# Relative FFA Formation and Lipid Oxidation of Commercially Milled Unseparated, Head, and Broken Rice

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**ABSTRACT:** This study was conducted to determine the relative rate of FFA formation and lipid oxidation of unseparated (head and broken), head, and broken rice and the effect of water washing on the lipid quality of broken rice. A regression model was developed with surface FFA or conjugated diene (CD) content vs. incubation time to determine the rates of FFA formation and lipid oxidation. The surface lipid contents of unseparated, head, and broken rice were 0.40, 0.38, and 0.50% of rice, respectively. FFA formation during storage showed three phases: an initial rapid formation, followed by a period of very little or no formation, and finally a phase of gradual formation. In contrast, CD formation initially showed a slow increase but later increased gradually with storage time. The relative rates of FFA and CD formation of unseparated, head, and broken rice were 0.0028, 0.0027, and 0.0036 and 0.192, 0.188, and 0.377, respectively. Water washing reduced the rates of FFA formation and lipid oxidation of broken rice to 0.0015 and 0.2192 from initial values of 0.0031 and 0.369, respectively. Water washing appears to be a simple and practical means of lowering the rates of FFA formation and lipid oxidation in broken rice.

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**KEY WORDS:** Broken rice, conjugated diene, lipid oxidation, free fatty acid, head rice, FFA formation, milled rice, storage study, water washing.

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Annual world rice production is about 585 million metric tons (2000–2001) (1). U.S. rice production in 2001 was 9.44 million metric tons, which is 30% higher than 1991 production and 285% higher than 1961 production (1). Domestic rice consumption in the United States has more than doubled in the last 20 years. In the year 2001, per capita rice consumption was 28.3 lb (12.84 kg), including direct food use (62%), processed food use (22%), and use in beer (16%) (2).

As with many food products, the quality of rice is determined by its ability to produce the preferred end products. The most common form of rice consumed in the world is as milled whole kernels. Whole-kernel or head rice, rather than broken rice, is used in brewing, even though broken rice is less expensive. Broken rice is believed to have a higher lipid oxidation rate and greater off-flavor development compared to whole kernels. However, the quality of head rice is better controlled than that of broken rice. Off-flavor development in beer depends on the surface lipids located in bran streaks that remain on the surface of milled rice after milling. Decomposition of lipids on the rice surface occurs by hydrolysis and subsequent oxidation, resulting in off-flavors (3,4). The FFA content is an indicator of off-flavor development and is used by the brewing industry to determine the appropriateness of rice as a brewing adjunct. The accepted level of rice FFA for the brewing industry is 0.1% or less.

Factors affecting the rate of FFA formation and off-flavor development are temperature, time, exposure to oxygen, and the amount of residual bran present on the milled rice. A few studies in the recent literature have reported on the rate of FFA formation in model systems using purified lipase (5,6). Lam and Proctor studied the kinetics and mechanism of FFA formation on the surface of milled rice (7). They developed a predictive model for FFA formation on the surface of milled rice during storage at different temperatures. Monsoor and Proctor (8) described a water-washing method to remove the total surface lipids and FFA on milled rice. They found that the storage stability of milled rice was improved with water washing, as it lowered the rate of FFA and conjugated diene (CD) formation. However, there have been no reports on the relative formation and oxidation of FFA in unseparated (head and broken) rice, head rice, and broken rice kernels that justify the use of whole kernels over broken ones as a brewing adjunct, or on the effect of water washing on broken kernels to increase their oxidative stability.

This study was conducted to determine the relative rate of FFA formation and lipid oxidation of unseparated, head, and broken rice. The effect of water washing on the rate of FFA formation and lipid oxidation on broken rice was also evaluated. The specific objectives of this research were (i) to determine the comparative rate of FFA formation and lipid oxidation of unseparated, head, and broken rice kernels, and (ii) to determine the effect of water washing on the rate of FFA formation and lipid oxidation of broken rice.

## MATERIALS AND METHODS

*Rice samples.* Commercially milled long-grain unseparated (collected after rice milling), head, and broken rice was obtained from Riceland Foods (Stuttgart, AR). These samples were used to monitor FFA formation and lipid oxidation during storage.

*Comparative rate of FFA formation and lipid oxidation of rice samples. (i) Storage study*. The unseparated, head, and broken rice (2 kg each) was placed on aluminum trays in a laboratory humidity oven (Hotpack, Philadelphia, PA) at 37°C and

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70% RH. This condition was chosen to represent the optimal temperature and RH for rice bran lipase. Samples (50 g) were taken from the oven from each rice population at time 0, every 12 h for 7 d, and every day thereafter for a total of 30 d for lipid analysis.

