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Herring Fish (*Clupea harengus*) Oil Production and Evaluation for Industrial Uses

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It is a well known fact that the lipid (oil) extracted from various fish species can be of industrial benefit if properly extracted and processed. In this study herring fish oil was analyzed using quantitative and qualitative analysis in other to provide an assessment of the quality of the oil for industrial purposes. This work focuses on the production of oil from frozen herring fish (*Clupea harengus*) as the raw material readily available on the market, by evaluating by the oil using chemical and physical analysis and refining the oil by degumming, neutralizing, drying, and decolorizing. The experimental results revealed that the rate of extraction increases with time until maximum extraction took place using an average size of 780 μm. Every 10.64 g of dried sample used has about 4.34 g of oil extracted for five hours. The extracted herring fish oil contains two essential unsaturated fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which could be of great industrial importance.

Keywords Herring, fish oil, *Clupea harengus*, PUFA, EFA, DHA

INTRODUCTION

There is a sizeable and growing world market demand for high quality fish meals and oil, and production can be quite profitable if suitable raw materials are available. Herring and sprat provide the largest single source of raw material in the production of fish meal and oil. They may be classified as fatty although the fat content may vary from 2 to 40% depending on species and season. The food industry handles the product from gutting, filleting, and other fish processing operations with care because these have proven to be a good raw material for fish meal and oil production (Aidos 2002). In this study herring fish was analyzed using different methods of quantitative and qualitative analysis of the lipid in other to provide an assessment of the quality of the oil for industrial purposes. This work focuses on the production of oil from frozen herring fish (*Clupea harengus*) as the raw material that is readily available on the market. Some of the objectives are to evaluate the oil using chemical and physical analysis and to refine the oil by degumming, neutralizing, drying, and decolorizing.

The composition of several fish species varies from season to season due to their natural cycle, maturity, and geographical locations. Herring fish (*Clupea harengus*), being a typical pelagic fatty fish, goes through a natural cycle showing considerable variation in lipid content composition (Hall 1994). The industry takes advantage of this fat by providing typical products such as frozen herring, cured herring, and kippers, which are produced for different times of the year; they are encouraged by health authorities to be consumed as a source of beneficial poly unsaturated fatty acids (PUFAs) (Aidos 2002). During the processing of herring a considerable amount of by-products are originated, which have to be processed further or disposed of. Following successful experience in upgrading herring into stable crude fish oil, good quality fish oil could be produced from stored product (Martins 1994).

Biogenic amine levels have been used as a quality index in fish (Martins 1994). Immediately after capture of the fish, the concentration of endogenous antioxidant substances such as ascorbic acid, glutathione peroxides, and tocophenol in muscle start to decrease continuously with storage time. Simultaneously, there is an increase in levels of oxidative catalytic substances such as low muscular weight and iron with increasing storage time (Aidos 2002). During processing and storage, fish quality may thus decline as a result of several factors, for example, oxidation is promoted by blood. Fatty fish species contain polyunsaturated fatty acids, which are prone to oxidation, producing off flavors and odors (Aidos 2002). Their generation represents a significant quality in loss in PUFA-containing foods.

In recent years, utilization of marine resources for human consumption has increased rapidly worldwide. This has been furthered by recognition of the health benefits of polyunsaturated fatty acids, in particular those of the family that exists

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in a high proportion in fish species with a high fat content. In some fatty fish processing, after the filleting operation a substantial amount of fish and fish leftovers is not used. In a time when depletion of the marine resources has become all too real, there is a clear need for more efficient utilization. A 100% utilization of fish processed for human consumption can be achieved by processing heads, fins, viscera, and so on into fish meal and fish oil. Converting herring products into fish oil is an opportunity to add value to products. Polyunsaturated fatty acids are interesting from a nutritional point of view, but at the same time can adversely affect product sensory quality due to oxidation (Aidos et al. 2002; Rajasilta 1992; Linko et al. 1985).

INDUSTRIAL UTILIZATION AND ECONOMIC IMPORTANCE OF FISH OIL

Fish oil is different from other oils mainly because of the unique variety of fatty acids it contains, including high level of unsaturated fatty acid. In fish oil, the major free fatty acids (FFA) present are eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). Marine oils are an important source of the already synthesized EPA and DHA. There are indication that EPA and DHA exert a positive influence on human health, related to proper neural development, the ability to see and learn, and by modulation of lilosanoids synthesis, decreasing the risk of cardiovascular disease (arteriosclerosis, thrombosis, stroke), cancers, diabetes, depression, immune disorders, and other diseases.

The market for liquid fish oil for human consumption can be divided into three areas: as a pharmaceutical component, as a healthy food component, and as a commodity for the food industry. Fish oil can be an important constituent of aquaculture feeds, contributing essential fatty acids needed by fish for normal growth, health, and reproduction. In principle, fish oil may be used in any food item that contains fat. However, the use of fish oil may result in sensory problems; the products can have a "fishy" taste. Additionally, due to susceptibility of fish oil to oxidation, the shelf life of the product may be seriously reduced (Aidos 2002; IFIO 1986; Alfred and Patrick 1985; Williams 1966; Eckey 1954).

