Physical Refining of Rice Bran Oil in Relation to Degumming and Dewaxing

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ABSTRACT: Physical refining of rice bran oil (RBO) with acidity between 4.0 and 12.4% has been investigated in relation to degumming and dewaxing pretreatments. It appears that physical refining after combined low-temperature (10°C) degumming-dewaxing produces good-quality RBO with respect to color, free fatty acid, oryzanol, and tocopherol content.
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KEY WORDS: Degumming, dewaxing, physical refining, rice bran oil.

Rice bran oil (RBO) of edible grade contains 2.0–20.0% free fatty acids (FFA), depending on the quality of bran. It is difficult to refine RBO because of its high FFA, unsaponifiable matter (UM), and color.

Among the various approaches for refining high- as well as low-FFA RBO, the most widely used steps are degumming, dewaxing, neutralization of FFA, bleaching, and deodorization. However, the major problems of chemical refining are production of large quantities of soap stock, high refining losses, and environmental pollution (1).

Bhattacharyya *et al.* (2) proposed a process for obtaining edible-quality oil from high-FFA RBO by a combination of miscella dewaxing and miscella refining. Deacidification of high-FFA RBO (15–30%) by re-esterification with glycerol and alkali neutralization also has been proposed (3,4). This combined process, followed by bleaching and deodorization, yields good-quality oil.

Biorefining, i.e., removal of FFA by esterification with added glycerol and specific lipases, is a newer approach. Bhattacharyya *et al.* (5) have successfully developed a process to bring down the FFA from 30 to 3.6% for RBO, and subsequent alkali refining, bleaching, and deodorization produced excellent-quality RBO. The main barrier of this process is the cost of the enzyme.

There has been growing interest in physical refining of RBO. The process is attractive because of its simplicity, lack of environmental impact, low oil losses, and good-quality product (6). Physical refining removes the FFA, thereby eliminating soap stock and reducing neutral oil losses to minimal levels. Prabhakar *et al.* (7) have reported that the higher refining loss of RBO and darkening of color is due to the existence of wax, oryzanol, and phosphatides. Practical experience has shown that acceptable results may be obtained during physical refining if good-quality raw material is used. Incomplete removal of undesirable components during pretreatments also affects the quality of the final product.

The removal of lipid and nonlipid components during degumming, dewaxing, and bleaching is therefore of prime importance. This investigation has focused on the removal of gummy materials and waxes under various conditions prior to physical refining, so that the quality of RBO as a final product is not impaired.

MATERIALS AND METHODS

Crude RBO of varying acidity were supplied by local oil mills.

FFA, peroxide value (PV) and UM in crude and refined oils were determined according to standard AOCS methods (8). Color of the crude and refined oils was determined with a Lovibond Tintometer (8).

Total gum and wax content was estimated as the percentage acetone-insoluble matter in the oil. The determination involved the crystallization of gum and wax from an accurately weighed quantity of oil in a conical flask, held at 4°C in a bath for 4 h after addition of five times the volume of acetone. After this period, the insoluble mass was filtered and washed with cold (4°C) acetone. The solvent was removed from the filter paper (at room temperature, 32°C) by applying vacuum (30 mm Hg pressure) in a vacuum desiccator. The residue was weighed and expressed as percentage total gum and wax.

Oryzanol content was determined by measuring the optical density of the oil in hexane (b.p. 65–70°C) solution at 315 nm and using the specific extinction coefficient for oryzanol (9).

Total tocopherol content was measured with an ethanolic solution of α, α′-bipyridyl reagent by following a spectrophotometric method (10). The spectral reading was taken at 520 nm, and a standard curve was prepared previously from pure tocopherol.

Degumming. Crude RBO (100 g) was weighed in a beaker (250 mL), and 5% (w/w) water or 0.2% phosphoric acid as

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10% solution in water was added, after heating to 65°C with constant stirring. Stirring was continued for 1 h. The oil was then centrifuged at 10,000 rpm for 15 min, and the clear upper layer was decanted. After phosphoric acid degumming, the acid was neutralized by CaO and centrifuged. Finally the oil was washed free of inorganic acid with hot water.

Dewaxing. Degummed RBO was weighed into a tared beaker, and 5% (w/w) water was added with stirring after cooling the oil to the desired temperature. Stirring was continued for 1 h at the desired temperature. The oil was then centrifuged at 10,000 rpm for 15 min at the same temperature. The oil was decanted and dried under vacuum (30 mm Hg pressure, 90°C temperature).

