Development of lightly milled black rice with easy cooking and retaining health benefits

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Abstract Consumers are reluctant to eat pigmented rice due to cooking difficulties and harder texture than white rice. In this study, paddy samples of black rice (Hom Nil cultivar) were milled for 0, 10, 30, 60 and 100 s and degree of milling (DOM) ~ 0, 6, 12, 22 and 30% were obtained. Head rice yield, physicochemical properties, cooking qualities, nutrients, resistant starch content, antioxidant properties, and sensorial qualities were studied. Milling at 10 s (DOM ~ 6%) did not remove all bran fractions. Head rice yield retained at 70.33%. Lightness (L^*) and redness (a^*) of black rice remained constant until DOM ~ 20% but yellowness (b^*) gradually increased. Nutrients were embedded at different locations in grain kernels. All nutrients decreased with DOM but in different extents. Milling at 10 s generated loss of anthocyanin (70%), fat (44%), ash (33%) and phenolic compounds (31%). Comparably tiny losses were observed in protein (15%) and dietary fiber (25%). However, cooking qualities of black rice were substantially improved. Cooking time reduced from 22 to 15 min with increases in water uptake ratio and volume expansion ratio. Additionally cooked black rice had impressively softer texture. Panelist appreciated the change in odor, flavor, texture attributes and palatability of the rice.

Keywords Black rice · Milling · Cooking quality · Antioxidant · Resistant starch

Introduction

Rice (*Oryza sativa* L.) is the main staple diet in many Asian countries. With growing health concerns and enlarging markets of healthy food products, some particular rice cultivars are increasingly produced and introduced to consumers in Thailand and worldwide. Among these rice cultivars, black rice is unpolished rice that contains a high content of natural anthocyanin compounds such as cyanidin 3-glucoside and peonidin 3-glucoside in the aleurone layer (Hu et al. 2003). It has other valuable antioxidants, including polyphenolics, flavonoids, vitamin E, phytic acid, and γ -oryzanol. Black rice has received wide interest from consumers and food industry owing to antioxidative, anti-inflammatory, antiatherosclerotic, anticancer and lower cholesterol properties (Hu et al. 2003). In addition, black rice is a good source of fiber, minerals, and several essential amino acids (Itani et al. 2002).

In order to consume rice, the hull is removed from rough rice to obtain brown rice. Brown rice (hulled rice) composes of the embryo (2–3% by weight), surface bran (6–7%), and endosperm (around 90%). Milling (whitening process) subsequently removes germs and bran layers from hulled rice by abrasive or friction forces and provides well-milled, reasonably well-milled, lightly milled, and under-milled rice depended on degree of milling (DOM). DOM is expressed by the weight percentage of bran removed or indicated by visual examination, chemical composition, and optical measurements. Milling induces grain breakage resulting in reduction of head rice yield (Reid et al. 1998; Yadav and Jindal 2008) and causes losses of food nutrients including fat (Chen and Siebenmorgen 1997), neutraceutical lipid (Ha et al. 2006), protein (Lamberts et al. 2007), dietary fiber (Lai et al. 2006), ash (Singh et al. 2000; Lamberts et al. 2007), phosphorus, magnesium, calcium,

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copper, manganese, molybdenum, chromium (Doesthale et al. 1979), iron (Prom-u-thai et al. 2007), zinc (Liang et al. 2008) and selenium (Liu et al. 2009). For antioxidant properties, phenolic, flavonoids, and anthocyanin content and antioxidant activity decreased after milling (Hu et al. 2003; Zhou et al. 2004; Walter et al. 2011) because more than 50% of polyphenols is in removed pericarp.

Milling devalues the nutritional and health benefits of hulled rice. However, it improves the cooking and sensory quality of rice. Thus, the majority of the consumers prefer well-milled rice, especially in countries where rice is the principal food. Researchers have reported a reduction of cooking time and increases in water absorption during cooking, volume expansion ratio, and length expansion ratio after milling (Mohapatra and Bal 2006, 2007). As a result of change in cooking quality, improved cooked rice texture was observed which included decline in hardness, firmness and chewiness and increases in cohesiveness, adhesiveness and stickiness (Park et al. 2001; Mohapatra and Bal 2006). Moreover, alteration of sensory attributes in terms of texture and flavor intensity have been reported by Park et al. (2001). The panelists preferred cooked milled rice more than cooked brown rice (Piggott et al. 1991).

