

THE USE OF HYDROGENATED FISH OIL TO EXTEND VEGETABLE OIL¹

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SUMMARY

During the last four years, national production of fish oil has increased appreciably due to the expansion of the "reduction" industries (fish flour). Nevertheless, this production is almost totally destined to industrial use (lubricants, tannery, etc.). In contrast, some countries like Japan, Canada and Peru have been using oil from different fish species for human consumption.

In view of the above, the objectives of the present work were: first, to establish the experimental conditions for obtention of a hydrogenated fish oil and second, the formulation of fish and vegetable oil mixtures for use in the food industry.

The methodology followed comprised: 1) characterization of crude fish oil through physical and chemical analysis; 2) adaptation of the vegetable oil refining procedures to fish oil, and 3) development of fish oil with vegetable oils. A hydrogenated fish oil with a melting point of 36°C, iodine index of 80, and lovibond color, yellow 20, red 13, was produced.

Based on the results of the sensory test, the possibility of using up to 30% extension of this oil with vegetable oils for frying, and up to 50% extension for baking, without affecting acceptability of product, was established.

INTRODUCTION

In Mexico, as in other countries, the production of oleaginous seeds and edible vegetable oils varies as a result of seasonal changes, field conditions, market prices and industrial storage possibilities (1). Self-sufficiency has not been achieved and oleaginous seeds have to be imported at a high

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cost. It was therefore considered that the use of locally available raw materials for edible oil production could be advantageous.

Countries such as Japan, Norway and Peru, which also need to increase their edible oil production, are processing significant amounts of oils from marine species (1-3). This product is then mixed with vegetable oils to extend the available amount. In Mexico, a similar system could be applied. During the last 10 years, fish oil production has increased considerably (from 1,500 ton in 1976 to around 12,000 ton in 1986). This increase is a result of the increased demand for fish flour in the animal food industry (4). Nevertheless, the oil byproduct has so far been used for industrial purposes, as lubricating grease and for soap manufacture (5). It is important, therefore, to explore its possible uses in the food industry.

Marine oils which contain a large variety of fatty acids are obtained principally from herring, sardine, pilchard, menhaden and whale. Their exact composition varies widely, depending on the season, type of nourishment and reproductive cycle, as well as the capture zone of the different species (6). These differences in composition have little effect on the energy value of the product. The fatty acids are highly unsaturated and oxidize rapidly, producing disagreeable fishy flavors and odors (7-9). However, they become relatively stable upon hydrogenation and develop a characteristic sweet odor and flavor which are removed during subsequent deodorization (10-12). The objectives of the study herein described were, therefore, to develop a process for obtaining fish fat with a melting point of 35-50°C and an iodine index of 50-90, and to use this oil as extender of vegetable oil for its utilization for frying, and in bread production.

MATERIAL AND METHODS

A. Experimental

- *Characterization of the fish oil and vegetable fat* — Physical and chemical tests were performed on "sardine oil" donated by the "Asociación de Productores de Harina del Pacífico, A. C.", and vegetable fat from Anderson Clayton obtained in a supermarket in Mexico City.
- *Crude fish oil processing* — A procedure, similar to the one employed in the edible vegetable oil and fat industry was used (13), but in order to adapt it to the fish sample the following conditions were included:
 - a) In the *bleaching phase*, two activated carbon concentrations (3 and 5% in relation to oil weight) were employed along with a constant temperature of 105°C for 15 minutes.
 - b) In the *hydrogenation phase*, 150 and 200°C temperatures and nickel rod catalyst concentration of 0.1, 0.2, 0.4 and 0.6% were used. Two reaction periods of 4 and 8 hr were also included, maintaining the hydrogen pressure at 2.8 kg/cm².

- *Formulation of fish and vegetable fat mixtures* — The hydrogenated fish oil was heated to 55°C and then mixed with 0.05% commercial antioxidants (BHT) (12). The product was then mixed with vegetable fat in the following proportions:

Mixture 1: 50:50 fish oil to vegetable fat

Mixture 2: 30:70 fish oil to vegetable fat

Mixture 3: 10:90 fish oil to vegetable fat

The mixtures were then cooled to room temperature and stored for three days to allow the formation of a more stable crystalline structure (13 - 15) before being evaluated.

