Effect of Water Washing on the Reduction of Surface Total Lipids and FFA on Milled Rice

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ABSTRACT: A simple method for removing total lipids from the rice surface by water washing is described for brewing operations, where small FFA levels can have a considerable effect on end-product flavor quality. Commercially milled (first-, second-, and third-break) rice was washed with deionized water with constant stirring for 5 and 10 min. About 60 to 80% of total surface lipids were removed by water washing, with a reduction of FFA and conjugated dienes (CD) relative to unwashed control samples. The total surface FFA content of first-, second-, and third-break milled rice was reduced by more than 50% of the original value by washing. Increases in FFA and CD in washed rice after 7 d of storage at 37°C and 70% RH were much lower than those of unwashed controls, in which FFA and CD development was considerably greater and reached brewing quality. Water washing may be a practical means of reducing off-flavor development in milled rice.

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KEY WORDS: Conjugated dienes, free fatty acids, milled rice, storage study, total surface lipids, water washing.

Rice is the second-leading cereal grain in the world in terms of annual production (1). The storage stability of milled rice is very important, since it ensures the availability of high-quality rice. Degradation of surface lipids in milled rice is related to the deterioration of rice quality during storage (2). The surface lipids are located in bran streaks that remain on the surface of the milled rice. Rice surface lipid decomposition occurs by lipase hydrolysis and subsequent oxidation, which produce off-flavors (2–5). Factors affecting the rate of off-flavor development are temperature, time, exposure to air or oxygen, and the degree to which bran has been removed during milling. Milled rice surface lipids are mainly composed of glycerides from residual rice bran that hydrolyze to FFA through lipase action (5,6). Subsequent oxidation results in a rancid and stale flavor in stored rice. These FFA are easily oxidized by lipoxygenase and cause deterioration of the quality of rice (7). Rice lipid degradation occurs faster after milling when bran lipases are exposed to the bran oil (8). These changes have a minimal effect on the quality of table rice. However, the brewing industry is a major user of milled rice, and milled rice with FFA levels as low as 0.1% has an adverse affect on beer flavor. The FFA content is an indicator for future off-flavor development and is used by the brewing industry to determine the suitability of rice as a brewing adjunct. The accepted level of rice FFA for the brewing industry is 0.1% or less. A simple washing technique to selectively remove residual bran lipids without additional milling would enhance rice brewing quality without an accompanying loss of rice kernels by abrasion. Since lipase activity requires emulsified oil, it appears probable that the oil is present as an O/W (oil-in-water) emulsion with a hydrophilic surface. Therefore, water washing may remove this oil without a loss of rice kernel yield.

Many researchers have reported on FFA and flavor volatiles present in rice during storage. However, there are very limited reports on the inhibition of FFA formed in milled rice during storage. Champagne and Hron (9) treated brown rice kernels and flours with ethanol containing chelators/acidulants to inhibit lipase activity. They found that the inhibition of lipase activity reduced oxidation and subsequent FFA formation. Because the use of alcohol for ethanolic denaturation of rice lipase is not commercially practical, a need exists to develop an acceptable and practical way of inhibiting FFA formation in stored milled rice. Removal of surface lipids from milled rice will reduce the problem of instability. Removal of rice bran oil from milled rice by conventional Soxhlet solvent extraction is complicated and time consuming. The objective of this research was to determine the effect of water washing on milled rice total lipids, FFA (to measure lipid hydrolysis), and conjugated dienes (CD) (to measure the PUFA oxidation that precedes off-flavor development).

MATERIALS AND METHODS

Rice samples. Commercially milled long-grain first-break, second-break, and third-break rice were obtained from Riceland Foods (Stuttgurt, AR). Commercial rice milling is done in three steps. The first step, or break, is an initial abrasion of bran from the kernel. During the second break, a water misting of the abraded rice removes additional bran. The third break is a polishing step to remove flour and bran particles. The surface lipid content of milled rice depends on the degree of milling, i.e., how much bran has been removed. To obtain rice with different surface lipid contents, we collected milled rice from each milling step. Whole kernels of these samples were obtained using a Grainman shaker table (Grain Machinery Mfg. Corp., Miami, FL) with 12/64 trays. During this process, the loose bran particles were also removed.

Water washing. Milled rice samples (200 g) were extracted with either 200 or 400 mL of deionized water with constant stirring for 5 or 10 min. Rice suspended in water was filtered through cheesecloth to separate the rice, which was then

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placed in a forced-air oven for 1 h at 80°C. The dried rice samples were subjected to the storage studies, with unwashed milled rice samples used as controls. Milled rice samples (unwashed and water-washed) were placed on aluminum trays in a laboratory humidity oven (Hotpack, Philadelphia, PA) at 37°C and 70% RH. Rice samples from the oven were sampled at time 0 and after every 12 h for 7 d. The stored water-washed and unwashed rice samples were then subjected to lipid analysis.