Usually, DOM increases with milling time. But, deviations of obtained DOM could be detected among rice cultivars due to differences in kernel characteristics, grain morphological characteristics including grain thickness, grain length, and length-to-width ratio that play an important role in gained DOM (Chen and Siebenmorgen 1997; Prom-u-thai et al. 2007). Most of the reported works, however, involved rice grains with light brown pericarp color. For this reason, little is known about the effects of milling on DOM and the qualities of black rice.

Certainly, milling creates adverse effects but simultaneously amended rice qualities. However, these changes are dependent on the extent of milling. Thus, the objective of this study was to evaluate the effects of milling on qualities of black rice. The suitable degree of milling was assessed to produce easy-to-cook black rice that exhibit softer texture, desirable sensory quality, and reasonable nutritional and health benefits. It is anticipated that the results of this work will promote black rice consumption among the young generation.

Materials and methods

Dehusking and milling

Paddy of fragrant black rice, Hom Nil cultivar, was purchased from a local rice mill in Nakorn Sawan province, Thailand. Freshly harvested paddy was cleaned by air classifier to remove the filth. It was dried at 30 °C using a

circulated air incubator to a final moisture content of 12–14%. Paddy sample was stored dry and cool (~ 25 °C) less than 30 days before milling and analysis.

Paddy samples (250 g) were dehusked on a laboratory scale rubble roll husker (THU 35A, Satake, Japan). Whole and intact black rice kernels (150 g) were milled in triplicate for 0, 10, 30, 60, and 100 s in the laboratory scale abrasive rice polisher (SKD-DBKK, Satake, Japan) equipped with an automatic timer to obtain rice with different DOM (0–25%). The DOM (the weight percentage of kernel layers removed by milling) was calculated from the weight of rice before and after milling. The screen and rotor of the polisher were thoroughly brushed to remove rice bran and rice kernels. After the whitening process, broken kernels were removed using a test rice length grader set with a 6.2 mm groove grading screen and receiving trough set at an angle of 30° from vertical. (TRG05A, Satake, Japan). The head rice with different DOM was conveyed to quality analysis.

Determination of head rice yield, color and cooking quality

Head rice yield

After rice kernels milled at different DOM were graded, head rice was separated and weighed. Head rice yield was expressed as a percentage of the weight of milled head rice kernels to the total weight of paddy.

Color of rice grain

Color of rice grain was measured in terms of L* value (lightness), a* value (redness), and b* (yellowness) using a CIE LAB Color Meter (ColorFlex E2, Hunter Lab, USA).

Cooking time

In order to assess the cooking time (C_T), five gram of rice sample was cooked in boiling water (rice: water = 1:20). Cooking time was recorded when nine from ten kernels were completely gelatinized.

Water uptake ratio, volume expansion ratio, length expansion ratio

Water uptake ratio (W_{UR}), volume expansion ratio (V_{ER}) and length expansion ratio (L_{ER}) were determined by cooking 1 g of rice in 15 mL boiling water until the pre-determined cooking time (Mohapatra and Bal 2006). The water uptake ratio was determined by the weighing of initial raw rice and cooked rice using a digital balance. It was expressed as the ratio of water absorbed during

cooking to uncooked rice weight. For volume expansion ratio, the volume of raw rice and cooked rice was measured using the toluene displacement method. The ratio of cooked rice volume to raw rice volume was reported. Similarly, lengths of rice kernels before and after cooking (20 kernels per replicate) were determined by a digital micrometer. The length expansion ratio was presented as the ratio of cooked rice length to raw rice length. In order to evaluate overall cooking quality, the cooking index (CI) was calculated by the formula as follows

$$CI = \frac{V_{ER} \times L_{ER} \times W_{ER}}{C_T}$$

Cooked rice hardness

For cooked rice hardness, 10 g of black rice kernels were placed in a beaker and added with 15 mL of water. The rice was cooked in an automatic rice cooker for 45 min with 800 mL of water was poured into the inner pot. The cooked rice sample was kept in the rice cooker for 10 min more. The samples were taken out and cooled at room temperature for 45 min. Then, the texture of cooked black rice was measured using back extrusion tests with a texture analyzer (TA 500, Lloyd Instruments, UK) equipped with a 50 kg-capacity compression load cell. The crosshead speed was 50 mm/min. The back extrusion test cell consisted of a stainless steel cylinder and a spherical-shaped stainless steel plunger. About 4 g cooked rice sample was placed in the cylinder. The plunger was allowed to move downward until it stopped 1 mm above the cell base. The hardness of cooked rice was determined from the maximum extrusion force in terms of Newton (N).

