tive of this study was firstly to focus on reducing the amylose content of BRF to less than 2% and then examined the physico- chemical properties of the product. Each experiment on the treat- ment process was carried out in triplicate. The effects of glycerol concentration, NaOH, treatment time and ultrasonication on pro- duct composition are listed in lower part of Table 1. 3.1. Effect of glycerol concentration on amylose removal Glycerol is regarded as GRAS (Generally Regarded as Safe) sub- stance for food and drugs application. The effect of glycerol con- centration used in treatment on amylose content of starch is presented in Table 1. Amylose content of rice flour starch decreased after treatment. By employing 77% alkaline glycerol, amylose content of BRF can be reduced to 1.43% with a yield of 80.42%, which indicates that glutinous rice flour (coded as SYN- GRF) was successfully obtained. The result of this study conforms with the result of Montgomery and Senti (1958), which reported that solution containing 70–85 wt.% organic solvent can effectively free amylose from amylose–amylopectin strong bond, although some amylopectin can be leached out. This non-selectivity also can be seen from the GPC curve of SYN-GRF (Fig. S3) with the dis- appearance of low molecular weight part of amylopectin peak. No protein peak was seen in the GPC curve as observed also in the result of previous study that used non-purified rice flour directly for GPC analysis (Lu, Chen, & Lii, 1996). The absence of protein interference may be due to the precipitation of protein during the neutralization of flour dispersion (Ju, Hettiarachchy, & Rath, 2001; Shyur, Zia, & Chen, 1988). Precipitated protein can be removed easily by membrane filtration prior to injection to the GPC apparatus. Treatment using low glycerol concentration failed to consider- ably reduce amylose content. This may be because at lower glyc- erol concentration, fewer plasticizer (glycerol) can diffuse into the starch through flour matrix. Although more plasticizer is expected to ease amylose leaching, treatment using 85 wt.% glyc- erol resulted in opposite trend due to increasing viscosity of the system, which may hinder ultrasonic mixing of rice flour with sol- vent. In addition to the physical property of the mixture, decreased removal of surface protein and lipid under less alkaline condition may also hinder diffusion of amylose out of starch. The glycerol concentration affects not only to the extent of alkalinity, but also to the water content in the system. Sufficient water in the alkaline system can promote gelatinization of starch components, solubilization of protein, and reaction with Table 1 Proximate composition of rice flour samples. Parameters Amylose content (%) Yield (%) Composition (%) Starch Free sugar Fiber Protein Lipid Ash Characterization BRF COMM-GRF 27.27 ± 1.36 1.89 ± 0.29 – – 88.8 ± 0.4 91.2 ± 0.3 0.84 ± 0.01 0.31 ± 0.00 2.40 ± 0.01 2.01 ± 0.02 0.70 ± 0.02 0.50 ± 0.01 6.67 ± 0.03 5.20 ± 0.02 0.60 ± 0.01 0.74 ± 0.01 Glycerol concentration (%) 25 50 65 70 75 77 (SYN-GRF) 85 20.20 ± 0.42 12.01 ± 0.35 7.38 ± 0.41 5.84 ± 0.18 3.84 ± 0.20 1.43 ± 0.30 7.84 ± 