

IAFMM

FISH OIL BULLETIN

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THE QUALITY, PROCESSING & USAGE OF FISH OIL FOR EDIBLE PURPOSES

This paper is written from the oil user's point of view. The manufacturer of edible fat products in Europe has a considerable variety of raw material oils for his purpose. The choice is governed by the following factors:-

- product specification e.g. all vegetable
- product use
- price of raw materials
- product quality or grade
- restrictions imposed by legislation

By making full use of the properties of individual oils, a considerable degree of interchangeability of oil types is available to the manufacturer. Fish oil is of particular importance because of its price advantage in normal circumstances compared with vegetable oils, and because of its special properties which will be discussed

later. The use of fish oil is, however, limited by its quality, which must therefore be dealt with first.

1. QUALITY

1.1 General

Because fish oils contain polyenoic acids of a higher degree of unsaturation than vegetable oils they are, apart from their pharmaceutical uses which will not be dealt with in this paper, always used in the hydrogenated form. In this state they are comparable in oxidative stability with the hydrogenated products of the more highly unsaturated vegetable oils e.g. soyabean, rapeseed, sunflower oils.

The quality problems of fish oil result from the handling and storage of the raw material, the fish, the method and equipment used for oil extraction and the storage and handling of the oil prior to refining and hydrogenation. Basically the same factors affect the quality of vegetable oils, but with fish oil the raw fish can pass on more impurities to the oil, and the content of more highly unsaturated polyenoic acids makes the fish oil more susceptible to deterioration.

The refiner is interested in quality from two aspects. The first is the consistent production of a bland oil with good shelf life and light in colour. The second is the minimising of production costs e.g. low losses, low chemicals usage including hydrogenation catalyst, and low cycle time due to ease of treatment. To achieve a specified product quality at a minimum cost, quality assurance tests are carried out on the crude oil.

1.2 Quality Assurance

Bearing in mind the above aims, the refiner's quality assessment testing has to be broad because no one or two tests will give him all the information required to optimise the refining procedure. The test methods are therefore often divided into two groups, the first being applied on receipt of a consignment to check the fundamental parameters, and the second deeper examination as soon as possible thereafter but in any case before the oil is used in the refinery. The purpose of this second examination is to determine refining procedures, build up statistical information for quality assessment and, if necessary, to establish grounds for a claim that the oil is not of good merchantable quality. If possible, shipments should be segregated to prevent contamination of a good oil with one of poor quality and to permit "first in - first out" usage or controlled blending on the basis of test results.

The initial testing involves the following:-

Moisture: for contractual reasons and because moisture in the oil leads to the formation of rust in storage tanks with consequent accelerated oxidation of the oil catalysed by iron. Thus high moisture may be a contributory cause of high oxidation levels and a high trace iron content, which can also lead to colour problems in refining. Moisture in the oil is also responsible for the increase of free fatty acids (FFA) during storage.

Dirt: usually only visually, unless excessive.

Appearance: Lovibond colour has not been found to be useful, but a golden brown oil is usually easy to refine whereas a dull brown oil gives difficulties. A frothiness can indicate a high phosphorus content and thus a tendency to emulsification problems.

F.F.A.: for contractual reasons and because this is still the most reliable parameter for oil quality and yield assessment.

Soap: to check that the oil is not a blend of neutralised and crude oils.

Iodine Value (I.V.): for hydrogen usage and to ensure that the I.V. is in the region expected for the type of oil stated although these limits are very wide.

The second examination should include:-

Peroxide Value (P.V.), Anisidine Value (A.V.): to establish primary and secondary oxidation product levels. These compounds with others resulting from further decomposition are responsible for the hardening flavour. Of the two values the A.V. is the more indicative of quality state.

Ultra Violet (U.V.) Extinction Values at 233 and 269 n.m.: these figures quantify the conjugated dienes and trienes respectively, and are related to oxidation levels, but increases in these values are also obtained when an oil is overheated, resulting in colour fixation.

Trace Metals, Iron and Copper: both metals are pro-oxidants, that is catalysts for fat oxidation, copper being ten times more active than iron. It is, however, unusual to find high copper levels, but high iron levels occur all too frequently. A further problem with iron is that when sulphur is also present a darkening of the oil colour frequently occurs during deodorisation. The trace metal level can be reduced using acids such as phosphoric and citric in the refining.

