Influence of Viscosity on Wax Settling and Refining Loss in Rice Bran Oil

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The role of viscosity on wax settling and refining loss in rice bran oil (RBO) has been studied with model systems of refined peanut oil and RBO of different free fatty acids contents. Wax was the only constituent of RBO that significantly increased the viscosity (81.5%) of oil. Monoglycerides synergistically raised the viscosity of the oil (by 114.2%) and lowered the rate of wax settling. Although a reduction in the viscosity of the oil significantly decreased the refining loss, the minimum loss attained was still 20% more than the theoretically predicted value. This led us to conclude that some chemical constituents, such as monoglycerides, must be removed before dewaxing; thereafter, oryzanol and phospholipids have to be removed. One can get an oil free of wax, recover other by-products and reduce processing losses.

KEY WORDS: Dewaxing, monoglycerides' influence on wax settling, refining loss, rice bran oil, rice bran wax, synergism between monoglycerides and RBW, viscosity, wax settling.

Processing of rice bran oil (RBO) by conventional alkali refining methods is expensive due to the presence of wax and high oil losses during refining (1,2). Wax occludes oil, resulting in high losses of oil during the dewaxing and refining steps (1–4). Understanding how the constituents of RBO influence the settling rate of wax could improve processing efficiency. The present study aims at understanding the nature of chemical constituents responsible for increasing the viscosity of RBO and the effects of viscosity on wax-settling and refining loss in peanut and rice bran oils.

MATERIALS AND METHODS

Materials. Refined peanut oil (PNO) and solvent-extracted RBO were purchased from the local markets in and around Mysore, India. Rice bran wax (RBW), RBO free fatty acids (FFA), RBO triglycerides, RBO partial glycerides, RBO oryzanol (OZ), soy lecithin (SL) and glyceryl monostearate (GMS) were used in the study. The details of their preparation/isolation and analysis have been described elsewhere (1). Known amounts of the above constituents were added to PNO, and then the mixture was heated on a water bath for dissolution. Oil samples were brought to room temperature (26 ± 2°C) prior to determining viscosity.

Preparation of monoglyceride free RBO. Crude RBO miscella was passed through a silica gel column (oil miscella/silica gel ratio of 5:1, vol/wt) as described in an earlier communication (5) (flow rate of miscella percolation increased by applying 38 cm vacuum), and the eluted oil miscella was collected and desolventized to get an oil that had reduced amounts of monoglycerides (starting oil 1.67%; after treatment 0.2%).

Preparation of oils with different viscosities. A combination of solvents and RBO was prepared by adding known amounts of water. Two layers of oil with different viscosities formed when the solvent–oil mixture contained about 1.4% water in the mixture. Therefore, a solvent–oil mixture was prepared by using hexane (225 mL), absolute ethyl alcohol (67.5 mL), RBO (250 mL) and water (7.5 mL). The solvent–oil mixture was shaken and allowed to stand for about 5 min at room temperature, which then separated into two distinct layers. The top and bottom layers were separated and desolventized to obtain low- and high-viscosity oils, respectively.

Degummed oil was prepared from crude RBO as outlined in an earlier communication (1); it had a slightly lower viscosity as compared to the initial crude RBO.

Methods. Refining loss was determined by using 10-g oil samples, as described previously (1). Oil viscosities were determined with an Ostwald viscometer of 25-mL capacity (6) in a constant-temperature water bath. The data were subjected to one-way (unequal sample size)/two-way analysis of variance, followed by Duncan's new multiple range test for segregating differences between means (7).

Wax settling experiments. Model wax-settling experiments were conducted at room temperature (26 ± 2°C) by placing PNO/monoglyceride-free RBO in graduated cylinders with or without added constituents such as RBW (3%), SL (2%) or GMS (1%), and then determining, at 4-h intervals to the end of the experiment, the volume of supernatant oil from which the wax had settled. The concentrations of individual constituents added to PNO were chosen on the basis of the levels at which wax, gums and monoglycerides are normally present in crude RBO (1).