Bleaching. The oil was bleached at 95°C, under vacuum (30 mm Hg pressure) with constant stirring for 20 min using 2% Tonsil, Supreme 131 (P.T. Süd-Chemie, Jakarta, Indonesia), earth optimum and 0.5% activated carbon (E. Merck, Darmstadt, Germany) (both on oil weight). The oil was then filtered under suction.

Caustic refining. The quantity of NaOH required was calculated and 10% excess NaOH over that required to neutralize the FFA was used. A 20° Baume (nearly 15% w/w) solution of NaOH (in water) was prepared with this NaOH. The oil was heated to 65–70°C (with constant stirring) and the NaOH solution was then added dropwise. After stirring for 20 min the oil was centrifuged at 12,000 rpm for 15 min. Finally the oil was washed with hot water to remove the soap completely and dried under vacuum (30 mm Hg pressure) at 90°C.

Combined degumming-dewaxing. Crude RBO (100 g) was placed in a beaker (250 mL) and 5% water (w/w) added with constant stirring. The temperature was brought to desired temperature (10, 17, 25, or 32°C) and kept for 1 h with stirring. The whole mass was then centrifuged to get the degummed-dewaxed oil and dried under vacuum as in the case of caustic refining.

Deodorization/physical refining. The deodorization process used was the conventional one. It was carried out by purging saturated steam at 185 ± 2°C under 5 mm Hg pressure. Physical refining was also carried out by purging saturated steam at 235 ± 5 to 265 ± 5°C under 5 mm Hg pressure.

The quality of the deodorized or physically refined oil was assessed through the measurement of color, FFA, PV, UM, total gum and wax, oryzanol, and tocopherol content.

RESULTS AND DISCUSSION

The physical and chemical characteristics of crude RBO samples are shown in Table 1.

In Table 2 the characteristics of combined water degummed-dewaxed (using 5% water), bleached, and physically refined RBO are shown.The results indicate that color, FFA, total gum and wax, oryzanol, and tocopherol content of the physically refined RBO are quite good for low-temperature (10°C) processing and acceptable at the moderately low-temperature (17°C) process. For combined degumming-dewaxing at room temperature (32°C) and slightly below room temperature (25°C), the quality of physically refined RBO is not acceptable, especially for the darker-colored and higher FFA crude oils.

TABLE 1
Physical and Chemical Characteristics of Crude Rice Bran Oil (RBO)

Characteristics	Crude RBO samples		
	Sample I	Sample II	Sample III
Color (Lovibond, 1″ cell)	30Y + 5R	30Y + 5.7R	40Y + 6R + 1.5B
Free fatty acid (FFA; % w/w)	4.0	9.5	12.4
Peroxide value (meq/kg)	16.0	18.4	19.32
Unsaponifiable matter (% w/w)	4.8	4.35	4.3
Gum and wax (% w/w)	3.8	3.71	3.76
Oryzanol (% w/w)	2.01	1.93	1.95
Tocopherol (% w/w)	0.15	0.14	0.11

TABLE 2
Characteristics of Physically Refined RBO After Combined Water Degumming-Dewaxing (at 10–32°C) and Bleaching[a]

Characteristics of physically refined RBO	Sample I (4.0% FFA)				Sample II (9.5% FFA)				Sample III (12.4% FFA)
	10°C	17°C	25°C	32°C	10°C	17°C	25°C	32°C	10°C
Color[b] (Lovibond, 1″ cell)	(10 ± 0.3)Y (1.0 ± 0.1)R	(8.0 ± 0.2)Y (1.0 ± 0.1)R	(20 ± 0.4)Y (2.2 ± 0.3)R	(20 ± 1.3)Y (1.5 ± 0.3)R	(15 ± 1.0)Y (2.0 ± 0.4)R	(16 ± 0.7)Y (2.2 ± 0.3)R	(20 ± 0.6)Y (2.8 ± 0.2)R	(20.3 ± 1.0)Y (3.0 ± 0.8)R	(16 ± 0.8)Y (3 ± 0.4)R
FFA[b] (% w/w)	0.2 ± 0.03	0.16 ± 0.04	0.18 ± 0.02	0.24 ± 0.02	0.18 ± 0.06	0.13 ± 0.05	0.21 ± 0.02	0.19 ± 0.03	0.24 ± 0.02
PV[c] (meq/kg)	0.94	1.08	1.30	1.85	1.23	2.20	1.89	1.34	1.03
UM[b](% w/w)	3.06 ± 0.20	3.30 ± 0.20	3.12 ± 0.30	3.42 ± 0.18	3.44 ± 0.20	3.34 ± 0.23	3.51 ± 0.09	3.41 ± 0.21	3.30 ± 0.20
Gum and wax[b] (% w/w)	0.48 ± 0.12	0.90 ± 0.09	1.60 ± 0.14	1.62 ± 0.03	0.57 ± 0.08	0.69 ± 0.03	0.98 ± 0.10	1.30 ± 0.20	0.53 ± 0.06
Oryzanol[c] (% w/w)	1.87	1.80	1.93	2.09	1.93	1.84	1.96	1.89	2.01
Tocopherol[c] (% w/w)	0.051	0.050	0.042	0.038	0.037	0.040	0.029	0.032	0.028

