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Enhancing the Stability and Production Economy of Salted and Dried Whole Capelin, *Mallotus villosus*

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Icelandic Fisheries Laboratories Report Summary

Title / titill:	**Enhancing the Stability and Production Economy of Salted and Dried Whole Capelin**, *Mallotus villosus*		
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Summary in English:

The aim of this preliminary experiment was to develop novel combined process for the production of salted/dried capelin, as a food item with extended storage stability. Capelin, *Mallotus villosus*, was treated in seven different ways, in weak acetic acid solution, by brining, brining with acetic acid, salting, desalting, neutralising with alkali and washing. These treatments where done in different orders prior to convection drying at 18-20°C. Chemical measurements were made after drying and after one month storage time at 39°C. Each group was measured for chemical composition (water, protein, fat and salt), lipid oxidation (free fatty acids, peroxide-value and TBA-value), as well as total volatile nitrogen (TVN), for comparing protein deterioration and finally the pH was measured to see the influence of the acid treatment. Results of these preliminary findings showed that brining in salt/acid brine gave the lowest water content, the lowest pH value and the most lipid oxidation of all treatments. Weak acid treatment alone had very little influence on chemical composition or lipid oxidation. All washing treatments decreased the salt content of the capelin. No complications turned up when treating the material this way and this method seems to by economical.

English keywords: Capelin, brining, drying, stability

Ágrip á íslensku:

Tilgangur þessa forverkefnis var að þróa nýtt vinnsluferli við framleiðslu á saltaðri og þurrkaðri loðnu sem matvæli með langt geymsluþol. Loðna, *Mallotus villosus*, var meðhöndluð á sjö mismunandi vegu; í 1-2% ediksýru lausn, pækluð í saltlegi, pækluð með ediksýru, söltuð, útvötnuð, hlutleyst með basa og þvegin. Meðhöndlunin var gerð í mismunandi röð á tilraunahópunum áður en loðnan var þurrkuð við 18-20°C. Efnamælingar voru gerðar strax eftir þurrkun og aftur eftir eins mánaðar geymslutíma við 39°C. Mæld var efnasamsetning (vatns-, prótein-, fitu- og saltinnihald) og þránun (óbundnar fitusýrur, peroxíðgildi og TBA-gildi) í hverjum tilraunahópi, svo og TVN-gildi sem mælikvarði á niðurbrot próteina og loks var pH-gildi mælt til þess að athuga áhrif sýrumeðhöndlunarinnar. Niðurstöður þessara frumathugana sýndu að loðna sem var pækluð í salt- og sýrulegi fyrir þurrkun varð þurrust, súrust og mest þrá af öllum meðferðarhópum. Meðhöndlun með veikri sýrulausn hafði lítil áhrif á efnasamsetningu eða þránun. Allur þvottur á loðnunni dróg úr saltinnihaldi hennar. Vinnsla á loðnu með þessum hætti hafði engin vandkvæði í för með sér og aðferðin virðist vera hagkvæm.

Lykilorð á íslensku: Loðna, söltun, þurrkun, stöðugleiki.

CONTENTS

1. INTRODUCTION

The aim of the experiments in this protocol is to study the feasibility of acid treatment as a part of novel combined process for the production of salted/dried small fatty fish, in particular capelin, as a food item with extended storage stability. A traditional and cheap method of stabilising and storing fish is salt or brine storage at low temperature in bins or plastic containers. Since capelin can be pumped as a whole it is possible to store big quantities of capelin mixed with salt or brine in tanks (>100 tons). However the microbiological and enzymatic processes going on during storage, chemical changes, changes of fish texture and other physical properties and the loss of dry mass into the brine have to be understood much better as they are to date. Also new technical means have to be found to mix the salt or the brine uniformly into the fish. Due to water transport limitations in fish skin and fat layers, drying of whole fatty fish on convection dryers is usually a very slow process, taking at least four days even for small fish like capelin. This can lead to microbiological spoilage of the fish until sufficiently low water activity is reached and to fat oxidation with pronounced rancid smell. The end moisture content usually differs between different fish bodies and between different parts of a single body making it difficult to achieve good storage stability throughout the whole product. According to Gildberg/Raa, 1979 and Wood, 1982 a mild acid treatment of the fish prior to drying is expected to ameliorate water transport properties of fish skin and fatty fish tissues. Because the acid treatment partly relies on the activity of collagenase enzymes, it has to be carried out before brine storage of the fish, which inactivates most of the enzymes.

