PRODUCTION OF FISH OIL FROM MAATJES HERRING BY-PRODUCTS

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Keywords: fish oil, herring by-products

Abstract

At present, the Dutch fish industry sells their waste to fish meal plants in Germany and Denmark to be converted into fish meal, pet food and fish oil. This fact does not take advantage of the freshness and quality of the fish by-products. An attempt of upgrading by-products from the maatjes herring production into fish oil has been made using a pilot plant with a heat exchanger and a three-phase decanter. The crude herring oil obtained had an initial peroxide value, anisidine value and free fatty acids of 3 meq/kg of fat, 8.9 and 2.9%, respectively. EPA and DHA polyunsaturated fatty acids were present in considerable amounts (99 and 91g/kg respectively). After processing, the FFA content remained low (< 3%), even after 35 days of storage at 50°C. Unfortunately, at 50°C the totox value increases to unacceptable levels. However, when the crude oil is stored at ambient temperature in the dark environment the characteristics of the oil remain stable. This opens the possibility for fish oil production using salted herring by-products.

1. Introduction

There is a good world market demand for high quality fish meal and oil, and production can be quite profitable if suitable raw material is available. Clupeids (e.g. herring and sprat) provide the largest single source of raw material for production of fish meal and oil. They may be classified as fatty although the fat content may vary from 2% to 30% depending on species and seasons (FAO, 1986; Ackman, 1979). The industry should take care of the by-products from filleting, gutting and other fish processing operations because these have proved to be a good raw material for fish meal and oil production. Skåra and Cripps (1997) have found

that by-products from farmed salmon can be used to produce fish oil of a quality that is well suited for human consumption. Besides salmon, also by-products from other fatty fish species as herring and mackerel might be used as a source of raw material. In the Netherlands the main fatty fish species that is processed for human consumption is herring. The amount of by-products from herring that is processed by the three major companies in the Netherlands is estimated at about 15,400 tons/year. At present, the Dutch fish industry sells their by-products to fish meal plants in Germany and Denmark. The by-products are transported to these countries and then converted into fish meal, fish oil and pet food of not so high quality due to long transporting times. For this reason it is better to process the herring waste near the source where it is produced. If possible the fish by-products should be held under chilled conditions to minimise the effect of microbial and enzymatic attack on the fish tissue. This spoilage is responsible for increased free fatty acid contents and increased oxidative breakdown by e.g. peroxidases.

The maatjes herring, a very popular product in The Netherlands, is produced mainly from fresh herring landed and gibbed in Denmark and subsequently lightly salted. Production is also possible from herring frozen in blocks. Gibbing is the removal of gills, liver, heart, intestines, stomach but not the pyloric appendix. The lightly salted herring is transported from Denmark to the Netherlands in barrels and after arrival it is sorted and packed in smaller buckets. A brine is added and the herring is frozen in order to kill the nematodes and to preserve the herring. Large processors make maatjes herring fillets to be sold to retailers. In lightly salted herring the ripening effect by the enzymes from the pyloric appendix is mainly on the texture of maatjes herring and not on the taste and odour of the product (Luten, 1997). A flow chart of the process is represented in figure 1. The by-products of maatjes herring processing consists of heads, frames, skin, and fins and can be used for the recovery of oil. The total amount of maatjes herring by-products that is available from the major Dutch companies is approximately 2100 tons/year. However, these by-products had been treated with salt, which may affect the quality of the oil. Oxidation may be initiated and promoted by several organic and inorganic substance like e.g. Cu and Fe, often present in salt (Huss, 1995).

In order to investigate the possibility of using such salted by-products as raw material source for fish oil production, a study has been made. The study, using a plant scale method, aimed at upgrading the herring by-products by the production of high quality fish oil. This study has been carried out in co-operation with Alfa Laval and a Dutch herring processor. This paper focuses on the quality change during processing and storage of the oil from maatjes herring by-products.

