Quality enhancement of canned sardine (Sardina pilchardus) by a preliminary slurry ice chilling treatment

Study of the quality of canned sardine (Sardina pilchardus): Effects of previous conditions of chilled storage

Abstract:
This study was focused on the improvement of quality of the canned sardine after a previous chilled step based on the use of slurry ice and how it affects the final canned product. Sardine was processed under sterilization conditions (115°C, 15 min) with a previous chilled storage in slurry and flake ice during 0, 2 and 5 days. Then, sardines were cooked and canned with sunflower oil as liquid cover. Physical and biochemical analysis were checked in the canned product. The obtained results showed a light inhibition in the sardines with a previous chilled storage in slurry ice in some biochemical indices as fluorescence in the organic phase of the muscle, fluorescence in the organic phase of cover liquid, TMA-i and cohesivity. Other analyses as induction time, alpha-tocopherol and anisidine value showed significantly higher values in the canned sardines with a previous refrigeration in slurry ice when compared to the canned sardines with a previous refrigeration in flake ice. Results confirm the practical advantages of using slurry ice as a previous treatment to the canned of sardines.

Keywords: sardine, canning, previous chilling, slurry ice, quality.

INTRODUCTION

The canning is a process of great technological importance in many countries of the world. From the capture of the fish until the canned product arrives at the consumer the raw material is submitted to a diverse industrial treatments. It is necessary a conservation process as refrigeration and frozen mainly, and a baking to reduce the excess of humidity and to inhibit endogenous enzymes. Is necessary an energetic treatment (sterilization) to inactivate the microorganisms and is necessary a later storage to guarantee a good taste of the product. When marine species are processed at high temperatures, PUFA damage can lead to the formation of significant quantities of primary and secondary lipid oxidation products, which can finally produce browning (Pokorny J, 1981), fluorescent compounds (Smith G et al., 1990; Maruf F et al., 1990) and off-flavour (Kunert-Kirchhoff J and Baltes W., 1990) and the loss of essential nutrients (Nielsen et al., 1985; Hidalgo et al., 1992).
Refrigeration has been widely used as a previous step of other technological treatments as smoked, canned, frozen and restructured fish products and the importance of this previous step in the quality of the end product has been demonstrated. Different preservation methods such as traditional flake icing (Mendes R, et al. 2001), refrigerated sea water (Kraus R, et al. 1992), storage under a modified atmosphere (Ruiz-Capillas C and Moral A. 2004), immersion in brine solutions (Xiong S, et al. 2002) and the incorporation of chemical preservative agents (McEvily A, et al. 1991) have been successfully applied to aquatic food products.

Slurry ice is also know as liquid ice, fluid ice, slush ice and flow ice and is an ice-water suspension at subzero temperature that provide several advantages as its faster chilling rate –due to a more rapid heat exchange–, and the reduced physical damage caused to seafood products by its spherical microscopic particles, as compared with the conventional flake ice. Additionally, full coverage of the fish surface, thus avoiding the formation of air pockets, prevents direct contact of the fish material with oxygen, with the subsequent benefits derived from minimisation of oxidation and dehydration events. From a technical point of view, the slurry ice mixture can be pumped, thus allowing a more hygienic fish handling and process automatization. Previous studies have reported good results in the application of slurry ice systems to farmed sea bream and turbot (Huidobro A., et al (2001); Rodriguez O., et al (2005) and to wild albacore, hake, and sardine (Price R., et al (1991); Losada V., et al (2004a); Losada V., et al (2004b). In the case of sardine, slurry ice systems showed statistical differences in the chilled storage of Sardine pilchardus (Campos C., et al (2004); Losada V., et al (2004).

Sardine (Sardina pilchardus) is a small pelagic fish. With the exception of the negligible amounts sold as retail, this species is mainly used as fresh or frozen raw material destined for further processing. One of the factors limiting its commercial use is the difficulty of its preservation at low temperature. Thus, the shelf life of sardines may be limited by rapid bacterial degradation and lipid oxidation mechanisms, which may cause off-flavors and flesh discoloration.