RESULTS AND DISCUSSION

Constituents responsible for increasing viscosity of model oil. To determine how wax settling is influenced by the constituents of crude RBO, a large quantity of pure RBO (*i.e.*, triglycerides) was necessary. Because RBO triglycerides and PNO (both contain triglycerides with approximately similar fatty acid compositions) behaved similarly with respect to viscosity and refining loss (see Tables 1 and 4, shown later), all model oil experiments were conducted with PNO instead of RBO triglycerides. Of the constituents individually added to PNO, FFA, OZ, SL and GMS did not significantly influence viscosity of the oil (Table 1). RBW alone increased the viscosity of the model oil by 81.5%. In combination with other constituents, RBW also significantly affected the viscosity of the oil (55.7–114.2%) (Table 2). SL and OZ individually reduced the viscosity of RBW in model oil to 55.7–59.4% over PNO, whereas GMS, along with RBW, synergistically increased the viscosity of the model oil (114.2%). It is interesting to note that GMS alone did not significantly increase the viscosity of the model oil (8.7%) (Table 1). Also, OZ reduced the synergistic effect of GMS with RBW on viscosity (114.2%) to that of the initial value for RBW alone (81.5% for RBW and 78.3% for model oil containing GMS, RBW and OZ). SL also behaved like OZ in that it reduced the synergistic effect of GMS with RBW on viscosity, but to a significantly lesser extent (96.8%). SL and OZ in combination completely eliminated the synergistic effect of GMS with RBW in the model oil. The mechanism by which viscosity changes were brought about by the addition of RBO constituents to model oil is not yet understood.

TABLE 1

Individual Effects of RBO Constituents on Viscosity

Sample oil[a]	Viscosity at 30 ± 0.1°C cP[b]	Increase over PNO (%)
PNO	34.5[c]	0.0
PNO + 6.8% FFA	36.0[c,d]	4.4
PNO + 3% RBW	62.6[e]	81.5
PNO + 1% OZ	37.4[c,d]	8.4
PNO + 1% GMS	37.5[c,d]	8.7
PNO + 2% SL	41.4[d]	20.0
RBO triglycerides	36.6[c,d]	—
Commercially refined RBO	37 ± 2.0	—
SE_m (35 df)	± 2.06	—

[a]PNO, refined peanut oil; FFA, rice bran oil (RBO) free fatty acids; RBW, rice bran wax; SL, soy lecithin; OZ, oryzanol; GMS, glyceryl monostearate; SE_m, standard error of mean values; df = degrees of freedom.
[b]Any two means having different superscripts (c–e) are significantly different ($P \leq 0.05$).

TABLE 2

Combination Effects of RBO Constituents on Viscosity

Sample oil[a]	Viscosity at 30 ± 0.1°C cP[b]	Increase over PNO (%)
PNO	34.5[c]	—
PNO + 6.8% FFA (APNO)	36.0[c]	4.4
APNO + 3% RBW	62.6[e]	81.5
APNO + 3% RBW + 2% SL	55.0[d]	59.4
APNO + 3% RBW + 2% GMS	73.9[g]	114.2
APNO + 3% RBW + 1% OZ	53.7[d]	55.7
APNO + 3% RBW + 1% GMS + 2% SL	67.9[f]	96.8
APNO + 3% RBW + 1% GMS + 1% OZ	61.5[e]	78.3
APNO + 3% RBW + 1% GMS + 1% OZ + 2% SL	55.1[d]	59.7
SE_m (16 df)	± 0.4519	—

[a]APNO, peanut oil acidified with 6.8% of RBO FFA; other abbreviations as in Table 1.
[b]Any two means having different superscripts d–g are significantly different ($P \leq 0.05$).
[c]The data of PNO and APNO were not included for analysis of variance.

