Mackerel (*Scomber Scrombrus*) Oil Extraction and Evaluation as Raw Materials for Industrial Utilization

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Abstract

The extraction, evaluation and refining of fish oil from mackerel (*scomber scrombrus*) has been conducted in this work. The total percentage oil yield using solvent extraction and total moisture content was 28.24% and 56.50 %respectively, which were found to increase linearly with time. The analytical properties of the crude and the refined oil were evaluated. It was observed that the crude oil consist from: acid value 2.5 mg/KOH, peroxide value 2.19 mEq/kg, saponification value 201.6 mgKOH/g, iodine value 108.09 I_2/100g, specific gravity 0.911, refractive index 1.485 and reddish brown colour. The refined oil was also evaluated as follows: acid value 2.27 mg/KOH, peroxide 1.00 meq/kg, saponification value 147.84 mgKOH/g, iodine value 106.93 I_2 /100g and golden brown colour. These values fall within the acceptable standard values. The refining of the oil brought about a notable improvement in the analytical properties of the oil. Thus, leads to a high quality fish oil in terms of the taste, colour, odours, shelf life and market value. Based on the improved characteristics of the oil, it could be suitable for applications in pharmaceutical and food industries.

Keywords

Mackerel, Scomber Scrumbus, Fish oil

Introduction

Mackerel are long bodies, rather thick appearing fish known as high sea fish. In December 1973, a conclusion was reached by Food and Agriculture Organisation (FAO) Technical conference held in Tokyo that conversion of fish is necessary for prevention of waste while ensuring the beneficial exploitation, which cannot be gainfully used for direct human consumption [1]. This among other things necessitated various researches into the production of fish oil. Apart from its various uses as consumable oils and other beneficial uses, the production of fish oil is necessary in the utilization of those fish species regarded as un-saleable and unpalatable; and those species too small and which quickly turn rancid for economic storage. Fish oil is the lipid fraction extracted from fish and fish by products. *Scombroids* (mackerel) and *clupeids* (herring) provide the largest single source of raw material for production of fish oil and fishmeal. They are regarded as fatty species, having fat content well distributed throughout the body. Generally, fish oils are more complex than land-animal oils or vegetable oils due to long – chain unsaturated fatty acids [2]. Fish oil is considered as liquid oil, but, in fact contains triglycerides of intermediate melting point for the oils to be partially solid at 20°C. Fish oils are unique in the variety of fatty acids of which they composed and their degree of un-saturation [3]. Refined fish oils are rich in polyunsaturated fatty acids of the linolenic acid family. Current medical research suggests that these fatty acids might have a unique role to play in prevention of coronary artery disease and the growth of different types of cancers. The oil is industrially used in leather tanning, production of soap and glycerol, and other products. Presently, the production of fish oil is becoming more demanding, as there is a sizeable and growing world market demand for high quality fish oils. In other to meet the demand of the society there is the need to locate new oil fish and further research to know their characteristics and usefulness. The project is aimed at the solvent extraction of the oil from mackerel (*scomber scombrus*) in relation with time of extraction as the only optimising parameters, while keeping other parameters (e.g. particle sizes, temperature etc.) constant. It also refines the extracted oil and carries out analytical test of the crude and refined oil to ascertain some of its physical and chemical properties. These include the moisture content, appearance, specific gravity and refractive index, iodine value, saponification value, acid value, peroxide value.

Omega–3 Fatty Acids

Omega-3 fatty acids are long chain polyunsaturated fatty acids (18-22 carbon atoms in chain length) with the first of many double bonds beginning with the third carbon atom (when counting from the methyl end of the fatty acid molecule).