*(ii) Total surface lipid content*. Surface lipids on the rice samples were extracted with 8 mL of isopropanol by vortexing 10 g of rice sample, and the surface lipid content of the extracts was determined by the method of Lam and Proctor (9).

*(iii) FFA formation and lipid oxidation*. The formation of FFA on the surface of milled rice was measured by the method of Lam and Proctor (9) using isopropanol as the extraction solvent. The CD content of the isopropanol extracts was measured by absorbance at 233 nm (10).

*(i) Rate of FFA formation and lipid oxidation*. To determine the relative rate of FFA formation and lipid oxidation, a linear regression model was developed with one independent ($X$) and one response variable ($Y$), and described as $Y = \beta_0 + \beta_1 X + \varepsilon$, where $Y$ is the total surface FFA content or total surface CD content, $X$ is the incubation time in days, and $\varepsilon$ is the random error term. The slope ($\beta_1$) of the regression model was calculated to determine the rate of FFA formation and lipid oxidation.

*Effect of water washing on the rate of FFA formation and lipid oxidation of broken rice. (i) Water washing*. Broken rice samples were washed with equal volumes of deionized water for 5 min as described by Monsoor and Proctor (8). Water-washed broken rice samples were filtered through cheesecloth to separate the rice, which was then placed in a forced-air oven at 70°C for 1 h along with the control (unwashed broken rice). The dried water-washed and unwashed broken rice was subjected to storage studies. The storage conditions and sampling method were similar to those in the previous Storage Study Section. The rates of FFA formation and lipid oxidation of these samples were determined by the procedure described in the previous section.

*Statistical analysis*. Student's $t$-test was used to analyze the results of three replications. LSD values were used to differentiate mean values, with significance defined at $P < 0.05$ (11).

## RESULTS AND DISCUSSION

*Comparative rate of FFA formation and lipid oxidation. (i) Total surface lipids*. The total surface lipid contents of unseparated, head, and broken rice were 0.40, 0.38, and 0.50% of rice, respectively. The surface lipid contents of unseparated, head, and broken rice samples after 30 d of storage were 0.39, 0.35, and 0.48% of rice. The changes in content of total surface lipids during the storage period were not statistically significant for all unseparated, head, and broken rice (data not presented).

*(ii) FFA formation*. The formation of FFA on unseparated, head, and broken rice during storage at 37°C and 70% RH is presented in Figure 1. The initial FFA contents of the total, head, and broken rice samples were 0.018, 0.016, and 0.021% of rice, respectively. The higher levels of FFA in the broken rice corresponded with a relatively high amount of surface lipids in the broken rice. Three separate phases or steps were identified in the FFA formation curve. The first step involved an initial rapid rise of FFA (0.05 to 0.06% of rice) within 5 or 6 d of storage, followed by a lag period of 3 to 4 d and then a final phase involving a gradual increase with storage time (Fig. 1). Lam and Proctor (12) also reported that FFA formation of partially and fully milled rice followed three distinct phases during storage at 37°C and 70% RH. The initial rapid rise of FFA is probably due to the activity of rice bran lipases. The slower rate of FFA formation in the second phase may be attributed to the feedback inhibition of rice bran lipases owing to increased production of FFA in the first phase. The third phase is probably due to the activation of rice bran lipases by alosteric regulation and/or the presence of microbial lipases (13). The FFA contents of unseparated, head, and broken rice were increased to 0.099, 0.096, and 0.121% rice after 30 d of storage at 37°C and 70% RH. Within 18 d of storage, the FFA level of the broken rice had increased to the critical value of 0.1%.