2. MATERIALS AND METHODS

2.1. Raw material

Capelin (*Mallotus villosus)* from frozen blocks (7 kg) were used in the experiments. The capelin was females with roe and of variable size graded from males by size, but the grading results in particle mixture of male (10-20 %). The capelin was caught in February, frozen into blocks and kept in frozen storage (7-8 months) until used for the trials. Before treatment the capelin was thawed in open air at 18-20°C for 24 hours and divided into seven treatment groups (1-7).

2.2. Experimental setup

The capelin was treated in seven different ways, either in acetic acid solution, by brining with 18% fine NaCl-salt solution, brining with acid, salting with fine NaCl-salt, desalting, neutralising with alkali (NaOH) and washing. The pH was measured with a digital pH meter (Sentron 3001, Sentron BV, Netherlands) at the surface of 4-6 capelins to follow up the pH during treatments. These treatments where done in different orders for each group (see also Appendix 1):

Group 1: Untreated capelin.

Group 2: Brining in 18% brine, capelin/brine (1:1.8) for 24 hours.
Dry salting, capelin/salt (1:0.25) for 7x24 hours.
Desalting, capelin/water (1:13) for 18 hours, followed by desalting, capelin/water (1:2) for 18 hours.

Group 3: Acid solution (1%), capelin/acid sol. (1:2) for 0.5 hours.

Group 4: Acid solution (2%), capelin/acid sol. (1:2) for 0.5 hours.

Group 5: Acid solution (1%), capelin/acid sol. (1:2) for 0.5 hours.
Washing by dipping capelin in water for 1-2 minutes followed by rinsing.
Brining in 18% brine, capelin/brine (1:1.8), for 24 hours.
Dry salting, capelin/salt (1:0.25) for 7x 24hours.
Desalting, capelin/water (1:13) for 18 hours, followed by desalting, capelin/water (1:2) for 18 hours.

Group 6: Brining in 18% brine, capelin/brine (1:1.8) for 24 hours.
Dry salting, capelin/salt (1:0.25) for 7x24 hours.
Desalting, capelin/water (1:13) for 18 hours, followed by desalting, capelin/water (1:2) for 18 hours.
Acid solution (1%), capelin/acid sol. (1:2) for 0.5 hours.
Neutralising with alkali (pH 12).
Washing by dipping capelin into water bath for 1-2 minutes followed by rinsing.

Group 7: Brining in 18% salt/1% acid brine, capelin/brine (1:1.8) for 24 hours.
Dry salting, capelin/salt (1:0.25) for 7x24 hours.
Desalting, capelin/water (1:13) for 18 hours, followed by desalting, capelin/water (1:2) for 18 hours.
Neutralising with alkali (pH 11.3).
Washing by dipping capelin into water bath for 1-2 minutes followed by rinsing.

Finally the treatment groups were dried by convection drying at a temperature between 18-20°. All groups got the same time in the drying cabin; 236 hours. The drying time was not significant because the drying equipment was not running continuously all the time.

2.3. Shelf life test

Shelf life test was carried out at 39°C in order to speed up changes and imitate warm climate as expected in the transport and distribution of this kind of product. After drying, each treatment group was stored in open polyethylene bags and kept in a heated oven at 39±1°C and about 30% moisture content. One sample from each treatment group was taken for chemical measurements directly after drying and again after one month storage time at 39°C. For comparison, one sample from the raw material was also taken for chemical measurements.

2.4. Chemical measurements

Each sample was measured for chemical composition (water, protein, fat and salt), lipid oxidation (free fatty acids, peroxide value and TBA value). Each sample was also measured for total volatile nitrogen (TVN), for comparing protein deterioration and finally the pH was measured to see the influence of the acid treatment. Samples were homogenized in a food processor prior to measurements.
Water content was measured according to A.O.A.C, Ca 20-45 and IAFMM Analytical methods for fishmeal. Protein content was measured according to ISO 5983. Salt content was measured according to A.O.A.C 937.09, using water agitation instead of boiling with acid.
TBA value (thiobarbituric acid) was measured according to Tarladgis, 1954 using antioxidants as in Vynke, 1970.
Peroxide value (PV) was measured according to A.O.C.S Cd 8-53. Free fatty acids (FFA) were measured according to A.O.C.S Ca 5a-40. PV and FFA were measured on a lipid extract of the capelin samples. Lipid extraction was done according to Bligh and Dyer, 1959, with additions according to Hanson and Olley, 1963. Lipid content in the lipid extract was evaluated gravimetrically.
Total volatile nitrogen - TVN was measured according to Antonacopoulos, 1968.
Measurements on pH were done using a glass electrode on a 1:1 mixture of sample/distilled water.

