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⁂Effect of Caustic Refining, Solvent Refining and Steam Refining on the Deacidification and Color of Rice Bran Oil

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ABSTRACT

Degummed rice bran oil was deacidified by caustic, solvent and steam refining processes. The steam refining process was optimized through a series of experiments with varying refining times (1-5 hr), temperatures (220-280 C) and amounts of steam (4-20%), at a pressure of 4 mmHg. The most significant factors affecting the degree of deacidification were the refining temperature and amount of steam. The correlation coefficient between quadratic equation obtained and experimental results was 0.96. Acid value and color of steam refined oil were not as good as those of caustic refined oil, but steam refining showed better retention of natural antioxidants than caustic or solvent refining. Steam refining is preferred for deacidification of rice bran oil because of reduced neutral oil loss and elimination of soap production.

The important criteria in selecting a deacidification process are known to be the degree of deacidification, neutral oil loss, effect on bleaching and production of soapstock (2,8-10). In comparing caustic refining, solvent refining and steam refining, caustic refining of degummed rice bran oil resulted in satisfactory acid values and color but showed the worst result in neutral oil loss and produced large amounts of soapstock. Solvent refining was not shown to be efficient because of poor deacidification, high losses of neutral oil and darkening of color. Steam refining also was less effective than caustic refining in deacidification and bleaching. However, the degree of deacidification could be improved by development of a process to remove all the free fatty acids (8), and the color problem could be eliminated by including a preliminary bleaching step before steam distillation (10). The application of steam refining to rice bran oil will result in many advantages such as reduced neutral oil loss, no production of soap, and the production of high purity, industrial fatty acids.

INTRODUCTION

Rice bran oil has been difficult to refine because of its high content of free fatty acid, unsaponifiable materials and color (1,2). Rice bran oil has been deacidified in industry by caustic refining, but this process gives considerably greater losses of neutral oils than caustic refining of many other vegetable oils with similar free fatty acid content (3,4). The solvent extraction method (2) and progressive acetylation of hydroxylated compounds in the oil (5) also have been used to reduce the refining loss of neutral oil of rice bran oil in the deacidification process. In liquid-liquid extraction refining, furfural-naphtha (6), liquid propane (7) or alcohols (2) have been used as the fractionating solvent. Alcohol extraction in combination with alkali refining has been used to give satisfactory deacidification, reduction of refining loss and color removal.

In recent years, steam refining of crude oils with high free fatty acids has been used to avoid both excess losses of neutral oil and production of large quantities of soapstock which require expensive waste-water treatment before discharge (8,9). Furthermore, steam refining gives savings on equipment, space, time and labor in comparison to caustic refining; it also yields high quality fatty acids (9). However, with dark-colored oils having a high free fatty acid content, the steam refining process is not as successful as caustic refining in achieving a low free fatty acid refined oil which gives satisfactory oil-color during the subsequent bleaching step. However, the bleaching problem of dark crude oils has been solved by inserting the bleaching process prior to steam refining (10,11).

At present, steam refining is used mostly in the palm oil industry. It also has been applied successfully to soybean oil, coconut oil, palm kernel oil, peanut oil, sesame oil and olive oil, tallow and lard (8,9). Optimization studies of steam refining concerning time, temperature and the amount of steam for any fats and oils are very scarce (8), and information about steam refining of rice bran oil is not found anywhere. In this study, rice bran oil was deacidified by steam refining, conventional caustic refining and solvent extraction method in order to compare the neutral oil loss and characteristics of the oil after each deacidification process. In the steam refining process, the independent variables were analyzed statistically in order to identify the factors affecting free fatty acid content and color. The residual contents of tocopherol and oryzanol also were measured to observe the effects of the deacidification processes upon the removal of natural antioxidants of neutralized oil.

MATERIALS AND METHODS

Materials

Crude rice bran oil was obtained from a local refinery and was laboratory degummed with 4% oxalic acid at a level of

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20 ml/Kg crude oil. The phosphorus content, acid value and peroxide value of degummed oil were 10.3, 26.5 and 7.1 ppm, respectively. Color of degummed oil was 12.2 red, 35.2 yellow and 6.4 blue, by Lovibond Tintometer with 1-inch cell. All solvents and reagents used were of analytical grade unless otherwise specified.

Caustic and Solvent Refining

The degummed rice bran oil was caustic refined with 0.5% excess NaOH solution at 70 C for 15 min. The oil and soap were separated by centrifugation, and oil was further washed with hot water.

In solvent refining, the oil and solvent (methanol, ethanol and 94.7% isopropanol) were mixed and shaken for 1 min and then allowed to separate into two phases. Solvents in oil phase were removed by vacuum evaporation. The colors of methanol-refined oils were measured (Table I).

