Separation of Saturated and Unsaturated Acids from Rice Bran Oil

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Rice bran oil, a by-product of rice milling, is an excellent source of a variety of fatty acids. Saponification yielded C_{16} saturated and C_{18} unsaturated acids. Saturated and unsaturated acids were separated by solvent crystallization. Hexane and methanol were both investigated as solvents. Gas-liquid chromatography and iodine value showed that hexane was the more effective crystallization solvent at a solvent/oil ratio of three and crystallization temperature of 5°C. The percent yield and purity of 88.8% and 91% unsaturated acids, respectively, and of 65% and 59% saturated acids were obtained. A process description is proposed for an integrated process.

KEY WORDS: Fatty acids, oils separation, rice bran oil, saturated fatty acids, unsaturated fatty acids.

Fats and oils are a mixture of various triglycerides. Fatty acids are manufactured by hydrolysis of fats and oils (fat splitting), yielding glycerine as a by-product. Besides the combined fatty acids in the form of glycerides, most fats and oils also contain some free fatty acids, due to the enzymatic hydrolysis in the parent oil bearing material before extraction. Fatty acids have diversified applications in various industries, such as textiles, plastics, foods, pharmaceuticals, etc., both "as is" and as the derivatives.

Local production of these strategic chemicals must take into consideration the strict governmental regulations on utilization and processing of edible oils. Therefore, making use of a local nonedible oil source was an attractive alternative.

The average annual production of Egyptian rice-bran oil amounts to 10,000–15,000 metric tons per year (1). After milling, the lipase enzymes split the intact glycerides into free fatty acids and glycerol. The bran quickly turns into a rancid, nonedible waste product. The fatty acid composition of different varieties of local rice bran oils as determined by gas-liquid chromatography (2) showed that these were made up of about 77% unsaturated acids (oleic and linoleic acids) and 23% saturated acids (palmitic acid). It is not possible to separate unsaturated and saturated acids by fractional distillation when they have the same chain length. Fractionation according to the degree of unsaturation present is usually carried out by crystallization processes, where solid saturated and liquid unsaturated acids are separated from each other. Three processes of crystallization separation are presently available (3): i) Panning and pressing process; ii) solvent crystallization process; and iii) Henkels/Lurgi wetting methods.

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The present work is devoted to the separation of fatty acids—saturated (palmitic) and unsaturated (oleic and linoleic)—from crude rice bran oil. The study, carried out on bench scale experiments, covers all the important factors affecting the separation process.

EXPERIMENTAL PROCEDURES

The separation of free unsaturated fatty acids from the saturated acids was conducted by solvent crystallization. Two different methods using hexane and methanol as solvents are proposed.

Pre-treatment of rice bran oil. Rice bran oil (one kg of crude oil) was filtered under vacuum to remove the waxy fraction and suspended matter. Saponification was carried out by mixing the filtered oil with 140 g KOH and 1 L methanol. The mixture was boiled under reflux on a water bath for 10–12 hr. Heating was discontinued and cold water was added to dissolve the saponified matter. Unsaponifiable matter was removed by extracting the mixture with diethyl ether several times until removal of all fatty acids which are in the form of K salts of fatty acid (aqueous layer).

Fatty acids were liberated by dropping about 1 L of 10% diluted sulphuric acid into the soap pasty layer until the fatty acids formed a clear, oily layer at the top. After separation, the fatty acid layer was washed several times with tap water until free of mineral acid.

Solvent crystallization. Two solvents, hexane and 90% methanol, were used for comparison and selection of the suitable solvent. Samples of 50 g of the fatty acids were dissolved in hexane at different acid to solvent ratio, ranging from 1:1 to 1:5 weight by volume. The solutions were chilled (+5°C) overnight, to crystallize out saturated acids. The crystals were separated from the mother liquor by filtration under vacuum and were washed several times with hexane.

The unsaturated acids were recovered from the mother liquor by distillation of hexane. A second crystallization was performed by dissolving the liquid phase obtained in an equal amount of hexane.

The methanol separation process is quite similar to the hexane separation, except that cooling was accomplished at −15°C overnight. The degree of unsaturation of the solid and liquid phases obtained was determined by evaluating the iodine value (IV).

