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Changes in the Physical and Chemical Properties of Thai Brown Rice Caused by High-Temperature Treatment

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The market for healthy food in Thailand is increasing rapidly due to growing recognition that food ingredients can causes diseases such as cancer and type 2 diabetes. Healthy food from natural products, and especially from whole grains such as brown rice, has become a priority for Thai consumers. Brown rice is rich in nutrients such as fiber and vitamins. However, brown rice has a high glycemic index and is therefore not suitable for patients with type 2 diabetes, since blood sugar and insulin levels increase rapidly after ingestion of this rice. The Khao Dok Mali 105 cultivar of brown rice has a low amylose content (12% to 17% by weight), and is popular in Thailand because of its flavor, aroma, and soft texture. However, cultivars such as Phisanurok 3 and Suphan Buri 1 with high starch amylose contents (23% to 26% by weight) are also in demand. Thai rice varieties normally contain degrees of crystallinity of A-type amylose, with a medium to fast digestion rate. Recently, researchers found that high-temperature treatment (130 to 150℃) influenced the glycemic index of brown rice. Gelatinization was produced during the processing, and affected physical and chemical properties such as texture and starch digestibility. The processing decreased the degree of crystallinity (i.e., increased the proportion of V-type amylose) and produced amylose–lipid complexes in the brown rice, which slow digestion of the starch. Our study is the first to confirm these previous results for three popular Thai rice cultivars.

Key words: brown rice, glycemic index, high-temperature treatment, Thai rice

Introduction

The market for healthy food in Thailand is increasing rapidly due to growing recognition that food ingredients can cause diseases such as cancer and type 2 diabetes. Healthy food from natural products, and especially whole grains such as brown rice, has therefore become an increasingly popular choice for Thai consumers. The nutrients in brown rice, such as dietary fiber, minerals oils, and vitamins, may prevent a variety of diseases (Houston and Kohler, 1970).

Researchers have recently discovered that the physical and chemical properties of rice can be altered by high-temperature processing (Wiset *et al*., 2005). Paddy rice with high initial moisture content can become partially gelatinized because the starch granules absorb water. In regions with a sufficient water supply, drying at high temperatures causes starch that is rich in water to absorb the water and undergo physical and chemical changes as gelatinization proceeds. In contrast, starch does not change form when the water supply is insufficient (Owen, 1996). The natural process of gelatinization can be simulated by heating starch granules in the presence of sufficient water, leading to partial gelatinization and a loss of crystallinity so that the starch granules become amorphous (Jenkins and Donald, 1998).

The glycemic index of brown rice can also be changed by high-temperature processing (Jaisut *et al*., 2009). When raw starch granules are processed at high temperatures, the resulting disruption of the starch structure affects the rate of digestion of the starch (Zhejiang

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and Bergman, 2004). Tetens *et al*. (1997) reported that parboiling decreased the digestion rate of rice starch. Rashmi and Urooj (2003) found that steaming rice could create resistant forms of starch. During steaming, amylose changes from a coil form to a helix form (referred to as A or B amylose) and guest molecules enter the central cavities of the amylose helices. This conformational ordering promotes aggregation of the helices, resulting in a partially crystalline amylose structure referred to as V-amylose (Biliaderis, 1992; Eliasson and Krog, 1985; Osman *et al*., 1961). In addition, complexation between lipids and the starch can occur, leading to binding of the lipids inside the amylose helix (Godet *et al*., 1993). The formation of such complexes provides more stability and higher resistance to enzymatic hydrolysis.

Although these processes are reasonably well understood, the effects of heating on the physical and chemical properties of the rice grains of Thai rice varieties has not been studied. In the present study, our goal was to investigate the effect of high-temperature drying on changes in the physical and chemical properties of Thai brown rice; to do so, we used three popular cultivars (Phisanurok 3, Suphan Buri 1, and Khao Dok Mali 105). The effects of drying temperature on the degree of gelatinization, on head brown rice yield, and on the rice's glycemic value were examined.