Determination of pasting property

Black rice samples were ground and screened through a 100-mesh sieve. Paste viscosity of black rice flours was determined with a Rapid Visco Analyser (RVA, Model 4D, Newport Scientific, Australia) using the AACC Approved Method 61-02 (AACC 2000). The pasting parameters were peak viscosity, breakdown (peak viscosity-minimum viscosity), final viscosity, consistency (final viscosity-minimum viscosity), and setback (final viscosity-peak viscosity).

Determination of nutrients

The protein content of black rice was determined by the combustion method, whereas fat content was measured after solvent extraction (AOAC 2000). Ash content was measured using the AACC Approved method 08-01

(AACC 2000). Dietary fiber was determined by the AOAC Method 985.29 (AOAC 2000).

Determination of phenolic content

Black rice samples were ground and screened through a 40-mesh sieve. Total phenolic content was extracted by modifying the method of Liyana-Pathirana and Shahidi (2006). Black rice flours (1 g) were extracted at room temperature with 8 mL of 80% ethanol containing 2 mL of NaOH (6 mol/L) in a shaker at 150 rpm for 24 h. Around 2 mL of HCl (5 mol/L) was added to adjust pH of extracts to 1–2 and the flasks were shaken for another 10 min. The extracts were subsequently centrifuged at 12,000g for 10 min and the supernatants were pooled and stored at 4 °C.

Total phenolic content was measured by the Folin-Ciocalteu colorimetric method. Extracts (2 mL) were mixed with 1 mL Folin-Ciocalteu reagent (0.5 N), and the reaction was neutralized with saturated sodium carbonate (75 g/L). They were incubated at 25 °C for 1 h before the blue color occurred was measured at 760 nm using a spectrophotometer (Spectronic 21, Milton Roy Company, USA) and ethanol as a blank. A calibration curve was prepared using a gallic acid solution. Total phenolic contents were expressed as mg of gallic acid equivalent per 100 g of rice (mg GAE/100 g).

Determination of anthocyanin content

Anthocyanin in the black rice flours was extracted by the method described by Zhu et al. (2010) with slight modification. Black rice flours (1 g) were extracted by mixing with 10 mL of 80% ethanol acidified with 0.5 mL of HCl (5 mol/L) and stirring on a shaker at 150 rpm for 24 h. The extracts were centrifuged at 12,000×g for 10 min, and the supernatants were decanted to amber bottles for anthocyanin determination.

The total anthocyanin content in black rice was measured by the pH differential method. The anthocyanin extracts (≤ 10 mL) was diluted with 0.025 mol/L potassium chloride buffer (pH 1.0) and 0.4 mol/L sodium acetate buffer (pH 4.5), and subsequently, the absorbance of diluted test portions were read at 520 and 700 nm. Anthocyanin content was expressed as cyanidin-3-glucoside equivalents, as follows:

$$\text{Anthocyanin pigment (cyanidin - 3 - glucoside equivalents, mg/L)} = \frac{A \times MW \times DF \times 10^3}{\epsilon \times 1}$$

where $A = (A_{520\text{nm}} - A_{700\text{nm}})_{\text{pH } 1.0} - (A_{520\text{nm}} - A_{700\text{nm}})_{\text{pH } 4.5}$; MW (molecular weight) = 449.2 g/mol

for cyanidin-3-glucoside (cyd-3-glu); DF = dilution factor; l = pathlength in cm; $\epsilon = 26\,900$ molar extinction coefficient, in $L \times mol^{-1} \times cm^{-1}$, for cyd-3-glu; and 10^3 = factor for conversion from g to mg.

Determination of DPPH radical scavenging activity

Black rice flours (1 g) were extracted by mixing with 25 mL of 80% ethanol acidified with HCl (1% v/v) and stirring on shaker at 150 rpm for 24 h. The extracts were centrifuged at $4000\times g$ for 15 min, and the supernatants were decanted to amber bottles for anthocyanin determination.

Each 1 mL of crude extract was added to 3 mL of 2,2-diphenyl-1-picrylhydrazyl (DPPH) (0.05 mmol/L). The mixture was vigorously shaken and left to stand for 30 min at room temperature in the dark. The absorbance of the reaction solution was then measured at 515 nm using a spectrophotometer (Spectronic 21, Milton Roy Company, USA) and ethanol as a blank. A calibration curve was prepared using an ascorbic acid solution. DPPH radical scavenging activity was expressed as mg of ascorbic acid equivalent per 100 g of rice (mg AA/100 g).