Lipid analysis. Total rice surface lipids and FFA were measured by the method of Lam and Proctor (10) by isopropanol extraction (11); FFA were subsequently measured colorimetrically. CD content of the extract was determined by the method of Peers *et al.* (12) to monitor oxidation development (13).

Statistical analysis. Student's *t*-test was used to analyze the results of three replications. Least significance difference (LSD) values were used to differentiate mean values, and significance was defined at $P < 0.05$ (14).

RESULTS AND DISCUSSION

Total surface lipid content. The change in total lipid content (% rice, dry basis) of the first-break rice sample during storage is shown in Figure 1A. Initially, the total surface lipid of the first-break rice was 0.99%. However, water washing significantly reduced the total lipid content of all rice samples. About 60 to 70% of surface lipids were removed by water washing. After water washing, the surface lipid content of the first-break rice samples varied between 0.29 and 0.40%. The changes in total surface lipid content during the storage period were nonsignificant for all the water-washed and unwashed first-break rice samples. Figure 1B presents the changes in total surface lipid content (% rice, dry basis) of second-break rice samples during storage. Water washing removed about 70 to 80% of the initial total surface lipid of 0.60%; the changes in total surface lipid content during the storage period were also not significant for second-break examples. Water washing of the third-break rice showed similar results (Fig. 1C). The initial surface lipid content of third-break rice was 0.46%, 70 to 80% of which was removed during water washing. The changes of surface lipid content during storage were also not significant.

Experiments with all three breaks of rice showed that water washing was equally effective on the rice samples tested. Piggott *et al.* (15) showed that the total surface lipid and FFA contents of milled rice depended on degree of milling. They found that undermilled rice had more surface lipid than well-milled rice, and after storage at 30°C it had higher levels of FFA content. The initial surface lipid contents of first-, second-, and third-break rice samples were 0.99, 0.60, and 0.46% respectively. About 60 to 80% of the total surface lipids were removed from all rice samples by water washing. Among the washing conditions, the most effective one was the 10 min washing with milled rice and water (ratio 1:2, wt/vol) for all samples. It was also observed that the differences in surface lipid content of 5-min (1:2) and 10-min (1:2) washings for first- and third-break rice were not significant. Hence, the ratio of milled rice to water had a greater impact on surface lipid extraction than did the extraction time.

FFA content. Total rice surface FFA content (% rice, dry basis) of the first-break rice sample during 7 d of storage is shown in Figure 2A. There was a significant increase in FFA during storage. In similar studies, Lam *et al.* (16) found a significant increase in FFA level within 48 h of storage at 37°C and 70% RH immediately after milling. The initial FFA content of the first-break long-grain rice was 0.036%, which was reduced to 0.004 to 0.011% during water washing. There was a significant increase in total surface FFA content of the unwashed first-break rice sample during storage. After 7 d of storage, the FFA level increased to 0.20%, which was much higher than the upper limit of FFA content (<0.1% of rice) required in the brewing industry. Lam *et al.* (16) found that the