Although the emphasis has been on the marketability of the free fatty acid related health benefits of fish oil, it is known that fish oil and fish liver oil contain other interesting compounds, such as vitamin A and D. With improved separation techniques and more gentle processing methods, these oils might play an even more important role in the pharmaceutical and food industry in the near future (Kelbel et al. 1999; Sargent 1997; Kinsetta 1990; Lee 1990; Jangard 1987; http://www.healthylivingeating.com/health9_newsl_4/healthnews9.htm).

METHODOLOGY

The frozen fish samples were cleaned, dried, and weighed and size reduction was carried out before being transferred into the Soxhlet extraction apparatus for continuous extraction by solvent (petroleum ether) (Macrcic et al. 1993; Treybal 1981; ISO 1988, 1975). The process flow diagram for the extraction is shown in Figure 1.

RESULTS AND DISCUSSION

Tables 1–7 show the results obtained from this research work. Table 1 shows the result of the moisture content present in the herring fish. Oil was extracted from the sample with initial moisture content of 67.1%, which is about 0.7% less than the standard value, which may be as a result of weather changes. The standard value of moisture content in herring fish is 67.8% (Martins 1994). The extraction yield with time for an average particle size of 780×10^{-3} mm is presented in Table 3, is while that of saponification is in Table 4.

The average size of sample used for the extraction was 780 μm, which gave the best oil content for about five hours of extraction. The extraction yields of oil when 10.64 g of

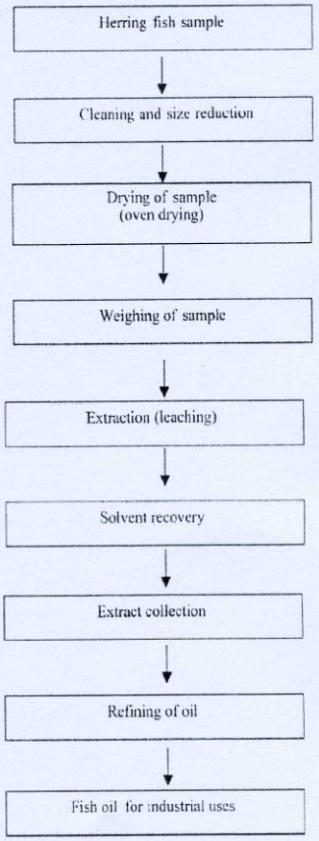

FIG. 1. Extraction process of herring fish (*Clupea harengus*) oil.

TABLE 1
Moisture content at various drying times (1–8 hours drying)

Drying time (h)	Mass of sample before drying (g)	Mass of sample after drying (g)	Percentage moisture content (%)
1	85.80	60.50	29.50
2	60.50	45.83	47.20
3	45.33	33.90	60.50
4	33.90	30.45	64.50
5	30.45	30.05	65.00
6	30.05	29.27	65.90
7	29.27	28.36	67.00
8	28.36	28.22	67.10

dried fish sample was used are: 2.55 g; 3.02 g; 3.62 g; 4.32 g, and 4.34 g from one to five hours (Table 3). The experiment was observed to be in accord with the fact that the higher the time, the more the extraction yield until a greater proportion of the oil was extracted from the fish sample. The percentage oil content from the dried herring fish sample was 40.79% after five hours of extraction, which represent; the percentage of oil left in the dried species. At the same time the fish oil composition of the extracted oil was about 13.42%; this is attributed to the fact that the composition of several fish species varies from season to season due to their natural cycle, maturity state, and geographical location (Aidos 2002). Herring, being a typical pelagic fatty fish, goes through a natural cycle showing considerable variation in lipid content composition (Aidos et al. 2002; Hall 1992; Ackman 1989; Hildrich and Williams 1984). The optimum amount of oil extracted from dried herring fish was 4.34 g for five hours; it was not economical to continue the extraction after this time since the result obtained for four hours was close enough to that of five hours, which means that at this time most of the oil in the fish was extracted.

TABLE 2
Percentage extraction of oil (1–5 hours)

Average size of sample (mm)	Time of extraction (h)	Mass of sample before extraction (g)	Mass of sample after extraction (g)	% of oil extracted
780×10^{-3}	1	10.64	8.09	7.90
780×10^{-3}	2	8.09	7.62	9.40
780×10^{-3}	3	7.62	7.02	11.20
780×10^{-3}	4	7.02	6.32	13.36
780×10^{-3}	5	6.32	6.30	13.42

TABLE 3
Content of oil present in dried fish sample in (%)

Time (h)	Extraction yield of oil (g)	Percentage of oil in dried fish (%)
1	2.55	23.97
2	3.02	28.38
3	3.62	34.02
4	4.32	40.60
5	4.34	40.79

