# Recent Accomplishments in the Fish Oil Utilization Program

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THE BUREAU OF COMMERCIAL FISHERIES, with the advice and assistance of the members of the Industrial Products Division of the National Fisheries Institute, four years ago undertook to support a full-scale program of research into the chemistry and technology of domestic fish body oils. The objectives of this program were to supply such basic information as would be necessary for development of new markets for these oils, and to support applied research in possible uses of fish oils which looked promising. These uses, if successfully developed, would give the industry additional market outlets for its product, pending completion of the possibly more rewarding basic research studies.

Such an extensive research program requires justification. Approximately one half of the total poundage of fish annually landed in the United States is destined for industrial usage. Such an important phase of the fishing industry merits research assistance by the Bureau. Further, the foresight of the Bureau and of the industry in supporting research designed to lessen our dependence on a single major outlet has recently been vindicated. The recent formation of the European Common Market may adversely affect our large export of fish oils destined for use in margarine manufacture. Finally, we should point out that any knowledge gained through this program of fish oil oxidation mechanisms would be of inestimable benefit to all phases of the fishing industry. The familiar "rusting" and yellowing of frozen edible fishery products, for example, is just another form of *in situ* oxidation of fish body oils.

The utilization research program is in its fourth year and has been carried out on a national basis at both Bureau laboratories and, by contract, at several research institutions. Foremost among the latter have been the Hormel Institute and the University of California. The basic research aspects of the investigation have been studied from many angles. We are investigating the mechanisms involved in enzymatic and in autoxidation of the oils to find the weak spots where such deterioration takes place and, more important, to determine what we can do to strengthen them. We are taking apart, molecule by molecule, the very complex mixtures that comprise fish oils to study and characterize each molecule through its physical and chemical constants. We are studying, with a view to prevention of their formation, the chemical nature of the volatile degradation products that appear to give fish oil its rather penetrating odor. We are investigating the chemical reactivities of the fatty acids derived from fish oils to determine whether some unique, commercally-desirable compounds may be formed through reactions at the carboxyl groups or at any of the many points of chemical bond unsaturation on the fatty acid molecule. We are testing the fatty acids for their nutritional value, for possible growth promoting effects, for possible physiological value in regard to the so-called essential fatty acid syndrome, and for possible beneficial effects on the serum cholesterol levels in blood. Our applied research efforts have been in the following fields, (1) possible inclusion of fish oils in animal rations as an energy source, (2) possible utilization of fish oils in the preparation of leather, (3) possible utilization of

fish oils in ore-flotation, and (4) possible utilization of fish oils in insecticides.

The present paper is a review of findings to date. The majority of the work mentioned has not been published and while we anticipate no major change in the findings, they are not final.

## Basic Research

### *Characterization of Fish Oil Fatty Acids*

Fish body oils are largely composed of triglycerides. These are molecules composed of three fatty acids linked together by a glycerine molecule. Our first step has been to break down these triglycerides, to release the fatty acids. We then intend to separate out each different fatty acid in chemically pure form for characterization and study. This has been an enormously difficult job, and has through the years discouraged research into fish oil fatty acids. The acids are easily destroyed or altered during fractionation by distillation or other known methods of separation. To complicate the job still more, an acid, in addition to differing in molecular length, may differ also in numbers and placement of points of chemical unsaturation on the molecule. To date, after much effort, we have separated in chemically pure form only two fatty acids. They are the eicosapentaenoic and 4, 7, 10, 13, 16, 19-docosahexaenoic acids. We have these acids under study. We know their characteristic infra-red, and ultra-violet spectra, their boiling and freezing points, and other physical and chemical constants. More important, however, we now have what may be a reproducible, essentially non-destructive, laboratory technique for the isolation of individual fatty acids.

If this is confirmed by work now in progress, we can look forward soon to achieving a full and complete characterization of the fatty acids commonly found in fish oils.

### *Oxidation of Fish Oils*

The Bureau's studies on the problem of oxidation of fish oils, both extracted oils and oils remaining in the fish flesh, have been undertaken from two approaches. The first approach, that of catalytically or enzymatically induced oxidation, has yielded much useful information. We now know, for example, that the hematin in fish meal catalyzes deterioration of the residual oil in the meal and that a similar reaction is involved in the discoloration of canned tuna. We have, in the laboratory, developed techniques to guard against the occurrence of such oxidative deterioration and are now field-testing these techniques.

