

Cereal Chemistry

Vol. 52

January-February 1975

No. 1

Effect of Parboiling of Rice on the Rate of Lipid Hydrolysis and Deterioration of Rice Bran

A. B. SHAHEEN, A. A. EL-DASH, and A. E. EL-SHIRBEENY, Department of Food Technology, Al-Azhar University, Cairo, Arab Republic of Egypt

ABSTRACT

Two rice varieties, one short grain (Nahda) and one long grain (Arabi), were parboiled with either a soaking or a boiling pretreatment prior to steaming; the effect of such parboiling treatments on the rate of lipid hydrolysis during long-term storage was then investigated. Parboiling of rice reduced the development of free fatty acids (FFA) in the bran oil; although the bran of parboiled rice can be stored as long as 10 months with only minor deterioration, the bran of untreated rice cannot be stored for more than 1 month without serious deterioration of oil and bran quality. Unparboiled bran exhibited two distinct stages of hydrolysis, an initial rapid rate for the first 7 weeks of storage and a subsequent slower rate throughout the remainder of the storage period. This latter stage was independent of the variety. The long-grain variety (Arabi) showed a lower rate of lipid hydrolysis for both parboiled and untreated samples than the short-grain one, although preboiled, parboiled samples showed greater lipolysis of bran oil than presoaked, parboiled ones. The value of the parboiling process in reducing the rate of FFA development is somewhat offset by the loss in resistance to oxidation, as was evident from an increase in the peroxide value for the parboiled samples.

Improvement of the nutritional value of rice through parboiling is a well-established process. However, the industrial cost of the production of parboiled rice may be a limiting factor in preventing the introduction of such a nutritionally superior product into the low-income sector of society in the developing countries where it is badly needed. A better use of by-products or improved parboiling techniques to produce a better quality by-product, however, may favorably influence the introduction of parboiled rice to replace regular rice on a large scale in the underdeveloped and developing areas of the world.

The major by-products of the rice milling industry are rice bran and rice bran oil. The use of bran as feed and bran oil as edible oil, however, is hindered by the fact that the oil undergoes an extremely rapid deterioration. This deterioration is due to the mixing of the lipid-splitting enzyme lipase and lipoxygenase and the oil during the milling of rice, resulting in an oxidative rancidity and the production of an off-flavor. The hydrolysis is so rapid that 60% of the oil is destroyed in a month (1), resulting in a very serious economic loss to the industry. Because of inactivation of the lipase enzyme during parboiling, however, parboiled rice bran seems to be more stable to hydrolysis. The effect of different parboiling processes on the rate of bran oil hydrolysis and bran acidity may therefore aid in selecting the most efficient parboiling process.

MATERIALS AND METHODS

The two varieties of rice were selected on the basis of prevalence in the Middle East, one short grain (Nahda) and one long grain (Arabi).

Parboiling and Milling of Rice Samples

The two methods of parboiling used in this investigation were determined to give the maximum yield of milled rice with minimum quantities of broken grains for the chosen varieties (2). The methods differed according to pretreatment. One pretreatment consisted of boiling for 20 min.; the other involved soaking the grains at room temperature for 24 and 18 hr. for the Nahda and Arabi varieties, respectively, since these soaking times were found to be the optimum in obtaining the highest yield of milled rice. After pretreatment, all samples were drained and spread in small wire-mesh trays; they were then steamed for 15 min. under a pressure of 1.5 kg./cm.² and dried at room temperature to a proper moisture content, generally ranging from 12 to 14%. A control sample for each variety was washed with water and dried in the same manner. The samples were then milled with a Universal laboratory mill.

Storage of Bran and Evaluation of Quality

Bran samples were stored in air-tight glass containers at room temperature, and samples were withdrawn on a weekly basis for extraction of oil. The protein, oil, fiber, carbohydrate, and ash contents of the bran were determined after 3 and 10 months of storage according to AACC methods (3). After 10 months of storage the samples were badly infested with mold growth and the experiment was therefore discontinued.