2.8. Statistical analysis

Calculations of correlation coefficients (r) were done using Data Analysis Tool pack of the Microsoft Excel programme.

3. RESULTS & DISCUSSION

The treatments and condition for each group was as following:

Group 1: Capelin 7.72 kg, untreated.
Surface pH value: 5.3-5.4.
Drying start point: 70.8% MC.
Drying endpoint (236 hours): 2.63 kg, 14.3% MC.

Group 2: Capelin 7.92 kg.
Brining, salting, desalting.
Surface pH value: 6.0-6.3.
Drying start point: 74.9% MC.
Drying endpoint (after 236 hours): 2.25 kg, 11.6% MC.

Group 3: Capelin 5.52 kg.
Acid (1%).
Washing
Drying startpoint :73.5% MC.
Drying endpoint (after 236 hours): 1.79 kg, 18.3% MC.

Group 4: Capelin 5.65 kg.
Acid 2%.
Washing
Drying startpoint 73.5% MC.
Drying endpoint (after 236 hours): 1.86 kg, 21.9% MC.

Group 5: Capelin 8.56 kg.
Acid (1%), washing, brining, salting, desalting.
Surface pH value: 5.8-6.0.
Drying startpoint : 75.5% MC.
Drying endpoint (after 236 hours): 2.37 kg, 11.5% MC.

Group 6: Capelin 6.24 kg.
Brining, salting, desalting.
Surface pH value: 6.1-6.4.
Acid (1%).
Washing
Surface pH value: 4.4-4.7.
Neutralising, washing.
Surface pH value: 6.2-6.4.
Drying startpoint 73.9% MC.
Drying endpoint (after 236 hours): 1.75 kg, 6.9% MC.

Group 7: Capelin 5.23 kg.
Brining (18%salt/1% acid brine), salting: desalting.
Surface pH value 5.0-5.2
Neutralising, washing
Surface pH value 6.0-6.2
Drying start point 70.2% MC.
Drying endpoint (after 236 hours): 1.56 kg, 0.1% MC.

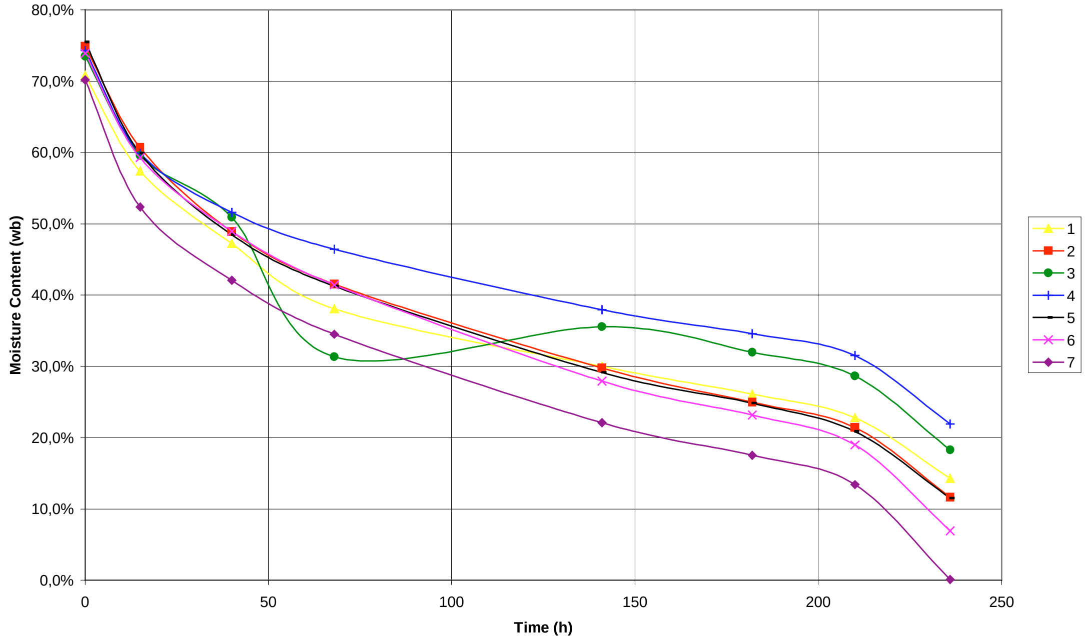

Figure 1. Drying curves of capelin. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

Drying curves are illustrated in Figure 1. There is obvious difference in drying rate between the groups. Group 7 is reaching 30% MC about 50 hours earlier than the next groups. For each group the initial moisture content was measured and then the drying process was followed up by weighing the product samples. There is a good uniformity between the groups through the whole drying period. One reading for group 3 after 68 hours is probably a wrong registration and at the final stage in the drying cycle the temperature was raised causing the steep in the curves. Unrealistic low final MC for especially group 7 (0.1% MC) might be due to inaccuracy in measurements and weighing.