Table 1. Average values of the composition of different Fish species

Fish specie	Protein (%)	Fat (%)	Ash (%)	Water (%)
Gadoids (Cod – like Fish)				
Blue whiting, North Sea	17.0	5.0	4.0	75.0
Sprat whiting, Atlantic	16.0	11.0	2.0	71.0
Hake whiting, South African	17.0	2.0	3.0	79.0
Norway Pont	16.0	5.5	3.0	73.0
Clupeids (herring)				
Anchoveta	18.0	6.0	2.5	78.0
Herring (spring)	18.0	8.0	2.0	72.0
Pilchard, south Africa	18.0	9.0	3.0	69.0
Anchovy, south Africa	17.0	10.0	3.0	70.0
Herring, winter	18.20	11.0	2.0	70.0
Scombroids (mackerel)				
Mackerel (spring), North Sea	18.0	5.50	1.60	75.0
Mackerel (Autumn), North sea	15.0	27.0	1.40	56.50
Horse mackerel, North sea	16.0	17.0	3.80	62.70
Horse mackerel, South Africa	17.0	8.0	4.0	72.0
Elasmobranches (sharks and rays)				
Dog – fish	19.0	8.90	2.30	70.0
Salmonoids (salmons and rays)				
Capelin, Norway	14.0	10.0	2.0	75.0

Adapted from Food and Agricultural Organization [1]

Table 2. Substances yielded from the non - triglycerides fraction of fish oils

Vitamins, pigments, other substances
Vitamin A_1 ($C_{20}H_{30}O$) Astacin, red ($C_{40}H_{48}O_4$) Activated 7- dehydrocholesterol($C_{27}H_{44}O$) Vitamin A_2 ($C_{20}H_{28}$) Fucoxanthin, yellow ($C_{42}H_{58}O_6$) Cholesterol ($C_{27}H_{46}O$) (e.g 3% in Atl. Cod) Vitamin D (calciferol) Xanthophyll, yellow ($C_{40}H_{56}O_2$) Lecithin - a mixed triglyceride linked to the chlorine ester of phosphoric acid Vitamin D_1 ($C_{56}H_{88}O_2$) Carothene, red to purple ($C_{40}H_{56}$) Monoglycerides esters Vitamin D_2 (calciferol) Taraxanthin, yellow ($C_{40}H_{56}O_4$) Hydrocarbons (e.g squalene, $C_{30}H_{50}$, α-$C_{28}H_{44}O$) highly saturated hydrocarbon that is often higher than 60% of shark liver oil) Vitamin D_3 ($C_{27}H_{44}O$) Zeaxanthin, yellow ($C_{40}H_{56}O$) Chlorophyll, green ($C_{54\text{-}55}H_{70\text{-}72}MgN_4O_{5\text{-}6}$)

Adapted from Hall [2]

Table 3. Quality specifications of fish oils

Characteristic	Free fatty acid	Moisture content	Un-saponifiable matter	Colour Gardner	Iodine value
Crude	Max. 3%	Max.1%	Max. 2.5%	10	160 - 190
Semi-refined	Max. 0.3%	Max. 0.3%	Max. 1.5%	9	160 - 170

Adapted from www.export-forum.com

It is concentrated throughout the food chain, but is most abundant in the oils of cold-water fish such as mackerel, salmon, sardines, herring and cod. Omega-3 fatty acids can be divided into three main categories – EicosaPentaenoic Acids (EPA), DocosaHexaenoic Acids (DHA) and Alpha-Linolenic Acids; out of which EPA and DHA have the most beneficial effects. EPA and DHA are found mainly in fish oils while Alpha-Linolenic is usually derived from plant sources [4]. However, there is an increase of awareness in the role of omega-3 fatty acids. Omega-3 fatty acids aids in the prevention and management of heart diseases. This can help in reducing one's risk of developing an abnormal heartbeat that can lead to heart problems and even sudden death. Omega-3 prevents asthma, hypertension, diabetes, cancer, and kidney dialysis and tends to inhibit the development or metabolism of these diseases in the body.

