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# Aging of low and high amylose rice at elevated temperature: Mechanism and predictive modeling

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## ABSTRACT

The objective of this research was to study the changes in physicochemical properties of rice during elevated temperature storage. Paddy of three rice cultivars with low amylose content (9–11%) and the other three with high amylose content (23–25%) was stored at 39.2 °C and 43.1% relative humidity up to 31 weeks. Drastic changes in moisture content and some parameters representing cooking qualities, cooked rice texture and pasting properties occurred during the first four weeks of aging. At similar aging time, low amylose rice had higher adhesiveness, peak viscosity and breakdown, but had lower pasting temperature than high amylose rice. Time-dependent change in adhesiveness and pasting temperature was predicted by fractional conversion model ($0.60 \leq R^2 \leq 0.94$). Difference among rate constant values of the data from low and high amylose rice was found. Proportion of high molecular weight proteins (>225 kDa) tended to increase over time. However, enthalpy of amylose-lipid complex melting fluctuated during storage. Changes in protein molecular weight pattern could thus be key mechanism of rice aging at elevated temperature. NIR-based predictive models for minimum cooking time, adhesiveness, pasting temperature, peak viscosity, and breakdown of rice samples were established ($R^2$ of calibration $\geq 0.81$; $R^2$ of validation $\geq 0.87$).

## 1. Introduction

Physical and physicochemical properties of rice generally change over time during storage. Those time-dependent changes, so called rice aging, result in the changes in head rice yield and color of milled rice, thermal and pasting properties of rice flour and starch, cooking qualities in terms of water uptake, volume expansion ratio, elongation ratio and solid loss, cooked rice texture and aroma. Rice aging greatly depends on storage conditions, particularly time and temperature (Tananuwong and Malila, 2012; Zhou et al., 2015). Although the quantitative changes in chemical composition of rice kernels were reported to be negligible (Tulyathan and Leeharatanaluk, 2007; Zhou et al., 2002), many qualitative changes in those components occurred during storage. The latter changes were postulated as mechanisms underlying changes in quality parameters of rice during aging. Recently, Zhou et al. (2015) proposed conceptual model of rice aging at cellular and molecular levels. The model was based on the changes in proteins, cell wall components and lipids. During aging, formation of disulfide linkages and other cross-linking reactions could occur in rice protein molecules, enhancing molecular weight of proteins. High temperature storage could induce cross-linking between phenolic acids and polysaccharides in cell wall remnants, and help strengthen the cell wall structure. During cooking of rice kernels, changes in protein and cell wall structure could retard moisture penetration to starch granules in the endosperm matrix, and further influence gelatinization process; for instance, swelling power of starch granules and amylose leaching were limited. Lipids could also be oxidized during aging, resulting in rancid off-flavor in aged rice. Apart from the recent conceptual model, other qualitative changes during rice aging were proposed, including amylose-lipid complex formation which might further restrict starch granule swelling (Moritaka and Yasumatsu, 1972) and amylase activity which could alter amylose:amylopectin ratio and average amylopectin chain length of the isolated starch (Patindol et al., 2005).

Despite the extensive study upon rice aging, study regarding effect of rice variety, particularly with different amylose contents, on the aging process was still limited. Mathematical modeling used to describe time-dependent changes in physicochemical properties of rice during aging was also scant. The objective of this research,

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therefore, was to study the changes in physicochemical properties of rice varieties with different amylose contents during high temperature storage. Six rice cultivars commonly grown in Thailand were selected as representatives of rice with low and high amylose content. Storage temperature selected in this study (39 ± 0.2 °C) approached ambient temperature during summer season of tropical countries, including Thailand. The elevated temperature could also enhance the rate as well as extent of the chemical changes during rice aging. Two important phenomena, formation of amylose-lipid complex and changes in protein molecular weight pattern, were monitored throughout the storage, to help elucidate the rice aging mechanisms. Kinetic modeling was introduced to predict the changes in some quality parameters during rice storage. NIR-based chemometric approach was also applied to the selected quality parameters of fresh and aged rice. Overall data from this study could help elucidate key mechanisms underlying aging of rice with different amylose contents. Feasibility of discerning rice quality changes during aging via NIR technique was also reported.

## 2. Materials and methods

### 2.1. Materials

Low amylose rice cultivars used in this study were Khao Dawk Mali 105 (KDML105) (10.01% amylose, dry basis (db)), RD45 (11.15% amylose, db) and Patumthani 1 (PTT1) (9.32% amylose, db). RD47, Pitsanulok 2 (PSL2) and Chainat 1 (CNT1), having amylose content of 24.27% db, 24.83% db and 22.79% db, respectively, were selected as the representatives for high amylose rice. Since storage condition and rice cultivar were the major factors considered in this study, rice samples were carefully selected in order to control other variables, particularly growing location and harvesting season. Hence, one lot of the samples per cultivar was used for the whole storage test. Paddies of KDML105 and RD45 were purchased from Prachantakham Agricultural Cooperative, Prachinburi. PTT1, RD47 and PSL2 paddies were obtained from Patumthani Rice Research Center. CNT1 paddy was purchased from Ratchaburi Rice Research Center. All samples were obtained within the crop year 2014. After harvesting, the paddy samples were sun-dried to the final moisture content of 10–13% wet basis (wb) before transporting to the laboratory.

