Extraction and Refining of Edible Oil from Extrusion-Stabilized Rice Bran

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ABSTRACT

Rice bran oil extracted from extrusion-stabilized bran was processed to a high quality salad oil. Stabilization prevented free fatty acid formation in rice bran prior to solvent extraction of the oil and thus increased the yield of refined oil. The flake form of the stabilized bran allowed rapid solvent percolation and efficient lipid extraction. Degumming soon after extraction removed a larger proportion of the gums and waxes and resulted in a higher yield of refined oil than if this procedure was delayed. Alkali refining was found to be most efficient with a concentration of 16° Bé (2.77M) NaOH and 0.5% NaOH excess. Acid activated clay was effective in removing color from the refined oil, and the addition of charcoal did not improve bleaching ability. Stabilization temperatures, within the range studied, did not appear to affect the bleached oil color. Color was measured spectrophotometrically at 537 and 612 nm.

INTRODUCTION

Production of edible oil from rice bran is practiced extensively in Japan, where 100,000 metric tons (MT) are produced annually (1), but only to a limited extent in other countries where rice is a major crop. This potential oil source is essentially unutilized in less developed countries because the delay between rice milling and bran extraction allows a high level of free fatty acid (FFA) to develop in the oil, and thus edible oil extraction is uneconomic (2).

Browne (3) demonstrated that the rapid accumulation of FFA in rice bran after milling was due to enzymatic activity and suggested that heat inactivation would prevent this problem. Reddi et al. (4) extracted rice bran with hexane within a few hours after milling and found that a high quality salad oil could be produced with about 20% refining loss from previously degummed and dewaxed oil. Many improvements in rice bran oil extraction and refining technology have been made in recent years, particularly in Japan. Processing technology was reviewed by Takeshita (5) and recently updated (1).

There has been a continuing interest in developing an economically viable process to inactivate the lipases in rice bran and provide a source of high quality, edible oil. The status of rice bran stabilization systems was reviewed by Sayre et al. (6), and Enochian et al. (2) analyzed the operational and financial feasibility of using an extrusion cooker for rice bran stabilization. A process has now been developed which prevents FFA accumulation in rice bran after milling by permanently inactivating the native lipases (7). The microbial load is also reduced to very low levels, which precludes lipase activity from this source. A simple autogenous extrusion cooker was used to heat the bran to 130 C; it was then held at ~99 C for 3 min prior to cooling (8).

The present research was conducted to demonstrate that high quality edible oil can be produced from rice bran stabilized by the extrusion cooking method. Traditional extraction and alkali refining procedures were used on a laboratory scale.

MATERIALS AND METHODS

Stabilization

Rice bran was processed through an extrusion cooker within 10 min after milling. Raw bran moisture was adjusted to about 12% by adding water to the bran at the extruder inlet if necessary. Extrusion temperature was 130 C, and the extruded bran was held at ~99 C for 3 min before air cooling to ~40 C and packaging (8).

Experiments to determine optimum oil processing conditions were all conducted using bran stabilized by the above conditions. Two experiments were conducted to determine the effect of stabilization temperature and FFA content of crude oil on the yield of refined oil. In one experiment, rice bran samples were collected either unprocessed or after extrusion at various temperatures within the range of 60 to 140 C. These samples were then stored at room temperature (~23 C) for six weeks prior to extraction. A second experiment compared oil from raw and stabilized bran which was stored at 3 C and extracted within 24 hr after milling.

Extraction

Extraction was conducted on a laboratory scale with a Soxhlet extractor. Commercial hexane (BP 64-69 C) was used, and hexane temperature during extraction was ~60 C. The extracted oil was desolventized in a vacuum evaporator at 70 C. Gum was removed by adding water to the oil to a level of 1% w/w, mixing at 60 C and allowing the gum to settle overnight at room temperature (20-23 C) before removal by centrifugation at 20-26 C. Wax was then removed by chilling the oil at 2-3 C for 48 hr or longer and centrifuging at 3 C.