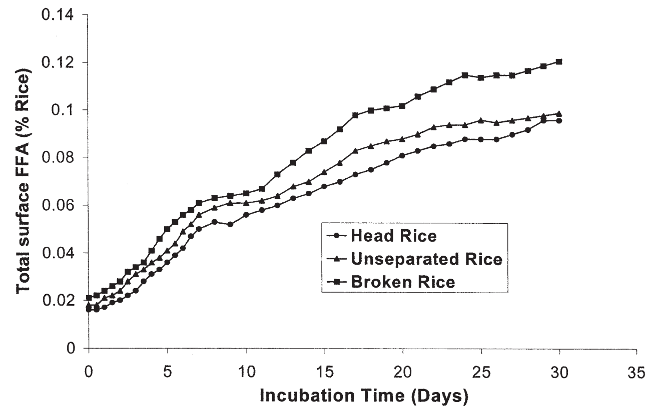


**FIG. 1.** Total surface FFA contents of unseparated, head, and broken rice during 30 d of storage at 37°C and 70% RH.

*(iii) Lipid oxidation*. The formation of CD in unseparated, head, and broken rice during storage at 37°C and 70% RH is presented in Figure 2. The initial CD contents of the unseparated, head, and broken rice were 9.96, 8.39, and 11.28 μM/100 g of rice, respectively. The differences in CD content among unseparated, head, and broken rice reflected the initial amount of total lipids and the FFA content of the samples. Unlike FFA formation, CD formation showed two distinct phases: initially, no or a very slow increase up to 10 and 12 d, then a gradual increase with storage time. The CD contents of unseparated, head, and broken rice increased by 1.61-, 1.71-, and 1.96-fold after 30 d of storage, whereas FFA contents increased by 5.50-, 6.00-, and 5.76-fold, respectively, for the same storage period. This indicated that the rate of FFA formation was relatively higher than the rate of lipid oxidation. The CD contents of the unseparated, head, and broken rice samples after 30 d of storage at 37°C and 70% RH were 16.09, 14.41, and 22.07 μM/100 g of rice, respectively.

*(iv) Rate of FFA formation and lipid oxidation*. The rates of FFA formation and lipid oxidation of broken rice were significantly higher than those of head or unseparated rice (Table 1).

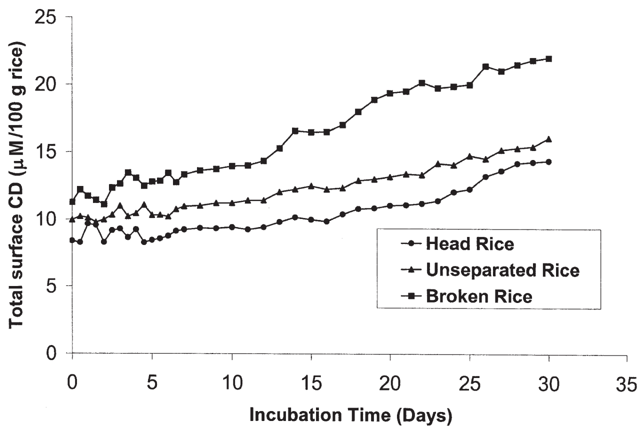


**FIG. 2.** Total surface conjugated diene (CD) contents of unseparated, head, and broken rice during 30 d of storage at 37°C and 70% RH.

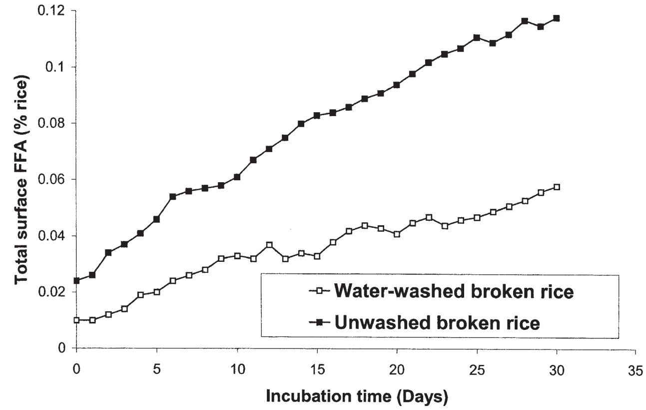


**FIG. 3.** Effect of water washing on the total surface FFA content of broken rice during 30 d of storage at 37°C and 70% RH.

We found that a smaller increase in lipid content had a greater effect on the rate of FFA formation. The rates of FFA formation on the surface of unseparated, head, and broken rice were 0.0028, 0.0027, and 0.0036% of rice per day, respectively. The rates of lipid oxidation on the unseparated, head, and broken rice, as indicated by the slope of the regression model, were 0.192, 0.188, and 0.377 μM/100 g of rice per day, respectively (Table 1). This explains the increased oxidation and off-flavor development associated with broken rice.

*Effect of water washing on the rate of FFA formation and lipid oxidation of broken rice. (i) Total surface lipids*. The initial surface lipid contents of unwashed and water-washed broken rice samples were 0.53 and 0.14% of rice, respectively. About 70% of the surface lipids on the broken rice sample were removed by water washing. The total surface lipid contents of unwashed and water-washed broken rice samples after storage were 0.46 and 0.12% of rice, respectively, with no significant changes observed over time.

*(ii) FFA formation*. The changes in surface FFA contents of the water-washed and unwashed broken rice samples after 30 d of storage at 37°C and 70% RH are presented in Figure 3. The initial surface FFA contents of the unwashed and water-washed broken rice samples were 0.024 and 0.010% of rice, respectively. The FFA contents of the unwashed control and water-washed broken rice increased to 0.118 and 0.058% of rice, respectively, within 30 d of storage. Water washing improved the storage stability of the broken rice, as the water-washed sample maintained FFA levels below the critical value of 0.1% after 30 d of storage (Fig. 3).