Materials and Methods

Materials

We obtained dried long-grain rough rice (Suphan Buri 1, Phisanurok 3, and Khao Dok Mali 105) from the Rice Research Institute in Pathumthani Province, Thailand. We rewetted the rice, sprinkled water on the rice, mixed the rice to ensure that all grains could contact the water, and then kept it in cold storage at 4 to 6℃ for 1 week prior to our experiments. The desired initial moisture content of the rewetted paddy rice was about 33% (dry-weight basis, DWB). Before starting each experiment, the paddy rice was stored in the lab until its temperature was close to the ambient temperature.

Preparation of the dried sample

We dried 1.8 to 1.9 kg of the rewetted sample in a fluidized bed dryer at temperatures of 130 to 150℃ using hot air as a drying medium, with a superficial velocity of 2.5 m/s. The desired moisture content after drying was approximately 23% (DWB), as recommended by Poomsa-ad *et al*. (2001). The rice was then tempered for 120 min to reduce the stresses created during drying. During the tempering step, the sample was kept in a closed jar to avoid moisture loss. Subsequently, the sample was ventilated in thin layer dryer, using ambient air at an air flow rate of 0.15 m/s until the moisture content reached 16% (DWB). This ventilation took 30 to 40 min. The sample was then kept at ambient temperature. The quality of the dried paddy rice (i.e., thermal properties, starch digestibility, and head brown rice yield) was subsequently determined and compared with reference which dried in shade. Dried of head brown rice was processed using an Ultracentrifugal Mill to produce particles with a size 0.25 mm in diameter.

Thermal properties of the rice

Thermal analysis of the brown rice flour was performed using a DSC-7 differential scanning calorimeter (Perkin Elmer, Norwalk, CT, USA). The brown rice flour was heated from 40℃ to 130℃ or 150℃ at a scanning rate of 10℃/ min. We weighed 3-mg samples into aluminum sample pans and added 10 μL of water. We then recorded the major parameters of the thermal profiles: the onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and transition enthalpy. The sample obtained under each combination of processing conditions was analyzed in triplicate. The degree of gelatinization (*SG*, %) was calculated from the first endothermic peak by using the following equation:

$$SG\,(\%)=\left(1-\left[\frac{\Delta H}{\Delta H_c}\right]\right)\times 100 \qquad (1)$$

where ΔH is the transition enthalpy of the treated brown rice (J/g dry matter) and ΔH_c is the transition enthalpy of raw brown rice (J/g dry matter).

In vitro kinetics of starch digestion

Brown rice starch digestion was determined according to the method proposed by Goni *et al*. (1997). *In vitro* starch digestion was measured immediately after cooking to avoid starch retrogradation. The enzymatic hydrolysis was performed on the following day in the same flask as the cooking to avoid losses of the sample. A sample of the rice (50 mg) was prepared in 30-mL Erlenmeyer flasks; 4 mL of distilled water was added and the sample was cooked at 180℃ for 30 min. Subsequently, 10 mL of HCl−KCl buffer at pH 1.5 was added, and the sample was homogenized for 2 min using a T25 Ultra Turrax homogenizer (IKA Labortechnik, Staufen, Germany). We then added 0.2 mL of a solution containing 1 mg of pepsin from porcine gastric mucosa (107195, Merck) in 10 mL of HCl–KCl buffer at pH 1.5 to each sample. We then incubated the sample for 60 min in a shaking water bath at 40℃. The volume was adjusted to 25 mL by adding 15 mL of Tris-maleate buffer (pH 6.9) and the pH was adjusted to 6.9.

To start the starch hydrolysis, another 5 mL of Tris-maleate buffer containing 2.6 IU of α-amylase from porcine pancreas (A-3176, Sigma) was added to each sample. The flasks were placed in a shaking water bath at 37℃ with moderate agitation. Aliquots (0.1 mL) were taken from each flask at 30-min intervals from 0 to 3 h. The α-amylase in these samples was immediately inactivated by placing the tubes containing the aliquots in boiling water for 5 min. We then added 1 mL of 0.4 M sodium acetate buffer at pH 4.75 and 30 μL of amyloglucosidase from *Aspergillus niger* (102 857, Roche) to hydrolyze the solubilized starch. The sample was then incubated at 60℃ for 45 min. Finally, the glucose concentration was measured using a glucose oxidase–peroxidase kit (510-A, Sigma). The rate of starch digestion was expressed as a percentage of the total starch hydrolyzed at different times (30, 60, 90, 120, 150, and 180 min). Each treatment was analyzed in triplicate.

