STUDIES ON THE CHEMICAL REFINING OF CRUDE RICE BRAN OIL

By

Mohamed Hamdy Taha Abou El - Fotouh

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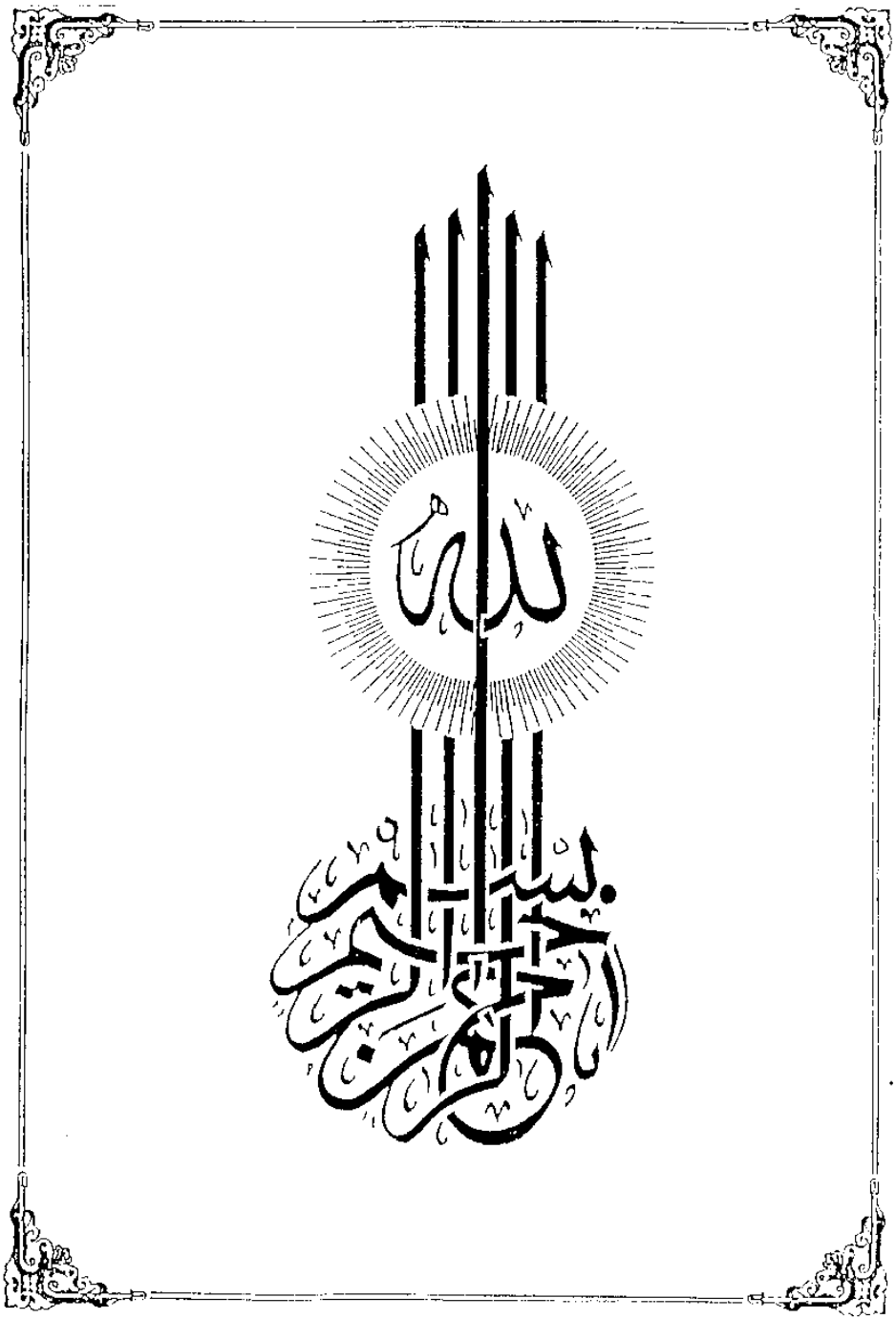

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CONTENTS

1. INTRODUCTION

The oil industry stands today as one of the most important food industries in Egypt, although the yield of vegetable oils is far from being sufficient for local consumption. Cottonseed oil is still considered, the main source of edible vegetable oils, and undoubtedly the road is quite open for cultivation and production of other oily seeds besides the fact that extensive research is unquestionably needed in that direction.

