Deacidification of High FFA Rice Bran Oil by Reesterification and Alkali Neutralization

A.C. Bhattacharyya and D.K. Bhattacharyya
University Colleges of Science and Technology, Department of Chemical Technology, 92, Acharyya Prafulla Chandra Rd., Calcutta 700 009, India

Rice bran oils of 15 to 30% free fatty acid can be deacidified to low levels by reesterification with glycerol after degumming and dewaxing. The reesterification can by combined with conventional alkali neutralization and bleaching to produce light color edible oil.

One of the methods of deacidification of a vegetable oil consists of the conversion of its free fatty acids (FFA) into neutral glycerides by reesterification with the free hydroxyl groups remaining in the oil or with added hydroxyl group through glycerol at high temperature in an inert atmosphere with or without catalyst system (1,2). This reesterification method has not been studied from the standpoint of the extent of deacidification and other characteristics of the deacidified oils. Anand and Vasishtha (3) have studied the esterification process for deacidifying high FFA rice bran oil, but have not examined the suitability of the process for converting rice bran oil into edible grade.

Reesterification is expected to increase the yield of neutral oil. The reesterified oil will have some FFA and can be further deacidified by alkali refining. An economical, integrated deacidification procedure would be valuable. It is necessary to critically evaluate the effect of reesterification on color and other chemical transformations that may occur during the reesterification process. A preliminary report (4) was made earlier on the reesterification behavior of degummed and dewaxed rice bran oil without giving details such as reesterifiation rate and characteristics of the reesterified samples or of the results when combined with alkali refining and bleaching.

In the present study the reesterification process has been investigated for commercial rice bran oil of varying FFA and color with respect to the effects of variables including temperature, catalyst, addition of glycerol and pretreatment (degumming and dewaxing) on the extent of reduction of FFA. The subsequent neutralization by alkali of the residual FFA in the oils obtained and the decolorization by bleaching earth also have been investigated.

EXPERIMENTAL

Crude rice bran oil of varying FFA content was obtained from local industries.

FFA and unsaponifiable matter in the crude and refined oils were determined by AOCS methods (5). Color of the crude and refined rice bran oil was determined by Lovibond Tintometer (6). Monoglycerides and diglycerides were estimated by separation from the oils by thin layer chromatography (TLC) (7) and then by color reaction of glyceride glycerol (8).

The reesterification reaction of the rice bran oil samples under investigation was carried out at temperatures from 120–200 C and at 5 mm pressure or in nitrogen atmosphere, with and without a catalyst and also with and without added glycerol. The reaction was conducted in a three-necked flask fitted with a stirrer, an arrangement for vacuum or nitrogen inlet, and a thermometer inlet. The flask was heated by a

TABLE 1

Deacidification of Raw Rice Bran Oil by Reesterification[a,b]

Time (hr)	Temperature (C)	% FFA in oil
2	200	9.6
	180	10.6
	160	12.8
	140	13.0
	120	13.6
4	200	8.0
	180	9.8
	160	10.6
	140	10.8
	120	10.8
6	200	7.6
	180	10.0
	160	10.2
	140	10.2
	120	10.2

[a]At high temperature without added glycerol and catalyst in nitrogen atmosphere.
[b]FFA in crude rice bran oil, 15.3%.

TABLE 2

Effect of Glycerol on the Deacidification of Raw Rice Bran Oil by Reesterification in Nitrogen Atmosphere[a,b]

Time (hr)	% Excess glycerol on theoretical	% FFA in oil
2	10	8.0
	20	7.6
	30	7.0
	50	6.2
4	10	7.4
	20	6.4
	30	6.0
	50	5.4
6	10	6.0
	20	5.6
	30	4.8
	50	4.0

[a]FFA in crude rice bran oil, 15.3%.
[b]Reesterification condition temperature, 200 C.

TABLE 3

Effect of Catalyst on the Deacidification of Raw Rice Bran Oil by Reesterification with Glycerol in Nitrogen Atmosphere

Time (hr)	Catalyst		% Excess glycerol on theoretical	% FFA in oil
	Nature	Amount % (on oil)		
2	Stannous chloride	0.2	20	6.9
			50	—
2	p-Toluene sulphonic acid	0.2	20	6.6
			50	5.5
4	Stannous chloride	0.2	50	5.4
4	p-Toluene sulphonic acid	0.2	50	5.3
6	Stannous chloride	0.2	50	5.1
6	p-Toluene sulphonic acid	0.2	50	5.0

[a]FFA in crude rice bran oil, 15.3%.
[b]Reesterification temperature, 200 C.

temperature controlled mantle. The reaction was continued on the basis of the reduction in FFA of the oil drawn periodically from the flask. The catalyst, like stannous chloride and p-toluene sulfonic acid (PTS) at 0.2% level by the weight of oil, were used.

After the desired reduction in the FFA level, the product was cooled to ca. 50 C and washed with distilled water saturated with brine until the catalyst was completely removed. The esterified oil was recovered by drying under vacuum of 750 mm at ca. 90 to 95 C. In some of the esterified oils, monoglycerides and diglycerides were estimated. Some of the esterified samples were further deacidified by the conventional alkali neutralization process. The oil sample was mixed with 20 Be' caustic soda solution containing 20% excess at ca. 50 C for 15 min by stirring. Soap stock was removed by centrifugation at 6,000 rpm. The neutralized and washed oils were dried and bleached with 2% Tonsil earth optimum at ca. 105 C and under ca. 730 mm Hg for 45 min. The bleached oil was recovered by filtration under vacuum.