The previous chilled is an important step in the canning process and the aim of the present study is tried to obtain a reduction in the alteration produced in the previous chilled step in flake ice and improvement the quality in the canned product with a previous chilled in slurry ice. This alteration was evaluate with sensory, physical and biochemical methods.
MATERIALS AND METHODS

Slurry ice and traditional flake ice
A slurry ice prototype (FLO–ICE, Kinarca S.A.U., Vigo, Spain) was employed. The composition of the slurry ice binary mixture was 40 % ice and 60 % water, prepared from filtered seawater (salinity: 3.3 %). The temperature of the slurry ice mixture was –1.5 °C.
Flake ice was prepared with an Icematic F100 Compact device (CASTELMAC SPA, Castelfranco, Italy); The temperature of the flake ice was –0.5 °C.
The fish specimens were surrounded by slurry or flake ice at a 1:1 fish to ice ratio, and stored in a refrigerated room at 2°C. When required, the flake ice and the slurry ice mixture were renewed.

Fish material, processing and sampling
Fresh sardine (Sardina pilchardus) were caught near the Galician Atlantic coast and transported on ice to the laboratory 10 h from the capture.
Upon arrival in the laboratory the fish specimens were neither headed nor gutted and were directly placed in slurry ice or flake ice in an isothermal room at 2°C. The length of the specimens was in the 16-21 cm range and the average weight was 150 g.
Samples were taken to prepare de canned product at days 0, 2 and 5. Sunflower oil like cover liquid was used.
Three months later the cans were opened and fish had been subjected to sensory and physical analysis, the white muscle was separated and employed for physical and biochemical analyses. All analyses were performed in triplicate.

Composition analysis
Water content was determined by the difference between the weight of fresh homogenised muscle (1-2 g) and the weight recorded after 24 h at 105 °C. Results are expressed as g water/100 g muscle.
Lipids were extracted by the Bligh and Dyer method. Quantification results are expressed as g lipid/100 g wet muscle.
NaCl content in fish muscle was calculated from the amount of chlorine by boiling in HNO$_3$ with excess of AgNO$_3$, followed by titration with NH$_4$SCN. Results are expressed as g NaCl/100 g muscle.

Biochemical analyses
The anisidine value was determined according to the official method AOCS Cd 18-19 (1989).
Formation of fluorescent compounds was determined with a Perkin Elmer LS 3B fluorimeter by measurements at 393/463 nm and 327/415 nm as previously described. The relative fluorescence (RF) was calculated as follows: RF = F/F$_{st}$, where F is the fluorescence measured at each excitation/emission maximum, and F$_{st}$ is the fluorescence intensity of a quinine sulphate solution (1 µg/mL in 0.05 M H$_2$SO$_4$) at the corresponding wavelength. The fluorescence ratio (FR) was calculated as the ratio between the two RF
values: FR = RF_{393/463} nm/RF_{327/415} nm. The FR value was determined in the aqueous phase resulting from the lipid extraction.

Trimethylamine-nitrogen (TMA-N) values were obtained by the picrate method, as previously described. The results were expressed as mg TMA-N/100 g muscle. Induction time was determined according the official method of A.O.C.S. Cd 12b-92 (1993). The Rancimat Metrhom equipment was used with a 679 detector. The conditions were: flow air 20 L/h and a 110 ºC temperature in the time of test.

α-tocopherol was determined according

**Physical analysis**

Texture properties were obtained according to Jonsson et al. 2000. Cohesivity was determined in a material test equipment (Lloyd Instruments Limited, LR-5K, Hampshire, England) with a cell of load of 500 N.

**Statistical analyses**

Biochemical data corresponding to the three chilling methods were subjected to one-way analysis of variance to assess significant (p<0.05) differences among treatments. Correlation analysis with time of the different parameters was studied. The SPSS 11.5 software for Windows (SPSS Inc., Chicago, II, USA) was used to explore the statistical significance of the results obtained, including multivariate contrasts and multiple comparisons by the Scheffé and Tuckey tests; a confidence interval at the 95% level was used in all cases.

Data from different biochemical analyses were subjected to one-way analysis of variance (p< 0.05). Correlation analyses among chilled time and biochemical indices were studied (Statsoft: Statistica for Macintosh., 1994).

**RESULTS AND DISCUSSION**

**General composition:**

The water content of canned sardine muscle ranged between 63.56 and 64.67 % while the lipid content was in the 1.13-1.89 % range. The differences in both constituents among specimens when are compare with fresh sardine values may be explained in terms of individual variations rather than being due to the sterilization of the canned product. However, when the canned product was compared with the fresh sardine it was observe that the medium values were 72.03 % in the water content and 3.01 % in the lipid content. It was obtained a great decrease in the lipid content and in the water content due to the canning process.

Both constituents exhibited fresh values similar to previous reports for fatty fish species (Piclet G.,1987; Losada V., 2004).