Our studies in enzymatic oxidation of fish oils indicate these oils to be the main energy source used to spark the metabolic processes of the live fish. No essential differences in form or rate of enzymatic breakdown of mammalian and fish fatty acids have been found. The well-known Beta oxidation and tricarboxyllic acid cycles processes of intermediary metabolism are operative in fishes. These findings are of fundamental importance for an adequate understanding of fish oil deterioration. In this regard, our scientists have compiled and annotated the first authoritative review of the world's literature on intermediary metabolism in fishes. We expect to publish this valuable work in the near future.

The second approach to the study of fish oil oxidation has been primarily through a study of the effects of antioxidants. Much light has been thrown on this controversial subject. The investigations strongly suggest that, to be successful, each antioxidant should be tailored for each specific use to which it is put. The presence of certain natural components in the oil, for example, monoglycerides, tocopherols, free fatty acids, certain organic amines or amino acids, or of metallic impurities can markedly affect, for better or for worse, the efficacy of any particular antioxidant. There is a very strong evidence that a compound which acts as a synergist to one antioxidant may well act as an antagonist to another antioxidant. All of these clues and many others not mentioned here are being fitted into the jigsaw puzzle of autoxidation which we hope to complete. A technique has been developed to detect rapidly and essentially simultaneously metallic impurities in fish oils at levels as low as two to four parts per million parts of oil. Such metallic impurities catalyze the breakdown of the oils. Mixtures of such impurities as cobalt tallate, lead octoate, copper naphthenate, and manganese octoate at levels of four ppm have been detected and characterized in a single sample of oil. A system of column-refinement of the oil to remove such impurities has been developed for use in the laboratory.

### *Nutritional Value of Fish Oils*

The total omission of fats from the diet of humans or animals results in a series of physiological disturbances known, in general, as the "essential fatty acid syndrome." These disturbances may include cessation of growth, breakdown of skin tissue, skin discoloration, etc. To these effects, there has been added the depression of blood-serum cholesterol levels, which are of interest because of possible implication in atherosclerosis therapy.

Inclusion of certain unsaturated fatty acids in the diet dramatically corrects these conditions. Investigations in this field with fatty acids derived from fish oils indicate that a major reassessment of the "essential" fatty acids activity theory may be necessary. Our researchers at Hormel Institute have reported that while fish oil fatty acids do not correct tissue breakdown conditions nor skin discoloration they do promote resumption of growth and do markedly depress blood-serum cholesterol levels. While tissue breakdown and skin discoloration are indices of extreme fatty acid dietary deficiencies, such cases are very rare in the United States. On the other hand, our serum-cholesterol levels, because of United States dietary habits, are sometimes quite high. If the present theory that cholesterol deposits are implicated in atherosclerosis is found to be valid, there is a strong possibility that the use of fish oil derivatives may become of therapeutic interest.

## Applied Research

### *Use of Fish Oils in Ore-Flotation*

Crushed metallic ores are customarily concentrated and enriched by exploiting the different "wetting" capacities of water and of oleic acid. Metals immersed in an oleic acid-water bath are preferentially wetted by the acid. The metals remain suspended in the acid while the useless gangue, wetted by the water, sinks to the bottom of the flotation tank. The acid, carrying with it the enriched metallic particles, is removed for further processing of the particles. Our contractors report that fish oil fractions, with iodine values of between 70

and 140 are excellent flotation agents fully equal to oleic acid now used. A large potential market exists if suitable fractionation of fish oil on an economically competitive basis can be developed.

Later work, undertaken on magnetically enriched low grade Mesabi taconite ores, indicated that the more highly unsaturated fatty acids (IV greater than 140) were extremely effective flotation agents in highly alkaline flotation baths. Under these conditions, acids "wet" and suspend the gangue while the metals sink. Using the combination of magnetic enrichment followed by alkaline flotation, silicate impurities in the ore concentrate have been reduced to as low as two per cent by weight. This "inverted" flotation process is less critically dependent upon the *ph* of the bath, possesses a wider tolerance to the presence of crushed ore "slimes," and owing to the absence of adsorbed fatty acids on the iron oxide, the concentrates so produced are more amenable to the pelleting process used with taconite ores. We will request a public service patent for this newly developed process.