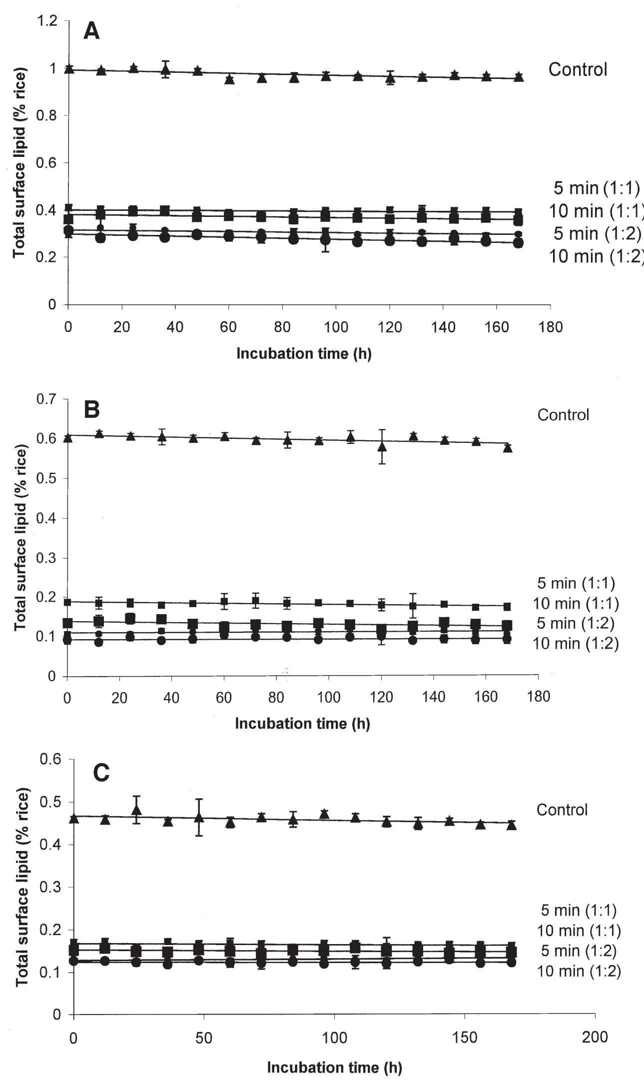

FIG. 1. Total surface lipid content of commercially milled long-grain rice at (A) first break, (B) second break, and (C) third break during 7 d of storage at 37°C and 70% RH. Error bars represent SD.

FFA content increased from 0.03% in freshly milled rice to 0.23% on day 50 of storage at 37°C and 70% RH. A study by Champagne and Hron (17) showed that the FFA level in brown rice increased from 3 to 24% within 6 mon of storage at 36°C. The total FFA content of first-break rice increased above the limit (0.1%) within 36 h of storage. In contrast, the FFA content in water-washed rice was significantly reduced, and changes in FFA content during the storage were also much lower compared to the control. Figure 2B presents the changes in total surface FFA content (% rice, dry basis) of second-break rice samples during 7 d of storage. The FFA content of the second-break rice increased threefold over the storage period (0.057% from the initial 0.019%). In contrast, the FFA content of water-washed second-break rice increased to a range of 0.019 to 0.020% from the initial range of not detected (ND) to 0.002%. During storage at 37°C and 70% RH, a similar pattern of FFA formation (% rice, dry basis) was observed with third-break rice (Fig. 2C). Within 1 wk of storage, the initial FFA content of 0.011% increased to 0.034% for third-break rice. The FFA content of water-washed rice increased to a range of 0.015 to 0.017% from the initial range of ND to 0.005%. The FFA content of unwashed rice was significantly higher than that of all water-washed rice samples. Champagne and Hron (17) found a similar effect on the accumulation of FFA in brown rice with ethanol extraction. Their research showed that FFA levels in kernels extracted with ethanol for 60 min at 24, 46, and 54°C increased from 2.0 to 3.8%, 1.5 to 2.7%, and 1.4 to 2.4% oil, respectively, within 6 mon of storage at 36°C.

Water washing of milled rice reduced the total surface lipid and FFA contents before storage and the rate of increase of FFA during storage. However, the rice/water ratio and washing time were not key factors affecting lipid and FFA contents.

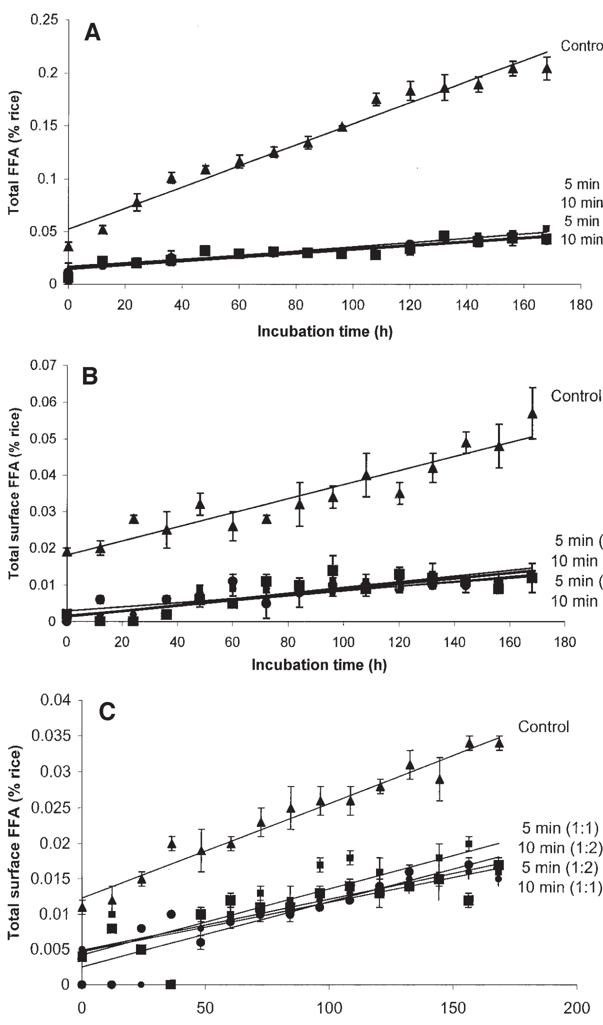

FIG. 2. Total surface FFA content of commercially milled long-grain rice at (A) first break, (B) second break, and (C) third break during 7 d of storage at 37°C and 70% RH. Error bars represent SD.

