Industrial Hydrogenation of Rice Bran Oil, a Substitute for Tallow

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The Indian soap industry's hard fat requirement was met until recent years by imported animal tallows. The search for alternate hard fats, consequent to the ban on the import of animal tallows in 1983, led to realization of the striking similarity in the fatty acid composition of mutton tallow and hydrogenated rice bran oil, except for the *trans* oleic acid content. This paper traces the course of compositional changes undergone by rice bran oil during industrial hydrogenation, employing gas liquid chromatography and infra red spectroscopy.

The availability in India of hard fats for the soap industry is limited. Until the mid-seventies, the hard fat requirement was met mainly by importing animal tallows. Later, such imports declined considerably, due to increased use by the organized soap industry of unconventional oils such as rice bran, neem, kusum, sal, karanja and castor. In 1983, the import of any fat of animal origin was banned by the government of India, leading to complete dependence on alternate sources for the tallow base.

Rice bran oil (RBO) has gained a commanding position as a raw material for soap. The reason for this is clear from the comparative fatty acid composition of distilled RBO fatty acids, distilled hydrogenated RBO (HRBO) fatty acids and animal tallow, as shown in Table 1.

Currently, about 80% of commercially available RBO in India is of the non-edible grade, with free fatty acid (FFA) content of 20 to 70%, a dark, dirty-green or brown color, a grassy odor, and the presence of waxes, gums, bran particles, mucilage, mineral matter, dust and traces of moisture and solvent. Hydrogenation of such RBO is not a straightforward operation.

Degumming (1-3), dewaxing (4-9) and miscella refining (10) to upgrade RBO to an edible grade has been investigated extensively. However, few studies relating to its actual industrial hydrogenation have been published, most reports being concerned with the development of suitable rugged catalysts, and the manipulation of process variables to enhance the rate of hydrogenation and achieve reduction in catalyst consumption (4,11). Following the course of reaction by examining intermediate products for their fatty acid composition by gas liquid chromatography (GLC) and infrared spectroscopy would make for better understanding of what happens. This paper reports such compositional studies made during plant-scale hydrogenation of RBO to produce a hard raw material for soap manufacture.

EXPERIMENTAL

The several lots used for hydrogenation were typical of RBOs of inedible quality, with FFA contents ranging

TABLE 1

Composition of Distilled RBO Fatty Acids, Distilled Hydrogenated RBO Fatty Acids and Animal Tallow by GLC

Composition[a]	RBO fatty acid	HRBO fatty acid	Animal tallow
14:0	0.5	0.5	1.0
16:0	19.0	19.0	21.0
18:0	2.5	30.0	30.0
18:1	48.5	44.0	43.0
18:2	29.5	6.5	5.0
trans-isomers	NIL	21.0	4.8
I.V.	99.5	53.2	42.2

[a]GLC on methyl esters.

TABLE 2

Details of Hydrogenation Runs, Silicate-Treated RBO, 0.1% Ni

Experiments	Batch (ton)	Hydrogen pressure (Kg/cm²)	Initial temperature (C)	Final temperature (C)
1	9.562	2.5	154	204
2	9.340	2.0	164	212
3	9.853	1.0	176	212

TABLE 3

Plant Hydrogenaton of Rice Bran Oil,[a] Analysis and Fatty Acid Composition

Time (hr)	Melting point (C)	Iodine value (Wijs)	Titer (C)	FFA/oleic (%)	Unsaponifiable matters (%)	Methyl esters (%)					% *trans* ΔIV	Linoleate selectivity
						16:0	18:0	18:1	18:2	*trans,* as methyl elaidate (%)		
0	27.2	94.5	27.3	46.8	5.14	19.8	3.5	43.5	33.2	—	—	—
1	34.1	80.8	32.0	—	—	19.1	10.0	51.7	19.2	8.5	0.62	2.15
2	40.1	72.5	38.9	—	—	19.9	15.1	50.2	14.8	15.7	0.71	0.86
3	46.8	61.1	45.4	—	—	18.7	22.9	47.3	11.1	21.7	0.65	0.47
4	48.5	59.8	47.1	—	—	18.8	24.1	46.4	10.7	23.2	0.66	0.33
5	50.1	54.9	48.9	—	—	19.3	28.3	43.9	8.6	24.1	0.61	0.50
6	51.2	52.3	46.8	45.6	5.83	18.4	30.6	41.7	9.2	22.5	0.53	0.26