*(iii) Lipid oxidation*. The changes in surface CD contents of the water-washed and unwashed broken rice after 30 d of storage at 37°C and 70% RH are presented in Figure 4. The initial CD content of the unwashed broken rice, 11.28 μM/100 g, was reduced to 6.02 μM/100 g by water washing. The differences in initial CD content in unwashed and water-washed broken rice reflect the total surface lipid and FFA contents of the unwashed and water-washed broken rice. This indicates that water washing can be used to eliminate or reduce the effect of higher amounts of initial surface lipids and FFA on the off-flavor development of milled rice.

*(iv) Rate of FFA formation and lipid oxidation*. The FFA and CD contents of unwashed and water-washed broken rice increased by 4.91- and 5.80-fold and by 2.00- and 2.14-fold from initial values after 30 d of storage at 37°C and 70% RH. The relative rates of FFA formation and lipid oxidation of broken

**TABLE 1**
**Rates of FFA Formation and Lipid Oxidation[a] of Commercially Milled Head, Unseparated, and Broken Rice Samples as Indicated by the Slope of the Linear Regression Model**

| Rice sample | FFA formation (FFA % of rice per day) | Lipid oxidation (μM CD/100 g of rice per day) |
|---|---|---|
| Head rice | 0.0027 ± 0.0003[b] | 0.188 ± 0.042[b] |
| Unseparated rice | 0.0028 ± 0.0002[b] | 0.192 ± 0.051[b] |
| Broken rice | 0.0036 ± 0.0004[a] | 0.377 ± 0.082[a] |

[a]Values with same roman superscript in each column (a,b) are not significantly ($P < 0.05$) different. CD, conjugated diene.

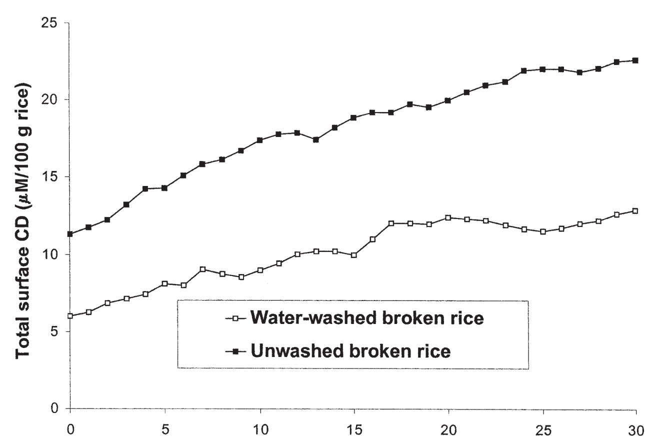


**FIG. 4.** Effect of water washing on the total surface CD content of broken rice during 30 d of storage at 37°C and 70% RH. For abbreviation see Figure 2.

**TABLE 2**
**Effect of Water Washing on the Rate of FFA Formation and Lipid Oxidation of Commercially Milled Broken Rice as Indicated by the Slope of the Linear Regression Model**

| Rice sample | FFA formation (FFA % of rice per day) | Lipid oxidation (μM CD/100 g of rice per day) |
|---|---|---|
| Unwashed broken rice | 0.0031 ± 0.0005[a] | 0.368 ± 0.037[a] |
| Water-washed broken rice | 0.0015 ± 0.0002[b] | 0.219 ± 0.043[b] |

[a]Values with same roman superscript (a,b) in each column are not significantly ($P < 0.05$) different. For abbreviation see Table 1.

rice were 0.0033% of rice per day and 0.368 μM/100 g of rice per day, respectively. The rates of FFA formation and lipid oxidation were lowered significantly by water washing, as indicated by the slope of the regression model for water- washed and unwashed broken rice (Table 2). The relative rates of FFA formation and lipid oxidation of water-washed broken rice were 0.0015% of rice per day and 0.219 μM/100 g of rice per day, respectively.

The rates of FFA formation and lipid oxidation of broken rice were significantly higher than those of unseparated and head rice. This may be due to the initial high content of surface lipids on broken rice compared to that of unseparated or head rice. Water washing reduced the surface lipid content and thus decreased subsequent hydrolysis and oxidation. Water washing also reduced the initial FFA and CD contents of the broken rice sample. Water washing seems to be a simple and practical means of removing surface lipids, FFA, and CD from broken rice to improve the quality. This technique may enable broken rice to be used for brewing.

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