Results of chemical measurements in the raw material are combined in Table 1.

Table 1. Chemical composition of capelin raw material.

	Water (%)	Protein (%)	Fat (%)	Salt (%)	pH	TVN mg/100g	PV meq/kg	FFA (%)	TBA mg/kg
Capelin	72.8	14.2	11.0	0.4	6.7	15.9	0.0	9.7	3.1

Results of chemical measurements of capelin after processing, drying and storage test at 30°C are compiled in Tables 2 and 3.

Table 2. Chemical composition of processed and dried capelin during storage at 39°C.

Capelin treatment	Days at 39°C	Water (%)	Protein (%)	Fat (%)	Salt (%)	pH
(1)-untreated	0	16.6	40.3	36.2	1.2	6.56
	30	4.7	48.2	38.5	1.3	6.37
(2)-salted-desalted	0	16.6	34.7	33.4	9.7	6.24
	30	3.8	41.8	38.9	10.4	6.04
(3)-1% acid	0	18.4	39.6	34.3	0.8	6.20
	30	4.0	48.7	39.3	0.9	6.19
(4)-2% acid	0	18.0	40.3	33.4	0.9	5.86
	30	3.9	49.7	37.3	0.9	6.06
(5)-1% acid-salted-desalted	0	17.5	32.9	35.8	9.8	5.98
	30	3.5	41.6	39.3	11.5	5.83
(6)-salted-desalted-1% acid-alkali	0	15.3	35.8	37.3	5.1	5.83
	30	3.6	42.9	42.0	6.0	5.86
(7)-salted/1% acid-desalted-alkali	0	12.9	39.5	39.1	4.8	5.34
	30	3.9	42.8	42.4	5.4	5.51

The average water content of capelin raw material was 72.8%. The water content decreased to average of 16.4% after drying and after one month storage to 3.9%. The difference in water content from the ones from the drying curve in Figure 1 is hard to explain and several factors may be involved. The highest difference was found in the driest samples. These samples may be very hygroscopic and susceptible to weight gain from atmospheric humidity during grinding and preparation of samples. As said before, unrealistic low final MC (Figure 1) might be due to inaccuracy in measurements and weighing.

The average protein and fat content increased after drying and storage with decreasing water content. Group 7 had far the lowest water content after treatment and drying, but group 3 had the highest water content. After one month storage at 39°C there was almost no difference between groups in water content, except that the untreated group (1) had the highest water content, see Figure 2.

The fat content between groups varied also a little. Groups 6 and 7 had the highest fat content, but group 4 had the lowest fat.

The salt content varied greatly between groups, see Figure 4. Groups 6 and 7 had markedly lower salt content compared to groups 2 and 5. These groups differ in the neutralising and rinsing treatment, that seems to lower the salt content. The acid treatment (groups 3 and 4) did also lower the salt content compared to untreated capelin (group 1).

The pH varied somewhat between groups, see Figure 5. The pH was lowest (highest acidity) in group 7, where the acid-brine acted for 24 hours and highest in the untreated group (1). In general the pH seems to get lower during drying and storage, except in group 4, where the strongest acid was used and in group 7, where the acid-brine acted for 24 hours. In both these groups the pH got higher after one month storage.