Determination of resistant starch content

Resistant starch was analyzed according to Goni et al. (1997). Around 50 mg of rice flour sample (dry weight) was added with 5 mL distilled water, adjusted pH to 2.0 and incubated with 0.2 mL pepsin solution, which was prepared by dissolved pepsin enzyme with enzyme-to-protein ratio of 1:17 in 0.01 mol/L HCL, at 37 °C for one h. Then it was hydrolyzed at 37 °C for 16 h after adjusting pH to 7.0 and adding 100 μ L of α -amylase. Samples were subsequently centrifuged, and the precipitate was added with 2 mL of 2 mol/L KOH. The solution was incubated with 0.1 mL of amyloglucosidase enzyme from *Aspergillus niger* at 50 °C for 30 min after pH was adjusted to 3.6–4.2. After centrifugation, glucose concentration in the supernatant was determined using the glucose oxidase–peroxidase kit. A factor of 0.9 was applied to convert glucose concentration into starch content.

Assessment of sensory properties

For sensory analysis, black rice samples were cooked in an electric rice cooker for 45 min using rice to water ratio of 1:1.5. Sensory evaluation was performed by 30 Thai students in the Division of Food Science and Nutrition, Srinakharinwirot University, Thailand. A hedonic scale (1 = extreme dislike, 9 = extreme like) was applied to determine panelist's preference to cooked rice samples. Sensory attributes of cooked rice that were subjected to

evaluation were appearance, color, odor, flavor, texture, and overall acceptability.

Data analysis

The milling treatments and all analyses were performed in triplicate. Data were subjected to analysis of variance followed by Tukey's range test to compare means at $p < 0.05$ using SPSS v. 12.0 software. Regression coefficients obtained for the relationship between DOM and black rice qualities were subjected to analysis of variance using SigmaPlot software v.11.0.

Results and discussion

Relationship of milling time and degree of milling

Black rice was abrasively milled for 0–100 s and various DOM (0–30%) was obtained. Changes of DOM during milling are shown in Fig. 1. DOM was not linearly increased with milling time. The alteration rate (slope) differed during the milling process. A power function relationship between milling time and DOM was indicated ($R^2 = 0.9951$). A decreasing of the slope was observed when milling time was less than 20 s (DOM < 9%). A lower gradient was consistently observed when milling time was during 20–100 s (DOM > 9%).

Around 9% rice layer removal was indicated as the bran fraction. Lamberts et al. (2007) further designated 9–15%, 15–25% and > 25% removal as outer, middle and core endosperm fraction respectively. Hardness of rice bran was different from that of endosperm. Outer layer of rice bran was harder than inner layer, whereas the hardness of the

Fig. 1 Effect of milling time on the degree of milling of black rice

three fraction of endosperm was similar. Thus, decreasing of the slope was noticed in the rice bran layer (DOM < 9%) and the shift of slope was subsequently perceived at the edge of bran and outer endosperm fraction (DOM > 9%). This agreed with the findings of Lamberts et al. (2007).

Additionally, fragrant black rice (Hom Nil cultivar) was easily milled. Milling at 100 s yielded high DOM (~ 30%), whereas it was around 25% for long-grain brown rice (Lamberts et al. 2007). Grain morphology affected DOM, particularly in grain length and length-to-width ratio (Prom-u-thai et al. 2007). At the same milling time, DOM of long-slender grain was higher than other shapes. The grain of Hom Nil rice was long (length of 7.2 mm) and slender (length-to-width ratio of 3.61). Thus comparatively high DOM was noticed. Singh et al. (2000) also reported that the percentage of bran removed at successive milling intervals differed significantly in different cultivars due to differences in shape and grain hardness. The loss of bran during milling increased with the length-to-width ratio as well.

Head rice yield

Figure 2a shows the quadratic equation for the relationship between head rice yield and DOM ($R^2 = 0.9732$). The removal of bran layers increased with milling duration and consequently, head rice yield (HRY) reduced. At the beginning (milling at 10 s or DOM ~ 6%) HRY was 70.33% and reduced remarkably to 58.97% at 20 s (DOM ~ 9%). A gradually slow reduction of HRY was subsequently noticed with successive milling. It was 27.50% at the end of milling (DOM ~ 30%).