Rice milling progressed considerably in recent years due to the continuous increase in the areas cultivated with rice especially after construction of the High Dam. Rice bran is an important by-product of rice milling industry where 10 million tons of rice could yield approximately one million tons of bran annually which in turn could be a source of 100000 tons crude oil. The keeping quality of the oil in rice bran is improved when the oil is extracted immediately since the oil deteriorates very quickly, on account of the unusually active lipase in the bran and subsequently becomes rancid in a considerably short time. Such a situation necessitated the extraction of the oil from the bran in the shortest possible time.

The rice bran oil produced locally is highly acidic and could not be refined by the usual alkali refining method since such a process is accompanied by a great loss in yield

and subsequently the refining process is impractical and far from being economical. In addition, the locally produced crude rice bran oil did not find its way easily or successfully in soap manufacturing for many reasons related to the inferior qualities of the resulting soap.

It is apparent from such an information that a quick and a satisfactory method is needed to save the oil from becoming rancid and converting it into a reasonably useful form. In other words, the proper chemical refining of rice bran oil will undoubtedly produce larger quantities of edible rice bran oil, about 100,000 tons annually, and such a quantity could serve a great deal in supplying the market where there is always an exceedingly high demand for vegetable oils.

The present investigation represents a study of rice bran oil from the standpoint of refining with the hope of developing a suitable technique to obtain edible rice bran oil from the bran. The most common method, employed to remove the acidity of vegetable edible oils, is the alkali refining process. The alkali refining involves the treatment of the crude oil with caustic soda in a amount equivalent to the free fatty acids, and such a process is usually accompanied with a considerable loss in the yield of the refined oil equivalent to 2 to 3 times the amount of free fatty acids orginally

present in the oil. The nutritional value of any edible vegetable oil stresses on complete absence of free fatty acids. The present dissertation deals primarily with the various aspects related to refining of rice bran oil and the possible isolation of an edible oil from such a by-product which is usually neglected in rice milling industry.

11. REVIEW OF LITERATURE

The refining process of crude vegetable oils is quite complicated and various workers tackled the problem from various angles since it is directly related to the economical value of the oil in question. The purpose of such a refining process involves the separation of various contaminants of the oil with the object of preparing the oil in a form suitable for human consumption.

The literature dealing with the subject is presented under different headings to point out clearly the relationship between refining and the contaminants of the oil.

(1) Extraction of wax from crude rice bran oil:

The separation of wax from crude rice bran oil attracted the attention of several research workers in the field of oil chemistry.

Tsuchiya (1948) obtained the pure wax by filtering, washing the crude waxes three times with methanol and then three times with acetone followed by rewashing with ether and finally with chloroform.

Nishimura (1949), obtained the best yield of waxes from crude rice bran oil at 20 - 25°C by filtering rice bran oil in unglazed porcelain cylinders covered with filter cloth under suction at 50 mm.

Marumo (1953), dewaxed crude rice bran oil by mixing it with 5 parts of 10% calcium chloride solution and the mixture was then centrifuged. The dewaxed oil represents almost 75% of the original crude rice bran oil.

George et al (1953), separated gums and waxes from rice bran oil by mixing the bran oil with water, after which the mixture was gently heated, agitated, cooled slowly and centrifuged. The resulting sludge was mixed with a gelatin solution and heated to 200°F. and then recentrifuged to obtain the crude dewaxed rice bran oil.

Kitsuta (1953), indicated that waxes could be extracted from crude oil with benzene.