Extraction of Oil from Bran

Every week during the storage period, a 200-g. portion of the bran was mixed with 500 ml. hexane (40° to 50° C.) and shaken for 3 hr. The hexane was then

TABLE I. EFFECT OF PARBOILING AND STORAGE ON THE CRUDE OIL CONTENT OF RICE BRAN

Parboiling Treatment	Duration of Storage (months)		
	0 %	3 %	10 %
Nahda¹			
Untreated	11.70	11.53	9.77 ²
Preboiling	12.01	11.92	10.05 ²
Presoaking	13.05 ³	13.01	10.83 ²
Arabi			
Untreated	13.51	13.50	11.48 ²
Preboiling	14.11	14.00	12.86 ²
Presoaking	15.01 ³	14.89	12.63 ²

¹P < 0.01 between varieties.

²P < 0.01 as compared to 0 time of storage for same treatment of same variety.

³P < 0.05 as compared to untreated rice of the same variety.

poured off and fresh hexane added, followed by vigorous shaking for an additional 3 hr. The extraction procedure was repeated twice in the same manner. The solvent was collected and evaporated to recover the oil. Oil samples were then dried under vacuum at 70°C. to ensure removal of any traces of hexane.

Free Fatty Acid Determination

The free fatty acid (FFA) content of the extracted oil was used as an index of bran and oil deterioration and was determined weekly over a 10-month period according to the method of Karon and Altschul (4) using 0.1N potassium hydroxide for titration of FFA.

Chemical Properties of Bran Oil

Saponification number, iodine number, and peroxide value were determined according to the AACC methods (3).

RESULTS AND DISCUSSION

Rice bran, a by-product of rice milling, makes up approximately 7 to 10% of paddy rice. It contains 10 to 15% protein, 10 to 15% oil, and 8 to 15% fiber, as well as a high quantity of carbohydrates, ash, and vitamins, making it nutritionally valuable for animal feed.

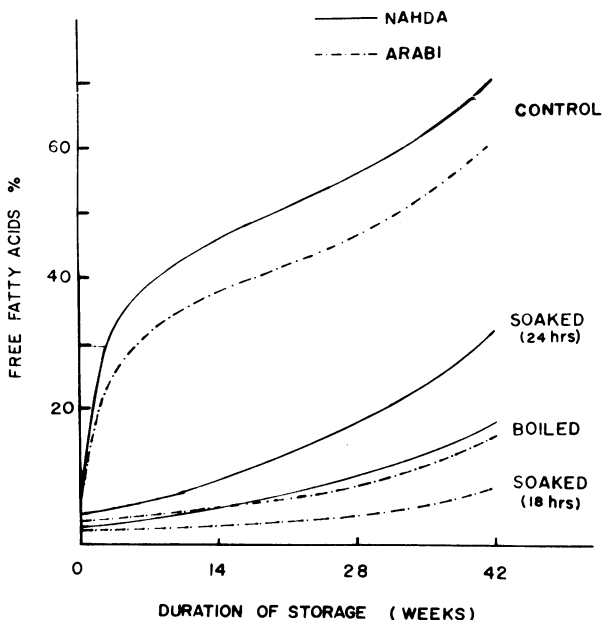


Fig. 1. Effect of parboiling of rice and storage of bran on the free fatty acid content of bran oil.

Effect on Major Constituents of Rice Bran

Parboiling and storage had no effect on the content of the major bran constituents: protein, fiber and ash; however, the bran oil content was influenced as shown in Table I. Upon soaking prior to steaming, bran oil of the Nahda and Arabi varieties underwent apparent increase of approximately 11% ($P < 0.05$). Upon the boiling pretreatment, however, the increase was not significant. A similar observation was reported by Subrahmanyam et al. (5).

It seems that the soaking of rice prior to steaming affects the separation of the bran layer during milling (degree of rice milling), resulting in an increase in the oil content of the separated bran. Such an explanation is supported by the fact that one of the most reliable methods presently available for measuring the extent to which the bran layers and germ have been removed from the rice endosperm is the amount of fat extracted from whole milled rice. It was found (6,7) that the amount of fat extracted is linearly related to the amount of bran removed, up to 6% of the original by weight.