The presence of NaCl in the chilling medium, characteristic of the slurry ice system, did not led to a increase of the NaCl content in the canned sardine muscle during the experiment except at day 5 of previous refrigeration in the slurry ice batch (0,91 ± 0,15) that led to a little increase as compared to the flake ice batch (0,83 ± 0,03). The value of
NaCl at day 0 was 0,68 ± 0,16. This finding is in agreement with a previous study performed with sardine (Losada V., 2004). However, when we compared the NaCl fresh sardine value (0,07 ± 0,02) we can observed that these values are smaller than canned sardine at day 0 that was 0,68 ± 0,16. This result is due to the canning process.

Texture properties:
Cohesivity showed a great decrease in both treatments during the day 2 and 5 of previous chilling refrigeration when compared with the canned sardines at day 0. As we can see in table 1 values of cohesivity do not showed greater differences between flake and slurry ice at day 2 and 5 of previous refrigeration. However values of canned sardines with previous refrigeration in slurry ice showed higher cohesivity than the flake ice ones.

Biochemical analysis:
As we can observe in Figure 1, the induction time showed greater values in the canned sardines with previous refrigeration in slurry ice that the sardines with previous refrigeration in flake ice throughout the experiment. These differences are statistically significant at day 5 of the experiment where we can observe a higher induction time in the canned sardines with a previous refrigeration in slurry ice (4,761 ± 0,839) that the flake ones (3,959 ± 0,422). This result is due a lower oxidation in the canned sardines with a previous refrigeration in slurry ice.

The strong heat treatment and the presence of some catalysts in the fish muscle can favor nonenzymatic lipid oxidation and hydrolysis so that detrimental flavor and essential nutrient losses can be produced (Hsieh and Kinsella, 1989; Harris and Tall, 1994).

Formation of interaction compounds (Table 2):
Fluorescence detection of interaction compounds during food processing has largely been carried out by measuring the fluorescence formation at a single excitation/emission maximum (Smith G., et al. 1990; Maruf F., et al. 1990). Previous work carried out on thermally treated fish muscle indicated a bathochromic shift of fluorescence related to an increase of lipid oxidation which was dependent on the time and temperature of processing (Aubourg S., et al. 1992; Aubourg S., et al. 1995). The fluorescence shift ($\delta F$), calculated as the ratio between two of the maxima investigated (393/463 nm and 327/415 nm), correlated with quality.

The detection of fluorescence in organic phase in the muscle showed a sharp increase when compared the initial canned sardines (0.83 ± 0.11) with the fresh samples (0.18 ± 0.03). However when compared the canned product there were differences between the sardines with previous chilled storage in slurry ice that sardines previously chilled in flake ice that showed higher values from the second day of previous chilled refrigeration.

Similar results were observed in the fluorescence in organic phase in the liquid cover, that no showed differences between the fresh sardines (2.66 ± 0.08) and the canned sardines at day 0 (2.56 ± 0.13). However at day 5 of previous refrigeration it were differences between the canned sardines refrigerated in slurry ice and the canned sardines previously refrigerated in flake ice.

A previous work showed that fluorescent compounds are formed in the oils during canned storage by condensation reactions of lipids and other compounds present in the starting oil. At the same time, fluorescent compounds are also progressively formed as a
result of the interaction between the packing oil and some constituents of the fish muscle.

TMA-N content showed (Table 2) a great increase of the order of 100 greater times when compared the canned product (6.92 ± 0.01) with the fresh sardines (0.06 ± 0.01). However the values were similar when compared the days of previous chilled refrigerated in both treatments. The values observed in the canned sardines with previous chilled storage in slurry ice were lowers than the sardines previously chilled in flake ice. The final value observed was 7.48 TMA-N/100 g muscle at day 5 of previous refrigeration in slurry ice, whereas it was 8.16 TMA-N/100 g muscle in flake ones at day 5. This is a value close to the legal limit of 12 mg/100 g set for TMA-N (Directive 91/493 ECC). In this experiment canned sardines with a previous refrigeration in slurry ice showed slowed down TMA-N formation in comparison with the previous refrigeration in flake ice.

In the determination of the no-volatile products of secondary oxidation measurement through the anisidine value, it was observed how increased the values in the chilled time being the greater average values in the case of the sardines that were previous chilled in flake ice than the previous liquid ice chilled ones.

As we can see content of alpha tocopherol decrease with the time of refrigeration being greater these decrease in the case of the canned sardines with a previous refrigeration in flake ice. At day 5 of refrigeration the values of content in alpha –tocopherol in canned sardines with a previous refrigeration in flake ice was 235.76 mg/Kg fat whereas in the case of canned sardines with a previous refrigeration in slurry ice was 291.22 mg/Kg fat.