0.34 37.1 ± 0.2 68.5 ± 0.3 72.2 ± 0.2 76.5 ± 0.3 82.6 ± 0.3 80.4 ± 0.4 80.7 ± 0.4 66.4 ± 0.3 82.1 ± 0.4 84.5 ± 0.4 90.9 ± 0.3 91.5 ± 0.3 91.0 ± 0.3 90.6 ± 0.4 0.20 ± 0.01 0.08 ± 0.00 0.09 ± 0.00 0.03 ± 0.00 0.04 ± 0.00 0.07 ± 0.00 0.30 ± 0.00 5.93 ± 0.02 3.30 ± 0.01 3.14 ± 0.01 2.98 ± 0.01 2.77 ± 0.01 2.85 ± 0.02 2.92 ± 0.01 7.32 ± 0.02 3.97 ± 0.02 3.94 ± 0.02 3.85 ± 0.01 3.65 ± 0.01 3.99 ± 0.01 4.09 ± 0.02 0.56 ± 0.01 0.25 ± 0.01 0.18 ± 0.00 0.15 ± 0.00 0.13 ± 0.01 0.11 ± 0.01 0.18 ± 0.01 19.59 ± 0.03 10.28 ± 0.04 8.11 ± 0.05 2.07 ± 0.01 1.91 ± 0.01 1.95 ± 0.02 1.96 ± 0.01 Alkalinity Without NaOHa 16.92 ± 0.31 84.8 ± 0.4 91.1 ± 0.4 0.13 ± 0.01 2.73 ± 0.01 5.06 ± 0.01 0.31 ± 0.00 0.70 ± 0.00 Time (min)b 30 45 60 75 90 20.46 ± 1.10 12.99 ± 0.67 7.84 ± 0.98 6.24 ± 0.90 6.17 ± 0.70 82.5 ± 0.3 81.2 ± 0.4 80.7 ± 0.4 79.9 ± 0.2 79.8 ± 0.4 89.6 ± 0.2 90.3 ± 0.3 90.6 ± 0.4 91.5 ± 0.8 91.6 ± 0.4 0.05 ± 0.00 0.09 ± 0.00 0.30 ± 0.00 0.19 ± 0.01 0.00 ± 0.00 2.89 ± 0.01 2.91 ± 0.02 2.92 ± 0.01 2.95 ± 0.00 2.95 ± 0.03 6.09 ± 0.03 5.21 ± 0.03 4.09 ± 0.02 3.34 ± 0.04 3.34 ± 0.01 0.47 ± 0.01 0.27 ± 0.02 0.18 ± 0.01 0.09 ± 0.00 0.09 ± 0.00 0.89 ± 0.01 1.23 ± 0.02 1.96 ± 0.01 1.97 ± 0.00 2.04 ± 0.01 Mixing modeb Ultrasonication Without ultrasonication 7.84 ± 0.98 10.22 ± 0.46 80.7 ± 0.4 84.4 ± 0.4 90.6 ± 0.4 91.3 ± 0.4 0.30 ± 0.00 0.07 ± 0.00 2.92 ± 0.01 2.78 ± 0.01 4.09 ± 0.02 3.92 ± 0.01 0.18 ± 0.01 0.21 ± 0.01 1.96 ± 0.01 1.76 ± 0.01 a Glycerol concentration 85%. b Glycerol concentration 85%, 1 N NaOH. alkaline-vulnerable moieties (lipid saponification and lignin hydrolysis). In the treatment process of starchy feedstock, starch gelatinization can irreversibly dissolve starch granule in water, thus less or no starch remains in the solid residue. In Table 1, treat- ment using 25 wt.% glycerol resulted in the lowest yield and the highest ash content. This was attributed to the substantial loss of starch by starch gelatinization and the inclusion of more Na+ into residual flour solid from NaOH introduced to the system. Severe loss of starch granules in the 25 wt.% glycerol treatment is por- trayed microscopically in Fig. S1. By decreasing the water content (increasing glycerol concentration to 50 wt.% and so on), starch gelatinization could be minimized so that only partial gelatiniza- tion occurred, which preserved the yield of residual solid. Investi- gation on the mass balance indicated that fiber was mostly retained during the treatment, while protein and lipid were remarkably reduced due to alkaline extraction mechanism. 3.2. Effect of NaOH on amylose removal The absence of NaOH in glycerol solution resulted in more than two times final amylose content (16.92%) in starch than that of treated in the presence of NaOH (7.84%). Alkaline condition also had significant impact on the solubilization of lipid and protein (Table 1). Since NaOH can dissolve both amylose and amylopectin, significant drop of amylose content may only be attributed to the increase of solubility of amylose in water, which can occur due to random substitution of hydroxyl group of amylose. Increasing solubility of amylose in water can be explained by the increase of its