Effect of added monoglycerides on wax settling in model oil. In the model oil, GMS increased the volume of wax settlings by 31.6%, thereby reducing the supernatant oil content by 87.8%. This was attributed to the elevation in the viscosity by 43.7% of the model oil by GMS (Table 3). The same effect was also observed for the RBO monoglyceride fraction added to the model oil. For example, the monoglyceride fraction isolated by silica gel treatment (identified as oxidized monoglycerides, Ref. 8) increased the viscosity of the model oil by 15.5%, resulting in decreased supernatant oil content by 58.3% and increased volume of wax settlings by 18.4%. Therefore, any attempt to increase the settling rate of wax in the oil without prior removal of native monoglycerides would meet with little success.

It is not presently clear as to how GMS/monoglycerides of RBO caused an increase in viscosity of the model oil. It is probable that an interaction between hydrophobic groups of RBW and partly hydrophilic groups of GMS/SL might be operative to produce an oil-in-oil type of solid-liquid emulsion.

Effect of removal of native monoglycerides from RBO on wax settling. When monoglyceride-free RBO was subjected to the wax-settling experiments, the volume of wax settlings was reduced from 41 mL (for control oil) to 17 mL (for monoglyceride-free oil), a 58.5% reduction. This resulted in a 40.7% increase in the yield of supernatant oil, thereby confirming that the removal of monoglycerides from RBO accelerated the settling of wax and increased oil recovery.

Effect of varying the viscosity of RBO on refining loss. For this set of experiments, RBO was partitioned between hexane and aqueous ethyl alcohol to get oils with low and high viscosities. These oils differed in composition, in that the low-viscosity oil contained mostly triglycerides, whereas the high-viscosity oil contained a greater proportion of the partial glycerides, wax, phosphatides and OZ [as indicated by a qualitative thin-layer chromatographic examination of the oils (1)]. Interestingly, these oils had the same FFA content as the starting RBO. Although the refining loss increased with increased viscosity (37.8–75.3 cP oils studied), it could not be reduced to that of the control PNO by lowering viscosity alone (Table 4). Irrespective of FFA content (6.8–11.8% FFA oils studied), the refining loss increased by 20–42% in all cases. However, PNOs of varying FFA contents (1.1–6.8% FFA in the oils

TABLE 3

Effect of Viscosity on Wax Settling in Model Systems (26 ± 2°C)

Sample oil[a]	Viscosity (cP)[b]	Volume of wax settlings after 191 h (starting volume, 100 mL)	Volume of supernatant oil after 191 h (mL)[b]
PNO + 3% RBW + 2% SL	53.6[d]	76 ± 0.5	24.7[l]
PNO + 3% RBW + 2% SL + oxidized monoglyceride fraction isolated from RBO (1%)	61.9[e]	90 ± 2.0	10.3[m]
PNO + 3% RBW + 2% SL + 1% GMS	77.0[f]	97 ± 0.5	3.0[n]
SE_m (df)[c]	± 0.2176 (15)	—	± 0.924 (6)

[a]Abbreviations as in Table 1.
[b]Any two means having different superscripts d–f or l–n are significantly different ($P \leq 0.05$).
[c]The number in parentheses indicate df.

TABLE 4

Effect of Viscosity on Refining Loss in Model Oil and RBO[a]

Sample oil	FFA (%)	Viscosity at 30 ± 0.1°C (cP)[c]	Refining loss (%) Predicted[b] (A)	Observed[c] (B)	% Increase over predicted loss (B − A/A) 100
PNO	1.1	34.46[m]	6.4	6.3[d]	—
	4.3	35.80[m,n]	13.5	13.4[e]	—
	6.8	35.80[m,n]	19.0	18.7[f]	—
RBO	6.8	41.20[p,q]	19.0	23.0[g]	21.1
	10.1	45.15[r]	26.2	32.0[i]	22.1
	11.8	42.33[q]	30.0	36.0[j]	20.0
	6.8	41.20[p,q]	19.0	23.0[g]	21.1
	6.8	49.74[t]	19.0	27.0[h]	42.1
	6.8	52.07[u]	19.0	27.0[h]	42.1
	11.8	37.78[o]	30.0	36.0[j]	20.0
	11.8	47.20[s]	30.0	40.0[k]	33.3
	11.8	75.29[v]	30.0	53.4[l]	78.0
RBO-fraction (triglycerides)	6.2	36.65[n,o]	17.6	17.6	—
SE_m (df)	—	± 0.4972 (36)		± 0.299 (39)	—