Tarayama and Kanji (1953), treated crude rice bran oil with ethylene trichloride and methanol at 40°C., and after cooling at 0°C, crystals of waxes floated and separated by filter pressing technique.

Misonou et al (1957), mentioned that waxes could be extracted from rice bran oil with 2-propanol because waxes are sparingly soluble in this solvent at room temperature while glycerides and fatty acids were soluble. The gummy substances in the crude oil were allowed to settle below 70°C.

Feuge and Cousins (1957), used acetone for the extraction of waxes from the crude oil or its sludge.

Yamauuta and Tei (1957), cooled the crude rice bran oil below 20°C and the waxes that separated were purified by dissolving in acetone followed by evaporation of the solvent at a temperature below the melting point of waxes.

Sugata (1958), separated waxes from the sludge of rice bran oil by mixing with 5 - 10% of its weight of water and heating to 70°C. to facilitate the separation of the wax in plate-crystal sheped forms. The separated oily waxes were mixed with two to four times their weight of 2-propanol and filtered. The filtrate was distilled to separate dewaxed rice bran oil.

(2) Bleaching of acidic rice bran oil:

Bleaching of acidic rice bran oil is quite important to convert the dark crude oil to a yellowish green color.

The A.O.C.S. official method (1950) of bleaching crude vegetable oils involved the use of bleaching earth in sufficient amounts for decolorization i.e 4%. The mixture is thoroughly mixed at about 250 ± 10 r.p.m. and heated immediatly to 120°C for not more than 50 minutes. The mixture was filtered through dry filter paper and the product was entirely clear.

Cocks and Rede (1962), suggested a method for bleaching highly acidic oils (e.g. rice bran oil) by introducing carbon dioxide on the surface of the oil (200 gm.) and heating at 70°C with continuous stirring. Heating was stopped followed by addition of the proper quantity of the bleaching agent and the mixture was shaken gently until the powder became submerged. After replacing the lid, carbon dioxide was introduced with stirring and the temperature was raised to 100°C in about 5 minutes with continuous stirring for 30 minutes. The mixture was allowed to cool to 90°C followed by filtering through a Buchner funnel.

Rice bran oil is reported by the same authors (1962) to exhibit the following characteristics, specific gravity at 25°C 0.9160 - 0.9610, refractive index at 25°C 1.470 - 1.473, iodine number 99 - 108, saponification number 181 - 189, unsaponifiable matter % 3 - 5, titer, °C 24 - 28, and acid value 4 - 120. Rice bran oil containes 15 - 20% of saturated and 80 - 85% of unsaturated fatty acid, distributed as follows: myristic 0.4 - 1%; palmitic 12 - 18%; stearic 1 - 3%; C_{20} - C_{22} saturated 1%; oleic 40 - 50%; linoleic 29 - 42%; linolenic tr. - 1%; palmitoic 0.2 - 0.4%.

Kenzo Yokochi (1972), bleached rice bran oil with phosphoric acid (0.02 - 0.05%) added to dehydrated oil at

35 - 40°C. After stirring for 30 minutes, activated clay (2%) was added and stirred under vaccum. When the temperature reached 80°C, more active clay (2 - 3%) was added. The temperature was raised further under vacuum. When the temperature reached 80°C, more active clay (2 - 3%) was added. The temperature was raised further under vacuum to 120 - 150°C with stirring before being passed through a filter press.

3) Esterification of acidic rice bran oil:

A variety and range of conditions were described for esterification of glycerol with higher fatty acids, but a few kinetic investigations were conducted to study the rate of such reactions.

Stager and Van Loon (1927), esterified dry glycerol with the theoretical quantity of petroselinic acid and 2% of powdered zinc as a catalyst. The reaction mixture was maintained at 180°C. under a partial vacuum while a stream of carbon dioxide was passed through to provide agitation and to assist in removing water formed during esterification. After 5 hours, the acid value did not suffer any further decrease.

Garner (1928) obtained nearly the theoretical yields of homotriglycerides by heating fatty acids and glycerol at 200°C. in the presence of carbon dioxide.