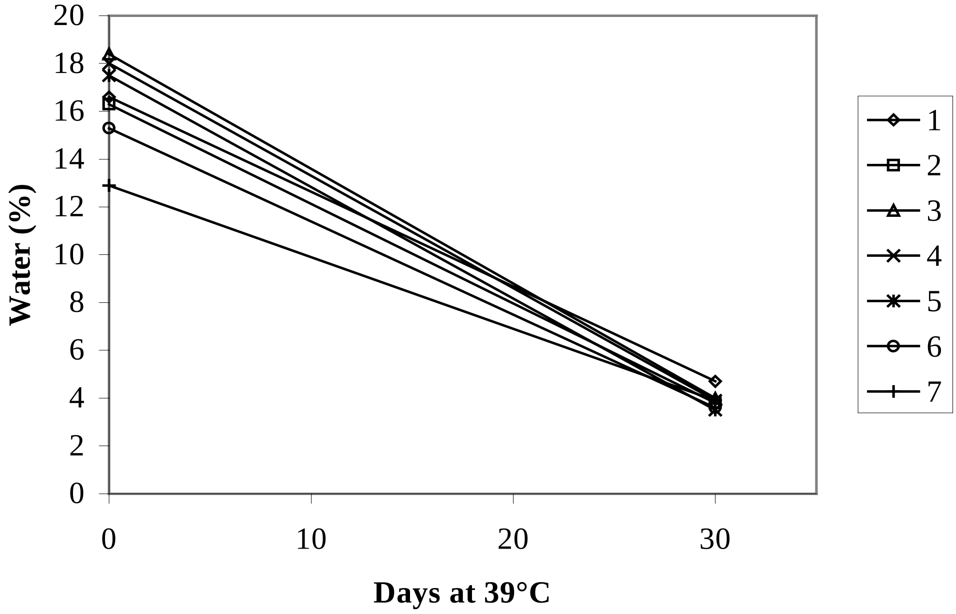

Figure 2. Water content in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

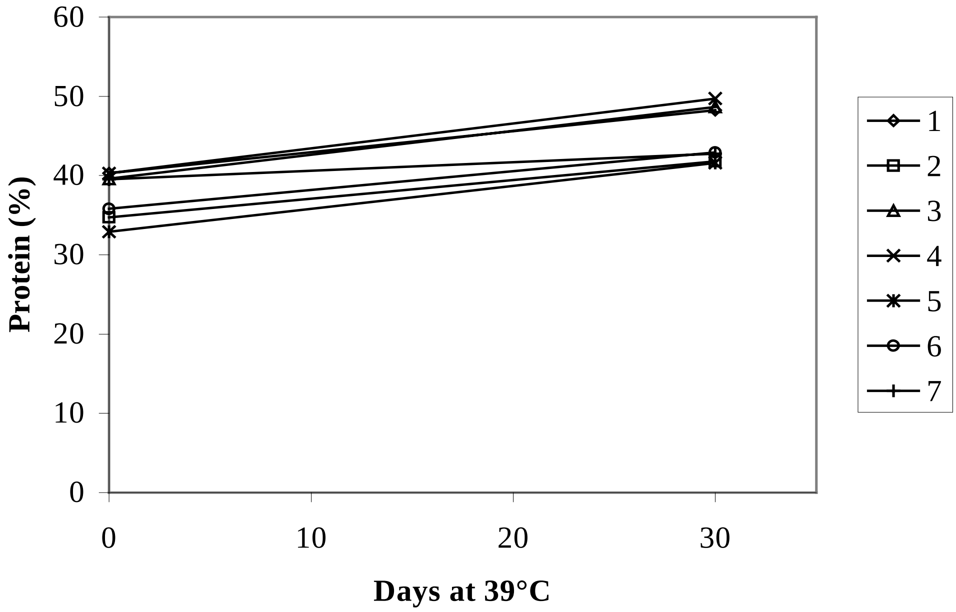

Figure 3. Protein content in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

