9. Fish Oil and Human Health

Jeyakumari A., L. Narasimha Murthy, Laly, S. J. and Abhay Kumar

Mumbai Research Centre of ICAR- Central Institute of Fisheries Technology, CIDCO Admin Building, Sector I, Vashi, Navi Mumbai, Maharashtra – 400 703

Introduction

Fish is a richest source of two essential fatty acids like α- linolenic acid (ALA) and linoleic acid. α- linolenic acid is an omega (ω) – 3 fatty acid whereas linoleic acid is an ω – 6 fatty acid . Fish is also a richest source of two pharmaceutically important ω – 3 fatty acids like eicosapentaenoic acid (EPA) and docosahexaenoic (DHA). Oil-rich fish, such as salmon, trout, mackerel, herring and sardines, are an excellent source of Omega-3 fatty acids, which are essential to our diet. Eating oil-rich fish provides the Omega-3 fatty acids needed for the body. Omega-3 oils from fish have a lowering effect on blood fats. This decreases the chance of the blood vessels clogging with cholesterol. Omega-3 can also make blood less "sticky", and it therefore flows more easily around the body. This can reduce the risk of a heart attack. They also help to reduce blood pressure a little and keep the heart beat steady. Omega-3 oil in fish can reduce the risk of dying from heart attacks. Schizophrenia symptoms can be eliminated or at least vastly diminished by oral supplementation with EPA. DHA is the building block of human brain tissue and is particularly abundant in the grey matter of the brain and the retina. Low levels of DHA have been associated with depression, memory loss, dementia and visual problems.

Fish oil: Fish oil can be extracted from whole fish and liver. Fish oil extracted from both resources has industrial and medicinal uses. Details

are given below;

Fish body oil

Fish body oils are usually produced during the wet reduction process. The press liquor is the oil-water emulsion containing dissolved proteins and other substances as well as particulate matter. The press liquor is passed through a series of settling tanks or a series of centrifuges. The amount of particulate matter depends on the degree of cooking, condition of the fish when processed and also the manner of pressing. Cooking is an important step because, if the cooking time and temperature is too low, the fluids (oil + water) will not be released from the protein and pressing out will be difficult. If the material is overcooked, the fish will become a soft mush and there will be an insufficient build-up of pressure in the press to expel the liquids.

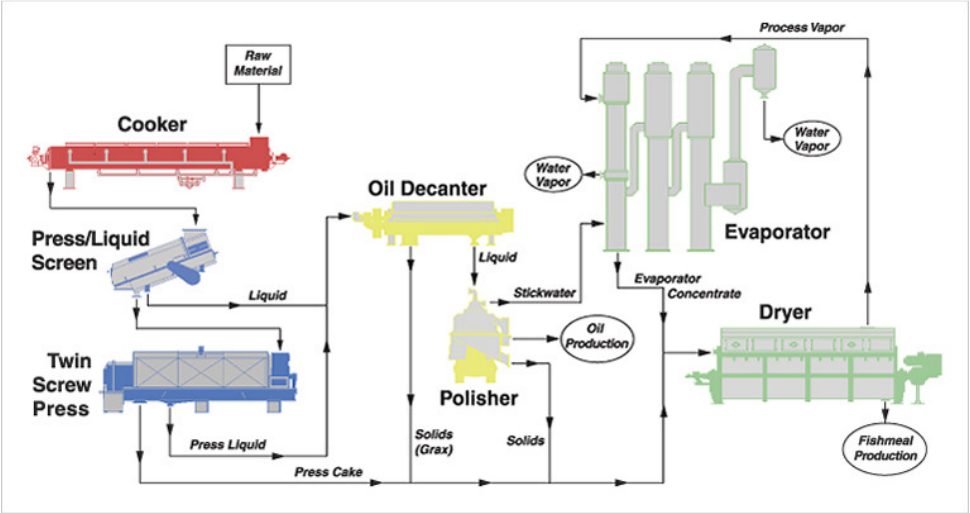

Fig.1. Process flow diagram for fish meal and fish oil production

Extraction by settling tank system

The settling tanks are heated to assist break up of the emulsion and prevent solidification of the stearin portion of the liquids. In a series of five or more

heated tanks the press liquor is admitted to the first at a point below the surface. Oil rises to the top and is passed to the bottom of the second tank containing water and the process is repeated in succeeding tanks. Finally oil is heated to evaporate the remaining water

Centrifuge system of extracting fish body oil

In this system, centrifuge is heated and water phase is spun off and almost clean oil is obtained. Further to get clean bright oil, oil is heated to about 94 degree, mixed with clean water of same temperature and passed to the polishing centrifuge. Oil produced through centrifuge system is finer, cleaner and brighter and has lower moisture content than oil from a settling tank system. Oil produced by pressing in dry reduction process is dark in colour due to contact with the metal surfaces and of poor quality.