[a]Experiment 1, hydrogenation of silicate-treated RBO with 0.1% Ni at 2.5 kg/cm², 154-204 C.

from 40 to 50%. All the oils were given a mild pretreatment with sodium silicate (0.2% on oil basis) at 70 C, followed by water washes. This procedure is used regularly in India. It removes iron and some mucilaginous matter, partly neutralizes the oil while yielding a firm soapstock, reduces the amount of hydrogenation catalyst needed subsequently, and minimizes catalyst poisoning.

Treated RBO was hydrogenated with wet-reduced nickel catalyst containing 23.72% Ni in a batch stainless steel autoclave of the oil circulation type. The reaction conditions are given in Table 2. The analytical results on samples withdrawn periodically are recorded in Tables 3, 4 and 5. The zero-hour sample corresponds to the time when the catalyst was well mixed with the oil soon after its addition.

Methyl esters were analyzed on an AIMIL MODEL 5500 gas chromatograph with a flame ionization detector, on a 12 × 2 mm i.d. DEGS column (15% DEGS on Chromasorb/W) programmed 180–220 C at 2 C/min with nitrogen as carrier gas (40 ml/min measured at column). The injection port and detector were maintained at 230 C and 250 C, respectively. Peaks were identified using reference methyl esters.

Infrared analyses were carried out on the methyl esters with a Perkin-Elmer model 289 infrared spectrophotometer having NaCl optics. The isolated *trans*-isomer content of the methyl esters was calculated as methyl elaidate following AOCS Method Cd 15-61 (12). Linoleate selectivities were calculated using AOCS Method Tz 16-79 (12).

At each stage, the amount of *trans* acid formation with drop in I.V. and the linoleate selectivity with respect to oleate (% linoleate disappeared divided by % stearate formed) were calculated.

RESULTS AND DISCUSSION

Fatty acid compositional changes during a typical plant hydrogenation of RBO (Experiment 1) (2.5 kg/cm^2 pressure, 0.1% Ni) are shown in Table 3. In the earlier half of the reaction, hydrogenation of linoleate proceeds extremely rapidly, along with far less hydrogenation of oleate to stearate, in other words with high selectivity. Later in the reaction, selectivity falls to very low levels as mostly oleate is being reduced. At this high pressure of 2.5 kg/cm^2, the rate of *trans* acid formation remains steady throughout the reaction.

In a mixture of glycerides and free fatty acids, the selectivity in the FFA part is known to be quite different from that of the glycerides (4). However, when dealing with an RBO containing typically 40–50% FFA, as in the present raw materials, one is more interested from a practical standpoint in the overall compositional changes that occur during the course of the process, rather than in the individual course of reaction in the FFA and glyceride portions of the oil.

TABLE 4

Plant Hydrogenation of Rice Bran Oil,[a] Analysis and Fatty Acid Composition

Time (hr)	Melting point (C)	Iodine value (Wijs)	Titer (C)	FFA/oleic (%)	Unsaponifiable matters (%)	Methyl esters (%)					% *trans* ΔIV	Linoleate selectivity
						16:0	18:0	18:1	18:2	*trans*, as methyl elaidate (%)		
0	27.0	99.8	24.3	44.6	4.09	19.9	2.7	44.2	33.2	—	—	—
1	31.3	81.5	31.0	—	—	18.7	8.1	50.4	22.8	15.4	0.84	1.93
2	39.5	72.2	37.4	—	—	18.1	19.4	49.4	13.1	23.8	0.86	0.86
3	43.4	63.8	40.7	—	—	17.3	25.1	48.9	8.8	17.3	0.52	0.75
4.5	47.0	58.0	44.9	—	—	18.9	27.5	45.9	7.7	20.0	0.48	0.46
5.5	47.5	52.6	46.4	43.0	4.37	18.8	29.8	43.2	8.2	19.4	0.41	0.22

[a]Experiment 2, hydrogenation of silicate treated RBO with 0.1% Ni at 2.0 kg/cm^2, 164–212 C.

