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The influence of long-term storage, temperature and type of packaging materials on the lipid oxidation and flesh color of frozen Atlantic herring fillets (*Clupea harengus*)

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ARTICLE INFO

Article history:

Received 29 July 2013

Received in revised form

7 November 2013

Accepted 11 November 2013

Available online 21 November 2013

Keywords:

Herring

Freezing

Oxidation

Long-term storage

ABSTRACT

The oxidation and color characteristics of Atlantic herring fillets were examined during the long-term frozen storage at -25 and -45 °C. The effects of packing materials with low and medium oxygen barriers were studied as well. At the temperature of -45 °C, the peroxide value (PV) and thiobarbituric acid reactive substances (TBARS) formation were significantly inhibited. The same desirable effect was detected for packaging material with a medium oxygen barrier at -25 °C. A regression model of the herring fillets' oxidation was verified. The storage time, temperature and packaging materials affected the color alteration. The differential scanning calorimetry (DSC) analyses of herring oil revealed a melting between -60.67 °C and 21.40 °C. The liquid fraction in the fish oil was determined. It was high for all the storage temperatures, thus the oxygen concentration in the package was considered to be the dominating factor for the herring's oxidation during frozen storing.

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Influence de l'entreposage à long terme, de la température et du type de matériaux d'emballage sur l'oxydation lipidique et de la couleur de la chair de filets de harengs (*Clupea harengus*)

Mots clés : Hareng ; congélation ; oxydation ; entreposage longue durée

1. Introduction

Atlantic herring is less stable than Atlantic salmon or Rainbow trout during frozen storage. The decrease in quality is caused

by lipid oxidation, but the rate of oxidative reactions is significantly different in these species. For example, the PV in pre-rigor frozen salmon did not exceed $1.82 \text{ meq O}_2 \text{ kg}^{-1}$ of fat when stored for 375 days at -25 °C (Indergård et al., 2013). On the other hand, herring fillets stored at -30 °C showed

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<http://dx.doi.org/10.1016/j.ijrefrig.2013.11.014>

Nomenclature

A	The initial concentration of PV and TBARS
C*	Chromaticity, points
c	Concentration of oxygen, mol m ⁻³
DSC	Differential scanning calorimeter/calorimetry
E	Energy, absorbed by sample during heating, J
h*	Hue, °
k	The modified OTR to introduce concentration
L*	Lightness, points
LNCS	Liquid nitrogen cooling system
M	Molar mass of oxygen, kg mol ⁻¹
m	melted mass, kg
MDA	Malondialdehyde
OTR	Oxygen transmission rate, cc ³ m ⁻² day ⁻¹
Ox	The concentration of PV or TBARS
PV	Peroxide value, meq of O ₂ kg ⁻¹ of fat
S	Surface of oxygen penetration, m ²
T	Temperature, °C
TAG	Triacylglycerides
TBARS	Thiobarbituric acid reactive substances, mg of malondialdehyde kg ⁻¹ of fish
V	Porous volume, m ³
z	Reaction rate constant, day ⁻¹ ;
ΔH	Heat of fusion, J kg ⁻¹
ε	Porosity, %
ρ	Density, kg m ⁻³
τ	Time, days

Subscripts

ap	Apparent
av	Average
atm	Atmospheric
b	Bulk
m	Melting
mt	Material
T	Temperature
τ	Time
0	Initial

11.6 meq O₂ kg⁻¹ of fat after 14 weeks (Hamre et al., 2003). Such a difference in the oxidation rates can be explained by varieties in the concentration of natural antioxidants and pro-oxidants, and also by processing peculiarities (Hultin, 1987).

The influence of the natural pro-oxidants like myoglobin and hemoglobin could be reduced by a proper slaughtering and pre-processing storage, where the blood is removed and the pre-storage period is extremely short. The storage of the herring at chilling temperatures prior to freezing initiates the enzymatic activity which leads to several deteriorative processes. This will lead to a decreased shelf-life during frozen storage. For example, herring fillets stored in ice for 6 days before freezing showed a PV of 25 meq O₂ kg⁻¹ of fat after 80 days at -18 °C, while herring stored in ice 3 days showed a PV of 7 meq O₂ kg⁻¹ of fat after 80 days at -18 °C (Undeland and Lingnert, 1999).

A comparative research devoted to lipid oxidation in herring fillets with and without skin showed that the PV reached 35 meq O₂ kg⁻¹ of fat in skinless fillets after 30 weeks at -18 °C,

while fillets with skin reached a value of 20 meq O₂ kg⁻¹ of fat at the same conditions and length of time. The oxidation of skinless herring from the outer side, where the concentration of pro-oxidants is the highest, was 3 times higher than from the backbone side. Hence, the skin provided a good barrier for oxygen (Undeland et al., 1998).

A plastic vacuumed packaging also gave a significant reduction of lipid oxidation in Atlantic salmon during frozen storage. The combination of packaging material and storage at -25 °C had a similar effect on PV and TBARS formation as storage at -45 °C with lower quality packaging material (Indergård et al., 2013).

The reaction rate of lipid oxidation during the exponential phase normally follows the Arrhenius equation; thus, lowering the storage temperature can inhibit the oxidation processes in fish tissues (Kamal-Eldin and Yanishlieva, 2005). An overall analysis of fish quality showed an increase in the shelf-life with a decrease of temperature. For example, the rancid odor of herring fillets stored at -20 °C for 12 months was strong, while fillets stored at -80 °C maintained a high quality for 18 months. (Hyldig et al., 2012). However, such a low temperature is unacceptable for industrial use, due to the high investment and running costs.

We believe that not skinning the fillets, decreasing their time spent in cold storage prior to freezing, and the application of packaging materials which prevent oxygen penetration are the most effective ways to preserve quality.

At the same time there is a lack of information in the literature about the thermal transition of fish oil, and it is difficult to decide which will be the dominant factor in the inhibition of the oxidation process of fish lipids: the oxygen concentration, the amount of the solid fraction of oil in the system at a given temperature, or a combination. Thus, the necessity of the application of packaging material with high barrier properties has not been validated.

The scope of this study is a comparison of the fat oxidation and color alteration in herring fillets with respect to the storage temperature and application of packaging material. The fish's stability was analyzed along with the fat solidification and oxygen permeation inside the product at storage temperatures.

2. Methods of experiment

2.1. Experiment description

Atlantic herring (*Clupea harengus*, November, 2011) was delivered by Sjøset Pelagic AS (Træna, Norway). The fish was stored at -1.0 ± 0.5 °C in sea water during transportation to a factory (2–3 days total). At the factory all the fish were filleted on filleting machines, washed, and then packed in cardboard boxes (20.0 ± 0.5 kg) with polyethylene. The freezing took place in a tunnel freezer at -35.0 ± 1.0 °C (MMC Kulde AS, Ålesund Norway) during 23.0 ± 0.5 h, until the central part of the fish blocks reached a temperature of -25.0 ± 1.0 °C. Thereafter, boxes with fillets were delivered in a refrigerated container to the laboratory (4–5 days, temperature -25.0 ± 1.0 °C), where the blocks were cut into four pieces (5.0 ± 0.1 kg). Each piece was repacked in packaging material and vacuumed in a Webomatic,

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