The crude oil content of the bran of untreated and parboiled samples showed no change upon storage for a period of 3 months at room temperature, although after 10 months a reduction of approximately 9 to 17% of the crude oil was observed for all samples ($P < 0.01$). The reduction of bran crude oil on storage may be the result of the formation of polar oxygen-containing compounds and polymers which decrease the solubility of glycerides in the nonpolar solvents used to extract the oil. Another possible explanation concerns associative forces (oil fixation) between glycerides and bran, causing a reduction in the amount of solvent-extractable oil. A similar phenomenon has been observed in corn oil upon storage (8).

Deterioration of Bran Oil

Deterioration of rice bran during storage is the result of complex chemical and biological reactions. Deterioration of bran and bran oil is considered as the most serious obstacle for economic production of a high-quality edible oil, as well as the use of bran as animal feed.

Effect on FFA Content. The FFA content is used as an index of deterioration of oil and oil-containing materials. A high FFA content is considered a serious detriment. The FFA content of the oil extracted from untreated samples was compared with that of the parboiled samples of the two rice varieties over a 43-week period, as shown in Fig. 1. It is evident from these results that parboiling of rice reduced the development of FFA in bran oil and, consequently, the deterioration of the bran quality. The pronounced effect of the parboiling process on lipid hydrolysis and the subsequent reduction of FFA were indicated by the fact that after nearly 10 months of storage at room temperature the FFA content of parboiled samples was less than that of the untreated ones after only 3 weeks of storage. Thus, while bran of unparboiled rice cannot be stored for more than 1 month without serious deterioration of oil quality, the bran of parboiled rice could be stored as long as 10 months with only minor deterioration of quality.

Several investigators (4,9,10,11) have reported that extremely active lipolytic enzymes are the principal factors in bran deterioration during storage. Although parboiling of rice destroys most of the lipolytic enzymes, however, a slight hydrolysis of fats during storage of the parboiled samples was evident. The short-

grain Nahda rice variety soaked for 24 hr. before parboiling had the highest FFA content and therefore suffered the greatest quality deterioration of all parboiled samples examined in this study. This may be explained because short-grain varieties have a larger surface area per unit weight than long-grain varieties. This larger surface area in combination with the longer soaking period (24 hr.) may result in a faster lipid hydrolysis during the soaking period. Therefore, soaking short-grain rice varieties for a long period (e.g., 24 hr.) enhanced the lipolytic action more than did the boiling pretreatment. However, soaking the long-grain Arabi variety for a shorter period (18 hr.) before steaming was quite effective in decreasing lipid hydrolysis and consequently reducing the deterioration of the bran oil.

Effect on Production Rate of FFA. The lipolytic rate depends upon the biological system as well as the conditions surrounding the system such as temperature, humidity, light, and surface area exposed. The rate of hydrolysis of bran oil can be expressed by the general equation

$$\frac{d\text{FFA}}{dt} = K(\text{FFA})(100 - \text{FFA}) \quad (1)$$

where t is the reaction time, FFA represents percentage of free fatty acids produced, $100 - \text{FFA}$ represents the unhydrolyzed portion of the glycerides, and K is the reaction constant.

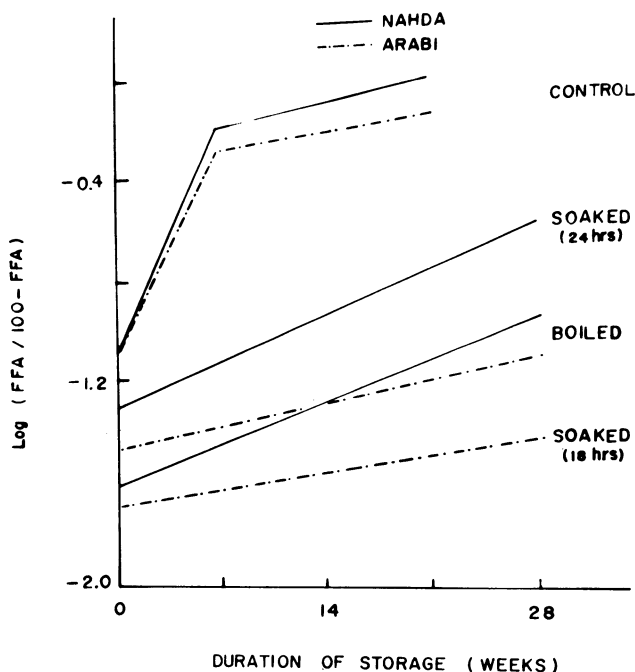


Fig. 2. Rate of lipid hydrolysis of bran oil from unparboiled and parboiled rice bran.