Refining

The clear oil was titrated with standard NaOH to the phenolphthalein endpoint by AOCS Official Method Ca 5a-40 (9) to determine the FFA content as oleic acid. Alkali refining was done according to AOCS Official Method Ca 9a-52 (9) with some modifications. For tests, rice bran oil (200 gm) was placed in a tall beaker and moved between water baths of the appropriate temperatures. NaOH solutions ranging from 12° Bé to 24° Bé (2.00M to 4.47M) were prepared. For each strength tested, the volume of solution added to the oil was sufficient to neutralize the FFA content and to provide excess NaOH from 0.25 to 0.75% (w/w, dry basis) of the oil. The alkali was added to the oil during rapid stirring without incorporating air, and stirring was continued for 20 min at 22 C. The beaker was transferred to a 65 C water bath and the emulsion agitated slowly for 15 min, then allowed to stand at 65 C for 30 min. Finally the oil was cooled in a 22 C water bath and centrifuged at 5 C for 10 min at 30K × G.

Bleaching

Refined rice bran oil was bleached using acid activated clay and activated charcoal, either separately or in combination. Three grades of acid activated clay were obtained from the Filtrol Corporation. According to the supplier, Grade 4 was designed specifically for edible oil processing and did not cause an increase in FFA during bleaching. Grade 105, which was recommended for hard-to-bleach oils with high chlorophyll contents, had a greater residual acidity and lower pH. Grade 105 FAC reportedly had bleaching qualities similar to Grade 105 but did not promote hydrolysis of the neutral oil during bleaching. Activated charcoal samples from four different sources were tested for bleaching ability.

Bleaching was accomplished by heating the oil under N_2 in an oil bath thermostat with vigorous stirring. When the rice bran oil reached the desired temperature within the range of 90-130 C, the bleaching agents were added, and stirring was continued for periods of 5 to 20 min. The bleached oil was cooled rapidly to room temperature, celite was added to a level of 2% w/w of the oil and the oil filtered through coarse and then fine sintered glass. The FFA content of the clear oil was determined.

Color Measurement

Oil color was measured using a double beam spectrophotometer with automatic wavelength scanning and recording capabilities. Cuvettes with a 1 cm light path were used, and absorbance from 350 to 750 nm was recorded after zeroing the instrument at 750 mm. Absorption was measured either on pure oil or on a 5% w/w solution of oil in CCl_4 using CCl_4 in the reference cell. The Lovibond color scale is commonly used in commercial practice to evaluate oil color and is used as part of Japanese Agricultural Standards for rice bran salad oil. Since Lovibond color measurements were not made in this study, a sample of commercial rice bran salad oil was obtained from Japan to use as a color reference.

RESULTS AND DISCUSSION

Rice bran oil, with low FFA content, can be extracted from extrusion stabilized bran which has been stored at ambient temperature for six weeks or more. Stabilized bran used in this study contained about 6% moisture and 20% hexane extractable lipids. The physical form of the rice bran was transformed from a fine powder to small flakes. Only 7 to 12% of these flakes passed a 25 mesh screen compared to 85% of raw bran (8). The extraction characteristics of these flakes were examined by El-Amin (10), who found that the flow rate of 58 C hexane through a 60 cm bed was 563 to 620 $l/m^2/min$. Reiners et al. (11) reported that a minimum percolation rate of 367 $l/m^2/min$ was required for a basket type extractor. The oil extraction rate was rapid; 96% of the oil was removed within 5 min, and after 1 hr extraction, the residual lipids were only 0.7% (dry basis). Pelleting of extrusion stabilized bran prior to extraction was not required.