Purification of Fish oil

The process is also known as hardening of oil. Crude oil has number of impurities such as free fatty acids, phospholipids, diglycerides, monoglycerides, pigments, pigment decomposition products, oxidation products, sulphur compounds, proteinaceous compounds, aldehydes, ketones, pesticides residues (preferably organochlorine pesticides and polychlorinated biphenyls accumulate in fatty fish species which are generally used for fish oil production. As lipophilic compounds these molecules tend to be sequestered in lipid rich tissues and finally find place in the fish oil. Fish oil may be contaminated with toxic heavy metals (such as Cd, Hg, Pb, Cu, Zn, etc. Cu and Zn are known for their distinct pro-oxidant effect. Spoiled raw material is responsible for the increased level of FFA, oxidative products and increased level of nitrogen and sulphur by

protein degradation and increased metal contents. Oil extracted from spoiled fish is discoloured and brown and foul smelling not characteristic of fish oil. The refining is done in following five steps:

Refining

Treatment of temperature oil with an aqueous alkaline solution which reacts with the free fatty acids to form soaps and remove any mucilages.

Bleaching

Bleaching materials commonly used are natural or activated clays and activated carbon. It removes any coloured matter, natural pigments and some of the suspended mucilages. These adsorbent substances are also effective in the reduction of oxidation products, phosphorus, to a lesser extent sulphur compounds and heavy metals and non metals.

Hydrogenation

It is the process by which hydrogen is added directly to the unsaturated bonds in the fatty acid chain. Gaseous hydrogen, liquid oil and solid catalyst are brought into intimate contact at an elevated temperature (usually 170 – 204^0 C) under a suitable pressure of hydrogen. The catalyst commonly employed is nickel, which is prepared in suspension and normally added to the oil at a level of 0.05 % to 0.1 %. When hydrogenation reach the desired point, the gas is turned off and the oil is cooled down rapidly. Lastly oil is filtered to remove catalyst. Hydrogenation process cannot be advocated where aim is to have an oil as the source of PUFAs, particularly those belonging to omega-3 family.

Further refining

It is the process of second refining of oil before deodourization, to improve

flavour stability

Deodourization

It is done by steam distillation under high vacuum (2 – 5 mm absolute pressure). Dry steam (free from oxygen and temperature range 170 – 230^{0}C) is used, which is passed through the oil under vacuum for prolonged period (may be upto 5 h in a batch process). This step removes free fatty acids, decomposition products of hydroperoxides such as aldehydes and ketones, odouriferous and other volatile impurities. This step is very critical one. If time and temperature are not strictly controlled as per schedule, the most valued components of the fish oil undergo distinct deterioration. Extended exposure of α-linolenic acid at a temp of 250^0 C produces geometric isomers. EPA and DHA are more susceptible to isomerisation. When retention of EPA and DHA are the concern then a temperature not exceeding 170^0 C is recommended.

Bleaching with silica gel

As an alternative to activated clay and carbon, the treatment of fish oil dissolved in hexane with silica gel gives a nearly colourless oil. It has been presumed that mono- and di-glycerides are the sources of odour and are retained in the silica gel.

Winterisation

It is a cold clearing process, additional operation for refining fish oil. When the oil is cooled sufficiently, the saturated triglycerides (have high melting points) commence to solidify and separate out. Solid fraction is designated as 'stearine'. Cooling must be gradual by circulating cold brine. Sudden chilling (or shock chilling) is to be avoided. The process is terminated when

temp of oil start rising due to release of latent heat as a result of crystallization of saturated glycerides

Preservation and storage of Fish oil

- Deterioration of fish oil results from the development of free fatty acids and oxidative rancidity
- Hydrolytic rancidity is caused by lipases present in the oil by contaminating microorganisms
- Oxidative rancidity is caused by atmospheric oxygen and lipoxygenases present in the fish or contaminating microorganisms
- Flavour reversion also takes place due to oxidation

Deterioration of fish oil can be avoided by

- ✓ Controlled heating to 80 – 100 degree for 15 – 20 min
- ✓ By adding antioxidants
- ✓ By halogenation
- ✓ Storing under inert gas such as nitrogen

Use of Fish body oil

- Unlike vegetable margarines, fish margarines have an excellent plastic consistency
- Fish oils can be used in manufacture of rubber, detergents, lubricants, printing inks, leather and cosmetics.
- Fish oil can be used in animal feed as carriers for the oil soluble vitamin A and D

Fish liver oil

Fish liver oils are an important source of vitamin A and D. Two most important sources of liver oils are cod and halibut (both are cold water

species). Other sources are tunas and allied species and some sharks. Although tuna's liver is small in comparison to its body weight but its oil is rich in vitamin A & D. The vitamin contents of shark liver vary greatly. Certain varieties such as tiger shark, black fin shark, hammer headed shark and saw fish are commercially important. The oil content is upto 80% of the liver. With decreasing fat content the colour of the liver changes from yellow to brown and texture from soft to firm. Presently shark liver is valued for highest unsaponifiable matter (squalene) which is present in the liver of certain deep sea sharks. Depending on the oil content and vitamin A potency, fish livers are generally classified into:

- ✓ Low oil content ---------- high vitamin A potency
- ✓ High oil content ---------- low vitamin A potency
- ✓ High oil content ---------- high vitamin A potency.