### *Use of Fish Oils in Leather*

Fish body oils have been used only to a very limited extent in leather processing because of a pronounced tendency toward combustion or charring during sulfonation. Also, leather prepared from such oils sometimes was alleged to exhibit "spew" when aged. Our researchers, in the course of a very detailed and authoritative research into the characteristics of fish oil containing leather, both aged and fresh, developed a novel adaptation of the sulfonation process which effectively prevented combustion of the oils. An exhaustive, comparative statistical analysis of controlled routinely prepared leathers and fish body oil containing leathers indicated that no significant differences exist. Both leathers were judged to be excellent.

Since domestic fish body oils are, at present, cheaper than raw oils, there would appear to exist a large potential market for fish body oils in the leather industry. The oil processors, wishing to develop this market, however, must accept the fact that education of the leather manufacturer is necessary and that further unforeseen developmental research may be necessary. A public service patent is being obtained by the Bureau for the newly developed sulfonation procedure. The studies indicated that the use of chemically-saturated oils produced soft leathers while the more unsaturated fish oils produced firm leathers. Again, if an economical system of fractionation of fish oils on the basis of chemical unsaturation can be developed, there exists a strong potential market for fish oils in the manufacture of both soft and firm leathers.

In essence, all of our work has indicated that future studies should be concentrated, to a large extent, on the autoxidation and odor problem. This we feel is the key-log in the log-jam which has held up the commercial exploitation of fish oils. To this end, we have planned to hold a two-day symposium on autoxidation and fish oil odor studies at our Seattle Laboratory during March 1959. We are asking that all technical persons, who are interested in oil utilization, attend the symposium and to bring with them notes and their observations as to the causes and cures of autoxidation and odor-causing deterioration.

We are convinced that industry should now undertake careful studies into the feasibility of further processing of their fish oils into three or more fractions as a function of degree of unsaturation. Such fractions will, undoubtedly, be the

first form of exploitation of fish oils. We cannot undertake this work without unduly dissipating our research effort. We feel it to be more fitting for us to continue our emphasis on the more basic research. We will, of course, do all in our power to assist the industry in establishing commercially feasible fractionation processes.

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# Exploratory Fishing For Sardine-Like Fishes in the Gulf of Mexico

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### *Introduction*

It is convenient, for present purposes, to recognize two fundamental regions in the marine environment, namely, the benthic or bottom region, and the pelagic region comprising everything above the bottom. Each division contains its own unique fauna and, as far as fisheries are concerned, poses its own specific problems.

Present knowledge of bottom fishery resources is fairly well advanced as compared to the pelagic. Modern otter trawling methods have undergone a progressive evolution and now occupy a place of prominence in world fisheries. In the Gulf of Mexico shrimp and ground-fish trawl fisheries are major components of the industry. In addition, oyster, scallop and clam fisheries, and to a large extent, the blue crab fishery are all dependent upon benthic stocks and bottom gear.

Regarding the pelagic division, however, knowledge is less complete. This area may be subdivided into a surface layer and a midwater region, again for convenience.

Most pelagic fisheries now existent depend upon the fauna of the surface layer. In the Gulf purse seining, gill netting, trammel netting, and some beach seining have been carried out in the bays and along the coast line. Menhaden, mullet and Spanish mackerel have been among the principal species sought to date. Sporadic observations of additional life in the surface layer have been made throughout the years on a subjective and more or less hit or miss basis by persons primarily engaged in other pursuits. Lack of adequate gear and methods of coping with the smaller school fish often reported and a lack of market have combined with a low level of interest to prevent progress in this field. The accumulative impact of the reports has, however, resulted in increasing interest in the past few years.

### *Recent Interest in Pelagic Fisheries*

With the increase in overhead and other expense associated with the complexity of large, modern, refrigerated menhaden vessels and gear, this fishery has become interested in increasing its operations, presently occupying the factory equipment for only a few months of the year, to a full time basis. They have, thus, recently been seeking information on school fishes other than menhaden for reduction use in the off season.