Upon integration and conversion to common logarithms, equation 1 may be expressed as

$$\text{Log (FFA/100 - FFA)} = 100 \text{ Kt}/2.3 + \text{Log FFA}_0/100 - \text{FFA}_0 \quad (2)$$

where FFA_0 is the original percentage of free fatty acids (4).

Therefore, plotting $\text{Log FFA}/100 - \text{FFA}$ against time gives a straight line with a slope equal to $100 \text{ K}/2.3$. When the data on FFA obtained in this study were plotted in such a fashion, the points fell as shown in Fig. 2. The rate constant of hydrolysis was then calculated and is presented in Table II. Untreated bran exhibited two distinct stages of hydrolysis, an initial rapid rate for the first 7 weeks of storage ($\text{K} = 1.28 \times 10^{-3}$ and 9.43×10^{-4} for Nahda and Arabi, respectively) and a subsequent slower rate ($\text{K} = 2.1 \times 10^{-5}$) throughout the remainder of the storage period. This latter rate was identical for both varieties, indicating that this stage of hydrolysis is independent of variety. Lipolysis of untreated bran is due exclusively to enzymes already present in the active state which may undergo a rapid hydrolysis, followed by a slower stage as a result of inhibition of the enzymes by the reaction products. Since the enzymes of parboiled samples are generally inhibited, lipolysis depends primarily on nonenzymatic reactions which are characterized by a slower rate of reaction. The long-grain Arabi rice showed a lower activity for both parboiled and unparboiled samples than the short-grain Nahda rice. This may be the result of varietal difference and/or a smaller bran surface area for the long-grain variety in comparison to the short-grain one. Preboiled samples showed greater lipolysis of bran oil than presoaked ones.

Effect on Chemical Properties of Bran Oil. The parboiling process had no effect on the saponification number of oil of the two rice varieties. The saponification numbers were 190.1 and 190.9 at the time of milling and 187.2 and 188.8 for the parboiled samples of Nahda and Arabi rice, respectively. Storage for 10 months caused a slight reduction (5%) in the saponification value of the extracted oil.

The iodine number of the Nahda and Arabi varieties was 99.2 and 98.6, respectively. Parboiling caused a 6.5 and 8.5% reduction in iodine number,

TABLE II. EFFECT OF PARBOILING AND STORAGE ON THE RATE OF HYDROLYSIS OF RICE BRAN OIL

Parboiling Treatment	Constant Rate of Hydrolysis (K)	
	First Stage	Second Stage
Nahda		
Untreated	1.28×10^{-3}	2.10×10^{-5}
Preboiling	1.70×10^{-4}	...
Presoaking	1.52×10^{-4}	...
Arabi		
Untreated	9.43×10^{-4}	2.10×10^{-5}
Preboiling	1.44×10^{-4}	...
Presoaking	1.24×10^{-4}	...

whereas storage of untreated samples for 10 months caused a 13 and 8.5% reduction in the same varieties. However, parboiled samples stored for 10 months showed only a slight decrease in iodine number. This decrease in iodine number indicates the saturation of double bonds of fatty acids upon parboiling or storage.

The effects of parboiling and storage on the peroxide value are presented in Fig. 3. The pronounced effect of the parboiling process on the peroxide value and subsequent fat rancidity was indicated by the fact that all parboiled samples had a higher peroxide value than the controls. This effect may be due to destruction of antioxidants by the steaming step of the parboiling process. Therefore, the value of the parboiling process in reducing the rate of FFA development is somewhat offset by the loss in resistance to oxidation. Storage of the rice bran for 3 months tripled the peroxide value of the oil of untreated samples, although the peroxide value for the parboiled samples stored for the same period was more than tripled. At the end of the 10-month storage period, the peroxide value rapidly decreased for each sample in question. This indicates that in the advanced stages of oxidation, various volatile compounds of low molecular weight are produced and is in agreement with the previous reports that the peroxide value of oil decreases after reaching a maximum (12).