Methods of preservation of Livers for oil extraction

- By freezing : 0 – 5^0C for 24 h/ at -18^0C for several months
- By salting: 10% salt with pieces of liver
- By formalin treatment: 0.25% by weight
- By alkali treatment:
    - ✓ In soln. of 2%Na_2CO_3 & 2& germicide (formaldehyde, phenol, resorcinol, cresol or alcohol)
    - ✓ By soda ash and sodium nitrate: 3% (by vol.) of soln. containing 9 parts soda ash & 1 part $NaNO_3$

Oil extraction

- **High oil-low vitamin A livers**: Livers are cooked directly or indirectly that results thermal rupture of the cells and releases the oil.
- **Low oil-high vitamin A livers/ High oil-high vitamin A livers**: Hence steaming will not release the oil without degradation of vitamin A, protein is digested and solubilized to release the enclosed oil and vit A or a solvent is used to extract oil.

Alkali such as NaOH (@1-2% by weight) or Na_2CO_3 is mixed with the ground liver and heated to 80-90^0 C by live steam with stirring. The digested liquor is centrifuged while hot to separate the oil.

Use of fish liver oil:

Nowadays liver oil is mainly used in the textile and tanning industries and in the production of cosmetics, pharmaceutical products, and lubricants.

Fish oil properties

The oils contain mainly triglycerides of fatty acids (glycerol combined with three similar or different acid molecules) with variable amounts of phospholipids, glycerol ethers and wax esters. It is characteristic of the oils that they contain a wide range of long-chain fatty acids with the number of carbon atoms ranging mainly from 14 to 22, and high degree of reactivity (unsaturation) ranging up to six double bonds per molecule. The complex nature of fish oil depends upon a number of factors. The fatty acid patterns of the oils vary widely with fish species and, to some extent, with the

composition of the plankton and the time of year. These influence the properties of oils both in regard to edible as well as technical applications. The oils contain variable, but small amounts of unsaponifiable components, such as hydrocarbons, fatty alcohols, waxes and ethers, and these also influence the properties of the oils to some extent.

In order to manufacture oil of desirable properties, one should observe the following:

a. the fish should be as fresh as possible;
b. the oil should be cooled before delivery to the storage tank and should be pumped in near the bottom of the tank (not right at the bottom) and removed from the top. The sludge and water should be regularly drained from the bottom to prevent an increase in FFA during storage.

Commercial value of fish oils

The market value of fish oil depends on its chemical analysis. Normally, a basic sales value is established for oil containing a certain level of free fatty acids (2% to 3%), unsaponifiable matter (3.5%), and water and dirt (0.3%). If these levels are exceeded, the price is reduced accordingly. The price may also be reduced if the oil is dark coloured or malodorous.

Standard for Fish Oils (Codex Stan 329-2017)

Fish oils, fish liver oils, concentrated fish oils, and concentrated fish oils ethyl esters shall comply with the following:

- ✓ Acid value ≤ 3 mg KOH/g
- ✓ Peroxide value ≤ 5 milli equivalent of active oxygen/kg oil
- ✓ Anisidine value ≤ 20
- ✓ Total oxidation value (ToTox)[2] ≤ 26

Fish oils with a high phospholipid concentration of 30% or more such as krill oil shall comply with the following:

- ✓ Acid value ≤ 45 mg KOH/g
- ✓ Peroxide value ≤ 5 milli equivalent of active oxygen/kg oil

Vitamins: Fish liver oils except of deep sea shark liver oil shall comply with following;

- ✓ Vitamin A ≥ 40 µg of retinol equivalents/ml of oil
- ✓ Vitamin D ≥ 1.0 µg/ml

The following additives may be used in Fish oil:

Additives	**Additive name**	**Maximum level**
Antioxidant		
E300	Ascorbic acid, L-	GMP
E 304, 305	Ascorbyl esters	2500 mg/kg, as ascorbyl stearate
E307a, b, c	Tocopherols	6000 mg/kg, singly or in combination
Emulsifier		
E322	Lecithin	GMP
E471	Mono- and di-glycerides of fatty acids	GMP