Non-linear relationship between HRY and DOM was confirmed with Yadav and Jindal (2008). They found that the reduction in HRY was a power function of the milling duration. Sun and Siebenmorgen (1993) informed dissimilar findings of a linear relationship between DOM and HRY, which implied that rice was milled to greater extents, the HRY decreased linearly. However, the cultivar and milling moisture content significantly influenced the rate at which HRY changes with DOM (Reid et al. 1998). The decrease in HRY with DOM was smaller at high moisture content at which the rice was milled. Bran layers were more easily removed when milling moisture content increased. Moreover, there was an indication of a relationship between kernel thickness of a cultivar and the HRY versus DOM slope. Kernel thickness distributions affected interkernel abrasion in friction milling. Lower HRY was obtained when a thickness less than 1.88 mm or more than 2.03 mm (Sun and Siebenmorgen, 1993). Black rice (HOM Nil) has a thickness of 1.77 mm; thus comparatively lower HRY was reported. These factors might

Fig. 2 Effect of degree of milling on **a** head rice yield and **b** color of black rice

contribute to the different relationships between HRY and DOM observed among the studies.

Grain color, cooking quality, texture and pasting property of black rice

Figure 2b presents the quadratic equation for the relationship between Lightness (L*), redness (a*), yellowness (b*), and DOM. R^2 were 0.9807, 0.9439 and 0.9534 respectively. Lightness (L*) of black rice sharply increased (22.8–56.2) until DOM ~ 15% and the increase was subsequently gradual (62.1–69.4). Then L* remained almost constant at DOM ~ 25%. At 15% DOM, bran and outer endosperm were completely removed. Redness of black rice (a*) remained almost constant (4.9–4.3) until DOM ~ 20% before it was gradually decreased (3.5–0.9). Yellowness (b*) of black rice gradually increased (3.1–9.9)

until DOM $\sim 20\%$ and then it remained almost constant (11.0–11.3).

The bran hull (outermost layer of black rice) contains high anthocyanin content, which contributes to the dark purple color of the black rice kernel. Changes of grain color during milling black rice indicated that the amount of pigment decreased from the bran surface to the middle endosperm fractions. Bran and outer endosperm fraction contained more pigments than the other portions. The distribution of pigments was consistent in the core endosperm in which the pigment extent was meager. Although Chen and Siebenmorgen (1997) reported the linear relationship of grain whiteness and DOM, Lamberts et al. (2007) and Yadav and Jindal (2008) confirmed a rapid increase of grain lightness at the beginning and a gradual increase in latter stages of milling. They claimed that the bran layer was quickly removed when compared to a mixture of bran and starchy endosperm layer. Distribution of pigments in brown rice kernels might be slightly different from those in black rice kernels. In brown rice, lightness remained unchanged in the middle and core endosperm fraction due to the removal of red and yellow pigments mostly located in bran layers. Distinct increase at the early stage of milling was due to significant loss of purple pigment in bran layers. However, the lightness of black rice still increased in middle endosperm fraction. This occurred concurrently with an increase of yellowness.

Cooking qualities of black rice milled for different milling times are shown in Table 1. The cooking time of black rice was around 22 min, and it was significantly shortened to 15 min ($p < 0.05$) at 10 s milling (DOM $\sim 6\%$). The water uptake ratio (0.66) and volume expansion ratio (1.39) significantly increased ($p < 0.05$) when milling at 10 s as well. There was no significant difference between the length expansion ratio and milling time ($p \geq 0.05$). Conclusively cooking index significantly increased ($p < 0.05$) with 30 s milling.

In addition to cooking quality, the texture of cooked black rice changed with different milling time (Table 1). Cooked black rice had a hardness of 34.75 N, but the substantially softer texture was noticed when milling only 10 s (22.37 N). Milling for a longer time (30–100 s) did not generate notable changes of texture ($p \geq 0.05$).

Good cooking qualities of rice are high volume expansion ratio, length expansion ratio, water uptake ratio and minimum cooking time. Removing of bran layers after milling assisted more water diffusion into the kernels during cooking because total protein content and surface lipid reduced. Starchy endosperm without fibrous bran layer was easily cooked and had a short cooking time. Positive effects of the degree of milling on water uptake, volume expansion, and cooking index were exhibited in the study of Mohapatra and Bal (2006) and Mohapatra and Bal

Table 1 Effect of milling on cooking qualities and pasting viscosity of black rice