Sulphur: the effect of sulphur as a catalyst poison is recognised but the poisoning effect depends on the chemical form in which the sulphur is present, and this is not as yet fully understood. All that can be said is that below 30 ppm in the crude oil (15 ppm in the neutralised oil) sulphur is not a problem, but that a significant poisoning effect is often encountered at higher levels.

Phosphorus: phosphorus is present in fish oil as phosphatides which are emulsifiers. These should be substantially removed from the oil by washing and/or phosphoric acid treatment prior to caustic soda refining so as to improve yields of neutral oil. The phosphorus content must be determined so as to calculate the required amount of phosphoric acid used to denature the phosphatides. The black residue which results from the treatment cokes the insides of solid bowl centrifuges and incomplete "degumming", as the reaction is known, can give separation difficulties when the soap-stock is split with sulphuric acid.

"Standard" Hydrogenation Test: this test is the definitive test for the forecasting of plant hydrogenation performance but, as can be seen from the above, it does not give all the information needed by the refiner to produce a high quality oil at optimum cost for that oil. Other catalyst poisons exist e.g. chlorine, bromine, iodine, which cannot easily be determined in a works laboratory and for this reason the hydrogenation test should be carried out in addition to the sulphur determination. (Update Note February 1983. At the time of writing there is no national or international Standard Test Procedure for the hydrogenation test but individual refiners/hydrogenators have their own internal "standard" methods).

The chromatographic loss test is useful for predicting a budget yield for a particular shipment, but it does not give the refiner the information he needs for optimising his processes and a budget yield can quite easily be worked out from the results of the tests mentioned.

The unsaponifiable matter determination in itself is of no great help apart from a high figure raising doubts about possible mineral oil contamination. Little is known about the quality effects of non-glyceride components of oils or of their degradation products and thus the content in the oil of these chemicals taken as a group is practically without value.

From the tests which have been recommended, a set of values can be stated which helps to assess the quality of a particular oil. These do not form a specification, but one can state that problems can be expected if the oil has one or two parameters with results outside those given. For example, in the following figures unadulterated crude oils with ffa's of less than 4% have normally

been processed without trouble, whereas over 4% problems can be expected with bleaching or hydrogenation due to general deterioration of the oil.

The following can therefore be called refiners' quality assurance figures for fish oil:

% Moisture			0.3% maximum
% Suspended Solids			0.1% maximum
% FFA			4.0% maximum
Peroxide Value (m. equivs/Kg)			6.0 maximum
Anisidine Value			12.0 maximum
U.V. Extinction	E	1% 233 nm 1 cm	10.0 maximum
	E	1% 269 nm 1 cm	4.0 maximum
Iron Content			1.5 ppm max
Copper Content			0.2 ppm max
Sulphur (Crude oil			30.0 ppm max
(Neutralised oil			15.0 ppm max
Phosphorus			0.02% maximum

(Update note February 1983. The above figures were compiled from experience with northern hemisphere industrial oils having iodine values of about 150 and below. Recent experience, however, with oils of iodine value 180-200 has indicated that the values given are also of the right order of magnitude for the latter oils at the point of production).

2. PROCESSING

2.1 Refining

Advances in analytical methods and, in particular, the development of more sensitive analytical instruments enable the oils and fats chemist to check the effect of refining treatments and chemicals more specifically on individual impurities or classes of impurities.

In recent years there have been no fundamental changes in techniques or chemicals, but rather the development of existing ones. Thus the use of phosphoric acid remains the principal tool for the denaturing and removal from the oil phase of non-hydratable phosphatides, but improvements in analytical techniques have resulted in the development of more efficient mixing techniques to effect a higher level of removal from the oil phase thus enabling higher yields of neutral oil to be obtained during caustic soda refining. In this manner phosphorus levels can usually be reduced to about 1 ppm after neutralisation and bleaching.

In the case of poor quality oils a water or brine wash followed preferably by centrifugal separation is needed to hydrate and remove from the oil mucilaginous material which would otherwise adversely affect the yield from the subsequent phosphoric acid/caustic soda treatments.