We used the non-linear model established by Goni *et al.* (1997) to describe the kinetics of starch hydrolysis:

$$C = C_\infty(1 - e^{-kt}) \tag{2}$$

where C is the percentage of starch hydrolyzed at time t (min), C_∞ is the percentage of starch hydrolyzed after 180 min, and k is the kinetic constant (min^{-1}). The parameters C_∞ and k were estimated for each treatment based on the data obtained from the *in vitro* hydrolysis procedure. The area under the hydrolysis curve (*AUC*) was calculated using the following equation:

$$\begin{aligned} AUC = {} & C_\infty(t_f - t_0) - (c_\infty/k) \\ & (1 - \exp[-k(t_f - t_0)]) \end{aligned} \tag{3}$$

where t_f is the final time (180 min) and t_0 is the initial time (0 min).

The hydrolysis index (*HI*) was defined as the *AUC* for the treated sample divided by the corresponding area for white bread. Goni *et al.* (1997) showed that *HI* was a good predictor of the glycemic response. We therefore estimated the glycemic index (*GI*) by using the following equation (Goni *et al.*, 1997):

$$GI = 39.71 + (0.549HI) \tag{4}$$

Head brown rice yield

We dehulled a sample (250 g) from each treatment using a Satake bench-top dehusker. We then separated the sample by using a rotating indented cylinder to determine the head rice yield. Head rice yield was calculated by dividing the head rice mass by the initial rice mass before separation. Each measurement was performed in duplicate and the reported value represented the average of the measured values.

Results and Discussion

Changes in physical properties during high-temperature processing

The amylose content in the three Thai rice cultivars that we analyzed ranged from 14.8% for Khao Dok Mali 105 to 26.0% for Phisanurok 3, with an intermediate value of 23.0% for Suphan Buri 1. Suphan Buri 1 and Phisanurok 3 are therefore high-amylose varieties, whereas Khao Dok Mali 105 is a low-amylose cultivar. The different amylose contents of the rice affect the physical and chemical changes that occur during high-temperature processing (Chung *et al.*, 2011). Table 1 shows that the drying temperature affected the degree of gelatinization. At an initial moisture content of 33.3% (DWB), the degrees of gelatinization ranged from 45.1% to 57.0% at a drying temperature of 150℃ and a tempering time of 120 min. The degrees of gelatinization were lower, ranging from 38.9% to 46.8%, at a drying temperature of 130℃.

The degree of gelatinization increased with increasing amylose content. After drying at 150℃ and tempering for 120 min, Phisanurok 3 had the highest degree of gelatinization (57%) whereas Khao Dok Mali 105 and Suphan Buri 1 had degrees of 45.1% and 53.2 %, respectively.

Paddy rice with high initial moisture content can become partially gelatinized because starch granules can absorb water, leading to gelatinization. During drying at high temperature, starch that is rich in water will absorb the water and undergo changes as gelatinization proceeds. In contrast, where there is insufficient water, the starch does not change form (Owen, 1996). The natural process of gelatinization can be simulated by heating starch granules in the presence of sufficient water, leading to partial gelatinization and a

Table 1. Thermal analysis of the dried samples. All moisture contents (%) are expressed on a dry-weight basis. All durations represent the tempering duration.