The long-grain variety of rice (Arabi) exhibited a lower rate of lipid hydrolysis for both parboiled and untreated samples than the short-grain Nahda variety, although presoaking before steaming showed a lower rate of lipolysis of bran oil than preboiling. Therefore, the use of presoaking with the long-grained Arabi rice would yield a product with maximum storability and minimum loss of oil.

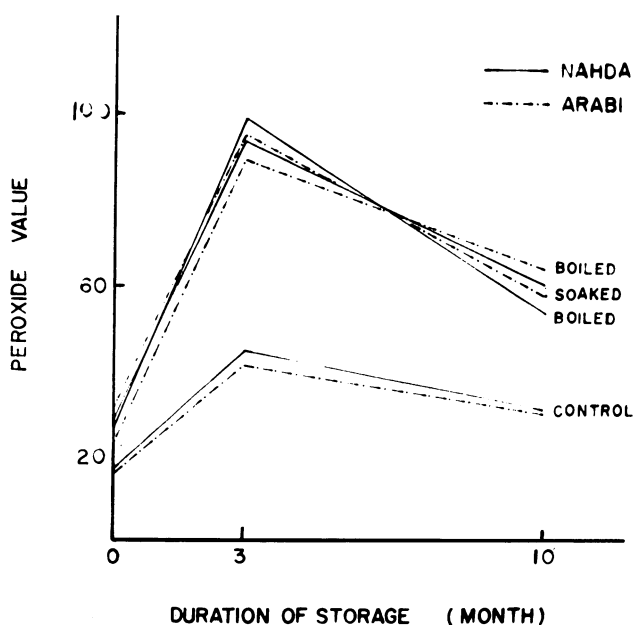


Fig. 3. Influence of parboiling and storage on the peroxide value of bran oil.

Literature Cited

1. GRIST, D. H. By-products of the rice industry. 2. Extraction of rice bran oil. *World Crops* 13: 154 (1961).
2. AHMED, E. A. Chemical and biological constituents of local varieties of rice with special reference to the effect of parboiling. Master's thesis, Ain Shams Univ. (1963).
3. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Approved methods of the AACC (7th ed.). The Association: St. Paul, Minn. (1962).
4. KARON, M. L., and ALTSCHUL, A. M. Effect of moisture and effect of pretreatment with acid and alkali on rate of formation of free fatty acids in stored cotton seed. *Plant Phys.* 19: 310 (1944).
5. SUBRAHMANYAN, V., SREENIVASAN, A., and GUPTA, P. H. Studies on quality in rice. I. Effect of milling on the chemical composition and commercial qualities of raw and parboiled rice. *Indian J. Agr. Sci.* 8: 459 (1938).
6. AUTREY, H. S., GRIGARIEFF, W. W., ALTSCHUL, A. M., and HOGAN, J. T. Effect of milling conditions on breakage of rice grain. *J. Agr. Food Chem.* 3(7): 593 (1957).
7. HOGAN, J. T., and DEOBALD, H. J. Note on a method of determining the degree of milling of whole milled rice. *Cereal Chem.* 38: 291 (1961).
8. BLACK, T. L., SPYRES, G. G., and BRAKKE, O. L. Effects of storage conditions on oil analysis of milled corn fractions by gas-liquid chromatography. *Cereal Chem.* 46: 63 (1969).
9. HUNTER, I. R., HOUSTON, D. F., and KESTER, E. B. Development of free fatty acids during storage of brown (husked) rice. *Cereal Chem.* 28: 232 (1951).
10. HOUSTON, D. F., HUNTER, I. R., and KESTER, E. B. Effect of steaming fresh paddy rice on the development of free fatty acids during storage of brown rice. *Cereal Chem.* 28: 394 (1951).
11. KARON, M. L., and ALTSCHUL, A. M. Comparison of respiration, free fatty acid formation and changes in the spectrum of the seed oil during storage of cotton seed. *Plant Phys.* 21: 550 (1946).
12. HOFFMANN, G. Vegetable oils. In: *Symposium on food: Lipids and their oxidation*, ed. by H.W. Schultz, pp. 215-229. AVI Pub. Co.: Westport, Conn. (1962).

[Received August 9, 1973. Accepted April 18, 1974]