hydrophilicity and stability in water (Wulff & Kubik, 1992). Addition of two hydroxyl groups from deprotonated glycerol for each substituted hydroxyl group in native amylose may enhance the hydrophilicity of amylose in water, while random position of substituent prevents amylose molecule from forming helical coil with non-polar outer side, which can precipitate out of water easily. Therefore, removal of amylose from starch granules using this approach can be achieved just by simple washing. The pro- posed reaction mechanism between deprotonated glycerol and the hydroxyl group of amylose is illustrated in Fig. S2. The differ- ence in nature between linear and branched structure of amylose and amylopectin allows amylose to react with other organic mole- cules, thus amylose is more easily extracted from starch (Reid, Tatsuta, & Thiem, 2008). After standing at 4 °C for 7 days, the ret- rograded amylose in the supernatant can be recovered for other applications. Qualitative iodine test on the pooled supernatant and retrograded amylose showed the existence of leached amylose as shown in Fig. S4. 3.3. Effect of treatment time on amylose removal During the treatment, it is obvious that amylose content decreased with increasing treatment time (Table 1). At the same time, protein and lipid that hinder amylose extraction decrease concurrently with the diffusion of amylose. Ash in the treated flour also increases due to the adsorption of Na+, while fiber content only increases slightly, which may be due to reduction of other components. Amylose content changed insignificantly after 60 min due to saturation, which is also reflected in the relatively unchanging proximate compositions (Table 1). Thus, in this study 60 min was chosen as the effective treatment time. 3.4. Effect of ultrasonication on amylose removal When white rice flour was treated with 85 wt.% glycerol in 1 N NaOH for 60 min, the amylose content of the resulted starch was 7.84% if ultrasonication was used while 10.22% was obtained if ultrasonication was not used. The result indicates that ultrasonica- tion has effect on decreasing amylose content due to the well- known effect of formation, growth, and implosive collapse of bub- bles in ultrasonic mixing. However, the result in Table 1 showed that ultrasonication has less effect on amylose reduction than other factors studied. This may be due to the indirect sonication provided by a classic ultrasonic bath used in this study which has low intensity. There are insignificant differences in the proxi- mate compositions between flours treated by sonication and with- out sonication (Table 1). 3.5. Physical properties of treated flour SEM images of the original white rice flour (BRF) and those of the treated rice flour (SYN-GRF) are shown in Fig. 1(a, c) and (b, d), respectively. It can be seen that before the treatment, starch granules appear as