The results of the fish oil analysis are shown in Tables 4, 5, and 6. The obtained saponification value was 1.343, the iodine value was 7.38, the acid value was 2.08, the pH value was 7.01 the refractive index was 1.46, and the specific gravity was 0.92 g/cm^3. The saponification value shows the mean molecular weight of fatty acids present in the oil, which in a saponification process will show the amount of alkaline required in saponifying the oil; this value is of great importance to the soap manufacturing industry. The value obtained was 1.343, which is less than the standard value of 1.36 (ISO 1988a,b, 1978, 1975; IFIO 1986; http://www.members.aol.com/oclainco/soapchart.htm). The deviation of the saponification value may be as a result of experimental error, or seasonal changes and the nature of the habitat where the sample species live. The acid value obtained was 2.08, which is moderate and falls within the standard value range of 0.5–5.0 this implies that the oil could be very reactive with oxygen when exposed to air, forming gum (Aidos 2002).

The iodine value shows the amount of unsaturated fatty acid present in the oil, which is an indicator of the reactivity of the oil. The iodine value obtained was 7.38. The peroxide value shows how stale the oil-bearing sample was; the sample used was a fresh sample from the refrigerator that was dried to remove moisture content, thus the peroxide value obtained was approximately zero since there was no color change, the same as the blank test (the blank test is the test with the absence of the sample, where other reagents are present like the real test). It could be concluded that the sample has negligible peroxide value. The physical characteristic of the oil was neutral with a pH of 7.01, which shows that the oil was neutral after extraction. The test for solubility shows that the oil was soluble only in organic solvent. The test for glycerol shows that the oil contains glycerol, which on heating will give an odor called accrolein (Martins 1994; Fernando and Akuyobi 1987; Gunstone and Norris, 1983; Plummer 1978).

The refractive index obtained was 1.46, which is in accordance with the standard value, which is 1.46 (www.frozenfish.com/pharm.html). The specific gravity obtained was 0.92 g/cm^3, which shows that oil is denser than water at 20°C (www.frozenfish.com/pharm.html). The oil was refined first by degumming to remove substances like phosphate

TABLE 4
Saponification value of fish oil

Mass of sample (g)	1st Titer value HCl vol. ($\times 10^{-3}$)(L)	2nd Titer value HCl vol. ($\times 10^{-3}$)(L)	Mean titer value HCl vol. ($\times 10^{-3}$)(L)	Saponification value
0.28	3.29	3.31	3.30	1.343
Blank test	7.77	7.77	7.77	

TABLE 5
Iodine value of the extracted fish oil

Mass of oil used (g)	1st Titer value $Na_2S_2O_3$ vol. (mL)	2nd Titer value $Na_2S_2O_3$ vol. (mL)	Mean titer value $Na_2S_2O_3$ vol. (mL)	Iodine value
0.4079	0.81	0.80	0.805	7.38
Blank test	24.50	24.50	24.50	

TABLE 6
Acid value of the extracted fish oil

Mass of oil used (g)	1st Titer value KOH vol. (mL)	2nd Titer value KOH vol. (mL)	Mean titer value KOH vol. (mL)	Acid value
0.4079	0.74	0.75	0.745	28.48
Blank test	0.10	0.10	0.10	

TABLE 7
Refining process analysis of the fish oil

Process of refining	Mass of oil before refining (g)	Mass of oil after refining (g)	Material removed from the refined oil
Degumming	15.0	14.60	Phosphate pigment, carbohydrate, protein
Neutralization	14.6	13.40	FFA, phosphate pigment, phospholides pigment, sulfur oil insoluble, water soluble
Drying	13.4	12.00	Water
Decolorizing	12.0	10.64	Pigment, oxidative product, sulfur, traces of soap

pigment, carbohydrate, and protein. It was found that there was about 0.4 g loss in weight from 15 g of oil after the degumming process. The oil was neutralize by removing free fatty acids (FFA), phosphate pigment, phosphotides pigment, sulfur, and others. The oil was reduced from 14.6 g to 13.4 g after the neutralization process. The oil was treated to remove water present in the oil due to the above processes, and a weight of about 1.4 g was removed from the fish oil (Table 7). The last process in refining the oil is the decolorization process where activated charcoal (animal bone) was used to remove the pigment, oxidation product, sulfur, and trace of soap, which causes the dark brown color of the oil. The pH was taken after refining and giving 8.59, which shows that the acid in the oil has been removed, and the oil is now alkaline in nature as a result of the final refining process, which would require further neutralization. The specific gravity reading of 0.918 g/cm^3 was obtained.

CONCLUSION

In this research work, the feasibility of producing quality fish oil from herring fish (*Clupea harengus*) and its evaluation was carried out. The oil extracted from herring fish was

relatively rich in essential polyunsaturated fatty acids such as eicosapentaeonic acid (EPA) and docosahexaenoic acid (DHA) and was relatively stable during storage. In most cases the level of free fatty acid increased over time. The refining procedure was thus a compromise between removing undesirable compounds and keeping beneficial component that might improve the oil quality. The currently obtained knowledge of herring fish oil suggests the possibility of using the oil in industrial-scale production such as the pharmaceutical, soap, and food industries.

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