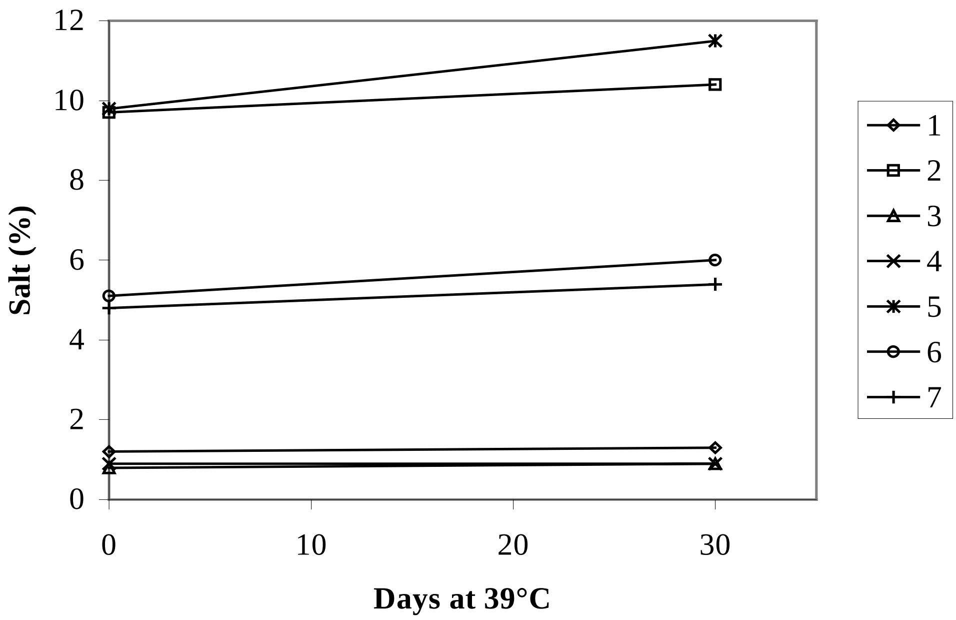

Figure 4. Salt content in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

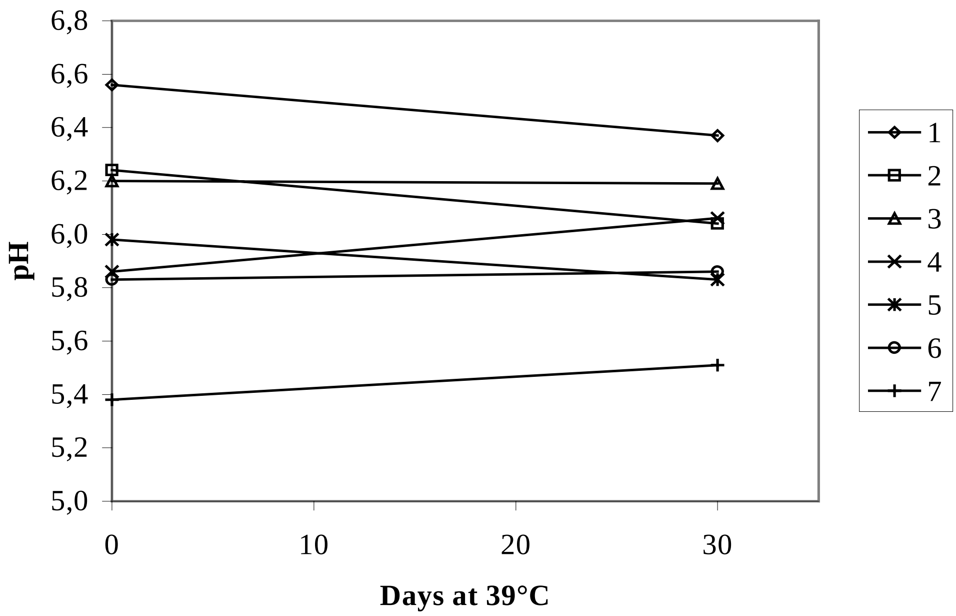

Figure 5. pH in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

Table 3. Chemical measurements of processed and dried capelin during storage at 39°C.

Capelin treatment	Days at 39°C	FFA (%)	PV (meq/kg)	TBA (mg/kg)	TVN (mg/100 g)
(1)-untreated	0	10.5	5.8	1.7	75.9
	30	18.3	0	1.0	133.3
(2)-salted-desalted	0	11.3	15.8	5.8	36.4
	30	18.0	< 2	3.1	65.8
(3)-1% acid	0	12.6	6.0	3.7	65.1
	30	22.6	0	1.5	111.3
(4)-2% acid	0	12.8	14.5	5.9	59.6
	30	22.8	0	1.6	109.7
(5)-1% acid-	0	10.9	15.9	12.9	33.9
salted-desalted	30	17.6	< 2	3.6	54.6
(6)-salted-desalted-	0	11.4	18.4	13.4	34.5
1% acid-alkali	30	18.2	< 2	3.6	67.8
(7)-salted/1% acid-	0	12.0	29.5	23.4	32.9
desalted-alkali	30	24.5	< 2	4.4	62.4