Milling time (s)	Cooking time (min)	Water uptake ratio	Volume expansion ratio	Length expansion ratio	Cooking index	Hardness of cooked rice (N)	RVA pasting viscosity (rvu)			Consistency	Setback
							Peak viscosity	Breakdown	Final viscosity		
0	21.9 ± 0.2a	0.66 ± 0.08d	1.39 ± 0.08c	1.04 ± 0.05a	0.05 ± 0.01b	34.75 ± 0.04a	89 ± 0c	31 ± 2c	122 ± 2b	64 ± 1b	32 ± 2a
10	14.9 ± 0.8b	1.15 ± 0.01c	2.22 ± 0.00b	1.03 ± 0.02a	0.18 ± 0.01b	22.37 ± 1.00b	115 ± 26c	51 ± 12c	133 ± 21b	69 ± 7ab	19 ± 5a
30	12.9 ± 0.1c	1.72 ± 0.11b	2.95 ± 0.08a	1.04 ± 0.01a	0.42 ± 0.04a	22.22 ± 0.39b	201 ± 6b	84 ± 4b	199 ± 1a	81 ± 1a	− 4 ± 2b
60	13.0 ± 0.0c	2.30 ± 0.18a	2.77 ± 0.18a	1.09 ± 0.05a	0.54 ± 0.09a	18.93 ± 3.68b	253 ± 1ab	120 ± 8a	204 ± 7a	71 ± 1ab	− 49 ± 9c
100	13.0 ± 0.0c	1.88 ± 0.03b	2.80 ± 0.1a	1.10 ± 0.01a	0.45 ± 0.04a	17.44 ± 0.77b	288 ± 12a	149 ± 4a	214 ± 6a	74 ± 2ab	− 74 ± 6d

All values are means $\pm$ standard deviation ($n = 3$)

Breakdown = peak viscosity–minimum viscosity, Consistency = final viscosity–minimum viscosity, Setback = final viscosity–peak viscosity

Different letters within the same column are significantly different at $p < 0.05$

(2007) as well. A sharp increase in cooking index was also observed at 9–14% DOM. Cooking qualities did not change much when most of the bran layer was removed at high DOM. However, they found a linear increase in length expansion with DOM. Thickness and surface area of fragrant black rice might differ from three varieties of brown rice used in their study. Similarly, DOM had a negative effect on the hardness of cooked brown rice. Existence of bran layer induced rigidity to cooked rice kernels. Moreover, the effect of DOM on cooking qualities varied with ranges of DOM, cooking method (cooking using fixed water-to-rice ratios or cooking using excess water), and pretreatment (parboiled rice or non-parboiled rice) (Brilliris et al. 2012a, b).

From Table 1, peak viscosity, final viscosity, and breakdown increased ($p < 0.05$) after milling. Significant difference ($p < 0.05$) was attained at 30 s of milling (DOM ~ 12%). But setback decreased ($p < 0.05$) significantly when milling at the same milling time. There was no significant difference found among consistency values ($p \geq 0.05$).

Total starch increased linearly with DOM when bran, outer, and middle endosperm fractions were removed (Lamberts et al. 2007). More starch portions in the flour sample increased peak viscosity, final viscosity, and breakdown of high DOM rice. Additionally, starchy endosperm without fibrous bran layer readily absorbed water and swelled comfortably. This finding agreed with Park et al. (2001). However, milling and grinding induced starch damage (Lamberts et al. 2007). Degradation of starch molecules lowered the reassociation of amylose and amylopectin when cooling. Thus low setback viscosity, which indicated a low rate of starch retrogradation, was noticed in high DOM rice.

Nutrients of black rice

Prominent nutrients of black rice are shown in Fig. 3a. The protein content of black rice decreased from 9.58 to 6.67 g/100 g during milling for 100 s. Milling for 10 s caused considerable reduction of protein ($p < 0.05$), and afterward, it was constantly diminished with consecutive milling. Black rice contained high ash content of 2.14 g/100 g. It significantly reduced ($p < 0.05$) to 1.43 g/100 g when milling for 10 s. Trivial changes were shown during milling 30–100 s. Ultimately the remained content was 0.37 g/100 g at the end of milling. Similarly fat content in black rice (4.63 g/100 g) decreased significantly ($p < 0.05$) to 2.61 g/100 g at 10 s because bran layers were removed. Fat content gradually decreased with successive milling. At 100 s milling, well-milled black rice was obtained with a fat content of 0.31 g/100 g.

Fig. 3 Effect of milling on **a** nutrients and **b** resistant starch content and dietary fiber content of black rice. In a group, bars with different letters were significantly different at $p < 0.05$ ($n = 3$)

Milling removes nutrients from rice kernels, but losses are varied. Protein, minerals, and fat were not consistently allocated in the black rice kernels. The effect of milling on protein content is less than fat content because a large amount of protein is in the endosperm. A similar finding on protein distribution was reported by Lamberts et al. (2007) that most of the protein in long-grain brown rice (~ 84.2%) existed in endosperm (DOM > 9%). For black rice, endosperm was attained when they were milled for longer than 10 s, and protein content in endosperm was around 82% of the entire protein in rice kernel. Protein in black rice still locates densely in the bran layer; thus substantial loss of protein (1.44 g/100 g) was displayed when almost bran fraction was removed (milling 10 s or DOM ~ 6%).