### 2.2. Sample preparation

Paddy was cleaned and packed in a plastic sack (1.5 kg/sack). The paddy samples were stored in a closed room with infrared heater to control the temperature at 39.2 ± 0.9 °C, 43.1 ± 2.8% relative humidity for 22 weeks. The experiment was done in duplicate, having 1 sack of the paddy as an experimental unit (1 replicate). Upon periodical sampling, moisture content of the paddy was measured by grain moisture meter (G-WON Hitech, GMK-303, Seoul, Korea). Paddy was dehusked with rubber roll huller. Brown rice was then whitened and polished to get milled rice. Head rice kernels were separated and used for the determination of cooking properties, cooked rice texture and absorption spectrum from near-infrared spectroscopy (NIR). Milled rice flour was prepared by grinding head rice with an electrical blender and sieved through a 100-mesh sieve. The moisture content of flour was determined by moisture analyzer HB43-S (Mettler-Toledo, Greifensee, Switzerland). The flour was used for the evaluation of pasting properties, thermal properties and rice protein pattern.

### 2.3. Determination of cooking properties

Cooking properties were determined by the method modified from Singh et al. (2005). One gram of head rice and 10 mL of water were added into a test tube before being heated in a boiling water bath. Minimum cooking time, water uptake, solid loss, volume expansion and elongation ratio were determined. Minimum cooking time was the shortest amount of time required for rice to be fully cooked; no white core existed at the center of rice grains once compressed between two cover glasses. The minimum cooking time was used in preparing cooked rice to be determined for other cooking properties. Water uptake was the percentage by weight of rice increased during cooking due to water absorption. Solid loss was the amount of solids in the remaining liquid left from cooking, reported as percentage of solids by weight of raw rice. Volume expansion was the ratio of the volume of cooked rice to that of raw rice. Elongation ratio was the ratio of the length of cooked rice to that of raw rice. The measurement was done in 4 replicates for the sample from each experimental unit.

### 2.4. Measurement of cooked rice texture

Textural properties of cooked rice were measured according to the method of Park et al. (2001) with slight modification. Twenty grams of head rice were mixed with certain amount of water (calculated from the water uptake value at specific aging time obtained from section 2.3), and steamed for the minimum cooking time recorded at the corresponding storage time (section 2.3). Cooked rice was kept in a sealed container for 30 min. Texture profile analysis of the samples was determined using Texture Analyzer TA-XT plus (Stable Micro Systems, Surrey, UK). Cooked rice kernels (1 g) were arranged in a single layer on a platform. The probe (P/100) was set at 30 mm above the platform, with test speed of 1 mm/s, post test speed of 5 mm/s, and holding time between cycles of 3 s. Textural parameters (i.e. hardness and adhesiveness) were determined via Exponent software version 6.1.5.0 (Stable Micro Systems). Thirty replicates of the measurement were performed for the sample from each experimental unit.

### 2.5. Determination of pasting properties

Pasting properties of rice flour were determined by Rapid Visco Analyzer (RVA-4, New Port Scientific Instrument and Engineering, Warriewater, Australia), using AACC Method 61–02.01 (AACC, 2000). Approximately 3 g of flour samples were mixed with 25 mL of distilled water. Pasting temperature, peak viscosity, breakdown and setback were determined by Thermocline for Windows version 3.11 (Newport Scientific Instrument and Engineering). Triplicate measurements were done for each experimental unit.

### 2.6. Evaluation of thermal properties

Diamond DSC (Perkin-Elmer Co., Norwalk, CT, USA) equipped with an Intracooler 2P (Perkin-Elmer) and nitrogen gas purge was used to determine gelatinization and amylose-lipid complex melting behaviors from rice flour samples. Approximately 16 milligrams of flour slurry with flour-to-water ratio of 1:3 were weighed into a large volume stainless steel pan (Perkin-Elmer kit no. 03190218), hermetically sealed, and equilibrated overnight at room temperature. The sample, as well as an empty reference pan, was scanned from 30 to 135 °C (10 °C/min). Onset temperature ($T_o$), peak temperature ($T_p$), conclusion temperature ($T_c$), enthalpy of the gelatinization endotherm ($\Delta H_g$), and amylose-lipid complex melting endotherm ($\Delta H_{al}$) were obtained via Pyris™ software version 11. Single measurement was done for the sample from each experimental unit.