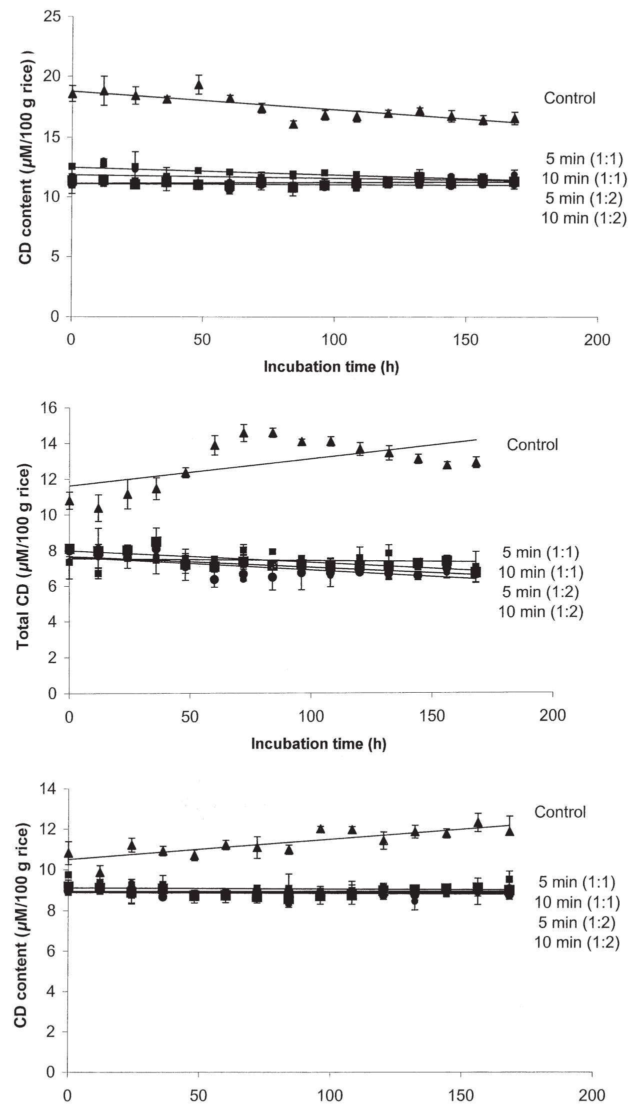

FIG. 3. Total surface conjugated diene (CD) content of commercially milled long-grain rice at (A) first break, (B) second break, and (C) third break during 7 d of storage at 37°C and 70% RH. Error bars represent SD.

CD content. Total surface CD content (μM/100 g rice sample, dry basis) of first-break rice during 7 d of storage at 37°C and 70% RH is presented in Figure 3A. The initial CD content of the unwashed rice sample was 18.58 μM/100 g, which was reduced to a range of 11.05 to 12.58 μM/100 g rice by water washing. The initial CD content of all water-washed rice and the unwashed control remained similar during the storage period. Figure 3B shows the total surface CD content (μM/100 g rice) of second-break rice during 7 d of storage. In second-break rice samples the CD content was initially 10.81 μM/100 g rice. The CD contents of water-washed rice samples were 7.34, 7.39, 8.12, and 7.99 μM/100 g rice for 5 min (1:1), 5 min (1:2), 10 min (1:1), and 10 min (1:2), respectively. The changes in CD content during storage were not statistically significantly different for the water-washed and unwashed rice samples. Figure 3C presents the CD contents of third-break rice during storage. The trend toward CD formation during storage was similar to that of first- and second-break rice. That changes in CD content during storage were not significant for all water-washed and unwashed rice samples may be due to the equal rate of CD breakdown and formation during storage.

Water washing improved the quality of milled rice by reducing the total lipid, FFA, and CD contents. Water washing appears to be a simple and practical means to reduce FFA formation in stored milled rice immediately prior to processing. This may allow lower degrees of milling to obtain higher head rice yields with low surface lipid contents.

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