Steam Refining

The apparatus used for steam refining is a modification of Sullivan's laboratory set-up as shown in Figure 1 (8). The working volume of the deacidification jar was 1-1.5 l. Steam distillation was conducted according to Sullivan (8). Pressure of the system was maintained at 4 mmHg, and time, temperature and amount of steam were controlled as needed (Table II).

TABLE I

Colors of Oils Refined by Methanol Extraction

Solvent (ml)/oil (g) ratio	Lovibond color (1-inch cell)		
	Red	Yellow	Blue
0.5	11.1	40.8	8.1
1.0	12.1	40.3	8.5
1.5	12.3	44.3	8.7
2.0	12.3	46.3	8.7
2.5	13.0	49.6	8.7
3.0	13.0	49.5	8.7
5.0	13.0	41.5	8.9
8.0	13.0	45.7	9.8
12.0	14.0	46.9	10.0

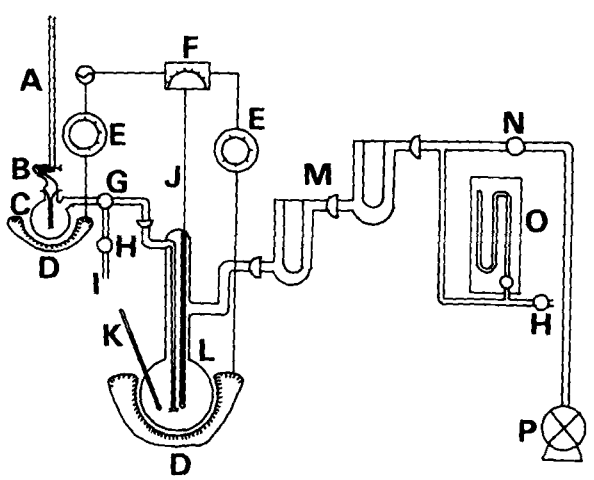

FIG. 1. Steam refining apparatus. A, burette; B, needle valve; C, steam generator; D, heating mantle; E, transformer; F, temperature controller; G, three-way vacuum cock; H, needle valve, bronze; I, nitrogen gas; J, thermocouple; K, thermometer; L, deacidifying jar; M, trap; N, two-way vacuum cock; O, U-manometer, and P, vacuum pump.

Analytical Methods

Acid value and peroxide value were measured by AOCS methods (12,13). Oil color was measured in a Lovibond Tintometer (Model E) with a 1-inch cell. Tocopherol content was measured as α-tocopherol by a modified Emmerie-Engel method (14), and oryzanol content was estimated by absorbancy at 315 nm (15).

Statistical Methods

Acid values from different steam refining conditions were correlated with three variables according to regression equation as follows (16):

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3$$

where Y = 1 n (AV of refined oil/AV of degummed oil)
X_1 = (time-3)/2 × 1.682
X_2 = (temperature-250)/30 × 1.682
X_3 = (amount of steam-12)/8 × 1.682 and
b_i, b_{ii}, b_{ij} = regression coefficients
Statistical significance of coefficients was determined by t-test.

RESULTS AND DISCUSSION

Caustic and Solvent Refinings

The acid value of rice bran oil deacidified by caustic refining was 0.36, and the peroxide value was 21.2. The color of caustic refined oil was 7.1 red, 43.1 yellow and 3.4 blue. The color of caustic refined oil was better than that of degummed oil.

Acid values and the neutral oil losses by solvent extraction methods are given in Figure 2. Generally speaking, acid values decreased and neutral oil losses increased with increasing solvent ratio. There was little difference among the three solvents in their ability to deacidify the oil. With a solvent/oil volume ratio of 12, acid values lay between 3.0 and 4.2. On the other hand, solvent type resulted in large differences in neutral oil losses (Fig. 2). With ethanol and isopropanol, neutral oil losses were as high as 85% compared to only 15% with methanol. Methanol was the obvious best choice for a refining solvent among the solvents tested.

Colors of methanol-refined oil were measured at certain ratios (Table II). As the ratio of solvent to oil increased, the oil became darker. This was considered to be due to concentration of coloring materials in the oil portion, while uncolored oil and fatty acids were removed in the solvent portion.

Steam Refining

The independent variables studied for steam refining were time, temperature and amount of steam. The pressure of the system was maintained at 4 mmHg while the other three variables were controlled at five different levels (Table II).

TABLE II

Levels of Independent Variables Used in Steam Refining

Levels	Time (hr)	Temperature (C)	Amount of steam (%)
	X_1	X_2	X_3
-1.682	1	220	4.0
-1	1.82	232	7.2
0	3	250	12.0
1	4.18	268	16.8
1.682	5	280	20.0

Acid values and color of oils are given in Table III. Regression coefficients (Table IV) were calculated and their significance was checked by a t-test. Finally, analysis of variance (ANOVA) of the equation is tabulated in Table V. From the results of Table IV, the regression coefficient (b_1) of variable time (X_1) was -0.1358 and was not significant at the 0.05 level. However, the regression coefficients of temperature (X_2) and amount of steam (X_3) had probabilities less than 0.001 and had statistically significant effects on the process. Regression coefficients of combined variables had higher probabilities and did not significantly affect the steam refining. The correlation coefficient between the predicted values and experimental values (Table III) was 0.96, which is considered excellent. It can be concluded that in steam refining, temperature and amount of steam are highly significant variables, while time is of little significance in the degree of deacidification.