Condition	Transition temp (℃) T_{o1}	Transition temp (℃) T_{p1}	Transition temp (℃) T_{c1}	ΔH_1 (J/g)	Degree of gelatinization (%)
Suphan Buri 1					
Reference 33.3%	63.4	72.4	76.1	7.9±0.01	—
T=130℃, 33.3%, 120 min	67.7	76.4	80.6	4.4±0.13	44.3±0.1^{b}
T=150℃, 33.3%, 120 min	72.8	78.1	84.0	3.7±0.02	53.2±0.1^{e}
Phisanurok 3					
Reference 33.3%	64.2	70.1	78.9	8.0±0.02	—
T=130℃, 33.3%, 120 min	67.5	72.4	80.8	4.2±0.01	46.8±0.5^{d}
T=150℃, 33.3%, 120 min	69.8	74.1	83.2	3.4±0.03	57.0±0.2^{f}
Khao Dok Mali 105					
Reference 33.3%	64.0	71.7	79.6	6.5±0.40	—
T=130℃, 33.3%, 120 min	69.5	74.2	82.2	4.1±0.07	38.9±0.5^{a}
T=150℃, 33.3%, 120 min	69.9	74.9	82.9	3.7±0.01	45.1±0.1^{c}

Table 2. Head brown rice yield. All moisture contents are expressed on a dry-weight basis. All durations represent the tempering duration.

Condition	Head brown rice yield (%)
Suphan Buri 1	
Reference 33.3%	63.8±0.9
T=130℃, 33.3%, 120 min	71.2±0.4
T=150℃, 33.3%, 120 min	72.5±0.6
Phisanurok 3	
Reference 33.3%	64.3±1.0
T=130℃, 33.3%, 120 min	75.3±0.5
T=150℃, 33.3%, 120 min	76.3±0.4
Khao Dok Mali 105	
Reference 33.3%	42.1±1.7
T=130℃, 33.3%, 120 min	39.1±1.4
T=150℃, 33.3%, 120 min	49.3±1.3

loss of crystallinity so that the starch granules become amorphous (Jenkins and Donald, 1998). A tempering process following high-temperature drying is important for grain quality, as this period allows the moisture in the core of the kernel to migrate to the outer layers along a moisture gradient without producing stresses that may crack the grain. During this stress-relaxation stage, starch properties can also be modified.

Table 2 shows the head brown rice yields of the samples dried at 130 and 150℃ and then tempered for 120 min. The yield improvement depended on the degree of gelatinization, with a higher degree of gelatinization producing a larger head rice yield. The head rice yields (49% to 76%) for degrees of gelatinization ranging from 45% to 57% obtained by drying at 150℃, were significantly higher than those with degrees of gelatinization ranging from 39% to 75%, obtained by drying at 130℃. The gelatinization of starch that occurred during drying and tempering helped to seal cracks inside the kernels, which therefore increased the head rice yield (Inprasit and Noomhorm, 2001; Taweerattanapanish *et al*., 1999). The higher increases for Phisanurok 3 and Suphan Buri 1 confirm that the amylose content plays an important role in gelatinization.

Starch Digestibility

Table 3 shows the maximum percentage of starch hydrolysis (*HI*) and the glycemic index (*GI*) under different processing conditions for Phisanurok 3, Suphan Buri 1, and Khao Dok Mali 105. The kinetics of starch hydrolysis were described well by Eq. (1), as indicated by the high R^2 value (0.99) for all analyses. All hydrolysis parameters of the samples subjected to the drying treatments were lower than those of the reference sample.

The *GI* value of reference brown rice ranged from

Table 3. Hydrolysis index (*HI*) and glycemic index (*GI*) of the dried samples. All moisture contents are expressed on a dry-weight basis. All durations represent the tempering duration.

Condition	*HI*	*GI*	R^2
Suphan Buri 1			
Reference 33.3%	53.2±0.011	68.9±0.0010^h	0.99
T=130℃, 33.3%, 120 min	39.7±0.009	61.5±0.0028^e	0.99
T=150℃, 33.3%, 120 min	31.4±0.021	56.9±0.0146^b	0.99
Phisanurok 3			
Reference 33.3%	49.4±0.009	66.8±0.0113^g	0.99
T=130℃, 33.3%, 120 min	40.2±0.018	59.2±0.0092^c	0.99
T=150℃, 33.3%, 120 min	28.8±0.018	55.5±0.0122^a	0.99
Khao Dok Mali 105			
Reference 33.3%	55.75±0.002	70.3±0.0009^i	0.99
T=130℃, 33.3%, 120 min	41.2±0.002	62.6±0.0010^f	0.99
T=150℃, 33.3%, 120 min	36.8±0.050	59.9±0.0277^d	0.99

Table 4. Crystallinities of the dried brown rice samples. All moisture contents are expressed on a dry-weight basis. All durations represent the tempering duration.