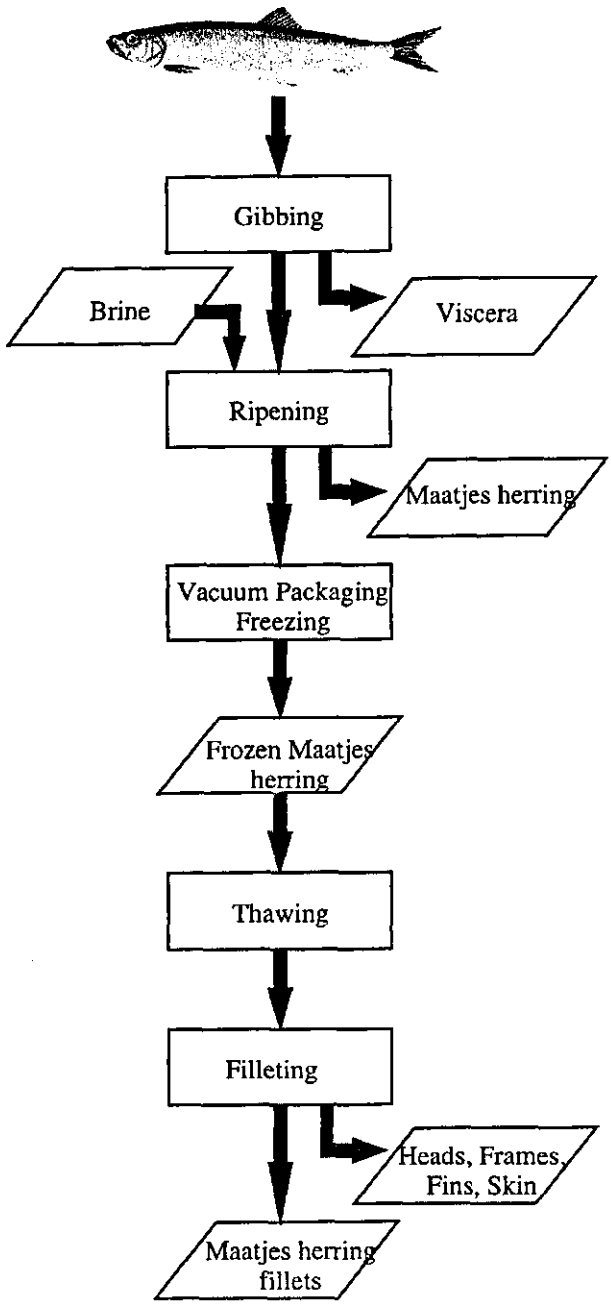

Figure 1– Maatjes herring production scheme.

2. Materials and methods

The raw material used in this study were herring by-products from frozen herring (*Clupea harengus*) used for the maatjes herring production.

2.1 Equipment

The recovery process is schematically represented in figure 2. In this experiment, about 1000 kg of maatjes herring by-products (heads, frames, skin, viscera, etc.) was minced (SAB, 49-033.2). Immediately, the minced by-products were pumped (mono-pump, SW 032, speed drive 50) and heated, using an insulated scraped-surface heat exchanger indirectly heated by steam (95±1°C, Alfa Laval Contherm®). The heated waste suspension was separated in a three phase decanter (Alfa Laval, NX 409S-11G) into a solid phase (called protein phase), a water phase (stickwater) and lipid phase (oil). All equipment parts being exposed to the products were made of stainless steel.

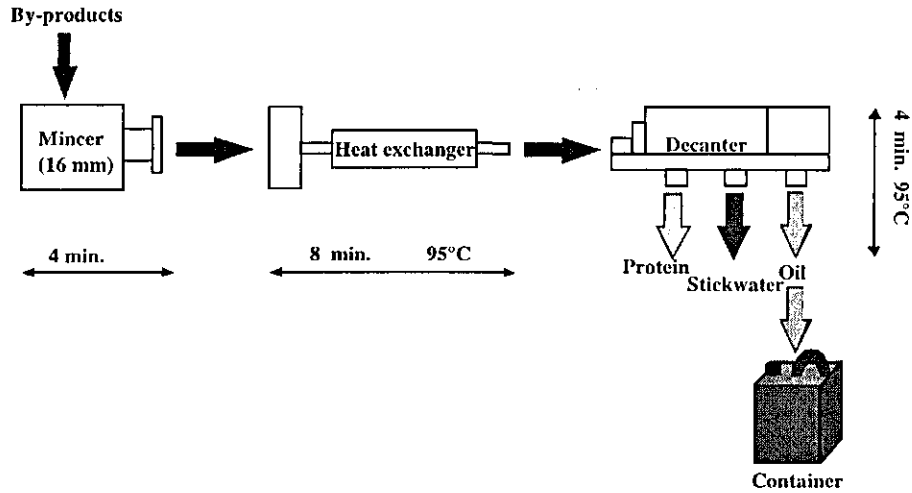

Figure 2- Scheme of the fish oil plant with processing time and temperature.