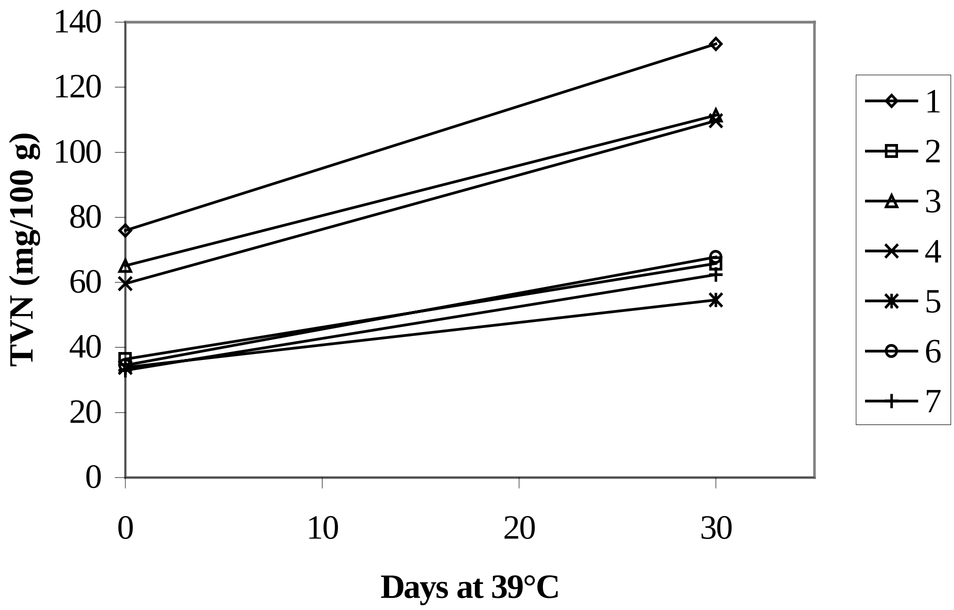

Figure 6. TVN in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

The TVN was highest in the untreated group (1) and the acid treated groups (3 and 4), both after drying and after one month storage at 39°C. In general the TVN value doubled during storage at 39°C for all groups, but least in group 5.

Free fatty acids in extracted lipids indicate the onset of lipid hydrolysis. The FFA increased very much in all groups during one month storage at 39°C. This was highly expected because fish lipids are unstable and prompt to lipid hydrolysis because of high content of unsaturated fatty acids. There was not much difference between groups in FFA after treatment and drying. But after one month storage at 39°C the

FFA was highest in groups 3, 4 and 7. These are the groups that got either the most acid treatment or were not neutralised after acid treatment.

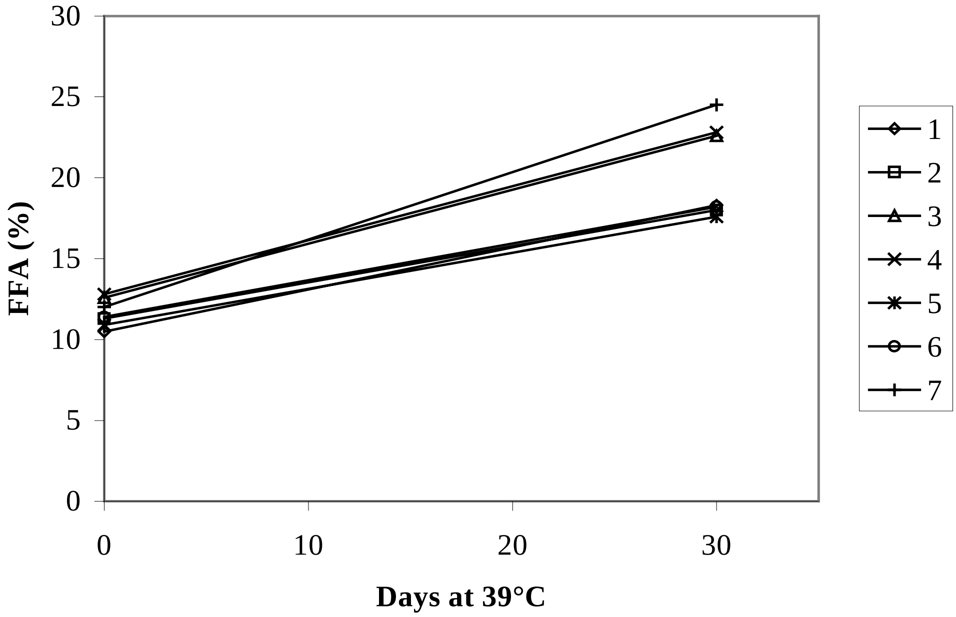

Figure 7. FFA in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

Peroxide value in extracted capelin lipids indicates primary oxidation. Peroxides are called primary oxidation products of lipid oxidation, because they are first produced and then they react further to produce secondary products of lipid oxidation. Because peroxides are very reactive, they have a limited lifetime, they either decompose or form other products. No peroxides were measured in the capelin raw material, indicating no or very low lipid oxidation in the raw material. Peroxides were detected in the treatment groups after drying, but declined almost to zero after one month storage at 39°C. Group 7 had the far highest peroxide value of all groups, followed by groups 6, 2, 5 and 4, but groups 1 and 3 had the lowest peroxide values.

