Relative Free Fatty Acid Formation and Lipid Oxidation of Commercially Milled Unseparated, Head, and Broken Rice

M.A. Monsoor and A. Proctor

ABSTRACT

This study was conducted to determine the relative rate of free fatty acid (FFA) formation and lipid oxidation of unseparated (head and broken), head, and broken rice and the effect of water washing on broken rice lipid quality. A regression model was developed with surface FFA or conjugated diene (CD) content versus 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. The 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, 0.0036 and 0.192, 0.188, 0.377, respectively.

INTRODUCTION

As with many food products, the quality of rice is determined by its ability to produce acceptable products. The most common form of rice consumed in the world is as milled whole kernels. Whole kernels or head rice are used in brewing rather than broken even though broken are less expensive. It is thought that broken have a higher lipid oxidation rate and greater off-flavor development relative to whole kernels. The off-flavor development in beer depends on the bran lipids that remain
on the surface of the milled rice after milling. However, head rice quality is better controlled than that of brokens. Rice surface lipid decomposition occurs by hydrolysis and subsequent oxidation, resulting in off-flavors (Aibra et al., 1986; Yasumatsu et al., 1966). The free fatty acid (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. There are a few studies that have reported in the recent literature on the rate of FFA formation in model systems using purified lipase (Fadiloglu and Soylemez, 1997). Lam and Proctor (2002) studied the kinetics and mechanism of FFA formation on the surface of milled rice. They developed a predictive model for FFA formation on milled rice surface during storage at different temperatures. However, there are no reports on the relative FFA formation and oxidation of the unseparated (head and broken) rice, head rice, and broken rice kernels, which justify the use of whole kernels as brewing adjunct over brokens. This study was conducted to determine the relative rate of FFA formation and lipid oxidation of unseparated, head, and broken rice. The objectives of this research was to determine the comparative rate of FFA formation and lipid oxidation of the unseparated, head, and broken rice kernels.

**MATERIALS AND METHODS**

**Rice Samples**

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

**Comparative Rate of FFA Formation and Lipid Oxidation of Rice Samples**

**Storage Study**

The unseparated, head, and broken rice (2 kg each) were placed on aluminum trays in a laboratory humidity oven (Hotpack, Philadelphia, Penn.) at 37°C and 70% relative humidity. This condition was chosen to represent the optimum temperature and relative humidity for rice bran lipase. Samples (50 g) from the oven were taken from each rice population at time 0 and every 12 hours for 7 days and thereafter every day for a total of 30 days for lipid analysis.

**Surface Lipid Content**

Surface lipid content of the rice samples were extracted with 8mL of isopropanol (IPA) by vortexing 10 g of rice sample and surface lipid content of the extracts were determined by the method of Lam and Proctor (2001).
**FFA Formation and Lipid Oxidation**

The FFA formation on milled rice was measured by the method of Lam and Proctor (2001) using isopropanol as the extraction solvent. The conjugated diene content of the isopropanol extracts was measured by absorbance at 233 nm (Fishwick and Swoboda, 1977).

**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 $Y$ = surface FFA content or surface CD content, $X$ = 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.

**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, with significance defined at $P<0.05$.

**RESULTS AND DISCUSSION**

**Comparative Rate of FFA Formation and Lipid Oxidation**

**Surface Lipid**

The surface lipid content of unseparated, head, and broken rice were 0.40, 0.38, and 0.50% of rice, respectively. The surface lipid content of unseparated, head, and broken samples were 0.39, 0.35, and 0.48% of rice after 30 days of storage. The changes in surface lipid content during the storage period were not statistically significant for unseparated, head, and broken rice (data not presented).

**FFA Formation**

The FFA formation of unseparated, head, and broken rice during storage at 37°C and 70% RH is presented in Figure 1. The initial FFA content of total, head, and broken rice samples were 0.018, 0.016, and 0.021% of rice, respectively. The higher FFA levels in broken rice corresponded with a relatively high amount of surface lipid in 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 five or six days of storage, followed by a lag period of three to four days and than a final phase involving a gradual increase with storage time (Fig. 1). Lam et al. (2001) 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 at the second phase may be attributed to the feed back inhibition of rice bran lipases.
due to increased production of FFA in the first phase. The third phase is probably due to the activation of rice bran lipases by allostery regulation and/or the presence of microbial lipases (Lam and Proctor, 2003). The FFA content of unseparated, head, and broken rice were increased to 0.099, 0.096, and 0.121% rice after 30 days of storage at 37°C and 70% RH. Within 18 days of storage the FFA level of the broken rice was increased to the critical value of 0.1%.

**Lipid Oxidation**

The CD formation of unseparated, head, and broken rice during storage at 37°C and 70% RH is presented in Figure 2. The initial CD content of the unseparated, head, and broken rice were 9.96, 8.39, and 11.28 µM/100g of rice, respectively. The differences in CD content between unseparated, head, and broken rice reflected the initial amount of total lipid and FFA content of the samples. Unlike FFA formation, CD formation showed two distinct phases; an initial no or very slow increase up to 10 and 12 days then a gradual increase with storage time. The CD content of unseparated, head, and broken rice increased by 1.61, 1.71, and 1.96-fold after 30 days of storage, whereas FFA content 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 content of the unseparated, head, and broken rice samples after 30 days of storage at 37°C and 70% RH were 16.09, 14.41, and 22.07 µM/100g of rice, respectively.

**Rate of FFA Formation and Lipid Oxidation**

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

**SIGNIFICANCE OF FINDINGS**

Broken rice had significantly greater surface lipid content than head and unseparated rice, which probably was due to the broken being undermilled relative to head rice. The surface lipid content was the major factor for FFA development and subsequent oxidation on milled rice during storage.
LITERATURE CITED


Table 1. Rate of FFA formation and lipid oxidation of commercially milled head, unseparated, and broken rice samples as indicated by the slope of the linear regression model.

<table>
<thead>
<tr>
<th>Rice samples</th>
<th>FFA formation (FFA % rice per day)</th>
<th>Lipid oxidation (µM CD/100g of rice per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head rice</td>
<td>0.0027 ± 0.0003 b</td>
<td>0.188 ± 0.042 b</td>
</tr>
<tr>
<td>Unseparated rice</td>
<td>0.0028 ± 0.0002 b</td>
<td>0.192 ± 0.051 b</td>
</tr>
<tr>
<td>Broken rice</td>
<td>0.0036 ± 0.0004 a</td>
<td>0.377 ± 0.082 a</td>
</tr>
</tbody>
</table>

* Values with same superscript in each column are not significantly (P<0.05) different.
Fig. 1. Surface FFA content of unseparated, head, and broken rice during 30 days of storage at 37°C and 70% RH.

Fig. 2. Surface CD content of unseparated, head, and broken rice during 30 days of storage at 37°C and 70% RH.