[a]Abbreviations as in Table 1. df, Degrees of freedom. The numbers in parentheses indicate df.
[b]Predicted loss = (2.2 × %FFA) + 4.0.
[c]Any two means having different superscripts d–v are significantly different ($P \leqslant 0.05$).

studied) and the RBO triglyceride's fraction (6.2% FFA oil) did not show higher refining losses than the predicted values. In an oil with high viscosity (75.3 cP), the refining loss was also significantly higher (78% increase compared with the low-viscosity control PNO). In low-viscosity oil (37.8 cP), the refining loss was significantly lower, but the losses were 20% more than the predicted value. However, in the fraction rich in RBO triglycerides (containing 6.2% FFA), the viscosity was similar to that of the control PNO, and the refining loss was also similar to the predicted value (Table 4). This indicated that by reducing the viscosity of RBO alone, refining loss cannot be reduced to a value less than 20% above the value predicted on the basis of FFA content of the oil. This 20% excess value was the lowest loss that was observed for RBOs with different FFA contents and viscosities.

Effect of processing crude RBO on viscosity and refining loss. The results of processing a typical RBO are presented in Table 5. The crude oil had high viscosity and produced high refining loss. Degumming RBO reduced the viscosity and refining loss by 5.6 and 4.6%, respectively; dewaxing degummed oil reduced these values by 21.8 and 64.6%, respectively. Furthermore viscosity reduction by purification into triglycerides reduced the viscosity by 30.4% and refining loss by 100%; the refining loss and viscosity were then similar to those of the control PNO with the same FFA content (Table 5). Reduction of crude oil viscosity therefore did not appreciably reduce the refining loss (viscosity 37.8 cP, refining loss 20% more than predicted value, Table 4), but reduction of viscosity, such as by isolation of triglycerides from RBO, yielded the predicted refining loss (viscosity 36.7 cP, Table 5). The partial glycerides-containing oil showed high viscosity (67.3 cP), and the refining loss was also appreciably high (78% increase compared to starting RBO). Therefore, OZ and monoglycerides need to be removed in addition to degumming and dewaxing before the oil is alkali-refined. Lowering crude oil viscosity for reducing

TABLE 5

Typical Viscosities and Refining Losses of RBO[a]

Sample oil	Viscosity at 27.8°C (cP)[b]	Refining loss (%) Predicted[c]	Observed[d]
Crude RBO (6.8% FFA)	52.67[k]	19.0	30.0
Phosphoric acid degummed	49.74[j]	19.0	29.5
Dewaxed by chilling	41.20[i]	19.0	22.9
Dewaxed oil fractionated into triglycerides (had 6.2% FFA)	36.65[h]	17.6	17.6
Dewaxed oil fractionated into partial glycerides	67.30[e,l]	19.0	53.4[f]
PNO (6.8% FFA)	35.80[g]	19.0	18.7
SE_m (18 df)	± 0.1378	—	—

[a]Abbreviations as in Table 1.
[b]Any two means having different superscripts g–l are significantly different ($P \leqslant 0.05$).
[c]Predicted loss = (2.2 × %FFA) + 4.0.
[d]Mean of duplicate values.
[e]Value increased by 28.0%; 83.6% increase based on triglycerides.
[f]Value increased by 78.0%; 185.6% increase based on PNO.

refining losses and increasing crude oil viscosity for a faster wax settling, therefore, is not by itself a solution to the problems encountered in refining and/or dewaxing of RBO.

This study indicates that: (i) RBW-settling rate is lowered by the presence of monoglycerides (GMS) through a rise in viscosity; (ii) any attempt to accelerate wax settling by altering viscosity of the oil, without removal of native monoglycerides, would meet with little success; and (iii) excessive refining loss is dependent not only on viscosity but also on constituents other than wax and monoglycerides [such as OZ, which may not have influence on viscosity individually, but has a synergistic/direct influence on increasing refining loss (1) in the oil systems studied].

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