One of the secondary lipid oxidation products is malondialdehyde that is measured in the TBA-value measurement. Secondary lipid oxidation is the consequence of primary oxidation and their products are usually more stable. The TBA-value declines very much during storage of capelin, most probably due to the high temperature (39°C) that promotes decomposition or even evaporation of malondialdehyde. The TBA-value of 3,1 in the raw material does not necessary indicate a poor raw material, because TBA-value is relative to lipid composition and can be variable from one fish species to another. Group 7 had the far highest TBA-value after treatment and drying followed by groups 5 and 6, but group 1 had the lowest value and group 3 was also rather low. After one month storage at 39°C the TBA- values had declined to 1-4 (mg/kg) but the group sequence was the same.

Although peroxide value indicates primer oxidation and TBA-value secondary oxidation, there was a good correlation between these measurements. These measurements had a correlation coefficient, r = 0.90.

Peroxide value had also a good negative correlation to pH, with r = -0.93. This indicates that the pH influences the peroxide value, in such way if we lower the pH value then we may expect higher peroxide value or lipid oxidation.

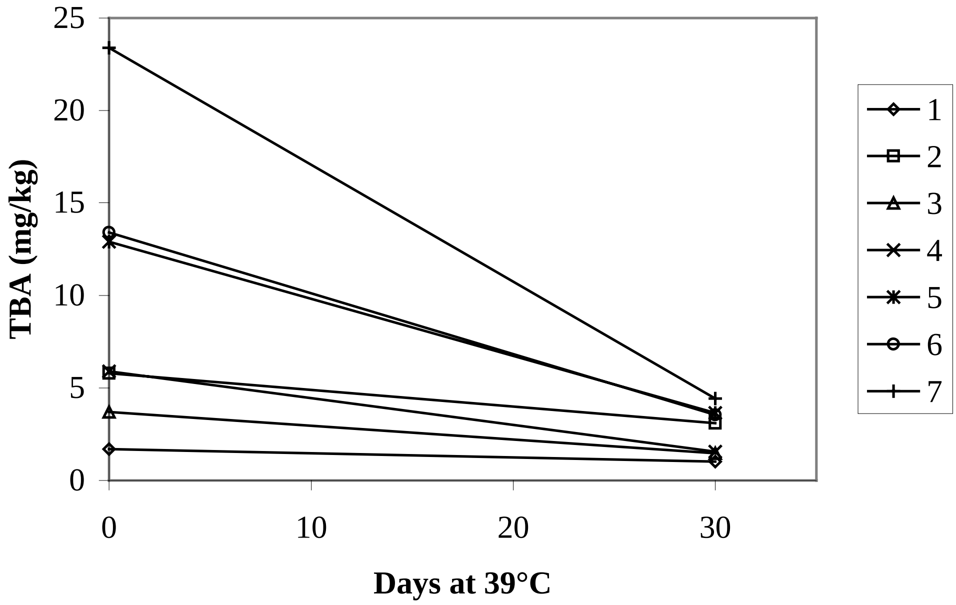

Figure 8. TBA value in processed and dried capelin during storage at 39°C. (1)-untreated. (2)-salted-desalted. (3)-1% acid. (4)-2% acid. (5)-1% acid- salted-desalted. (6)-salted-desalted-1% acid-alkali. (7)-salted/1% acid- desalted-alkali.

4. CONCLUSIONS

From these preliminary findings we can conclude that brining in salt/acid brine (group 7) gives the lowest water content, the lowest pH and the most lipid oxidation. Acid treatment alone (group 3) had very little influence on chemical composition or lipid oxidation. All washing treatment seems to lower the salt content and even the TVN-value.

The aim of this experiment was to get information about possible accommodation of pre handling raw material for drying with salt- and acid treatment. By this treatment it might be possible to reduce the cost by storing the raw material and by processing/drying the product.

Due to a preliminary product specification for salted/dried capelin, the requirement is maximum 30-35% moisture content and about 6 to 10% salt content. According to that, the above result shows that it is possible to keep the product within these limits.

The experiment did not show any complication by treating the material this way and it seems that this method is economical. To get this method further confirmed it is necessary to do a large-scale experiment and research.

It is essential to make further experiments concidering that treatment and storing of raw material in salt/brine tanks might be cheaper than freezing and storing in cold storage.

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APPENDIX 1

Capelin treatment groups