Research Note

Parboiling improved oxidative stability of milled white rice during one-year storage

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Abstract Parboiling was investigated to improve the long-term oxidative stability of milled white rice beyond its current application to paddy brown rice. White rice was steamed at 105°C for 20 min, 120°C for 5 min, or 120°C for 20 min without soaking in water, followed by drying at 70°C for 3 h. During one-year storage at 25 and 4°C, acid value as an index of oxidative deterioration of rice remained relatively constant in parboiled rice samples, while significant increases were observed in raw rice with higher acid values at 25°C compared with 4°C. This indicates that the parboiling improved the oxidative stability of white rice over the long period of time even at room temperature, therefore it can be an efficient alternative to retard the oxidative deterioration of white rice.

Keywords: parboiling, white rice, oxidative stability, storage, acid value

Introduction

Rice is a staple food that is an important nutrient source in the Korean population. Despite of the increase in rice production by 2.0% in 2015 (4.33 million tons) compared with 2014, per capita rice consumption has gradually decreased as Korean dietary patterns become more and more westernized (1). The abundant rice supply has led to increasing consumer demand for higher quality rice. However, white rice is susceptible to undesirable changes such as oxidation of fatty acids, which can be a food safety concern particularly when it is stored for long periods of time (2). To improve the oxidative stability, rice in East Asia is commonly parboiled in the state of paddy brown rice and then milled. As the time from rice harvest to consumer spending has been extended even up to a couple of years (1), there has been a growing need for development of a processing method which maintains the quality of milled rice. Nevertheless, to the best of our knowledge, no data are available on the oxidative stability of 'milled white rice' during long-term storage. Taking into consideration the economic efficiency and cost of storage, an alternative to ensure the quality of milled rice, possibly at room temperature, needs to be developed.

White rice contains about 1% lipids, over 65% of which is composed of unsaturated fatty acids (3). Free fatty acids are derived from acylglycerols by lipolysis and they undergo further oxidation to produce off-flavor in rice. The content of free fatty acid (i.e., acidity) has therefore been used as a good index of quality deterioration of rice during storage. Multiple factors such as rice constituent and

storage condition have been reported to affect the formation of free fatty acid during storage: (i) Temperature - white rice stored at higher temperatures showed higher acidity than that stored at low temperatures (2); (ii) Lipase/esterase - enzymatic hydrolysis of the ester bond of triacylglycerols in rice increased the concentration of free fatty acids, which in turn increased the acidity of stored rice (4); (iii) Water activity (moisture content) - presence of water beyond the boundary of zones I and II of moisture sorption isotherm in foods increased lipid oxidation (5). Accordingly, factors that catalyze the formation of free fatty acids as well as their oxidation should be inhibited as possible during long-term storage of rice.

In this study, in order to improve the oxidative stability of milled white rice for long-term storage, the rice was steamed to inactivate enzymes catalyzing hydrolysis of the ester bond of triacylglycerols, followed by air-drying to reduce the moisture. The objective of this study was to test the feasibility of parboiling as an alternative for improving the storage stability of 'milled white rice', beyond its current application to paddy rice. The change in acidity during one-year storage at room temperature (25°C) and refrigerated (4°C) temperatures was therefore monitored.

Materials and Methods

Sample preparation and storage White rice was purchased from an on-line Agricultural Cooperative market. No information about variety, fertilization, or post-harvest storage conditions was available.

The rice was divided into four portions: one remained as it was, and the others were processed under three different conditions. The steaming conditions were selected based on thermal treatments that are generally applied to the parboiling process on a laboratory scale. Aliquots of 150 g of the white rice was put into three stainless steel testing sieves, covered with aluminum foil, and then steamed in a laboratory autoclave (JS-AC 60; Johnsam, Bucheon, Korea) at 105°C for 20 min (first batch), 120°C for 5 min (second batch), or 120°C for 20 min (third batch). Then, the steamed rice was dried at 70°C for 3 h in a drying oven (OF-12; Jeio Tech, Gimpo, Korea) to reach a final moisture content of around 10%. The rice samples, raw and parboiled rice, were then packaged in polyethylene bags, labeled, and stored in a thermostatically controlled incubator at 25 or 4°C for one year. The former represents the room temperature at which rice is commonly stored at homes or storehouses, while the latter corresponds to a controlled condition for retarding the oxidation of fat in rice during storage. The rice was monitored for 365 days.