**FINAL REMARKS**

The employment of slurry ice had produced a partial inhibitory effect in the alteration and lipid oxidation obtained in some analysis. The obtained results in this study were showed inferior average values in the samples with previous chilled storage in slurry ice in some indices as fluorescence in organic phase of muscle, fluorescence in organic phase of cover liquid and TMA- i. Induction time, anisidine value and alpha tocopherol indices showed statistically higher values in the results obtained in the slurry ice samples when compared with flake ice samples during the experiment.

Cohesivity was reflected greater average values in the sardines with previous slurry ice that in the sardines with previous flake ice.

These results showed practical advantages in the use of slurry ice as a chilled method of previous refrigeration to the canned of sardines.
ACKNOWLEDGEMENTS

The authors wish to thank Kinarca S.A.U. for providing the slurry ice equipment and Justo López Valcarcel S.A. to provide the cans and for lend its equipment to make the canned product. This work was supported by the Secretaría Xeral de I+D from the Xunta de Galicia (Galicia, Spain) (Project PGIDTI02RMA18E). The authors also thank Mr. Marcos Trigo and Mrs. Mónica García for their excellent technical assistance.

REFERENCES

Tabla 1. Texture properties of the shears test in canned sardine with a previous chilled storage in slurry and flake ice

<table>
<thead>
<tr>
<th>Refrigeration time (days)</th>
<th>Treatment</th>
<th>Cohesivity (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Day 0</strong></td>
<td></td>
<td>47.9 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Slurry ice</td>
<td>36.1± ± 3.7</td>
</tr>
<tr>
<td></td>
<td>Flake ice</td>
<td>34.7± ± 2.7</td>
</tr>
<tr>
<td><strong>Day 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Slurry ice</td>
<td>33.7± ± 3.2</td>
</tr>
<tr>
<td></td>
<td>Flake ice</td>
<td>33.4± ± 1.9</td>
</tr>
</tbody>
</table>

* Mean values of four independent determinations (n=4) and standard deviations are indicated. For each refrigeration time, means followed by different letters (a-b) indicate significant differences (p<0.05) between both chilling systems.
Table 2: Results of biochemical analyses (Induction time, alpha-tocopherol, i-poliene, TMA-N, Anisidine value, fluorescence in organic phase of muscle and fluorescence in organic phase of oil) in canned sardine at 0, 2 y 5 days of refrigeration in slurry and flake ice.

<table>
<thead>
<tr>
<th></th>
<th>Day 0</th>
<th>Day 2</th>
<th>Day 5</th>
<th>Day 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slurry ice</td>
<td>Flake ice</td>
<td>Slurry ice</td>
<td>Flake ice</td>
</tr>
<tr>
<td><strong>Induction time</strong></td>
<td>4,679±0,072</td>
<td>4,272±0,474</td>
<td>4,087±1,251</td>
<td>4,761a±0,839</td>
</tr>
<tr>
<td><strong>Alpha-tocopherol</strong></td>
<td>313,538±1,461</td>
<td>298,990a±3,685</td>
<td>266,030b±34,503</td>
<td>291,220a±8,402</td>
</tr>
<tr>
<td><strong>i-Poliene</strong></td>
<td>1,06 ± 0,03</td>
<td>1,32 ± 0,20</td>
<td>0,86 ± 0,04</td>
<td>1,41a ± 0,07</td>
</tr>
<tr>
<td><strong>TMA-N</strong></td>
<td>6,92±0,42</td>
<td>6,83±0,87</td>
<td>7,94±0,73</td>
<td>7,48±0,71</td>
</tr>
<tr>
<td><strong>Anisidine value</strong></td>
<td>0,80±0,30</td>
<td>1,68a±0,41</td>
<td>1,91b±0,31</td>
<td>1,53a±0,26</td>
</tr>
<tr>
<td><strong>Fluorescence in muscle</strong></td>
<td>0,83±0,11</td>
<td>0,77±0,20</td>
<td>0,87±0,16</td>
<td>1,10±0,17</td>
</tr>
<tr>
<td><strong>Fluorescence in oil</strong></td>
<td>2,56±0,13</td>
<td>3,28±0,28</td>
<td>3,50±0,68</td>
<td>6,20±2,42</td>
</tr>
</tbody>
</table>

* Mean values of four independent determinations (n=4) and standard deviations are indicated. For each analysis and each refrigeration time, means followed by different letters (a-b) indicate significant differences (p<0.05) between both chilling systems.