Production of Fish Oil

The production of the fish oil deals with the separation of fatty substances (lipids) from other constituents of the fish. Generally, separation starts from the preparation of the raw material up to the purification of the product, which is the final stage of the process. One of the methods used industrially in obtaining fish oil is the batch hydraulic pressing, a process whereby the oil is obtained or expressed by hydraulic pressing from a mass of moderately cooked oil bearing fish samples. A recent development is in the extraction of oil from oil – bearing material using solvent. Solvent extraction, which is also referred to as leaching is a process whereby a soluble constituents present either as a solid or liquid is removed from a solid or from a liquid by the use of solvents [5]. In fact solvent extraction techniques are one of the most commonly used methods of isolating lipids from food samples (e.g. fish) and of determining the total lipid content of foods. The principle is based on the fact that lipids are soluble in organic solvents, but insoluble in water hence providing a convenient method of

separating the lipids components in the food samples from water-soluble components such as protein, carbohydrates and minerals [6]. For a successful extraction of oil the sample need to undergo specific preparations prior to solvent extraction [6]. In practice, the efficiency of solvent extraction depends on the polarity of the lipids present compared to the polarity of the solvent. Polar lipids (such as glycolipids or phospholipids) are more soluble in polar solvents (such as alcohols), than in non- polar solvents (such as hexane). On the other hand non – polar lipids (such as triacylglycerols) are more soluble in non-polar lipid than in polar ones. Soxhlet extraction is one of the most commonly used methods for determination of total lipids in dried samples. This is mainly because, it is fairly simple to use and is the officially recognised method for a wide range of fat content determinations. The main disadvantages of the technique are that: a relatively dry sample is needed (to allow the solvent to penetrate), it is destructive and it is time-consuming [6].

Methodology

Standard medium fish were used and pre-treated by washing, drying and particular size reduction, and acid hydrolysis before transferring into the soxhlet extraction apparatus for continuous extraction with petroleum ether [7]. Refining of the extracted crude oil was carried out through deguming, neutralisation, and deodorisation, filtering and bleaching process using methods as outlined by Hall ([2]). The refined oil was then characterised to determine the moisture content, values of acid, saponification, iodine, peroxide, the refractive index and specific gravity by employing the methods specified by International Standard Organisation ([8-10]).

Results

Table 4. Crude oil and refined sample oil overall analytical results

Characteristic	Acids mg/KOH	Saponification mg/KOH/g	Iodine I_2/100g	Peroxide mEq/kg	Refractive index	Specific gravity	Appearance
Crude oil	2.50	201.60	108.09	2.180	1.485	0.911	Reddish brown
Refined	2.27	147.84	106.93	1.00	N/A	N/A	Golden brown

Discussion

The extraction of the oil from the fish gave an appreciably percentage yield of 7.31%, 11.635%, 17.50%, 24.58%, 27.46%, 28.24%, 28.24% at varied extraction time of between 1 to 7 hrs while the corresponding percentage moisture content removed was 17.18%, 26.00%, 38.44%, 47.17%, 56.36%, 56.36% at varied evaporation time of between 1 - 6 hrs. From fig. 1, the highest moisture content of 56.50% was removed at a period of 5.4 hrs, after which it decreased and eventually became constant. Also from fig. 2, the optimum percentage lipid extracted was 28.24%, which remained considerably constant after 6 hrs. This could be attributed to the reduced concentration gradient of the oil in the sample as the extraction proceeded and a relative increase in the viscosity of the solvent used; since high viscosity does not support effective extraction, hence at this point the extraction of the oil ceased [5]. The percentage values are of 27.0% and 56.60% for the lipid and moisture content of mackerel could be said to be in conformity when compared to standard. However, the linear relationships between the two values is being supported by the fact that an increase in the lipid content of fish is usually accompanied by a decrease in the moisture content in almost linear proportion or vice versa [11]. This considerable high lipid content could be attributed to the season (summer) in which the experiment was conducted and the fish specie, since a higher lipid content is obtainable in mackerel silage in summer than in spring [12]. The oil was analysed by carrying out some physical and chemical tests on it. It was observed that though most of the results obtained were tolerable to the standard values, nevertheless some were outside the normal range. This according to research is due to the fact that most of the standard values from the literatures are dependent on geographical locations, seasons and purpose to which the oil will be used for [11]. The acid value of the oil was found to be 2.50 mg/KOH, which is within the standard value of less than 5 mg/KOH for fish oil. The peroxide value was found to be 2.18 mEq/kg against the standard value of less than 10 mEq/kg. The appreciably lower value in peroxide value could be attributed to the fact that the oil was left for very few hours prior to the analysis of the oil, which supported the fact that the lesser the period of the oil exposure to the atmosphere, the lesser the rate of the oxidation of the oil and consequently the lesser the peroxide value of the oil. The saponification value was found to be 201.60 mgKOH/g, which is slightly higher than that of standard value for fish oil (165 – 195 mgKOH/g). The iodine value was found to be 108.09 I_2/100g of the sample as against the