After degumming and dewaxing, one lot of clear crude oil, which contained 2% FFA, was used for single observation tests of refining and bleaching conditions. Scans of crude or refined, unbleached rice bran oil produced absorption curves similar in shape to the one reported by Reddi et al. (4). Peaks or shoulders were noted at 414, 454, 482, 537, 561, 612 and 671 nm (Fig. 1, a). The absorption maxima at 612 and 671 nm are characteristic of chlorophyll A (4), and absorption at 525-550 nm is closely related to Lovibond red (12). Absorption at 537 and 612 nm were found to be good indications of relative oil color (Fig. 1, c) and were used in this study. Bleaching the oil eliminated all of the peaks and shoulders on the absorption curve and produced a smooth curve with little absorption above 500 nm (Fig. 1, b). The reference sample of rice bran salad oil from Japan had an absorbance of 0.033 at 537 nm and 0.010 at 612 nm.

The effect of NaOH concentration is shown in Table I. NaOH concentration for neutralization reached a broad optimum for oil recovery at about 16°Bé, but oil recovery decreased as the lye concentration increased to 20°Bé and above. Color intensity, as indicated by absorbance at 537 and 612 nm, was reduced from that in the crude oil, but the different lye concentrations did not appear to have a significant effect either on color or residual FFA level.

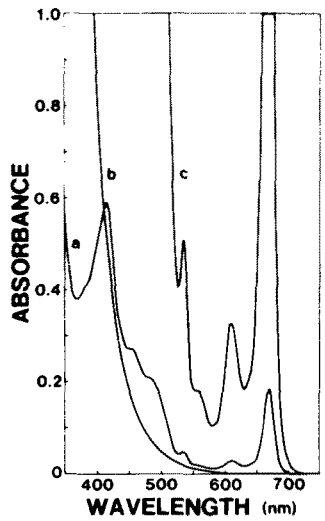

FIG. 1. Rice bran oil spectra. (a) Refined, unbleached oil, 5% w/w in CCl_4. (b) Refined, bleached, 100% oil. (c) Refined, unbleached, 100% oil.

TABLE I

Effect of NaOH Concentration on Refined Oil[a]

NaOH concentration		% Oil recovery	% FFA	Absorbance	
°Bé	M			537 nm	612 nm
0	0	–	2.01	0.775	0.520
12	2.00	91.1	0.10	0.415	0.270
14	2.38	91.7	0.10	0.416	0.269
16	2.77	91.9	0.08	0.417	0.266
18	3.17	91.4	0.07	0.394	0.253
20	3.59	90.6	0.06	0.407	0.262
22	4.02	89.7	0.10	0.394	0.254
24	4.47	84.3	0.11	0.388	0.248

[a]0.5% excess NaOH added.

TABLE II

Effect of Excess NaOH Level on Refined Oil[a]

% Excess NaOH	% Oil recovery	% FFA	Absorbance	
			537 nm	612 nm
0.25	90.2	0.11	0.436	0.283
0.40	90.3	0.08	0.421	0.272
0.50	91.9	0.08	0.417	0.266
0.60	91.3	0.07	0.400	0.259
0.75	91.0	0.08	0.396	0.258

[a]NaOH concentration 16°Bé (2.77M).

Based on these results, a concentration of 16°Bé (2.77M) NaOH was used in subsequent refining.

Excess lye, expressed as percent dry NaOH of oil weight and applied as a 2.77M solution, was tested against oil recovery, oil color and residual FFA content (Table II). An excess of 0.5% resulted in the highest yield of refined oil. Further increases in excess lye up to 0.75% did not appear to alter oil recovery. Residual percentage FFA in the refined oil was similar at all levels above 0.25% excess NaOH. Color of the oil tended to become lighter as the amount of excess alkali increased, but the changes were minor.

TABLE III

Effect of Acid Activated Clay Grade on Free Fatty Acid Formation and Oil Color[a]

Clay grade	% FFA	Absorbance 537 nm	Absorbance 612 nm
0 control	0.08	0.439	0.276
#4	0.13	0.118	0.064
#105	0.13	0.085	0.044
#105 FAC	0.11	0.056	0.024

[a]Activated charcoal present in all samples at 0.4%. Activated clay present in all samples at 4.0%. Bleaching temperature, 110 C; bleaching time, 15 min.

All of the activated clays used were effective in reducing oil color, but they also caused a small increase in FFA content of the oil (Table III). Grade #105 FAC was the most effective bleaching agent.