16**clump in the matrices of plant cell wall.**

Sonica- tion treatment releases starch granules by breaking plant cell wall matrices (Fig. 1b). Starch granule shape changed from nearly spherical before treatment (Fig. 1c) to polygonal (Fig. 1d). This polygonal shape can be reasoned as the artifact of NaOH abrasion of starch granule surface, which is commonly identified as amylo- plast. Since amyloplast is a non-pigmented plant organelle that is strongly associated with protein bodies (i.e., enzyme) for starch synthesis and stored lipid, removal of amyloplast also contributes to the

16**reduction of protein and lipid** content **in rice flour**

after treatment. Since low power ultrasound was utilized in this study, the surface of starch did not develop any remarkable pore or pitch (Jambrak et al., 2010). XRD peaks of BRF, COMM-GRF and SYN-GRF (Fig. 2) reflect typ- ical

15**peaks of A-type starch, which has strong diffraction peaks at** 2H = 15° **and** 23° **and a doublet at** 2H = 17° **and**

18°. Similar spec- tra of BRF and SYN-GRF indicate that the polymorphic form of starch remains the same, implying minimal effect of treatment on polymorphic crystalline structures. Amylose-lipid complex appears as weak intensity peak at 2H = 20° only for BRF (Zhu, Liu, Wilson, Gu, & Shi, 2011). Based on the crystallinity percentage (Table 2), it can be concluded that the treatment increases crys- tallinity of BRF by reducing amylose content. Gelatinization properties of BRF, COMM-GRF and SYN-GRF shown in Table 2 are in the range of the values reported in the study of

5**Singh, Singh, Kaur, Sodhi,** and **Gill (2003).** However **the** dif- ferences **in**

12**To (onset temperature), Tp (peak temperature), Tc** (con- clusion **temperature) and DHgel** (gelatinization **enthalpy)**

are insignificant due to low ultrasound power used in this study which had less effect on granule and properties of rice starch (Yu et al., 2013). Gelatinization temperature of COMM-GRF starch was lower BRF SYN-GRF COMM-GRF a.u. 5 10 15 20 25 30 35 40 2θ (degree) Fig. 2. X-ray diffraction pattern of rice flours. than that of BRF starch. This result agrees with the result of Varavinit, Shobsngob, Varanyanond, Chinachoti, and Naivikul (2003) about the relationship between amylose content and gela- tinization