TABLE 5

Plant Hydrogenation of Rice Bran Oil,[a] Analysis and Fatty Acid Composition

Time (hr)	Melting point (C)	Iodine value (Wijs)	Titer (C)	FFA/oleic (%)	Unsaponifiable matters (%)	Methyl esters (%)					% *trans* ΔIV	Linoleate selectivity
						16:0	18:0	18:1	18:2	*trans*, as methyl elaidate (%)		
0	26.2	94.2	28.5	42.7	4.92	19.0	6.1	42.1	32.8	—	—	—
1	29.6	87.0	30.1	—	—	19.3	11.0	51.5	18.2	16.3	2.26	3.00
3	36.4	77.6	35.2	—	—	20.5	12.2	53.6	13.7	16.5	0.99	3.75
4.5	42.7	68.6	39.9	—	—	20.0	15.7	53.8	10.5	20.0	0.78	0.91
5.5	45.0	64.5	42.5	—	—	18.5	25.0	47.1	9.4	23.2	0.75	0.12
7.5	48.0	55.0	46.8	—	4.81	16.0	33.2	44.6	6.2	19.1	0.49	0.39

[a]Experiment 3, hydrogenation of silicate treated RBO with 0.1% Ni at 1.0 kg/cm^2, 176–212 C.

Table 4 shows the compositional changes at the next lower working pressure of 2.0 kg/cm^2. At this pressure, selectivity to linoleate is initially fairly high and gradually declines, but at lower values all along than for the hydrogenation at 2.5 kg/cm^2. *Trans* acid formation per unit I.V. is high at the start and declines as the hydrogenation progresses.

Table 5 shows data for hydrogenation of RBO at a yet lower pressure of 1.0 kg/cm^2. Strikingly, the selectivity to linoleate is very high at the start, but decreases to a low figure as the reaction progresses because linoleate has been used up rapidly. At this low pressure, *trans* acid formation for a unit drop in I.V. is high at the start, and gradually declines as the reaction progresses.

Formation of *trans* acids during hydrogenation of a high-acid RBO shows that saturation of linoleate proceeds through a conjugation mechanism. Hydrogenations carried out under plant conditions in India, which are typically at low hydrogen pressures of about 1.0 kg/cm^2, lead to relatively low hydrogen coverage on the nickel surface. Such a condition promotes diene conjugation, and its quick hydrogenation to *trans* monoene forms. However, raising the pressure to 2.0 or even 2.5 kg/cm^2, while altering the course of the reaction, has little effect on the final level of 19–22% *trans* monoene acids that are present at the terminal I.V. of 53–55.

The fatty acid compositions of distilled HRBO and animal tallow are very similar, except that HRBO carries 19% *trans* acids. These *trans* acids have been found to persist in split HRBO and even in distilled HRBO fatty acids.

The composition of the fatty acids of tallow is such that up to 80% can be incorporated in soap formulations. For distilled HRBO fatty acids, the limit of incorporation is about 50 to 60%, since *trans* monoene acids have a higher melting point than *cis*. Reducing their formation during hydrogenation will enable higher percentages of HRBO to be used in soap formulations. It is also the experience in practice that a higher percentage of *trans* acids in HRBO fatty acids causes cracking of the soap on storage. Further study of process variables is needed to determine means of achieving a lower percentage of *trans* acids during hydrogenation of RBO.

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