Fissures and color observation Photographs of the raw and parboiled rice samples were taken using a digital camera (VLUU PL90; Samsung, Suwon, Korea), wherein fissures were visually observed. Color was measured with a CR400 handheld chromameter (Konica Minolta Sensing, Osaka, Japan) and expressed in values of lightness (L), redness (a), and yellowness (b).

Proximate analysis and gelatinization degree The rice samples were ground using a household blender (HM-331N; Hanil, Incheon, Korea). Proximate composition was then determined according to the AOAC approved standard methods (6). The degree of gelatinization was determined by enzymatic hydrolysis with diastase from *Aspergillus oryzae* (amylase $\geq 3,500$ U/g, Sigma-Aldrich, St. Louis, MO, USA) and then iodometric titration with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution according to the method of Nielsen (7).

Water-holding capacity One gram of rice powder was dispersed in 35 mL distilled water and then mixed for 30 min in a shaking water bath (BS-21; JeioTech, Seoul, Korea) at 25°C. After centrifugation at $3,061 \times g$ (5810R; Eppendorf, Hamburg, Germany) for 20 min, the supernatant was decanted, and the precipitate was weighed. Water-holding capacity ($\% = 100 \times b/a$) was determined by the amount of water held in the sample matrix, which was calculated as the percentage of matrix weight remaining after centrifugation (b) to the initial weight of the sample (a).

Acidity Fat acidity, an index of oxidative deterioration of rice during storage, was measured using an acid-base titration at 0, 1, 3, 6, 9, and 12 months after parboiling. Crude fat was extracted with diethyl ether using a Soxhlet extraction unit (E-816; Buchi, Flawil, Switzerland). After evaporation of the solvent, 50 mL of benzene:ethanol (1:1 v/v) mixture was added to dissolve the fat. The fat solution was then titrated with 0.005 N KOH in 95% aqueous ethanol containing a

phenolphthalein as an indicator. The acid value was expressed on a dry weight basis.

Statistical analysis All experiments were conducted in triplicate and expressed as average $\pm$ standard deviation (SD). Analysis of variance (ANOVA) and Duncan's multiple range tests were performed using the SAS program version 9.1 for windows (SAS Institute Inc., Cary, NC, USA) to evaluate the difference among samples.

Results and Discussion

Physicochemical changes of parboiled white rice Fissures were observed within the kernel of the parboiled rice, demonstrating that fissuring occurred during the steaming and/or air-drying, the extent of which became more distinct with increasing steaming intensity (Fig. 1). This indicates that internal stresses by steaming and drying exceeded the tensile strength of rice kernel. Kunze (8) demonstrated that the moisture gradient within a kernel created stress, which led to fissuring. These fissures possibly shorten cooking time for soaking and gelatinization by helping water embed easily into kernel. However, excessive fissuring in rice may lead to undesirable kernel breakage.

Transparency and yellowness of the parboiled rice increased as the steaming conditions became harsher (Fig. 1 and Table 1), indicating that gelatinization of the starch granules and non-enzymatic browning reactions increased with steaming. Of the steaming conditions, the harshest condition at 120°C for 20 min resulted in the highest transparency and fissuring in white rice, with more apparent fissures than the other conditions. This shows that fissuring is dependent on the steaming temperature and time.

The degree of gelatinization in the parboiled rice varied depending on the steaming temperature and time (Table 1), and was highest in rice steamed at 120°C for 20 min. The parboiled white rice had lower moisture content compared with raw rice (Table 1). This suggests that the parboiled white rice is less susceptible to fat oxidation. Moisture content is one of the factors influencing fat oxidation, which takes place on the lipid-water interface (9). The contents of protein and fat tended to be higher in the parboiled rice than in the raw rice, and the carbohydrate content differed significantly depending on the steaming temperature (Table 1). These compositional changes can be attributed to the loss of moisture during parboiling. It is in agreement with the results of Ibukun (10), demonstrating that parboiling resulted in the changes in the protein, lipids and ash content of rice kernel, and mainly, the loss of moisture.