temperature of starch. Theoretically, gelatinization is ini- tiated by granule swelling due to hydration and swelling of the amorphous region (Wani et al., 2012). During gelatinization, hydrogen bonds between amylose and amylopectin in semi- crystalline region in starch need to be disrupted first for water to be inserted, which inflicts higher gelatinization temperature in normal rice. Glutinous rice contains very small amylose content and since its crystalline region consists of short chain of glucose, thus it needs lower temperature to melt or dissociate. From Table 2, it can be seen that SYN-GRF has a slightly higher gelatinization temperature than that of the BRF. Sodium ions remained in starch, which cannot be removed completely by washing, enhanced the (a) (b) (c) (d) Fig. 1. SEM images of BRF (a and c) and SYN-GRF (b and d). Table 2 Physical properties of BRF, SYN-GRF and COMM-GRF. Flour samples Gelatinization (°C) Swelling power (g/g) Solubility (%) Crystallinity (%) To Tp Tc Tc–To DHgel (J/g) BRF SYN-GRF COMM-GRF 61.43 70.17 62.04 70.53 61.10 69.04 75.74 14.31 77.27 15.23 75.33 14.23 8.327 10.79 5.17 8.014 14.06 21.54 8.673 12.10 15.22 18.41 21.30 20.83 Table 3 Pasting properties of BRF, SYN-GRF and COMM-GRF. Flour samples PT (°C) tp (min) PV (RVU) HPV (RVU) BD (RVU) CPV (RVU) SB (RVU) BRF SYN-GRF COMM-GRF 62.9 62.6 62.2 6.4 104.8 ± 0.8 4.8 198.9 ± 2.4 2.9 195.6 ± 1.4 92.7 ± 0.5 93.4 ± 1.1 98.1 ± 1.2 12.1 ± 0.3 105.5 ± 1.3 97.5 ± 0.2 133.2 ± 2.4 106.1 ± 0.3 123.1 ± 3.3 40.5 ± 1.9 15.7 ± 0.8 25.0 ± 2.1 stability of starch granules

10**through electrostatic interaction between** these **ions and hydroxyl groups of starch**

(Ahmad & Williams, 1999; Karim et al., 2008) that resulted in the slight increase of onset and peak temperatures. Broader temperature range between onset and conclusion temperature of SYN-GRF is in accordance with its increase in relative crystallinity (Zobel, 1992). DHgel represents the phase transition of granules from an ordered state to a disordered one during heating in excess water. It involves melting of both crystalline and double-helical regions (Jambrak et al., 2010). The endothermic enthalpy of COMM-GRF starch is higher than that of the BRF starch because COMM-GRF contains higher portion of amylopectin, which forms crystalline region that needs more energy to be disordered than that of BRF. It is interesting to observe that DHgel of the treated sample is lower than that of original sample, although it possesses higher crys- tallinity. This can be interpreted as the effect of diffused ions in the starch granule that shaped molecular gap allowing water to readily diffuse through the compact structure of crystalline zone (Ahmad & Williams, 1999). The data obtained in this study show that SYN-GRF has the lar- gest swelling power, followed by COMM-GRF and BRF. The lower swelling power and solubility of BRF than other types of rice flour is due to its high amylose content, which tends to inhibit water mobility by the formation of less-opened double-helix structure (Sodhi & Singh, 2003). For the treated rice flour, swelling power increased significantly due to the removal of amylose, which per- mits starch granules to absorb more water and swell to a greater extent. The same trend in solubility and swelling power suggests that the increase in starch solubility is due to the effect of granule swelling, allowing the exudation of amylose into water (Techawipharat, Suphantharika, & BeMiller, 2008). The pasting properties reflect the behavior of starch granule during cooking or processing. The viscosity of starch dispersion may change during water penetration, swelling of granule, break- ing down of starch granular structure (gelatinization), and ret- rogradation of starch components. The pasting properties of BRF, SYN-GRF, and COMM-GRF measured by RVA are listed in Table 3. Reduced PT and tp in SYN-GRF compared to BRF showed acceler- ated swelling due to lesser amylose content, which gave less resis- tance towards water penetration (Park, Ibanez, Zhong, & Shoemaker, 2007). SYN-GRF showed relatively similar PV as COMM-GRF, indicating similar swelling behavior of the amylopectin-rich starch. Higher HPV and remarkable BD of SYN- GRF signified a waxy starch identity, which is easier to be dis- rupted than the non-waxy starch during heating. The lower set back and cold paste viscosity of SYN-GRF indicated weaker ret- rogradation potential, which correlated to the lower amylose content. It is also worth noting that no decrease in the HPV value of SYN- GRF proves that the integrity of starch granule was not disrupted by depolymerization during ultrasound-alkaline glycerol treat- ment (Lai, Karim, Norziah, & Seow, 2006). This statement is sup- ported also by the result of GPC analysis that showed insignificant shifting of amylopectin curves and their peaks towards lower molecular weight direction (Fig. S3). Thorough observation on the chromatogram showed that only the amylose peak experienced considerable depolymerization by alkaline glyc- erol that may cause overestimation in the result of iodine colori- metric technique. 4. Conclusion The amylose content of starch in broken white rice flour could be reduced from 27.27% to 1.43% by treating the flour using 77 wt.% glycerol in 1 N NaOH under ultrasonication for 1 h. Glyc- erol and alkali are responsible for amylose to have more solubility and stability in water. While there was an increase in ash content by adsorption of Na+, some components, such as protein, free sugar and lipid in rice flour were partly leached during treatment, which resulted in higher starch content in the treated flour. Low ultra- sound intensity has less effect compared to glycerol concentration, alkaline condition, and treatment time. SEM images revealed that the granule shape changed, with insignificant destruction on gran- ule surface due to application of alkaline condition and low sonica- tion power. The method used in this study increased relative crystallinity through amylose removal, but retained starch crys- talline structure as A-type starch. Sodium ions stabilize starch structure which increased gelatinization temperature while decreased gelatinization enthalpy. The treated rice flour (SYN- GRF) has higher swelling power and solubility than other rice flours. After the treatment, the pasting properties of the broken rice flour also changed, towards those similar to the commercial glutinous rice flour.

