# ผลของการเร่งอายุต่อการเปลี่ยนแปลงสัณฐานของเม็ดแป้ง สมบัติทางความร้อน และโปรตีนของแป้งข้าวที่เก็บเกี่ยวใหม่

Effects of Accelerated Aging on Changes in Starch Granule Morphology, Thermal and Protein Properties of Freshly-Harvested Rice Starch

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#### Abstract

This experiment aimed to investigate the effect of accelerated aging (AA) treatments on alterations of starch granule morphology, thermal property and protein property of freshly-harvested aromatic rice cv. KDML 105. Milled rice samples were accelerate-aged using an automatic autoclave setting at 100, 110 and 120°C for 100, 45 and 25 min, respectively. Observation of starch granule morphology using Scanning Electron Microscope (SEM) indicated that high temperature condition did not disrupt starch granular structure but caused change on the starch thermal property by increasing temperature of gelatinization and decreased gelatinization enthalpy ( $\Delta$ H) as determined by Differential Scanning Calorimeter (DSC). AA treatments increased number of disulfide bonds of protein sub unit and changed solubility of rice protein. Protein and starch thermal properties changes in AA rice occurred at molecular level of rice starch granule components. These were basis changes related to cooking, textural and pasting characteristics of rice.

Keywords: Aromatic rice, accelerated aging, starch property

#### าเทคัดย่อ

การทดลองนี้มีวัตถุประสงค์เพื่อศึกษาผลของการเร่งอายุต่อการเปลี่ยนแปลงสัณฐานของเม็ดแป้งข้าว สมบัติทาง ความร้อนและโปรตีนของข้าวหอมที่เพิ่งเก็บเกี่ยวใหม่พันธุ์ขาวดอกมะลิ 105 ข้าวสารตัวอย่างถูกเร่งอายุโดยใช้หม้อนึ่งความดัน อัตโนมัติที่อุณหภูมิ 100 110 และ 120 องศาเซลเซียส ด้วยระยะเวลา 100 45 และ 25 นาที ตามลำดับ การศึกษาสัณฐานของ เม็ดแป้งข้าวด้วยกล้องจุลทรรศน์อิเล็คตรอนแบบส่องกราด (SEM) พบว่า ความร้อนของปัจจัยการเร่งอายุไม่ก่อให้เกิดความ เสียหายต่อสัณฐานของเม็ดแป้ง แต่การเร่งอายุเปลี่ยนแปลงสมบัติทางความร้อนของแป้งโดยทำให้อุณหภูมิการเจลลาติไนซ์ ของแป้งข้าวเพิ่มขึ้นและปริมาณความร้อนที่ใช้ในการเจลลาติไนซ์ลดลงเมื่อวิเคราะห์ด้วยเครื่องดิฟเฟอเรนเชี่ยลสแกนนิ่งแคโล ริ-มิเตอร์ (DSC) การเร่งอายุเพิ่มจำนวนพันธะไดซัลไฟด์ระหว่างหน่วยย่อยของโปรตีนและมีผลต่อสมบัติการละลายน้ำของโปรตีน การเปลี่ยนแปลงสมบัติทางความร้อนและโปรตีนดังกล่าวเกิดที่ระดับโมเลกุลขององค์ประกอบเคมีของแป้งข้าว และเป็น พื้นฐานของการเปลี่ยนแปลงคุณสมบัติการหุงต้ม เนื้อสัมผัส และความหนืดชันของข้าว

คำสำคัญ: ข้าวหอม การเร่งอายุ สมบัติของเม็ดแป้ง

#### Introduction

Aging affects various rice physico-chemical properties which are related to changes in cooking and pasting characteristics of stored rice. These changes had been reported to associate with change in protein property (Hamaker and Griffin, 1990; Martin and Fitzgerald, 2002; Fitzgerald, et al., 2003). The main storage protein in rice was oryzenin and its molecular weight increased significantly during storage (Chrastil, 1990). This

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increase was correlated with an increase in disulfide bonding between cysteine (Chrastil and Zarins, 1992). The formation of disulfide bond of the protein sub unit decreased its solubility and could affect pasting property as studied via RVA (Zhou et al., 2003). Change in property of rice protein that occurs during natural aging may be enhanced by high temperature (Derycke et al., 2005). High temperature was also reported to influence thermal property (Altay and Gunasekaran, 2006). In this present study, AA of freshly-harvested milled rice was achieved by high temperature treatment, and thus the rice starch granule and its component would likely be affected. The experiment was thus designed to investigate changes in starch granule morphology, thermal and protein properties caused by AA treatments.