For brown rice, ash content distributed most in bran fraction (61%), and they uniformly scattered in the middle and core endosperm (Lamberts et al. 2007). Quadratic and exponential equations were presented for the relationship between ash content and milling duration (Singh et al. 2000). Similarly, most of the ash content in black rice

located in the bran fraction, and the remainder was in the endosperm. But it steadily reduced with milling time. Hence the relationship between ash content and milling duration varied among rice cultivars with different grain compositions and kernel shapes. High ash loss was noticed in a cultivar with a low length–width ratio (Singh et al. 2000). Moreover, losses of specific minerals (iron, zinc, and selenium) during milling differed in their locations in grain kernels (Prom-u-thai et al. 2007; Liang et al. 2008; Liu et al. 2009).

Fat in black rice is largely located in the bran layer (> 44%), and it decreased distinctly when bran fraction was removed. This was consistent with findings in studies done by Chen and Siebenmorgen (1997) and Ha et al. (2006), who reported a reduction of total fat content, surface lipid content, and nutraceutical lipid of brown rice with DOM.

Resistant starch and dietary fiber of black rice

From Fig. 3b, the resistant starch content of black rice (6.30 g/100 g) did not significantly change when milling for 10 s ($p \geq 0.05$), but it increased when milling for 100 s (16.66 g/100 g) ($p < 0.05$). However, dietary fiber of black rice (5.73 g/100 g) notably reduced ($p < 0.05$) to 4.27 and 0.79 g/100 g when milling for 10 s and 100 s, respectively.

Although an obvious trend was not exhibited, resistant starch slightly increased with DOM. This might be due to more starch fractions in high DOM rice. Dietary fiber mostly located in bran fraction, and it reduced with DOM. This agreed with Lai et al. (2006), who reported contraction of total dietary content in brown rice included pectic substance, hemicellulose, and cellulose with DOM. The total dietary fiber of brown rice was more than that of milled rice around 3–4%. However, milling of black rice for 10 s (DOM ~ 6%) did not remove much bran fraction, and dietary fiber still existed almost 75% of total dietary fiber.

Rice with the bran layer is not simply digested. Brown rice is classified as low and medium GI food, whereas milled rice was high GI food. Glucose released during digestion of brown rice was lower than those of milled rice (Leonora et al. 2006) because brown rice had more dietary fiber, fat, phytic acid, and polyphenols. Additionally, bran layers inhibited water and acid absorption and gastric juice diffusion during simulated gastric digestion; thus breakage, solubility, and digestibility of rice kernels was hindered (Kong et al. 2011).

Antioxidant properties of black rice

Black fragrant rice (Hom Nil cultivar) was claimed as a good source of antioxidants. It contained total phenolic and

Fig. 4 Effect of milling on phenolic content (mg GAE/100 g), anthocyanin content (mg/100 g) and DPPH scavenging activity (mg AAE/100 g) of black rice. In a group, bars with different letters were significantly different at $p < 0.05$ ($n = 3$)

anthocyanin content of 186.20 mg GAE/100 g and 24.55 mg/100 g, respectively (Fig. 4). Phenolic content sharply reduced to 127.82 mg GAE/100 g when milling for 10 s ($p < 0.05$), and then it gradually decreased to 61.01 mg GAE/100 g at 100 s milling. A similar pattern was observed in changes in anthocyanin content during milling. Anthocyanin in raw black rice suddenly decreased to 7.46 mg/100 g at 10 s milling ($p < 0.05$) before petty alterations were noticed during 30–60 s. Lastly, milling for 100 s completely removed anthocyanin pigments from black rice kernel. Antioxidants were eliminated during milling. Therefore, DPPH scavenging activity of raw black rice (227 mg AAE/100 g) indubitably reduced to 175 mg AAE/100 g when milling only 10 s ($p < 0.05$). Additional milling (30–100 s) caused a slight decline of DPPH activity to 118 mg AAE/100 g.