- *Physical, chemical and sensory evaluation of fish oil and mixtures* — Evaluation by physical and chemical procedures, plus sensory tests were undertaken as a last step, as follows:

B. Methods

- *Physical methods* — Humidity and volatile material were determined by the AOCS evaporation method (16), and insoluble impurities detected with hexane and petroleum ether (17). Lovibond color (18), melting point using the capillary tube method (19) and smoke point (20) determinations were also performed.
- *Chemical methods* — Acidity (21), non-saponifiable material and the saponification index (22) were determined. For the iodine index, Wij's procedure (23) was followed. The peroxide value (24-26) was determined on samples stored at room temperature (approximately 20°C) for periods of 7, 10, 15 and 30 days and 4 months.
- *Sensory tests* — To establish acceptability of the fish oil and its mixtures, as compared to that of vegetable oil, two types of products were prepared: a sponge cake, and a fried product containing mainly "tortillas". The preparations were evaluated by two groups of untrained judges, one group formed by 41 and another group by 49 persons. The odor, flavor and acceptability of the products were evaluated in questionnaires on a scale of 1 to 7 (27-30). The data were finally submitted to analysis of variance and Duncan's test (31).

RESULTS AND DISCUSSION

The characteristics of this crude fish oil product compared to those of other oils such as anchovy and sardine oils are very similar (Table 1). An important observation was the high iodine index of these samples, indicative of a high degree of unsaturation.

During processing of the fish oil, significant bleaching was obtained using activated carbon, especially with the 5% addition. Quantitative color determinations confirmed visual observations. Yellow-colored units diminished 25 and 42.5% for the 3 and 5% additions, respectively, and red-colored units decreased 94 and 96%. Reduction in the blue-colored units was 100% in both cases.

TABLE 1
 PHYSICAL AND CHEMICAL CHARACTERISTICS OF SOME CRUDE
 FISH OILS

	Fish ¹	Sardine ²	Anchovy ²
Humidity and volatile matter	0.16	—	—
Humidity and impurities, o/o	—	—	0.5 Maximum
Acidity (oleic acid), o/o	1.68	0.1 — 13	1 Maximum
Impurities, o/o	0.04	—	—
Unsaponifiable matter, o/o	1.40	0.5 — 2.0	3 Maximum
Iodine content	194	160 — 194	196 — 198.5
Lovibond color ³	40YW 28R 3B	—	—
Gardner color	—	—	9 Maximum

- 1 Fish oil — raw material used in the present investigation.
- 2 Data obtained from Fineberg, H. & A. G. Johanson. Industrial use of fish oils. In: *Fish Oils*. M. E. Stansby (Ed.). Westport, Conn., The Avi Publishing Co., Inc., 1967, p. 225.
- 3 YW = Yellow; R = Red; B = Blue.

During hydrogenation, iodine value decreased as the reaction period increased. In tests conducted at 200°C, the decrease in iodine value became more apparent as the catalyst concentration was increased. Nevertheless, at 150°C, the decrease in iodine value was greatest with the 0.4% catalyst concentration. In both cases, however, the hydrogenation rate reached its highest during the first four hours of the reaction. As Figure 1 shows, with constant catalyst concentrations and reaction times, the hydrogenation rate was proportional to the temperature. The optimal conditions for fish oil hydrogenation were a 0.4% nickel-rod catalyst concentration, a 200°C temperature and a minimum reaction period of four hours. The product obtained was a plastic fat, that is, a deformable non-flowable soft grease. The objectionable odor of crude fish oil was replaced by a sweet smell. During deodorization, the FFA content (expressed as oleic acid) was reduced to 5% and the sweet smell acquired during hydrogenation was replaced by a neutral odor. The flow diagram for the obtention of fish fat is shown in Figure 2.

With regard to oxidation during storage (Figure 3), the rate was greater in all samples during the first 60 days. This corresponds to the propagation period during which free radicals become oxidized. After this period, the oxidation rate was almost constant in all samples. During the 120-day test period, no unpleasant odors were detected in the fish fat, or in the 30 and 50% mixtures. A slight rancid smell, however, was detected in the vegetable fat and in the 10% fish-fat mixture. This may be a result of the high peroxide value detected in the vegetable fat when tests were initiated. When the peroxide value was less than 2.5 mEq/kg of fat, sensory characteristics were not altered, but with values of 3.75 mEq/kg, rancidity was detected in all cases.