The color of oil was changed considerably during steam refining. The red color increased as the time and temperature increased and as the amount of steam decreased (Table III). Possibly red pigments were developed by heat and decomposed by steam. On the other hand, blue color increased drastically during steam refining. Blue color developed more when the amount of steam was added at given times and temperatures. The amount of steam, therefore, seemed to be mostly related to blue color development among variables tested.

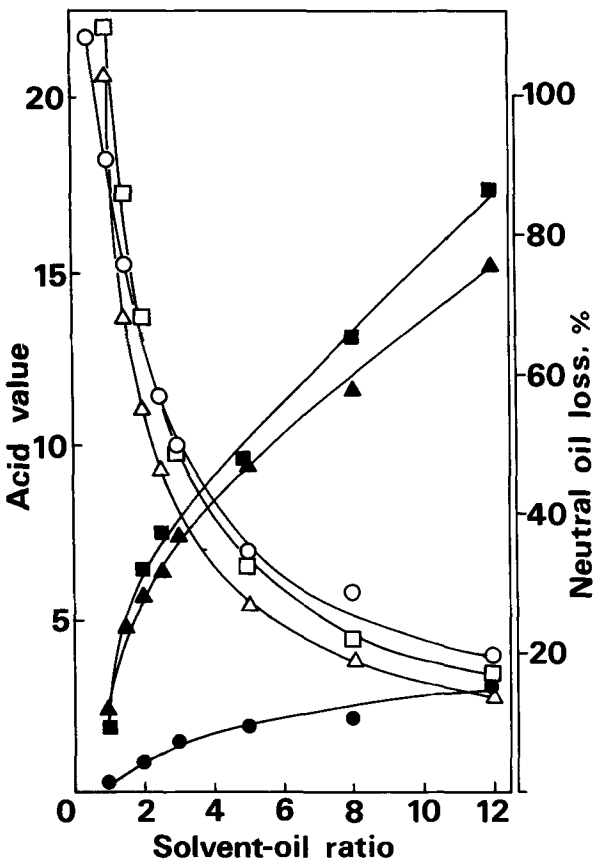

FIG. 2. Refining of rice bran oil by methanol, ethanol and isopropanol. Open symbols are for acid value. Closed symbols are for neutral oil loss. ○, Methanol; △, ethanol, and □, isopropanol.

TABLE III

Acid Value and Colors of Rice Bran Oil Steam Refined under Various Conditions

Batch No.	Time (hr)	Temperature (C)	Amt. of steam (%)	Acid value	Lovibond color		
					Red	Yellow	Blue
1	1	250	12	2.57	8.0	62.0	27.3
2	1.82	232	7.2	6.95	13.7	41.0	18.9
3	1.82	232	16.8	3.19	6.4	65.1	29.6
4	1.82	268	7.2	1.38	14.1	36.1	19.9
5	1.82	268	16.8	1.41	9.9	23.4	22.7
6	3	220	12	6.41	13.2	36.5	20.1
7	3	250	4	5.21	20.3	42.1	12.1
8	3	250	12	2.18	13.4	41.1	19.8
9	3	250	12	1.45	11.5	43.2	22.1
10	3	250	12	1.49	11.0	43.2	21.2
11	3	250	12	1.50	11.2	43.1	20.8
12	3	250	12	1.61	13.6	45.1	18.6
13	3	250	12	1.33	13.1	38.1	20.7
14	3	250	20	1.11	9.7	45.1	23.5
15	3	280	12	0.87	16.8	35.1	18.2
16	4.18	232	7.2	8.98	18.1	31.1	13.1
17	4.18	232	16.8	2.08	8.1	69.9	26.0
18	4.18	268	7.2	1.17	17.6	41.1	15.2
19	4.18	268	16.8	1.01	18.1	21.1	17.8
20	5	250	12	1.27	12.4	41.1	20.8

Tocopherol and Oryzanol Contents after Refining

Characteristic natural antioxidants in rice bran oil such as tocopherols and oryzanol impart longer storage stability considering the oil's high degree of unsaturation. The levels of antioxidants were measured after refining, and the results are given in Table VI. Caustic refining significantly reduced the contents of both tocopherols and oryzanol, but 97.7% of tocopherols and 91.7% of oryzanol were retained after steam refining. In solvent refining oryzanol was mostly retained but tocopherol was diminished considerably.