As bleaching temperature was increased from 90 to 130 C, the FFA content of the bleached oil increased slightly from 0.10 to 0.14%. Increasing the bleach time from 5 to 15 min at 120 C also resulted in FFA values within this range. Bleaching for 20 min at 120 C produced an elevation in FFA content to 0.22% of the bleached oil. Commercial standards for the FFA content of refined oil range from 0.05 to 0.15% (13). Oil color as indicated by absorbance at 537 and 612 nm decreased from 0.087 to 0.050 and 0.043 to 0.020, respectively, when bleaching temperature was increased from 90 to 100 C for 15 min. Further increases in temperature up to 130 C or bleaching times of 5 to 15 min at 120 C did not produce an additional reduction in color. When bleaching time was increased to 20 min at 120 C, absorption increased to 0.109 at 537 nm and 0.061 at 612 nm. This is consistent with reported optima of bleaching times and temperatures which are dependent on the kind of oil being bleached (14).

Four different lots and/or brands of activated charcoal were tested, and all were similar in their bleaching ability. In commercial practice, charcoal is added to bleaching clay at the rate of 5 to 10% (12). Various amounts and combinations of activated clay and charcoal were tested. Charcoal alone at 0.4% was not as effective in color reduction as 2% acid activated clay. The addition of charcoal did not appear to improve decolorization by the activated clay at any of the combinations tested. As bleaching clay was increased from 2 to 8% of the oil, absorbance at 537 and 612 nm decreased from 0.054 to 0.026 and from 0.020 to 0.008, respectively. Addition of 6% clay produced a very light colored oil with a slightly golden cast, which was similar in color to a sample of commercial Japanese rice bran oil. The amount of bleaching clay to use must be balanced between the desired degree of bleaching and economic considerations. Both the cost of the bleaching clay and the value of the oil absorbed by the spent clay must be taken into account.

TABLE IV

Absorbance of Refined and Bleached Oil Extracted from Rice Bran Processed at Various Temperatures

Processing temperature	Refined oil[a] 537 nm	Refined oil[a] 612 nm
Raw[1] [b]	.102	.037
Raw	.452	.264
60	.251	.136
80	.716	.488
100	.547	.387
120	.272	.167
130	.424	.283
130[2]	.338	.213
130[3]	.508	.330
140	.138	.079
	Bleached oil[c]	
Raw[1]	.021	.001
130[2]	.015	.000
130[3]	.021	.002

[a]NaOH concentration 16° Bé (2.77M), 0.5% excess NaOH added.
[b]Numbers indicate the source of the bleached oil.
[c]Filtrol 105 FAC, 4% of oil weight, 110 C, 15 min.

Absorption at 537 and 612 nm was measured on several lots of refined oil which had been extracted from either raw bran or bran extrusion cooked at various temperatures (Table IV). The color as indicated by the absorption values was quite variable and did not show a relationship to processing temperature. After bleaching, the absorption values were very low at both wavelengths and did not appear to be associated with the color of the source refined

TABLE V

Effect of Stabilization Temperature on Rice Bran Composition and on Oil Recovery after Various Processing Steps

Extrusion temperature, °C	Experiment A[a] R[c]	60	80	100	120	130	140	Experiment B[b] R	130
% Moisture in bran	10.6	8.9	7.7	7.3	6.3	5.7	4.8	11.3	6.3
% Oil in bran (dry basis)	20.1	21.4	21.4	21.0	20.7	19.3	20.6	19.7	20.0
% Lipase activity[d]	100.0	74.8	39.4	24.2	6.1	2.9	1.2	—	—
% FFA in extracted oil	33.5	24.2	11.2	5.4	3.1	2.6	2.3	3.0	1.7
% Oil recovery, degummed	92.1	91.5	91.7	92.4	90.2	88.2	89.5	84.4	82.8
% Oil recovery, dewaxed	58.6	75.0	76.1	81.4	80.5	78.8	80.3	79.9	77.2
% Oil recovery, refined (neutralized + washed)	9.2	32.2	47.1	60.0	63.1	62.1	61.9	65.3	66.1
% Refined oil recovery from degummed, dewaxed oil	15.7	42.9	61.9	73.7	78.4	78.8	77.1	81.7	85.6