1**Appendix A. Supplementary data Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2016.**

02.068. References Ahmad, F. B., & Williams, P. A. (1999). Effect of salts on the gelatinization and rheological properties of sago starch. Journal of Agricultural and Food Chemistry, 47, 3359–3366. Castillo, C. P. S., Dewey, P. J. S., Lara, J. J., Henderson, D. L., Solano, M. d. L., & James, W. P. T. (2000). The starch and sugar content of some Mexican cereals, cereal products, pulses, snack foods, fruits and vegetables. Food Composition and Analysis, 13, 157–170. Ding, W., Wang, Y., Zhang, W., Shi, Y., & Wang, D. (2015). Effect of ozone treatment on physicochemical properties of waxy rice flour and waxy rice starch. International Journal of Food Science and Technology, 50, 744–749. Doblado-Maldonado, A. F., Gomand, S. V., Goderis, B., & Delcour, J. A. (2015). Methodologies for producing amylose: A review. Critical Reviews in Food Science and Nutrition. Jambrak, A. R., Herceg, Z., Šubaric, D., Babic, J., Brncic, M., Brncic, S. R., ... Gelo, J. (2010). Ultrasound effect on physical properties of corn starch. Carbohydrate Polymers, 79, 91–100. Ju, Z. Y., Hettiarachchy, N. S., & Rath, N. (2001). Extraction, denaturation and hydrophobic properties of rice flour proteins. Journal of Food Science, 66(2), 229–232. Karim, A. A., Nadiha, M. Z., Chen, F. K., Phuah, Y. P., Chui, Y. M., & Fazilah, A. (2008). Pasting and retrogradation properties of alkali-treated sago (Metroxylon sagu) starch. Food Hydrocolloids, 22, 1044–1053. Khush, G. S. (2005). What it will take to feed 5.0 billion rice consumers in 2030. Plant Molecular Biology, 59, 1–6. Knorr, D., Zenker, M., Heinz, V., & Lee, D. (2004). Applications and potential of ultrasonics in food processing. Trends in Food Science and Technology, 15, 261–266. Lai, L. N., Karim, A. A., Norziah, M. H., & Seow, C. C. (2006). Effects of Na2CO3 and NaOH on pasting properties of selected native cereal starches. Journal of Food Science, 69(4), 249–256. Lu, S., Chen, C.-Y., & Lii, C.-Y. (1996). Gel-chromatography fractionation and thermal characterization of rice starch affected by hydrothermal treatment. Cereal Chemistry, 73(1), 5–11. Montgomery, E. M., & Senti, F. R. (1958). Separation of amylose from amylopectin of starch by an extraction–sedimentation procedure. Journal of Polymer Science, 28, 1–9. Nadiha, M. Z. N., Fazilah, A., Bhat, R., & Karim, A. A. (2010). Comparative susceptibilities of sago, potato and corn starches to alkali treatment. Food Chemistry, 121, 1053–1059. Nara, S., & Komiya, T. (1983). Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. Starch, 35(12), 407–410. Park, I.-M., Ibanez, A. M., Zhong, F., & Shoemaker, C. F. (2007). Gelatinization and pasting properties of waxy and non-waxy rice starches. Starch, 59, 388–396. Pigman, W. W., & Wolfrom, M. L. (1945). Advances in carbohydrate chemistry (Vol. 1). New York: Academic Press Inc.. Prasad, K., Anil, A., Singh, Y., & Sinha, A. S. K. (2013). Concentration dependent rheological behaviour of promising basmati and non basmati rice flour. International Food Research Journal, 20, 2005–2008. Reid, B. O. F., Tatsuta, K., & Thiem, J. (2008). Glycoscience: Chemistry and chemical biology. Berlin: Springer. Shih, F. F., Champagne, E. T., Daigle, K., & Zarins, Z. (1999). Use of enzymes in the processing of protein products from rice bran and rice flour. Nahrung, 43, 14–18. Shyur, L.-F., Zia, K. K., & Chen, C.-S. (1988). Purification and some properties of storage proteins in japonica rice. Botanical Bulletin of Academia Sinica, 29, 113–122. Singh, N., Singh, J., Kaur, L., Sodhi, N. S., & Gill, B. S. (2003). Review: Morphological, thermal and rheological properties of starches from different botanical sources. Food Chemistry, 81, 219–231. Sodhi, N. S., & Singh, N. (2003). Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. Food Chemistry, 80, 99–108. Techawipharat, J., Suphantharika, M., & BeMiller, J. N. (2008). Effects of cellulose derivatives and carrageenans on the pasting, paste, and gel properties of rice starches. Carbohydrate Polymers, 73, 417–426. Titapiwatanakun, B. (2012). Technical Assistance Consultant's Report (Vol. TA-REG 7495). Thailand: Kasetsart University. Varavinit, S., Shobsngob, S., Varanyanond, W., Chinachoti, P., & Naivikul, O. (2003). Effect of amylose content on gelatinization, retrogradation and pasting properties of flours from different cultivars of Thai Rice. Starch, 55, 410–415. Wani, A. A., Singh, P., Shah, M. A., Schweiggert-Weisz, U., Gul, K., & Wani, I. A. (2012). Rice starch diversity: Effects on structural, morphological, thermal, and physicochemical properties—A review. Comprehensive Reviews in Food Science and Food Safety, 11, 417–436. Wulff, G., & Kubik, S. (1992). Helical amylose complexes with organic complexands, 1 microcalorimetric and circular dichroitic investigations. Makromolekulare Chemie, 193, 1071–1080. Yu, S., Ma, Y., Menager, L., & Sun, D.-W. (2012). Physicochemical properties of starch and flour from different rice cultivars. Food and Bioprocess Technology, 5, 626–637. Yu, S., Zhang, Y., Ge, Y., Zhang, Y., Sun, T., Jiao, Y., & Zheng, X.-Q. (2013). Effects of ultrasound processing on the thermal and retrogradation properties of nonwaxy rice starch. Journal of Food Process Engineering, 36, 793–802. Yuliana, M., Huynh, L. H., Ho, Q. P., Truong, C. T., & Ju, Y. H. (2012). Defatted cashew nut shell starch as renewable polymeric material: Isolation and characterization. Carbohydrate Polymers, 87, 2576–2581. Zhu, Y., Chen, H., Fan, J., Wang, Y., Li, Y., Chen, J., ... Mundt, C. C. (2000). Genetic diversity and disease control in rice. Nature, 406, 718–722. Zhu, L. J., Liu, Q. Q., Wilson, J. D., Gu, M. H., & Shi, Y. C. (2011). Digestibility and physicochemical properties of rice (Oryza sativa L.) flours and starches differing in amylose content. Carbohydrate Polymers, 86, 1751–1759. Zobel, H. F. (1992). Starch granule structure. In R. J. Alexander & H. F. Zobel (Eds.), Developments in carbohydrate chemistry (pp. 18–19). Minnesota: American Association of Cereal Chemists. Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164 159 160 Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164 Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164 161 162 Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164 Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164 163 164 Y.D. Setyawati et al. / Food Chemistry 203 (2016) 158–164