TABLE IV

t-Test of Regression Coefficients

Regression coefficient		t-Value	Probability
b_0	-2.7023	—	—
b_1	-0.1358	3.2028	< 0.05
b_2	-0.6259	14.7588	< 0.001
b_3	-0.3637	8.5758	< 0.001
b_{11}	-0.0624	1.5116	< 0.2
b_{22}	0.1572	3.8069	< 0.02
b_{33}	0.1633	3.9442	< 0.02
b_{12}	-0.0411	0.7423	> 0.02
b_{23}	0.2646	4.7759	< 0.01
b_{13}	-0.1064	1.9199	< 0.2

TABLE V

Analysis of Variance (ANOVA) of Equation in Steam Refining

	Sum of squares	Degree of freedom	Mean squares	F-value
First order term	7.40883	3	2.46961	83.8008[a]
Second order term	1.34909	6	0.22485	7.6298[b]
Lack of fit	0.19975	5	0.03995	1.3556
Experimental error	0.14737	5	0.02947	
Total	9.10504	19		

[a]$P < 0.005$.
[b]$P < 0.025$.

TABLE VI

Natural Antioxidant Contents of Refined Oils

	Tocopherol (%)	Oryzanol (%)
Degummed oil	0.761	1.670
Caustic refined oil	0.537	0.977
Solvent refined oil	0.601	1.553
Steam refined oil	0.744	1.532

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⁂Determination of Peroxide Value by Conventional Difference and Difference-Derivative Spectrophotometry

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ABSTRACT

The spectrophotometric behavior of the system iodide-iodine-iodate-oxygen was studied, and a simple iodometric method to determine peroxide value by conventional, difference or difference-derivative spectrophotometry was developed. The procedures are carried out inside standard photometric cells containing iodide solution to which the sample is added. Absorbance or its first derivative with respect to wavelength is measured to determine iodine concentration by means of calibration curves. No special care to avoid iodide oxidation by atmospheric oxygen is necessary.

The method is applicable even to lipids that give emulsions with water, such as phosphatides, and precise results are obtained even at low peroxide values.

The use of a digital spectrophotometer with data processing and programming facilities allowed development of an interactive program for automatic operation, which is outlined.

INTRODUCTION

The autoxidation of lipids is a major cause of their deterioration and hydroperoxides formed by reaction between oxygen and the unsaturated fatty acid moieties are the primary products of this process. The peroxide concentration, usually expressed as peroxide value, gives therefore a measure of the early steps of lipid oxidation (1). The peroxide value (PV) is the concentration of substances, in terms of milli-equivalents of peroxide per 1000 g of sample, that oxidize potassium iodide to iodine.

The numerous methods described in the literature to determine PV were reviewed by Gray (2) together with other procedures to evaluate lipid oxidation.

Iodometric Determination of PV

The most widely used methods to determine PV are those based on the volumetric measurements of the iodine produced from potassium iodide by peroxide at room temperature in acetic acid-chloroform medium (3). According to Mehlenbacher (4), one of the principal sources of error in these methods is the oxidation of iodide by atmospheric oxygen, leading to high results (5,6). Besides variations in the reaction conditions such as temperature and time, it also has been established that other possible sources of error in the titrimetric methods include variation in the weight of sample, the type and grade of solvents used and the nature of the sample (2).

The iodometric AOCS Official Method Cd 8-53 (7), as it states itself, is highly empirical; any variation in procedure may result in variation in results. Besides, it fails for very low PV because of difficulties in the titration end point determination. Furthermore, it is inadequate for samples like phosphatides which give emulsions by shaking, also causing trouble with the end point observation.

Very low PV can be determined by a modification (8) of the titrimetric methods that involves the replacement of the titration step with an electrochemical technique in which the iodine liberated is reduced at a platine electrode maintained at a constant potential, while purified nitrogen is passed for deaeration.

Some colorimetric versions of the iodometric methods have been reported (9-13) in which the liberated iodine is measured either directly by means of the absorbance of the triiodide ion in the UV, or by measurement of the blue color of the starch-iodine complex. It has been suggested (12) that a main factor which has heretofore prevented the wide use of colorimetric methods is the deviation of the absorbance data due to air oxidation of the excess iodide. To avoid this deviation the reaction mixture must be protected from light, and deaeration of solutions by purging with carbon dioxide and exclusion of atmospheric oxygen with the same or other inert gas are necessary. Furthermore, in the procedures of Swoboda and Lea (11) and of Takagi et al. (12), the excess iodide is converted into the more stable cadmium-iodide complex ion. The use of colorimetric cells especially constructed to avoid autoxidation of iodide was proposed (14,15), but they are troublesome and not readily available (12).

The measurement of iodine concentration in the volumetric methods is carried out in an aqueous phase in the presence of an immiscible organic solvent in which the