[a]Rice bran was extruded without added water at the temperature indicated and held 3 min at the lower of either the extrusion temperature or 99 C prior to air cooling. All samples were held six weeks at room temperature (~23 C) prior to oil extraction with hexane at ~60 C.
[b]Stabilization conditions were the same as in Exp. A, but bran was stored at 3 C and was extracted within 24 hr after milling.
[c]Raw rice bran, no heat treatment.
[d]Based on FFA increase in oil extracted from bran adjusted to 11% moisture and stored 96 hr at 32 C.

TABLE VI

Percentage Loss of Extracted Lipid at Various Steps of Processing

Processing step	Oil loss as % of original extracted lipid	
	Experiment A[a]	Experiment B[b]
Degumming step	11	17
Dewaxing step	9	6
Neutralization & washing step	18	11
Total refining loss	38	34

[a]Stabilization and extraction conditions are described in Table V, footnote a. Data are means for samples extruded at 120, 130 and 140 C.

[b]Conditions are presented in Table V, footnote b. Data are from bran extruded at 130 C only.

oil. This indicates that, within the range studied, the temperature reached in stabilizing the bran did not affect the bleached oil color.

The influence of the degree of stabilization and the FFA content of extracted oil upon oil yield, at various steps in oil processing, are presented in Table V. In Experiment A, raw rice bran is compared with bran extruded at various temperatures. Moisture content of the extruded bran decreased as temperature increased, but the quantity of extractable lipid was not significantly affected. Each successively higher extrusion temperature reduced the lipase activity of the processed bran. This has been confirmed elsewhere using a sensitive fluorometric lipase assay (7). A definite transition in bran stability took place at extrusion temperatures of 120 C and above. Although the residual lipase activity was still 6% at 120 C, bran stored six weeks at ~23 C yielded oil with only 3% FFA content compared to slightly over 2% for bran processed at 140 C. At extrusion temperatures below 120 C, both lipase activity and FFA content of the extracted oil increased markedly with each decrease in extrusion temperature.

Extracted oil was stored six days at 3 C before gums were removed as previously described. Following centrifugation, oil recovery averaged about 90%. The precipitated gum was bulky, and no attempt was made to recover occluded oil. After crystallization and separation of wax, oil recovery increased as the bran extrusion temperature increased up to 100 C.

The clear, dewaxed crude oil was neutralized by adding the appropriate quantity of 16°Bé NaOH with an excess equivalent to dry NaOH at 0.5% of the oil weight. Only 9% of the original extracted lipid was obtained from oil containing 33.5% FFA. In oils containing 2-3% FFA, the final recovery was 62-63%. This recovery appears to be quite low, but it must be realized that the processing was carried out on a laboratory scale using small volumes. Consequently, the proportion of transfer loss is relatively high. Also, no attempt was made to recover residual oil from the gum, wax or soap stock. While these recovery figures are useful for comparing samples treated in a similar manner, they should not be considered predictive of absolute values which would likely be attained under industrial conditions.

Experiment B illustrates that oil extracted from raw bran at low FFA levels performs in a similar manner to oil from extrusion stabilized bran. In this experiment, the oil was processed immediately after extraction and was not chilled or stored prior to degumming. A greater loss after the degumming step, compared to Exp. A (Table VI), indicates that greater proportions of the gum and wax were removed. The oil was then chilled at 3 C for 48 hr prior to wax removal. Following the neutralization step, a four percentage point decrease in total loss was noted for Exp. B compared to oils with similar FFA content in Exp. A. This finding is consistent with the observation by Takeshita (5) that gums should be removed immediately after oil extraction. Removal of these gums allows a cleaner break of soap stock and reduced loss in the neutralization step.

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