2.2 Sample design

The recovered herring oil (pooled sample) was divided into three containers and exposed to three different storage environments:

- room temperature, closed dark container, flushed with nitrogen;
- room temperature in a closed transparent glass bottles placed in front of the

window during the months of July and August 1999;
- in an oven at 50°C in a closed dark containers.

Two oil samples were taken, at regular intervals, from each storage condition and analysed for level of oxidation products. In order to avoid further oxidation, all the samples were kept at -80°C freezer until being analysed. Prior to the analysis, the oil samples were thawed at room temperature for 30 minutes.

2.3 Analytical methods

Fatty Acid Composition

The fatty acid methyl esters (FAMEs) were prepared according to AOCS Official method Ce 1b-89 and analysed with regard to the amount of content of individual fatty acids. Three oil samples (n=3) have been analysed once (a=1). The different FAMEs were separated from each other with gas chromatography (GC) using a Fisons 8130 instrument, equipped with an auto-sampler (Carlo Erba A200S) and detected with a flame ionisation detector (FID). A fused silica capillary column (0.25 mm i.d. x 50m) coated with CP Sil-88 for FAMEs (film thickness 0.20 µm), from Chrompack (Middelburg, The Netherlands) was used. The chromatographic conditions applied were: column oven temperature 190°C, injection port and detector at 250°C; sample size of 0.1µl, with a split flow of 60 ml/min. Heliurn was used as carrier gas with an inlet pressure of 145 KPa. Fatty acid methyl esters were identified by comparison of their retention times with those of chromatographic standards (from Alltech and Sigma). Quantification was performed, using TurboChrom (version 4.2) software (Perkin Elmer), by integrating peaks on the chromatogram. Results are expressed as g/kg of lipid.

Free Fatty Acids

The amount of free fatty acids (FFA) of the oil samples was determined by titration according the AOCS Official Method Ca 5a-40 (n=2, a=1). The percentage of FFA was calculated as oleic acid. Internal reference materials were analysed together with the samples.

Peroxide Value (PV)

Peroxides value (PV) were determined according to the official AOCS method Cd-8b-90 (n=2, a=1). The content is expressed in terms of meq of peroxides per kg of lipid. Internal reference materials were analysed together with the samples.

Anisidine Value

The anisidine value of the herring oil was carried out according to AOCS official Method Cd 18-90 (n=2, a=1). Internal reference materials were analysed together with the samples.

Totox value (TV)

TV was calculated according to the formula TV=2xPV + AV. This value has been suggested for the assessment of oxidation in oils (Idris *et. al.*, 1992).

All reagents used were chemical grade.

3. Results and discussion

Table 1 shows that the fatty acid oil composition has, as expected, a high amount of monounsaturated fatty acids mainly C20:1, C22:1 and also contains a high proportion of ω-3 polyunsaturated fatty acids, in particular the important C20:5 (EPA) and C22:6 (DHA). It is known that the feed of the herring is mainly from copepods (natural marine zooplankton) from relatively high latitudes which is rich in these fatty acids (Ackman, 1982; Ackman, 1992; Sargent, 1995).

Table 1- Fatty acid profile in oil from maatjes herring by-products.

Fatty acids	(g/kg of lipid)[a]
Saturated	
Total	266 ± 16
Monoenes	
Total	368 ± 29
Polyunsaturated	
C20:5	99 ± 13
C22:6	91 ± 11
Total	277 ± 33

[a] Mean value ± SD, (n=3, a=1).

The value of FFA in oil is an important quality parameter. The reason is not only because usually the FFA value is checked due to contractual reasons (between the retailer and purchaser of the oil) (FAO, 1986) but also because the FFA are more susceptible to oxidation than esterified fatty acids (Labuza, 1971; Kinsella *et al.*, 1978). The results (figure 3) show that the amount of FFA present in the maatjes herring oil was low (2.9%) and remain constant during storage time for all the three

different storage conditions. This suggests that the hydrolysis of the oil did not occur during the storage period.