Black rice contains beneficial antioxidants comprised of polyphenolics, flavonoids, vitamin E, phytic acid, and γ -oryzanol. At 85% degree of milling, Kong and Lee (2010) found a large amount of free polyphenols and flavonoids in the bran fraction of black rice, and a small amount was in the endosperm. For Hom Nil black rice, a moderate amount of phenolic compounds (58.38 mg GAE/100 g or 31%) was eliminated after milling for 10 s (DOM ~ 6%). When all bran (calculated as the difference in contents of black rice and rice milled for 30 s or DOM ~ 12%) was entirely removed, phenolic compounds lost around 102.17 mg GAE/100 g or 55%. Other researchers (Zhou et al. 2004; Walter et al. 2011) reported a relatively higher amount of phenolic compounds in the light brown pericarp (70–90%) and black pericarp (92–97%). Variations were due to cultivar, particularly phenolic compounds contained in rice kernels, degree of milling, and extraction methods used to determine total phenolic content.

Table 2 Effect of milling on sensory qualities of black rice

Milling time (s)	Consumer acceptance scores					
	Appearance	Color	Odor	Flavor	Texture	Overall acceptability
0	4.9 ± 1.5b	5.0 ± 1.7a	6.0 ± 1.5ab	5.3 ± 1.4b	5.4 ± 1.2ab	5.5 ± 1.4a
10	5.6 ± 1.6ab	5.8 ± 1.5a	6.4 ± 1.0a	6.5 ± 1.1a	6.3 ± 1.2a	6.1 ± 1.3a
30	5.9 ± 1.4a	5.9 ± 1.5a	6.3 ± 1.2a	6.3 ± 1.1a	6.3 ± 1.3a	6.3 ± 1.3a
60	6.2 ± 1.3a	5.7 ± 1.1a	5.8 ± 1.4ab	6.0 ± 1.5ab	5.9 ± 1.5ab	5.9 ± 1.6a
100	6.2 ± 1.5a	6.0 ± 1.3a	5.2 ± 1.4b	5.7 ± 1.6ab	5.3 ± 1.7b	5.6 ± 1.4a

All values are means ± standard deviation (n = 30)

Different letters within the same column are significantly different at $p < 0.05$

Almost 85% of anthocyanin, which was one of the flavonoids, was in bran layers of black rice (Hu et al. 2003). In this study, milling at 10 s (DOM ~ 6%) did not remove all bran layer, and consequently, 30% of total anthocyanin remained in rice kernels.

Antioxidant activity reduced with decreasing in antioxidants after milling. Milling of black grains affected antioxidant activity similar to the effect on polyphenols. It reduced around 88% when black rice was polished (Walter et al. 2011). In this study, only 35% decline of antioxidant activity was perceived when all bran (milling for 30 s or DOM ~ 12%) was confidently removed. Black rice milled at 10 s (DOM ~ 6%) still had 77% of the antioxidant activity of black rice.

Sensory quality of cooked black rice

Black rice samples with different degrees of milling were cooked, and sensory qualities evaluated by the panelists are presented in Table 2. Overall, acceptability and color scores of raw black rice were not significantly different ($p \geq 0.05$) from those of black rice milled for 10–100 s. Appearance scores increased with milling time with obvious notice at 30 s (DOM ~ 12%) of milling ($p < 0.05$). However, panelists apparently preferred cooked rice milled for 10 s (DOM ~ 6%) when odor, flavor, and texture were inquired.

The outer seed coat of raw rice caused unpleasant flavor and texture. Removing a small portion of the bran layer produced cooked rice without strong bran flavor and tough texture. Panelists preferred mostly on well-milled and lightly milled rice. Park et al. (2001) described the detail of changes of sensorial qualities with DOM. Panelists detected decreasing of color, grain integrity, puffed corn flavor, raw rice flavor, wet cardboard flavor, hay-like flavor and bitterness of cooked rice, whereas glossiness, plumpness, sweetness increased. For texture, agglomeration, adhesiveness, cohesiveness, inner moisture, tooth packing of cooked rice increased, but hardness and chewiness decreased.

Improving odor, flavor, and texture acceptance of cooked black rice when milling at 10 s (DOM ~ 6%) concurrently perceived with reducing of instrumental textural hardness and fat content.

Conclusion

Milling definitely diminishes healthful compounds in black rice; however, losses depend on their locations in grain kernels. Milling at 10 s (DOM ~ 6%) did not remove all bran fractions. Small losses of protein (15%) and dietary fiber (25%) were noticed, whereas evident losses of ash (33%), fat (44%), phenolic compounds (31%) and anthocyanin (70%) were observed. In contrast, milling at 10 s appreciably improved the cooking qualities of black rice by reducing cooking time (~ 7 min) and increasing water uptake ratio and volume expansion ratio. Additionally, cooked black rice had impressively softer texture. Panelists preferred odor, flavor, and texture of cooked lightly milled black rice to cooked unmilled black rice.

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