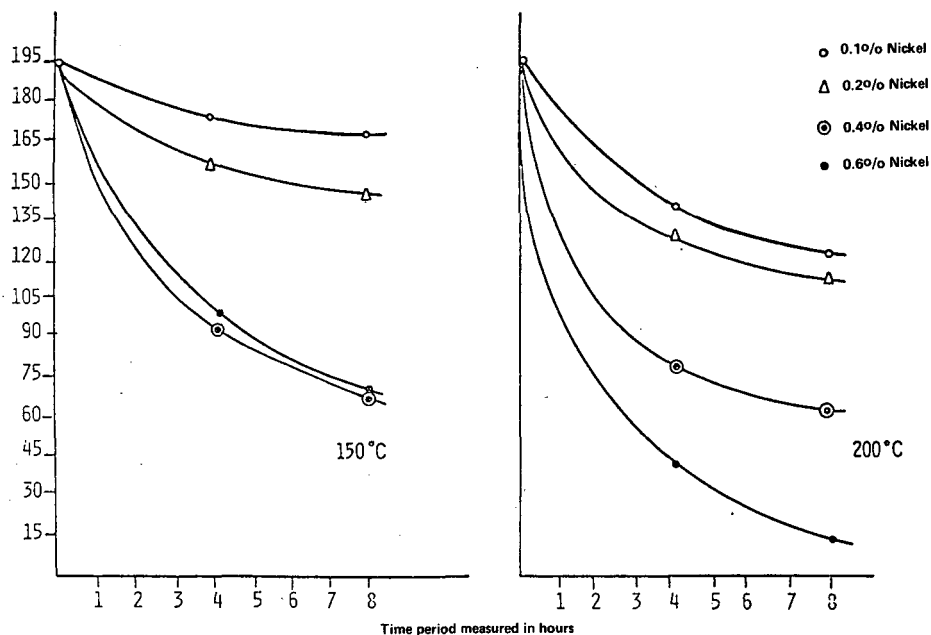


FIGURE 1

Temperature effect of the catalyst concentration and speed time for fish oil hydrogenation (Pressure: 2.8 kg/cm^2)

Sensory analysis of the baked products prepared with each mixture revealed no significant difference at the 95% level in any of the characteristics analyzed compared to those of the vegetable fat. Only 100% fish fat showed a significant difference. Tortilla fritters prepared with the 10 and 30% fish-fat mixtures were undistinguishable from those prepared with vegetable fat. Those prepared with 50 and 100% fish fat were unacceptable.

On the basis of our findings, we concluded that fish oil can be processed under the conditions laid out in this article, and extended with vegetable fat to form a product stable for at least four months at room temperature. Extensions of up to 50% for baking purposes and up to 30% for frying, are completely acceptable and undistinguishable from commercial, 100% vegetable fat.

We consider, however, that industrialization of food industry sub-products in Mexico requires more development to fully exploit the potential available.