standard value of between 135 to 190 I_2 /100g of the sample. The specific gravity of the oil was found to be 0.911, which is close to that of the standard of 0.907 to 0.915. The refractive index was found to be 1.485 which falls between the standard values .The appearance of the oil was reddish brown due to the prolonged heating period and the employed solvent extraction method which often oxidizes the product (i.e. the oil) and produces a reddish colour [2]. The extracted oil was refined and during deguming, 7% weight loss of the initial mass of the oil was obtained which is equivalent to the percentage mass of gums removed from the crude oil.

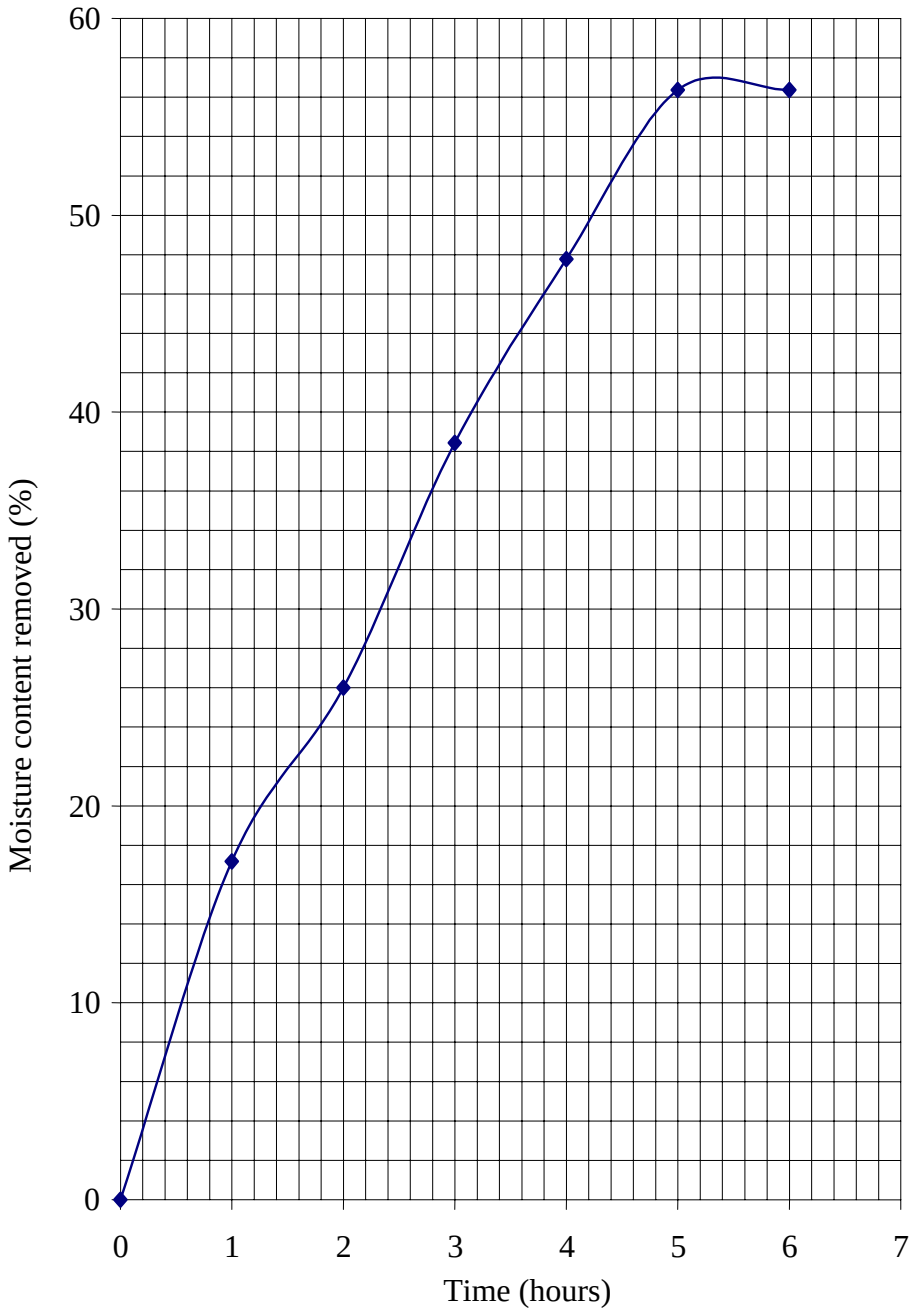

Fig. 1. Percentage moisture content removed against time (hours)