The compositions of both the original oil recovered from the saponification stage and the two separated phases for selected samples were identified using gas-liquid chromatography (GLC). The methyl esters of the samples were analyzed using a Varian 3700 gas chromatograph (Varian Associates, Palo Alto, CA) with dual flame ionization detection. The column was 6 ft. stainless steel, tubing 1/4″ internal diameter, packed with 20% diethylene glycol succinate on 60–80 chromosorb W. The following were the main analytical conditions: Column temperature, 195°C; injection tempera-

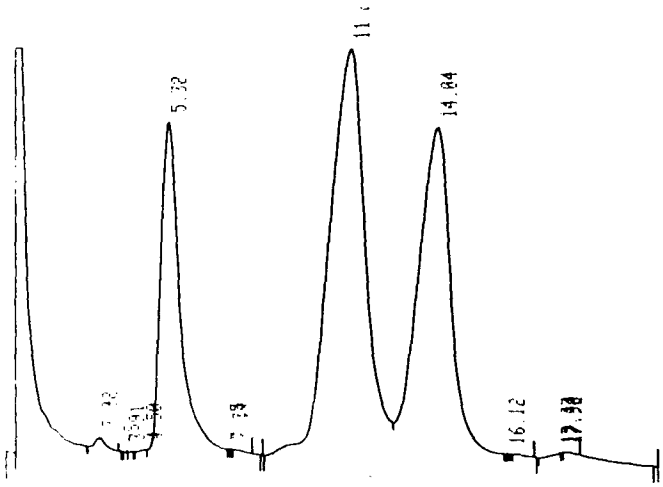

FIG 1. Gas-chromatographic chart of original sample.

ture, 220°C; detector temperature, 300°C; carrier-gas (He) flow rate, 30 mL/min; hydrogen flow rate, 30 mL/min; air flow rate, 300 mL/min; and attenuation, 8–32.

The qualitative analysis was done using pure esterified samples of palmitic, oleic and linoleic acids. The quantitative analysis was carried out using the peak area technique, which was calculated by the computer system attached to the gas-liquid chromatography apparatus.

RESULTS AND DISCUSSIONS

The recovery of the crude oil as free fatty acids from saponification stage amounts to 85% wt. The balance consists of phosphatides, sterols, resins, waxes and color bodies. The gas chromatogram of the original sample is represented in Figure 1. The equivalent amount of each acid was calculated from the corresponding ester, convert by the relation:

$$g\ acid = ester\ \% \times (acid\ mol.\ wt./ester\ mol.\ wt.)$$

The percentage of the individual acids was then determined from these data. The results of these calculations showed the following composition: palmitic acid, 20.2%; oleic acid, 45.9%; and linoleic acid, 33.5%, with minor constituents—myristic, stearic and linolenic acids, corresponding to 0.4%. Therefore, their value could be neglected in all subsequent calculations.

Figures 2 and 3 illustrate the change in weight of solid phase (saturated fatty acid, SFA) and liquid phase (unsaturated fatty acid, USFA), respectively, with change of solvent to oil ratio. The influence of the solvent amount on the separation is very pronounced. It is characterized by a sharp decrease in saturated acids accompanied by a corresponding increase in unsaturated acids. After reaching a certain minimum at about 3:1 ratio, in the solid phase, agreeing with maximum increase in the liquid phase, this trend shows no deviation with higher ratios. These facts indicate that, at lower solvent to oil ratio, excess unsaturated acids are retained in the pore structure of the crystallized phase, resulting in a deficiency of the separation process. This was confirmed by the determination of the IV for each sample, as illustrated in Table 1.

Even though we notice a decrease in the IV with respect to the saturated phase, accompanied by its increase with respect to the unsaturated phase, *i.e.*, more satisfactory separation, the cost limitation of the use of high concentration of solvent favors the 3:1 solvent to oil ratio as the optimum condition for extraction.

The calculated amounts of saturated and unsaturated acids, based on the chromatographic analysis of samples, corresponding to the above solvent to solute ratio, are represented in Table 2. Identification of the

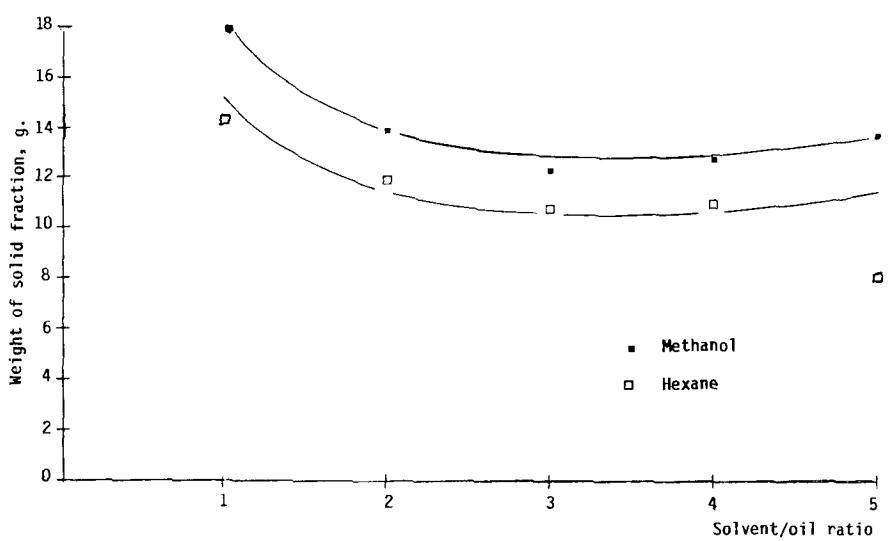

FIG. 2. Weight of solid phase vs. solvent to oil ratio.