Fatty acids and some pigments are still removed from fish oil primarily by caustic soda in either batch, semi-continuous or fully continuous plants. Physical refining, that is the removal of fatty acids by distillation, is unlikely to become widely accepted for fish oil because of the wide fluctuations of quality of the oil, and the difficulty of removal of such impurities as sulphur, phosphatides, halogens and trace metals to a satisfactory level prior to distillation. If these impurities remain in the oil at the time of distillation, the high temperatures employed (250°C) result in colour deterioration and fixation.

Trace metals are removed to a large extent by the phosphoric acid used primarily for degumming, and by bleaching earth. Removal is not total. In bad cases citric acid is used in conjunction with highly activated earths, but in such cases the refiner's aim of iron less than 0.15 ppm and copper less than 0.05 ppm is still rarely achieved with consequently poor oxidative stability of the final oil.

Sulphur levels are normally reduced by about 25% during neutralisation and by a similar amount during bleaching. Halogens are only slightly affected by both treatments. The only effective method currently known for the removal of these two impurities is adsorption on a used nickel catalyst, but this is expensive and rarely used in practice.

Oxidation levels are not affected by neutralisation, but bleaching converts peroxides to aldehydes and ketones thus reducing the P.V. to zero but increasing the A.V. It is these secondary oxidation products which are thought to be eventually responsible for the hardening flavour which is caused by the presence in the oil of such aldehydes as 6-nonenal and 2-trans-nonenal.

2.2 Hydrogenation

Batch hydrogenation and supported nickel catalysts are still favoured against continuous plant and copper or other heterogeneous or homogeneous catalysts for edible oil hydrogenation.

Recent plant developments have concentrated on increased efficiency measured by batch cycle time and energy conservation, and on automation. The latter is effected by hydrogen flow measurement under closely controlled autoclave conditions. In-line measurement of density, iodine value and refractive index is also being tried out but so far without much success.

To prevent the formation of carcinogenic polycyclic ring structures at the onset of the hydrogenation of fish oil, the reaction is begun at 150/160°C and the temperature is then allowed to rise to the normal 180/200°C.

Catalyst improvements in activity and selectivity have resulted from a better understanding of reaction centres in the catalyst particle. Filterability has also been improved.

2.3 Post-refining

In most modern plants the post-refining of hardened fish oil now consists of treatment with citric acid solution, drying, bleaching with activated earth and filtration. This is usually referred to as "white" filtration as distinct from the "black" filtration when the catalyst is removed, and should follow immediately after the nickel removal. The citric acid is used to split nickel soaps and to cause most of the nickel and other trace metals to be adsorbed by the bleaching earth.

The free fatty acids, about 0.2 to 0.4%, are removed together with the volatile aldehydes and ketones in a semi-continuous or fully continuous deodoriser at 220 to 250°C.

2.4 Interesterification

This process will be mentioned later in the paper under "Developments". Nature attaches fatty acids to glycerol by what is known as a "natural" rather than by a mathematically random arrangement. Certain chemicals, sodium methoxide and ethoxide, sodium metal and sodium/potassium alloy, can be used to bring about a randomisation of the fatty acid distribution of the glycerides in either a single fat or blend of oils and fats, thus effecting considerable changes in the physical properties of the fat or blend e.g. in the dilatation curve. Hardened fish oil can be so treated in blends such as to widen its usage.

2.5 Fractionation

Soyabean oil, like fish oil, does not possess good oxidative stability in its natural "soft" state. To improve this stability for use in salad oils, soyabean oil is lightly hydrogenated to an I.V. of 105/110 and is then fractionally crystallised to give a liquid oil of acceptable cold test and considerably improved shelf-life. The same can be done with fish oil hardened under conditions of maximum selectivity to a similar iodine value.

3. USE OF HYDROGENATED FISH OILS IN FOODS

3.1 Crystallisation

Glycerides may be liquid or solid at normal temperatures, depending on the character and the siting of the fatty acid radicals in the glyceride molecule. When the glycerides are solid they are polymorphic, that is to say, they can exist in more than one crystalline form, some of which are relatively unstable. In general, one form is more stable than the others, although not necessarily the same form for each class of glyceride.