The water-holding capacity of parboiled rice samples increased in a steaming-dependent manner (Table 1). There was a particularly great increase in the water-holding capacity when steamed at 120°C. This may be attributed to the greater extent of gelatinization of rice starch. It seems that the steaming disrupted the crystalline structure of starch, thereby resulting in higher absorption of water into the

Fig. 1. Fissures in raw (A) and parboiled milled white rice. Milled white rice was parboiled by steaming at 105°C for 20 min (B), 120°C for 5 min (C), or 120°C for 20 min (D) and following air-drying at 70°C for 3 h.

starch granule. However, there were no differences in the water-holding capacity between cold and hot water. These results indicate that rice was swollen through water absorption during steaming, and then the water was lost during the following drying process to create a porous structure. Therefore, the parboiled rice was easily rehydrated and held a large amount of water, even when immersed in cold water.

Oxidative storage stability of parboiled white rice Lipid hydrolysis is initiated by lipases in rice, and the resulting free fatty acids generate off-flavors in rice (11). Therefore, inhibition of the initial formation of free fatty acids is critical for controlling the lipid oxidation in rice. The high temperatures (105–120°C) employed in this study possibly led to the denaturation of lipase. Brunschweiler *et al.* (12) found that heat-treatment of rice bran at 110°C for only 5 min was sufficient to reach a very low residual lipase/esterase activity, which corresponds to 0.3% of the activity in raw bran. They found that the inactivation rate increased with increasing temperature and time. It is likely that the steaming (105°C, 20 min or 120°C, 5–20 min) employed herein was sufficient for the inactivation of lipase.

In addition, lipases may originate from microorganisms which proliferate on grain during storage, especially under humid storage conditions (13). Thus, storage temperature would be one of the factors influencing the growth of microbes, resulting in change of the reaction rate of hydrolysis and oxidation. In this study, the rice was stored at 4 and 25°C, which represent a refrigerated temperature and a room temperature, respectively. During one-year storage, differences in the acidity values of the rice samples were observed depending on the storage or steaming conditions (Table 2). Raw rice had a significant increase in acidity, with higher values at 25°C. It is in agreement with the result of Rehman (14) reporting a significant increase in the acidity from 37.20 to 54.52 in rice at 25°C while little change was observed at 10°C during storage. Lipase is more active at higher storage temperatures, and in turn causes the formation of more free fatty acids. In contrast, the parboiled white rice samples did not show significant changes in acid values for 365 days at both temperatures, with the harsh steaming conditions resulting in lower acid values (Table 2). In addition, the acid values of the parboiled white rice had no substantial differences between the two temperatures tested herein. There are a couple of possible explanations for the

Table 1. Physicochemical properties of raw and parboiled white rice¹⁾

	Degree of gelatinization (%)	Proximate composition				
		Moisture (%)	Protein (%)	Fat (%)	Ash (%)	Carbohydrate (%)
Untreated ²⁾	3.71	15.77±0.18 ^a	6.95±0.22 ^a	0.48±0.00 ^a	0.32±0.10 ^{ab}	76.27±0.02 ^c
105°C, 20 min	30.42	9.58±0.04 ^d	7.28±0.13 ^a	0.57±0.02 ^a	0.22±0.05 ^b	82.36±0.10 ^a
120°C, 5 min	92.53	11.28±0.07 ^b	7.19±0.07 ^a	0.43±0.19 ^a	0.32±0.13 ^{ab}	80.31±0.31 ^b
120°C, 20 min	107.44	10.84±0.06 ^c	7.09±0.12 ^a	0.48±0.04 ^a	0.45±0.05 ^a	81.14±0.18 ^b
<i>p</i> value		0.0001	0.2159	0.6102	0.0709	0.0001
	Color			Water-holding capacity (%)		
	Lightness (L)	Redness (a)	Yellowness (b)	Cold water	Hot water	
Untreated	88.71±0.23 ^b	-5.76±0.11 ^b	12.86±0.13 ^d	216.44±1.93 ^c	266.79±22.56 ^c	
105°C, 20 min	89.62±0.18 ^a	-6.29±0.03 ^d	14.24±0.25 ^c	270.70±20.11 ^b	299.28±27.54 ^c	
120°C, 5 min	86.89±0.05 ^c	-6.13±0.02 ^c	16.50±0.17 ^b	392.63±9.06 ^a	372.54±5.78 ^b	
120°C, 20 min	84.98±0.28 ^d	-5.19±0.03 ^a	18.06±0.10 ^a	413.63±7.10 ^a	426.47±31.69 ^a	
<i>p</i> value	0.0001	0.0001	0.0001	0.0001	0.0002	