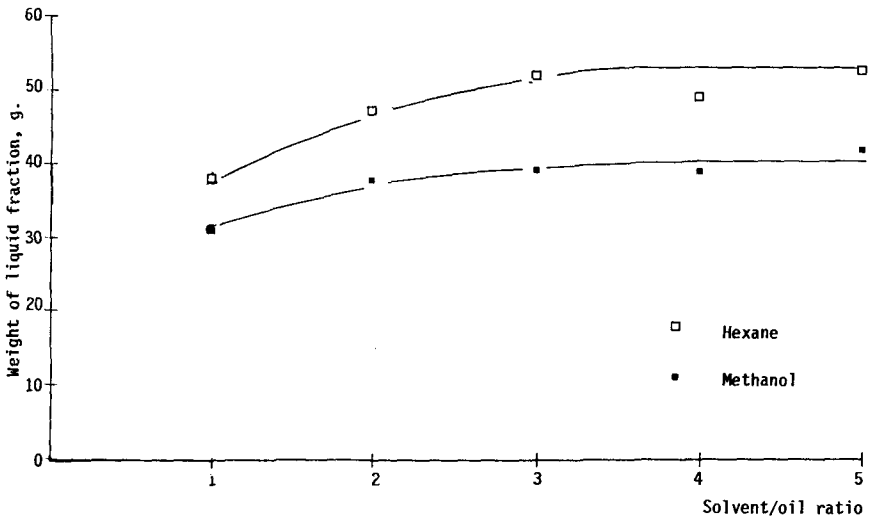

FIG. 3. Weight of liquid phase vs. solvent to oil ratio.

TABLE 1

Iodine Value of Saturated and Unsaturated Fatty Acids at Different Proportions of Solvent to Oil

	Hexane:solvent/oil					Methanol:solvent/oil				
Iodine value	1	2	3	4	5	1	2	3	4	5
Saturated acid (palmitic)	34	35	20	—	15	79	78	81	—	33
Unsaturated acids (oleic and linoleic)	100	110	142	—	152	116	115	130	160	—

TABLE 2

Saturated and Unsaturated Acids for the Two Stages of Extraction

	Hexane		Methanol	
Stage no.	Saturated (S) phase, g	Unsaturated (US) phase, g	Saturated (S) phase, g	Unsaturated (US) phase, g
1	3.2 (S acid) 1.7 (US acid)	38.3 (US acid) 6.8 (S acid)	2.4 (S acid) 4.0 (US acid)	36.0 (US acid) 7.6 (S acid)
2	6.5 (S acid) 4.0 (US acid)	35.5 (US acid) 3.5 (S acid)	5.4 (S acid) 7.6 (US acid)	31.4 (US acid) 5.4 (S acid)

TABLE 3

Acids Recovery Percentage and its Purity Percentage

	Hexane		Methanol	
Acid	Recovery %	Purity %	Recovery %	Purity %
Saturated (palmitic)	65.0	59.0	54.0	41.5
Unsaturated (oleic and linoleic)	88.8	91.0	78.8	84.8

chemical constitutions of the different products by GLC (Table 3) proved that the percent yield and purity of solid product (palmitic acid) is about 65% and 59%, respectively, with lower IV indicating lower content of unsaturated fatty acids. The percent yield of the liquified product, *i.e.*, oleic and linoleic acids, characterized by its high degree of unsaturation as indicated by its IV is about 88.9% with 91% purity.

An insight into the differences between the use of hexane and methanol as solvent can be obtained by noting that minimum recoveries of solid fractions are directly coupled to maximum recoveries of liquid fractions, and vice-versa in the case of hexane and methanol separation, respectively. Another difference is that, for methanol, multi-extraction steps could be used. Moreover, the use of hexane will possibly be superior to methanol, because crystalline acids are formed at a temperature of +5°C, compared to that at −15°C as in the case of methanol. Thus, lower energy consumption would be required.

Proposed integrated process. By incorporating the present work with processes described previously, it is now possible to completely utilize this by-product to obtain useful and profitable products. For example, by chilling and centrifuging the crude oil, an assay fraction is recommended which can be purified to produce waxes (4). The de-waxed oil can be utilized as an antifoam agent (5) or fractionated as described here to produce saturated and unsaturated fatty acids.

It is worth noting that different products, which are essential chemicals for many industries, could be obtained by rice bran oil processing. Therefore, the rice bran oil, locally produced as a nonedible waste product, has proved to have potential for production of a wide variety of products.

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