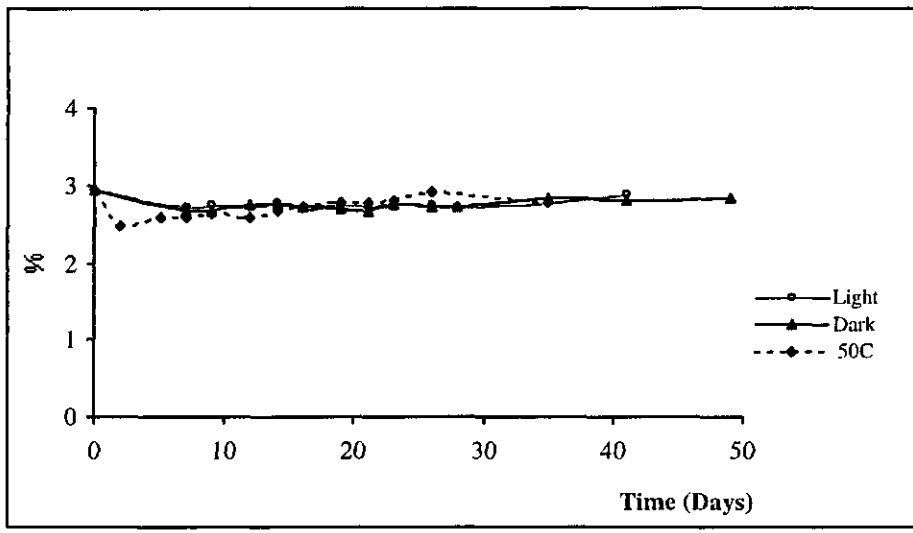

Figure 3- Free fatty acids of maatjes herring oil during storage.

The hydroperoxides, presented by the peroxide value (PV) are the primary oxidation products. The PV is an indicator of the first stage of the oxidation process. The amount of hydroperoxides in oil usually increases in time to a certain maximum and decomposes rapidly to the secondary oxidation products, leading to a decrease of the PV. In the maatjes oil, two peaks of peroxide values are shown for the conditions 50°C and light (figure 4). This phenomena can be caused by two different oxidation reactions with different speeds or initiation times (autoxidation and photooxidation, respectively). It is known that the oxidation of unsaturated lipids is accelerated by exposure to light (Frankel, 1998). Both reactions produce hydroperoxides. The oil stored under dark and nitrogen conditions is quite stable. The peroxide value in the oil remains very low. This fact is somehow peculiar particularly taken into account that fish oil is rich in polyunsaturated fatty acids and consequently very prone to oxidation. A possible explanation might be that this crude herring oil has some natural antioxidants that are protecting against oxidation.

Usually, the hydroperoxides are very unstable and decompose into secondary oxidation products: volatile and non-volatile end-products. The non-volatile end-products (high-molecular-weight saturated and unsaturated carbonyl compounds in triacylglycerols) can be measured by the anisidine value (AV). The AV provides useful information related to compounds formed in oils during processing (Frankel, 1998) and in many cases are associated with the term «oxidative rancidity» and are described as having objectionable off-odours and off-flavours (St. Angelo, 1996).

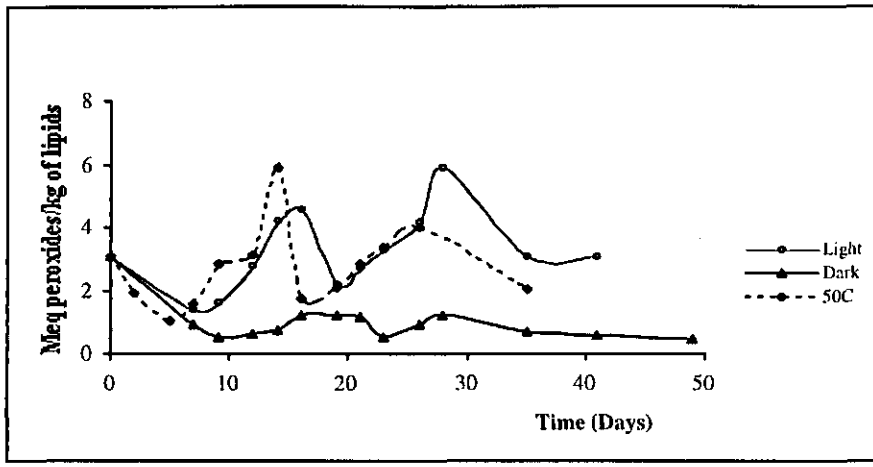

Figure 4- Peroxide value of maatjes herring oil during storage.

This type of deterioration can be serious in poorly processed oils containing ω-3 polyunsaturated fatty acids (Frankel, 1998). Figure 5 shows the anisidine values measured in the oil stored over time. In the oil kept at condition 50°C the development of the secondary oxidation products initiate within a few days after storage, which probably means that the primary oxidation products are decomposed to secondary oxidation products rapidly. The two maxima present for peroxide value at 50°C (figure 4) are also observed in the anisidine value at 50°C (figure 5).