Condition	A-type amylose (%)	V-type amylose (%)
Suphan Buri 1		
Reference 33.3%	22.9±0.1^h	1.5±0.1^b
T=130℃, 33.3%, 120 min	14.3±0.2^e	5.2±0.2^c
T=150℃, 33.3%, 120 min	9.2±0.3^{bc}	6.8±0.1^e
Phisanurok 3		
Reference 33.3%	19.9±0.3^g	1.6±0.1^b
T=130℃, 33.3%, 120 min	13.0±0.1^d	5.7±0.2^d
T=150℃, 33.3%, 120 min	8.6±0.4^b	8.4±0.2^f
Khao Dok Mali 105		
Reference 33.3%	14.9±0.1^f	1.0±0.2^a
T=130℃, 33.3%, 120 min	9.9±0.4^c	4.8±0.2^c
T=150℃, 33.3%, 120 min	7.6±0.3^a	6.0±0.1^d

66.8 to 70.3, which represents a medium to high glycemic index (Champ *et al*., 2003). After high-temperature drying, the *GI* value fell into the low to medium category, with values ranging from 55.5 to 62.6. The effect of drying temperature on the *GI* value was therefore significant. Our results show that to reduce the *GI* value, it is necessary to dry brown rice at temperatures higher than 130℃.

The decreasing *GI* values probably result from the formation of amylose-lipid complexes during the heat treatment; these complexes resist enzymatic digestion. The *GI* values suggest that the brown rice dried using the fluidization technique was less digestible than the untreated rice, and therefore might have beneficial health effects.

The results for Phisanurok 3 and Suphan Buri 1 (Table 3) showed that the amylose content of the brown rice may affect starch hydrolysis. The cultivar with the highest amylose content (Phisanurok 3) had the lowest *GI* value (55.5) when heated at 150℃ and a moisture content of 33.3% DWB, with tempering for 120 min.

Table 4 summarizes the crystallinities of the dried brown rice samples. The percentages of V-type amylose increased after drying. During the high-temperature process, amylose changes from coil form to helix form and guest molecules enter the central cavities of the amylose helices. This conformational ordering promotes aggregation of the helices, resulting in a partially crystalline amylose structure, which is referred to as V-amylose (Osman *et al*., 1961; Eliasson and Krog, 1985; Biliaderis, 1992). Table 4 clearly shows increased proportions of V-amylose and decreased proportions of the A-amylose as a result of the heat treatments. In addition, the complexation of lipids and starch can occur, leading to binding of lipids and other guest molecules inside the amylose helix (Godet *et al*., 1993). The formation of these complexes provides more stability and a higher resistance to enzymatic hydrolysis. This change is confirmed by the decreasing *GI* values shown in Table 3.

Conclusions

High-temperature processing using fluidized bed drying followed by tempering changed the physical and chemical properties of three cultivars of Thai brown rice, as was previously reported for non-Thai cultivars. Drying temperature had a clear effect on the head brown rice yield and the glycemic index. The increased degree of gelatinization that resulted from the high-temperature treatments could be attributed to the loss of polygonal starch granules, and the tempering improved the head brown rice yield. The effect of amylose content on starch hydrolysis in the dried samples may be an important cause of the decreased brown rice glycemic index as a result of the formation of amylose-lipid complexes, but to confirm this, it will be necessary to perform X-ray diffraction tests to confirm the conversion of some A-type amylose to V-type amylose, resulting in more amylose-lipid complexes and lower *GI*. Based on the results of this study, we recommend high-temperature processing of Thai rice using fluidized bed drying, followed by tempering and ventilation, to reduce the glycemic index of Thai brown rice from medium to high in untreated rice to low to medium in the treated rice (for Suphan Buri 1, GI decreased from 68.9 to 56.9; for Phisanurok 3, GI decreased from 66.8 to 55.5; for Khao Dok Mali 105, GI decreased from 70.3 to 59.9).

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