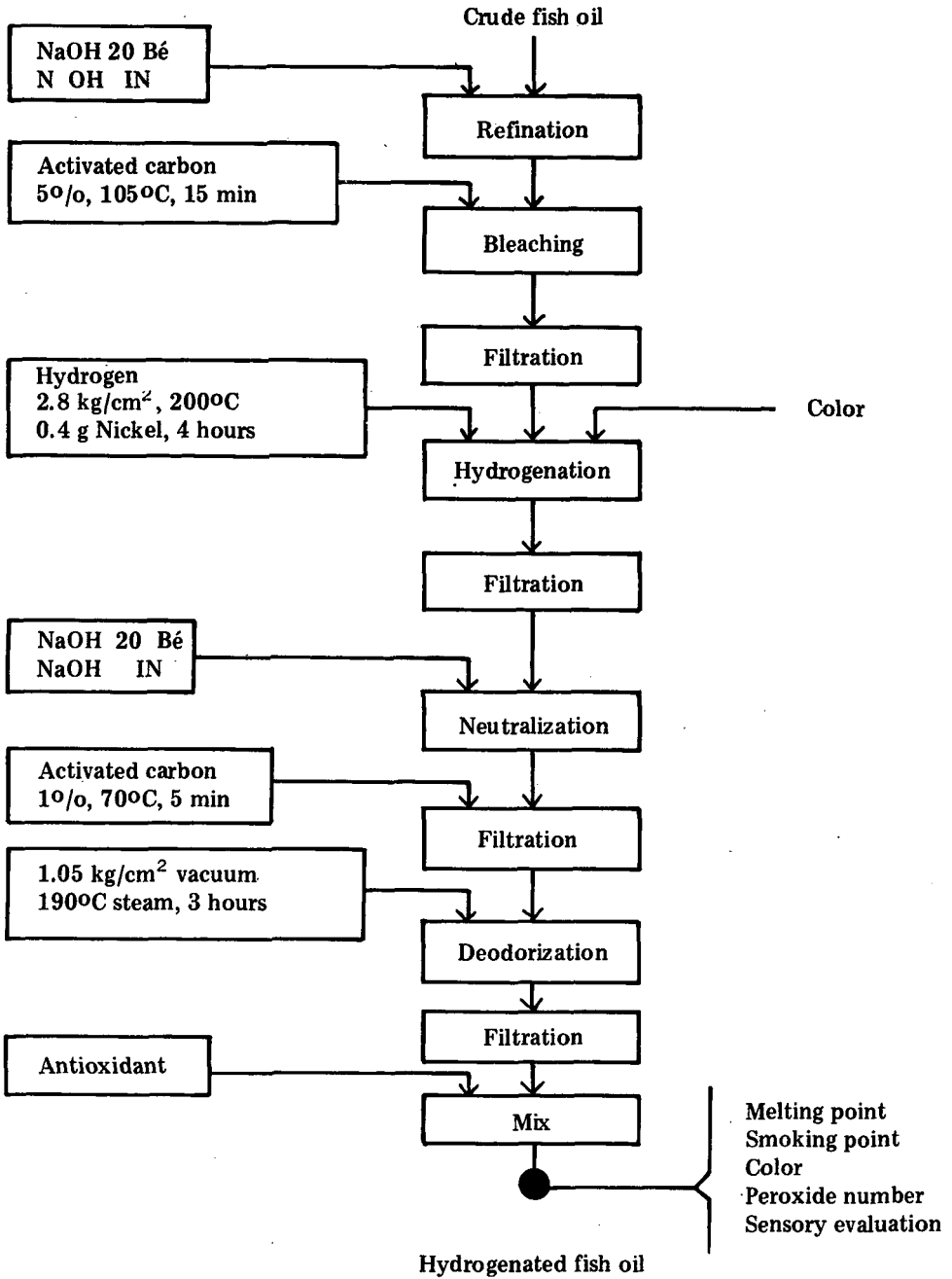


FIGURE 2

Procedure for the obtention of a hydrogenated fish oil

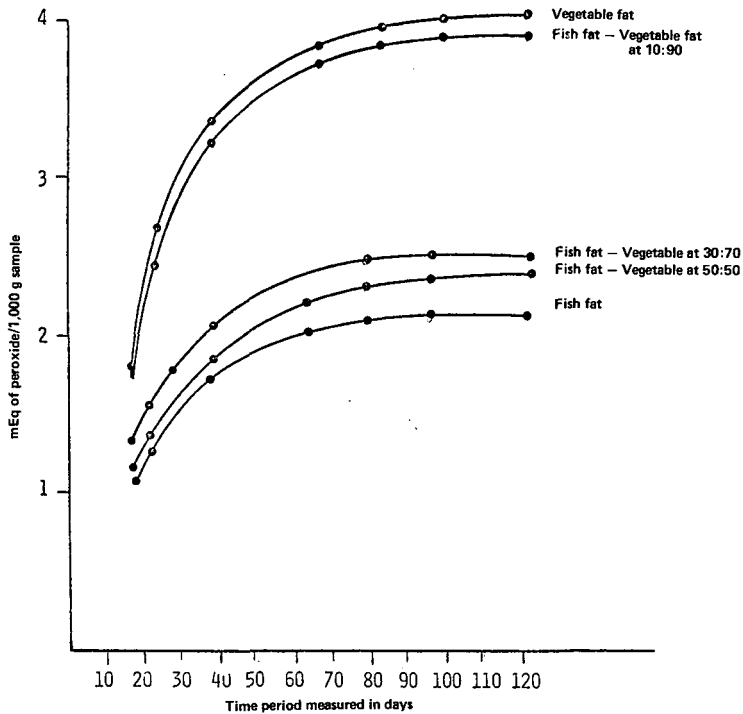


FIGURE 3

Stability for fish fat and its mixtures which lead to rancidity by oxidation

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RESUMEN

EL USO DE ACEITE HIDROGENADO DE PESCADO COMO EXTENSOR DE ACEITE VEGETAL

La producción nacional de aceite de pescado ha aumentado en forma sensible en los últimos cuatro años, en virtud de la expansión de las industrias de "reducción" (harina de pescado). Sin embargo, esta producción se destina, casi en su totalidad, a

usos industriales (lubricantes, curtiduría, etc.). Algunos países como Japón, Canadá y Perú han venido utilizando el aceite de pescado de diversas especies para consumo humano.

En vista de lo expuesto, los objetivos del presente trabajo fueron: primero, establecer las condiciones experimentales para obtener una grasa hidrogenada de pescado y segundo, formular mezclas de ésta con grasas vegetales para su utilización en la industria alimentaria.

La metodología comprende lo siguiente: 1) Caracterización del aceite crudo de pescado mediante análisis físicos y químicos; 2) adaptación del proceso de refinación de aceites vegetales al aceite de pescado y 3) elaboración de mezclas de grasa de pescado con grasas vegetales. Se obtuvo una grasa hidrogenada de pescado con punto de fusión 36°C, índice de yodo 80; punto de humeo 248°C, color lovibond, 20 amarillo y 1.3 rojo.

A partir de los resultados de las pruebas sensoriales, se estableció la posibilidad de utilizar una grasa vegetal "extendida" con grasa de pescado en un 30% para frituras, y en un 50% para productos de panificación.

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