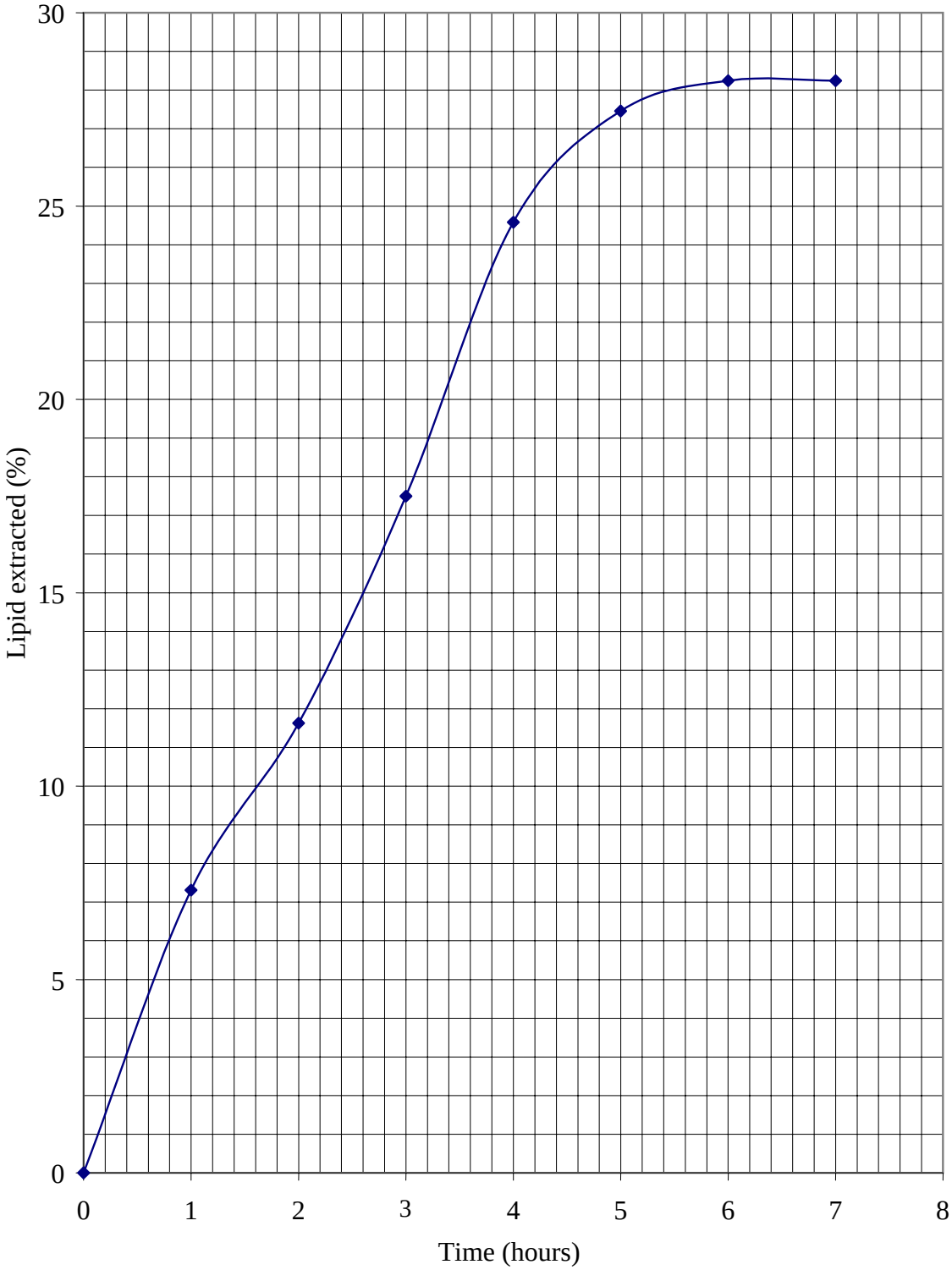

Fig. 2. Percentage lipid extracted against time (in hours)

During neutralization, 6.29% weight loss of the mass of oil was obtained which is equivalent to the percentage mass of free fatty acid removed. Bleaching process yielded 2.37% weight loss of the initial weight of oil equivalent to the percentage pigment removed. Also during deodorization process, percentage odorous component removed, i.e. the

percentage weight loss of the initial weight of oil was 5.68%. The refined oil was then analysed to ascertain the fitness of the oil for edible applications. The acid value of the refined oil was found to be 2.27 mg/KOH, which shows a considerable reduction from that of crude oil. The peroxide value of the refined oil was also found to be 1.00 mEq/kg. These reductions in acid and peroxide value imply that there is an improvement in the quality of the oil, as it reduces the susceptibility of the oil to rancidity and improve stability. The saponification value of the oil was reduced to 147.84 mgKOH/g in the refined oil. This reduction in the saponification value equals the calorific and weight loss by the oil. The Iodine value of the refined oil was found to be 106.93 I_2/100g of the sample which implies that few of the double bonds in the oil has been saturated, hence giving the oil wider applications. In addition, the colour of the oil was observed to be golden brown, which indicated the significance of the percentage pigments removed. Hence, bleaching contributed to the physical improvement of the refined oil. Finally from the graphs, it can be concluded that the percentage oil yield and the moisture content removed from the fish are directly proportional to the time of extraction and evaporation respectively.

Conclusions

In conclusion, the total percentage oil yield from mackerel (*scomber scrombrus*) using solvent extraction was 28.24%. The oil was evaluated and some of its physical and chemicals properties were determined. Although most of these analytical results obtained were tolerable to the standard values; nevertheless some were outside the normal range.

However, the refining of the oil brought about a notable improvement in the analytical properties of the oil. These properties were in conformity with standard values. All these resulted in improving the quality of the fish oil in terms of the taste, colour, odours, shelf life and market value. Based on the improved characteristics of the oil, it could be suitable for applications in pharmaceutical and food industries.

Recommendations

A lot need to be done in terms of investigating the effects of seasonal changes in relations to the oxidative stability and measurement of the free fatty acid quality index of the

oil. The excessive milling of fish in the course of extracting the oil should also be controlled in order to maximize the of the extraction process, as the solid residue may be unsuitable for sale as animal feeds hence posing a disposal problem. Finally the turning of high quality fish into fish oil and meal should be strictly discouraged.

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