By means of X-Ray diffraction three distinct crystallisation patterns have been identified in glycerides and fats and named alpha (α) beta (β) and beta prime (β^1). The alpha form is the lowest melting of the three and is unstable, changing to the β or β^1 form depending on which of these two is the stable form for the particular mixture of tryglycerides.

The desirable characteristics of margarines and shortenings are smoothness and plasticity, and are described by β^1 crystallisation. It can be seen from the following table that hardened fish oils crystallise in the β^1 form and therefore influence any blends of which they form part to crystallise also in that form, thus giving the desired characteristics to the product.

CLASSIFICATION OF FATS AND OILS ACCORDING TO CRYSTAL HABIT

Beta Type	Beta Prime Type
Soyabean	Cottonseed
Safflower	Palm
Sunflower	Tallow
Sesame	Herring
Peanut	Menhaden
Corn	Whale
Canbra	Rapeseed
Olive	
Coconut	Milk fat (butter oil)
Palm Kernel	
Lard	Modified lard
Cocoa Butter	

Source: JAOCS 1978, 55 (11), 823 - 829

Fats having β crystal forming habit can be crystallised in the β^1 form by suitable crystallisation techniques, but they remain unstable in the latter form, and under storage conditions may revert to the stable β form in which the product has a sandy texture.

A further advantage of hardened fish oil is its speed of crystallisation which is appreciably faster than palm oil, lard and hardened soyabean oil. This property simplifies the plant requirements and process control for blends containing a high level of hardened fish oil.

The crystal lattice obtained with tubular-chilled high hardened fish oil blends has particularly good creaming qualities i.e. air incorporation properties. Such products give high quality cakes and are widely used for this purpose even when a premium has to be paid for them.

3.2 Hydrogenated Fish Oils

Individual hardened fish oils and their uses are as follows:

(melting points are given as a range in °C e.g. 30/32)

HFO 30/32 : I.V. 85

Dilatation at 20°C (D20) = 600 mm³/25 gms

Although a HFO 25/27 was made some years ago in Norway, it is believed that the HFO 30/32 is the lowest melting product currently used in Europe. Because of its high I.V. it is inherently less stable to oxidation than the more usual HFO 33/35. HFO 30/32 is therefore only used when soft oils e.g. soyabean are expensive. In these cases the soft oil component of a blend can be considerably reduced e.g. 30% to 10%, or removed entirely.

HFO 33/35 : I.V. 75

D 20, 850

This is the most commonly used melting point. It is much valued as a "middle-melting" component of margarine and shortening blends due to its steep dilation curve, which, when shortenings with a longer plastic range are wanted, can be modified by the addition of a higher melting fat (40/42, 46/48 or tallow). Some blends contain up to 80% of this melting point.

HFO 46/48 : I.V. 35

D 20, 1650

This fat is used as the high melting component in industrial margarines and shortenings to give improved "body" or longer plastic range. It has a flat dilatation curve (solid fat curve) having a D 40 of about 950. Depending upon the purpose of the product up to 60% of the HFO 46/48 may be used. In table margarines because of the poor "mouth-feel" it imparts to the product its use is limited to about 5% and then usually only in summer.

HFO 36/38 : I.V. 65
D 20, 1200

HFO 40/42 : I.V. 55
D 20, 1500

The above are intermediate melting products used by some manufacturers to simplify blends and by others because of the "palate-cling" and poor nutritional properties of the relatively highly saturated 46/48 product.

3.3 Products

3.3.1 Margarines

Table Margarines: The use of hardened fish oil is limited to those not specified as being "all vegetable" and, in certain countries, to an amount such that the docosenoic acid (C22 monoene) content of the oil blend is not more than an agreed or legislated percentage of the total fatty acids, usually 5 or 10%. In such blending, notice must be taken of the docosenoic acid (erucic acid) input of rapeseed oil. However, due to the now widespread use of so-called "zero erucic acid" rapeseed oil, this is usually negligible, but the legislation or agreement still limits the inclusion of HFO to 25% or higher depending on its C22 monoene content.

HFO 30/32 and 33/35 are very suitable for both refrigerator and packet table margarines and are used at up to 70% of the oil blend. In the later stages of the life of the product the "hardening" flavour can be detected to a varied extent, depending on the quality of the starting oil.