#### Materials and Methods

Three replicates, each of 370 g of head milled rice from freshly-harvested paddy, cv. KDML105, were placed in aluminum containers and sealed. The containers were then exposed to three different aging treatments, 100°C for 100 min, 110°C for 45 min and 120°C for 25 min in an automatic autoclave. After exposure, the containers were left covered and cooled for about 2 hr at 21°C. Subsequently, the rice samples were poured into zip-locked plastic bags and kept at -20°C until the time of analyses. Change in starch properties of fresh and AA samples were investigated. Cross section of middle part of rice kernels including their flour samples were viewed on a Scanning Electron Microscope (JEOL Technics LTD., Japan) at an accelerating voltage of 15 kV. Thermal properties of flour samples were analyzed using a Differential Scanning Calorimeter (DSC, TA Q100, TA Instruments, Newcastle, DE). Thermal scan was performed from 35 to 110°C at a heating rate of 2°C/min. Increases in disulphide bonding of protein sub unit was done employing a Rapid Visco Analyser (RVA model 4, Newport Scientific, Warriewood, NSW, Australia). Flour (3 g on the basis of 12% MC) was poured into a RVA canister and the weight was made up to 28 g with distilled water or solutions containing 10 mM dithiothreitol (DTT, Fluka 43819). Differences in the RVA parameters between samples were then recorded and analyzed.

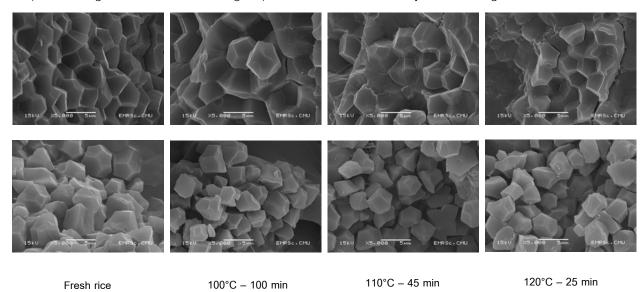
## Results and Discussion

## Investigation of changes in starch granule morphology

Kernel cross section and flour samples were scanned thoroughly to observe for gelatinization or disruption of the rice starch granules (Figure 1). This was done since gelatinization of starch molecule is associated with the disruption of starch granular structure. The result revealed that starch granules retained their polygonal morphology after AA treatments. SEM micrographs indicated that surface of the starch granules did not lose their flatness and smoothness. This suggested that the gelatinization of starch did not likely take place in the rice kernel though the temperature and exposure duration were sufficient for completion of its gelatinization. This was attributed to AA samples had low moisture content (approximately 13.3%wb) as compared to that of parboiled rice. Result indicated that high temperature condition of this present study enhanced aging process of fresh rice without disruption of its starch granular structure.

### Determination of changes in thermal properties

The thermal transition in terms of onset  $(T_0)$ , peak  $(T_p)$  and conclusion  $(T_0)$  temperatures of gelatinization, gelatinization temperature range ( $\Delta T = T_c = T_c$ ) as well as gelatinization enthalpy ( $\Delta H$ ) of AA rice significantly differed from those of fresh rice (Table 1). The results indicated that  $T_{c}$ ,  $T_{p}$  and  $T_{c}$  of the AA rice shifted to higher temperature. High gelatinization transition temperatures were an indication of aging (Zhou et al., 2003). Thus, increases in gelatinization temperatures implied that aging had already taken place in fresh milled rice after AA treatments. Increases in the transition temperatures of AA rice might be attributed to less solubility of their starch granules caused by AA treatments. The AA conditions of this study could enhance rate of oxidation process of rice constituents including oxidation of starch granule-bound protein. This protein could become more restricted to hydration and swelling of the starch granules which consequently retarded starch gelatinization and hence the temperature of gelatinization shifted to higher position when determined by DSC thermograms.