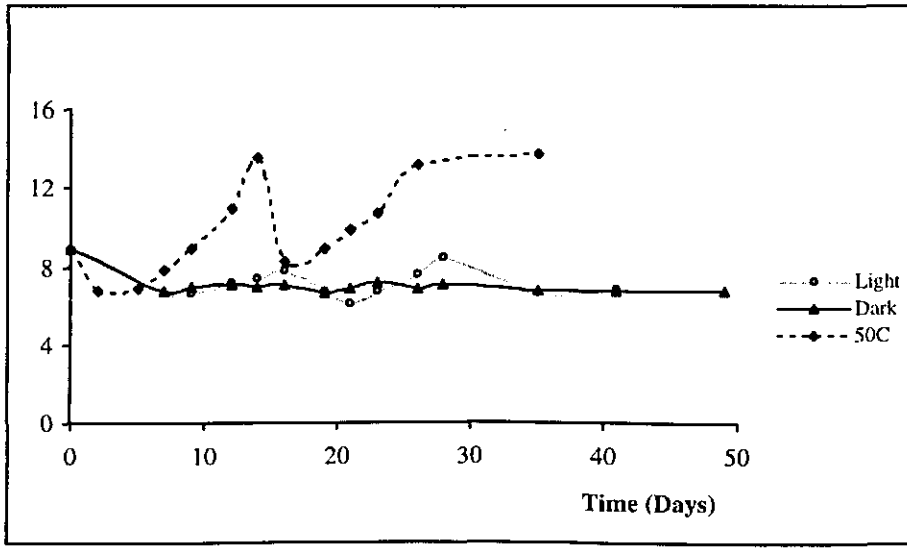

Figure 5- Anisidine value of maatjes herring oil during storage.

In the oil samples stored under light conditions, only two small peaks are present. Possibly, a termination reaction is favoured than a propagation reaction under such conditions. There is hardly any change in the AV for the oil kept at dark conditions. The oil in this situation is stable. Therefore, it might be concluded that high amounts of oxidation products are inhibited by a lack of oxygen and light.

The total oxidation value, shown in figure 6, is a calculation according to AV + 2PV. This totox value is used as a measurement of the precursor non-volatile carbonyls present in processed oil plus any further oxidation products developed after storage. In the present case, the conclusions taken are similar to those found from the anisidine value results.

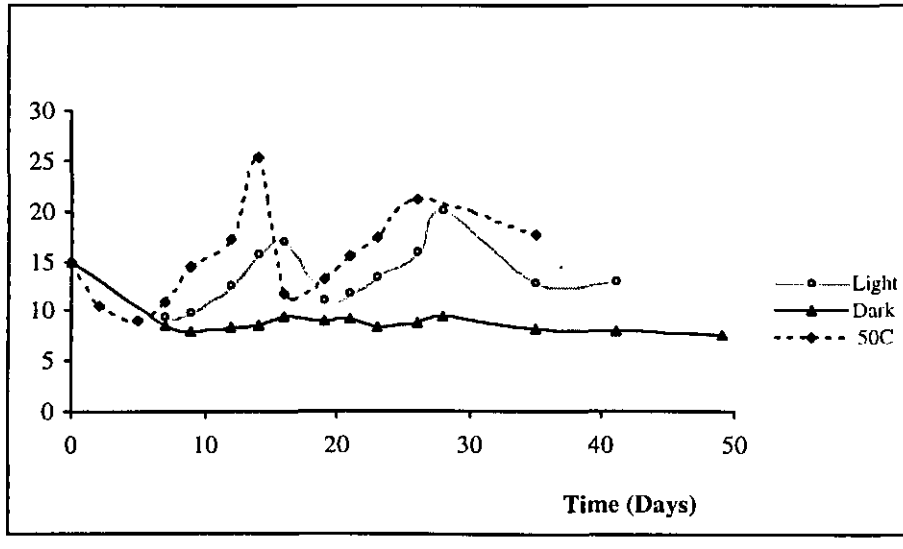

Figure 6- Totox value of maatjes herring oil during storage.

Summarising, our results shown that it is possible to produce fish oil from salted (maatjes) herring by-products. This oil, like the oils from fatty fish species, contains a high percentage of the valuable polyunsaturated ω-3 fatty acids, mainly EPA and DHA. The oxidation values found reveal that the crude herring oil obtained has low initial values of FFA, PV and AV. Of course, the storage under conditions like light and at high temperatures should be avoided. Fortunately, the oil is quiet stable in time when it was kept under dark conditions, in the absence of oxygen and at ambient temperatures. This fact shows that usage of maatjes herring by-products might be very promising for fish oil production.

4. References

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