The color and unsaponifiable matter of the reesterified and alkali neutralized and bleached oils were examined according to standard procedures.

RESULTS AND DISCUSSION

The effect of temperature on the rate of reduction of FFA of raw rice bran oil during reesterification without any added hydroxyl group and without any catalyst is shown in Table 1. It is evident that the rate at which raw rice bran oil reesterifies is at its maximum between 180 C and 200 C.

TABLE 4

Deacidification of Degummed [a] and Dewaxed[b] Rice Bran Oil[c]

% FFA in crude rice bran oil	Reesterification condition[d]		
	Time (hr)	% Excess glycerol on theoretical	% FFA in oil
15.3	2	30	6.0
		50	5.1
	4	30	4.7
		50	4.0
	6	30	2.8
		50	1.6
20.5	2	30	9.8
		50	9.0
	4	30	7.4
		50	6.5
	6	30	4.4
		50	3.1
30.2	2	30	12.2
		50	10.1
	4	30	7.8
		50	6.6
	6	30	5.2
		50	4.0

[a]Degummed by 85% phosphoric acid (1 kg/ton).
[b]Dewaxed by alkylated phenol ethylene oxide condensate (0.5% on oil as 2% aqueous solution).
[c]With glycerol (98%) under vacuum (5 mm pressure) in presence of 0.2% p-toluene sulphonic acid.
[d]Temperature, 200 C.

TABLE 5

Characteristics of Degummed[a] and Dewaxed[b] Rice Bran Oil After Reesterification[c]

% FFA in crude rice bran oil	Time (hr)	% FFA in the reesterified oil	% Mono-glyceride	% Di-glyceride	Lovibond color (1 cm cell)	
					Y	R
15.3	2	5.1	1.75	3.23	20.0	2.8
	4	4.0	1.72	3.52	20.0	2.8
	6	1.6	1.33	5.38	20.2	3.1
20.5	2	9.0	2.64	6.64	18.4	2.6
	4	6.5	2.24	6.76	18.4	2.7
	6	3.1	2.12	7.80	18.8	3.0

[a]Degummed by 85% phosphoric acid (1 kg/ton).
[b]Dewaxed by alkylated phenol ethylene oxide condensate (0.5% on oil as 2% aqueous solution).
[c]Reesterification at 200 ± 2 C with 50% glycerol and 0.2% p-toluene sulphonic acid.

TABLE 6

Characteristics of Degummed[a] and Dewaxed[b] Rice Bran Oil After Reesterification and Alkali Neutralization

% FFA in crude rice bran oil	% FFA in oil after		Lovibond color (1 cm cell)		Loss after refining (%)	Unsaponifiable matter (%)
	Reester-ification	Alkali refining	Y	R		
15.3	5.1	0.22	16.0	1.6	16.9	2.0
	4.0	0.20	16.0	1.7	16.5	2.0
	1.6	0.18	16.6	1.8	4.8	1.9
20.5	6.5	0.22	14.6	1.5	22.4	2.2
	3.1	0.20	14.8	1.6	6.8	2.0

[a]Degummed by 85% phosphoric acid (1 kg/ton).
[b]Dewaxed by alkylated phenol ethylene oxide condensate (0.5% on oil as 2% aqueous solution).

Table 2 contains data showing the effect of the addition of glycerol on the extent of deacidification of raw rice bran oil by reesterification. The use of glycerol in 50% excess of the theoretical amount to neutralize the FFA reduces the FFA from 15.3 to 6.2 in two hr at 200 C. At the same temperature when the reaction is conducted for four hr and six hr, the FFA is reduced by only 1 and 2%, respectively. The addition of glycerol increases the rate of reaction.

The effect of two catalysts, namely tin chloride ($SnCl_2$, $2H_2O$) and an aromatic sulphonic acid (p-toluene sulphonic acid) on the extent of esterification of fatty acids with added glycerol to raw rice bran oil is shown in Table 3. The use of catalysts does not influence the esterification rate, as can be noted from the FFA remaining in the oil.

The effect of degumming and dewaxing on the extent of deacidification of rice bran oil with glycerol and catalyst under vacuum is presented in Table 4. The high FFA rice bran oil samples can be effectively reesterified when the reaction is carried out on a degummed and dewaxed oil under vacuum.

The characteristics of two samples of rice bran oil after degumming and reesterification are shown in Table 5. It can be seen that the reesterified samples contain monoglycerides and diglycerides. The diglyceride proportion increases and that of monoglyceride decreases when the FFA decreases. The color becomes deeper in the red unit and light in the yellow unit.

The reesterified rice bran oil samples having FFA from ca. 2% to ca. 6% have been alkali-refined and bleached, and the characteristics of the oil samples obtained are included in Table 6. Alkali refining loss appears to be high, presumably due to the 1 to 2% monoglyceride in the reesterified samples.

The deacidification of high FFA commercial rice bran oils can be achieved by reesterification with an acid catalyst in the presence of added glycerol after degumming and dewaxing. The combination of reesterification and alkali neutralization does not improve the color. However, considering the original FFA of the oil and the ultimate amount of oils recovered by the

combination of reesterification and alkali neutralization, the combined process appears to be quite technically feasible for deacidifying high FFA commercial oils.

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