<u>Figure 1</u> Scanning electron microscopy of freshly-harvested KDML105 rice starch granule after accelerated aging with different conditions.

Table 1 Thermal transition in terms of onset  $(T_p)$ , peak  $(T_p)$ , and conclusion  $(T_c)$  temperatures and gelatinization enthalpy ( $\Delta$ H) of flour samples ( $J g^{-1}$ , 11% MC wb) of KDML 105 freshly harvested rice as affected by accelerated aging treatments.

Accelerated aging treatments (Temperature –time)		Transition temperature (°C)			
	T <sub>o</sub>	$T_P$	T <sub>c</sub>	T <sub>c</sub> - T <sub>o</sub>	$\Delta$ H (J g <sup>-1</sup> )
Fresh rice	57.52±0.135 <sup>b</sup>	65.02±0.061 <sup>c</sup>	72.34±0.111	14.83±0.061 <sup>a</sup>	7.79±0.128 <sup>a</sup>
100°C-100 min	58.13±0.053 <sup>a</sup>	65.31±0.031 <sup>b</sup>	72.47±0.113	14.35±0.075 <sup>b</sup>	7.20±0.108 <sup>b</sup>
110°C-45 min	58.08±0.083 <sup>a</sup>	65.33±0.094 <sup>ab</sup>	72.57±0.090	14.49±0.106 <sup>b</sup>	7.18±0.020 <sup>b</sup>
120°C-25 min	58.20±0.208 <sup>a</sup>	65.42±0.031 <sup>a</sup>	72.60±0.101	14.41±0.269 <sup>b</sup>	7.07±0.103 <sup>b</sup>

Means (± SD) followed by the same letters in a column are not significantly different by DMRT (P<0.05)

## Investigation of changes in protein properties

To investigate change at molecular structure of starch granular protein, pasting curves obtained from RVA were employed. Results indicated that AA treatment changed the freshly-harvested rice to become aged as observed by RVA viscograms in Figure 2A. AA rice flour samples performed their RVA pasting curves different from fresh rice. This was possibly attributed to the increase in cross-linking between the protein sub units caused by the AA treatments. During AA, disulfide cross-links may rapidly be generated between both intra and inter-links of the protein molecules and that the protein network became a barrier to water penetration, hydration and swelling of the starch granules. To verify whether changes in RVA viscosity of AA rice samples were due to cross-linking between sulfhydryl groups of cysteine units. DTT was utilized because of it has a specific effect to reduce only the disulfide bridge. The results showed that the pasting curves of AA operated with 10 mM DTT solution behaved almost similar to the typical viscogram of fresh rice as illustrated in Figure 2B. In the Figure, different responses to DTT between fresh and AA samples were observed. In the presence of DTT, pasting temperature, trough and final viscosity of the AA samples decreased markedly while peak viscosity increased. These significant changes resulted in a greater increase in breakdown and decrease in setback value.

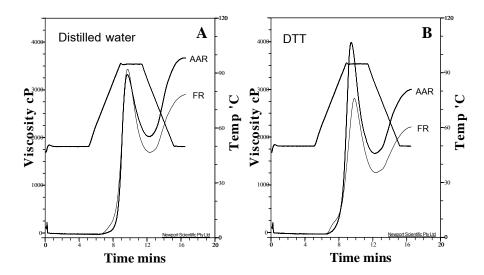


Figure 2 RVA viscograms of flour from freshly-harvested rice cv. KDML105 (FR) and the flour after accelerated aging with 100°C for 100 min (AAR) when operated with distilled water and with solution containing dithiothreitol (10 mM DTT).

#### Summary

This study revealed that AA treatments did not change morphology of the rice starch granule but had influence on thermal and protein properties of rice starch. These changes occurred at the molecular level of the rice starch granule components and exerted their influences on the physico-chemical properties that are related to cooking characteristics of rice.

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