[a]Physical refining done at 245 ± 2°C at 5 mm Hg presssure.
[b]Results are expressed as mean ± standard error.
[c]Results are expressed as arithmetic mean of three results. PV, peroxide value; UM, unsaponifiable matter. See Table 1 for other abbreviations.

TABLE 3
Effect of High-Temperature (65–70°C) Degumming and Low-Temperature (10–25°C) Dewaxing on Bleached/Physically Refined RBO Characteristics[a]

Characteristics of physically refined RBO	Type of degumming[c]	Sample I (water- or H_3PO_4-degummed) at different dewaxing temperature			Sample II (water-degummed) at different dewaxing temperature		
		10°C	17°C	25°C	10°C	17°C	25°C
Color[b] (Lovibond, 1″ cell)	*	(10 ± 0.4)Y (1.0 ± 0.2)R	(9.0 ± 0.2)Y (1.2 ± 0.1)R	(20 ± 0.4)Y (2.3 ± 0.5)R	(16 ± 1.0)Y (1.5 ± 0.3)R	(17 ± 0.6)Y (2.2 ± 0.4)R	(20.3 ± 0.6)Y (2.7 ± 0.3)R
	**	(12 ± 2)Y (1.2 ± 0.5)R	(15 ± 1.0)Y (1.2 ± 0.8)R	(15 ± 1.2)Y (1.3 ± 0.2)R	— —	— —	— —
FFA[b] (% w/w)	*	0.12 ± 0.02	0.18 ± 0.03	0.21 ± 0.03	0.20 ± 0.02	0.18 ± 0.03	0.19 ± 0.03
	**	0.13 ± 0.06	0.19 ± 0.02	0.18 ± 0.04	—	—	—
PV[d] (meg/kg)	*	0.84	1.93	1.03	0.92	2.01	0.82
	**	2.01	1.02	1.06	—	—	—
UM[b] (% w/w)	*	3.20 ± 0.30	3.00 ± 0.40	3.49 ± 0.30	3.06 ± 0.30	2.98 ± 0.40	3.29 ± 0.10
	**	3.10 ± 0.40	2.90 ± 0.20	3.20 ± 0.20	—	—	—
Gum and wax[b] (% w/w)	*	0.60 ± 0.20	0.71 ± 0.16	0.93 ± 0.27	1.00 ± 0.23	0.69 ± 0.32	0.82 ± 0.18
	**	0.71 ± 0.21	0.93 ± 0.20	0.80 ± 0.10	—	—	—
Oryzanol[d] (% w/w)	*	2.03	1.98	2.00	1.83	1.93	1.89
	**	1.99	1.93	2.01	—	—	—
Tocopherol[d] (% w/w)	*	0.041	0.045	0.033	0.029	0.023	0.026
	**	0.021	0.030	0.027	—	—	—

[a]Degumming done using 5% water or 0.2% H_3PO_4 on weight of oil, at 65–70°C.
[b]Results have been expressed as mean ± standard error.
[c]*Results are of water-degumming followed by water-dewaxing and **results are of H_3PO_4 degumming water dewaxing process. See Tables 1 and 2 for abbreviations.
[d]Results have been expressed as arithmetic mean of three results.

As expected and reported (11), the color of physically refined oil became darker under the same pretreatment steps, if the oil being processed was of high acidity (as depicted in Table 2).

In Table 3 characteristics of RBO refined with four operations including degumming (at 65°C), dewaxing at low temperature (10, 17, and 25°C), bleaching, and physical refining are shown. The results show that for 4% FFA oil, change of dewaxing temperature from 10 to 17°C does not affect the oil color markedly, whereas change of dewaxing temperature from 10 to 25°C yields worse color in physically refined oil. Similarly, UM, gum and wax, and tocopherol content were affected adversely. For 9.5% FFA oil, changes of dewaxing temperature from 10 to 17°C or from 10 to 25°C both worsen the color of refined oil. However, the UM, gum and wax, and tocopherol content in refined oil remained mostly unaffected if dewaxing was carried out at higher temperatures (17 or 25°C). The results indicate that low dewaxing temperature (10°C) offers better oil quality in terms of color, gum and wax, tocopherol, UM, and oryzanol content for both low- and high-FFA RBO.