¹⁾Values are expressed as average±standard deviation of triplicate measurements. Values with different superscript in the same column are significantly different.

²⁾Untreated raw rice

Table 2. Changes in the acid value of raw and parboiled white rice during storage for one year at 25 and 4°C¹⁾

	Acid value (mg KOH/100 g dry weight) at 25°C						<i>p</i> value
	0 month	1 month	3 month	6 month	9 month	12 month	
Untreated ²⁾	37.20±4.30 ^{abc}	30.71±2.60 ^{ac}	48.87±7.42 ^{aA}	47.81±0.09 ^{aAB}	56.42±0.10 ^{aA}	54.52±6.13 ^{aA}	0.0067
105°C, 20 min	26.11±4.75 ^{bA}	23.75±3.97 ^{bA}	29.88±0.77 ^{bA}	27.21±4.45 ^{bA}	27.11±0.16 ^{bA}	27.55±1.49 ^{bA}	0.5949
120°C, 5 min	21.44±1.06 ^{bA}	17.90±0.68 ^{bA}	20.15±1.49 ^{bCA}	20.75±4.94 ^{bA}	20.90±0.82 ^{CA}	23.41±1.03 ^{bCA}	0.3792
120°C, 20 min	21.97±0.11 ^{bA}	19.18±0.11 ^{bAB}	16.39±0.00 ^{CB}	22.33±3.02 ^{bA}	19.50±0.89 ^{CA}	16.76±2.40 ^{CB}	0.0416
<i>p</i> value	0.0243	0.0191	0.0035	0.0054	<0.0001	0.0014	
	Acid value (mg KOH/100 g dry weight) at 4°C						<i>p</i> value
	0 month	1 month	3 month	6 month	9 month	12 month	
Untreated	39.15±0.71 ^{abc}	37.53±1.04 ^{ac}	35.01±2.10 ^{ac}	44.29±4.04 ^{aAB}	35.17±2.76 ^{ac}	48.46±0.99 ^{aA}	0.0052
105°C, 20 min	26.47±5.82 ^{abB}	24.26±5.13 ^{bB}	26.10±0.07 ^{bAB}	33.74±0.70 ^{bA}	30.92±0.49 ^{aAB}	30.94±4.25 ^{bAB}	0.2070
120°C, 5 min	27.15±6.22 ^{abA}	21.63±1.78 ^{bA}	24.82±1.51 ^{bA}	24.17±1.60 ^{CA}	24.91±2.43 ^{aA}	20.88±0.94 ^{CA}	0.4097
120°C, 20 min	26.86±2.24 ^{abA}	22.60±2.90 ^{bA}	22.73±0.00 ^{bA}	21.85±0.24 ^{CA}	32.08±9.28 ^{aA}	29.62±2.29 ^{bA}	0.2016
<i>p</i> value	0.1107	0.0200	0.0025	0.0017	0.3468	0.0017	

¹⁾Values are expressed as average±standard deviation of triplicate measurements. Significant differences in the same column and row are presented as different lowercase and uppercase superscripts, respectively.

²⁾Untreated raw rice

observation. The rice steaming procedure herein probably led to (i) the inactivation of lipase or esterase (12), and (ii) the formation of a complex between remaining free fatty acids and amylose after starch gelatinization (15). Consequently, the acid values of the parboiled white rice remained relatively constant compared with the acid levels in raw rice for one-year storage, even at 25°C. These results indicate that the parboiling improved the oxidative stability of white rice over the storage period of one year. Further studies to evaluate the effects of parboiling on the lipase activity, complexation of free fatty acids with amylose, and textural properties of parboiled white rice are needed.

Disclosure The authors declare no conflict of interest.

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