Cake/Creaming Margarines

These margarines are required to give good air incorporation into the cake batter or cream, so that the product shall have a good volume and "light" texture. It has been found that a wide spectrum of triglyceride types helps to produce this effect. Hardened fish oil has such a spectrum as a result of the wide variety of fatty acids, ranging from C14 to C24, of which it is composed.

The quantities of the various hardened fish oils in the oil blend are altered depending upon the dilatation or solid fat index specifications of the margarine required. Up to 80% of hardened fish oil can be used.

The use of hardened fish oil in these margarines is limited by the preference in certain countries for all-vegetable products and, particularly when used for the production of synthetic creams, by the sensitivity of the product to the development of off-flavours.

Pastry Margarines : A plastic but tough product is needed in this case. To achieve this texture a flatter dilatation curve is used with a higher percentage of solid fat at bakery and mixing equipment temperatures (30 to 35°C). The fat blend melting point varies appreciably from country to country depending on local preference and ambient temperature.

The plasticity of this product is improved when a blend having a wide spread of triglyceride types is used. About 60% of HFO can be used but in this case it is all 46/48 or 40/42 or a mixture of 46/48 and 33/35.

3.3.2 Shortenings

These are 100% fat products which are blended and processed according to the use for which they are intended. The value of hardened fish oil lies in its creaming power e.g. for cake making, and therefore it is heavily used (up to 70% of 33/35) in premium products for this purpose. It is also used in "pumpable" shortenings, which are tanker loads of products normally supplied in cartons, but not in "liquid" shortenings.

Biscuit fats are not required to produce good air incorporation and so hardened fish oil is used to a lesser extent and dependent on competing oil prices. The same applies to fats used for pie crusts.

Hardened fish oil is also used in the cheaper varieties of ice cream fats. Again its dilatation curve is very suitable for this purpose at a melting point of 33/35°C and in consequence it is used to 80% of the oil blend. Flavour reversion is however a particular problem in this case.

3.3.3 Other uses

Bread Fats/Emulsions: Fat is used in bread recipes to give a moister crumb and better anti-staling properties. Usually lard is used for this purpose but, with the advent of modern dough mixing machines, a fat with more body at 35°C was required. To achieve this about 30% of HFO 46/48 can be used in admixture with, for example, beef tallow. The emulsions are cheaper versions of the same product. HFO 33/35 is also used as a bread fat.

Emulsifiers: These are prepared from various fatty raw materials including lard, palm oil, hardened soyabean oil and hardened fish oil. Two types of emulsifier for which hardened fish oil is used are low melting (ca 35°C) mono-diglycerides and polyglycerol esters of fatty acids. These compounds are used in the food industry to improve air incorporation e.g. in shortenings, whipped creams and ice cream.

4. DEVELOPMENT

4.1 Quality

The first priority in development work should be the investigation of the source and nature of impurities in the crude oil such that attention can then be turned to their reduction at source or during processing and their elimination during refining, prior to hardening.

4.2 Selective Hydrogenation

Although much work has been carried out on this subject, particularly using copper catalysts, it is worthy of continued research. The target should be a product equivalent to palm olein with a melting point not higher than 25°C and a D 20 of maximum 200. The success of such a project would be dependent on the removal of catalyst poisons before hydrogenation.

4.3 Selective Hydrogenation/Fractionation

This subject was discussed briefly under (2.5) above. It is a method of widening the use of fish oil but it is expensive and would be unlikely to find widespread use except in developing countries with a local fishing/fish oil industry and a shortage of hard currency which necessitated import substitution, or in a general shortage of vegetable soft oils such as occurred in 1974. The fractionation of hardened fish oil has been carried out on a production scale.

4.4 Ghee Substitute

Some developing countries in the Middle East are in the situation mentioned in (4.3) and have little or no other native supplies of oil bearing materials. It has been shown on a laboratory scale that a satisfactory ghee substitute can be produced from a blend of 80% HFO 40/42 and 20% palm oil. This subject is worthy of further attention.

4.5 Interesterification

The use of this process has been primarily confined to vegetable oils as reported in the literature, but certain work has also been carried out using hardened fish oil. Two areas of interest are the production of confectionery hard butters for coating or coverage use, and the formulation of margarine blends particularly those with high contents of polyunsaturated fatty acids.

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