Table 3 also shows the effect of H_3PO_4 degumming (at 65°C) and water-dewaxing at three different temperatures (10, 17, and 25°C) on the characteristics of bleached and physically refined RBO. The results indicate that color slowly darkens if higher dewaxing temperature is used. By comparing the results in Table 3 it is evident that the color of the refined oil obtained by H_3PO_4 degumming, low-temperature dewaxing (10°C), bleaching, and physical refining is slightly darker than that obtained after water-degumming at the same temperature (65°C) and water-dewaxing (10°C). The dewaxing carried out at higher temperatures (17 or 25°C) does not affect the color noticeably. However, the color of oil obtained after H_3PO_4 degumming, water-dewaxing (at 25°C), bleaching, and physical refining is better than the oil refined in the same manner by water-degumming in place of H_3PO_4 treatment. The contents of UM, gum and wax, oryzanol, and tocopherol do not vary much when the particular RBO is dewaxed at three different temperatures (10, 17, and 25°C). A closer view also reveals that tocopherol content of refined RBO degummed by the H_3PO_4 route is less than by the water-degumming route. The overall observation suggests that separate water-degumming (at 65°C) and low-temperature water-dewaxing (10°C) yield better-quality oil than H_3PO_4 degumming (at 65°C) and water-dewaxing.

The effect of the independent variable temperature on the color of physical refined oil is shown in Table 4. Clearly the best results may be obtained if higher temperature is maintained during operation, obviously demanding higher energy.

The sequences of alkali refining, bleaching, and deodorization after single-step degumming-dewaxing yield refined oil of better quality with respect to color while other charac-

Table 4
Effect of Temperature (studied on Sample I) on Physical Refining of Combined Water Degummed-Dewaxed Bleached RBO

Characteristics	Operating temperature for physical refining		
	235 ± 5°C	250 ± 5°C	265 ± 5°C
Color[a] (Lovibond, 1″ cell)	(12 ± 1)Y (1 ± 0.2)Y	(9 ± 1)Y (1.2 ± 0.1)Y	(8 ± 1)Y (0.8 ± 0.2)Y
FFA[a] (% w/w)	0.19 ± 0.02	0.16 ± 0.02	0.18 ± 0.02
PV[b] (meq/kg)	0.85	0.94	0.89
UM[a] (% w/w)	3.22 ± 0.20	3.40 ± 0.20	3.51 ± 0.20
Gum and wax[a] (% w/w)	0.50 ± 0.12	0.49 ± 0.15	0.59 ± 0.10
Oryzanol[b] (% w/w)	2.01	2.11	2.14
Tocopherol[b] (% w/w)	0.048	0.039	0.029

[a]Results have been expressed as mean ± standard error.
[b]Results have been expressed as arithmetic mean of three results. See Tables 1 and 2 for abbreviations.

TABLE 5
Characteristics of Combined Water Degummed-Dewaxed, Alkali Refined, Bleached, and Deodorized RBO[a]

Characteristics of RBO	Oil used		
	Sample I	Sample II	Sample III
Color[b] (Lovibond, 1″ cell)	(6 ± 1)Y (0.5 ± 0.1)R	(12 ± 1.2)Y (1.0 ± 0.5)R	(15 ± 1)Y (1.8 ± 0.2)R
FFA[b] (% w/w)	0.12 ± 0.02	0.20 ± 0.02	0.19 ± 0.02
PV[c] (meq/kg)	1.08	1.31	1.23
UM[b] (% w/w)	2.71 ± 0.40	2.84 ± 0.40	2.90 ± 0.40
Gum and wax[b] (% w/w)	0.51 ± 0.23	0.81 ± 0.21	0.68 ± 0.27
Oryzanol[c] (% w/w)	1.90	1.85	1.73
Tocopherol[c] (% w/w)	0.023	0.026	0.022

[a]Deodorized at 185 ± 2°C, under 5 mm Hg pressure.
[b]Results have been expressed as mean ± standard error.
[c]Results have been expressed as arithmetic mean of three results. See Tables 1 and 2 for abbreviations.

teristics remain nearly the same (Table 5). This process, however, suffers from higher refining losses.

The overall results indicate that single-step degumming-dewaxing at low temperature is a better approach than the conventional two-stage process of degumming and dewaxing in getting good-quality refined RBO, and also reduces the process by one operational step.

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