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The Investigation of Quality Changes in Marinades Obtained from Frozen African Catfish (*Clarias gariepinus*, B., 1822)

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Abstract: In this study it is aimed to investigate the suitability of African Catfish (*Clarias gariepinus*, B.,1822) caught intensively especially in Mersin-Silifke for marinating and determine its shelf life. After their heads and tails were cut off and they were eviscerated first and then washed and drained of the water, the samples were put into plastic refrigerator bags and kept at -18°C for 3 months. At the end of 3 months, the frozen samples were defrosted and boiled in boiling water for 5 min. They were put in brine after cooling and preserved at 4±1°C. In the raw material, raw protein, lipid, moisture, raw ash analyses of the samples kept frozen for 3 months and the marinated samples were done in order to monitor the changes in the food composition at 3 month intervals and Thiobarbituric Acid number (TBA), Total Volatile Basic-Nitrogen (TVB-N), peroxide number, pH and sensory analyses were done in order to monitor the changes in chemical quality.

Key words: African catfish, marinating, shelf life, quality, protein, lipid

INTRODUCTION

The ever-increasing world population exceeded 6 billion at the turn of the new millennium while it was 2,5 billion in the 1950s. The increasing population both creates a shortage on agricultural food products and necessitates alternative food production. The need for animal proteins is also on the increase in parallel with famines and malnutrition in the world.

Aquaculture products which have a major role in food production are consumed in a variety of ways in the country: fresh, frozen and processed (smoked, canned, marinated, salted, dried, etc.). Consuming processed aquaculture products enables both the conservation and a more profitable usage of the product.

Marinating technology is one of the oldest known methods of food conservation and dates back to the 7th century B.C (Gokoglu, 2002). The basic principle of marinating process is that the fish, subjected to one or more pre-processing techniques is rendered eatable by treating with acetic acid and salt. The products obtained this way are among the food items that can be consumed without any subjection to thermal treatment (Gram and Huss, 1996).

Maturing process the first phase of marinating is comprised of complex physical and chemical reactions. Marinating process takes place with the effect of neither acetic acid alone nor salt (Varlik *at al*., 2004). Salt and acetic acid which, although, have the same effect on fish meat are in fact, substances with opposite charges cancelling the effect of one another. While salt hardens the material, acetic acid softens it (Kilinc and Cakli, 2004).

In the maturing process, salt and acetic acid transfer into fish tissue continues until the salt and acetic acid levels in the fish tissue liquid are equal with the salt and acetic acid levels in the solution (Karl *et al*., 1994). Although it has been reported that this transfer is completed fast, generally in two day's time (Dokuzlu, 2000) it may still vary depending on temperature and meat thickness.

In marinated products it is aimed to provide the product with a longer shelf life by stopping the activities of present bacterial enzymes in the product with the effect of acetic acid and salt. Acetic acid and salt, along with the enzymes from fish, have an effect on the protein and lipid contents of fish although they cause destruction to a certain extent in the protein and lipid contents of fish and as a result, aromatic and delicious products are created (Schenderyuk and Byokowsky, 1990).

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In this study, it is aimed to achieve product diversity or and improve the quality of African Catfish which has a problem of marketing in our country and investigate how African Catfish can be integrated into economy to the benefit of fishing industry in the area.

MATERIALS AND METHODS

In the study, 40 kg of African Catfish (*Clarias gariepinus*) caught from Göksu Delta were used. The cleaned and skinned fish were washed with potable tap water. After their water was drained, they were put into plastic refrigerator bags and kept at -18°C for 3 months. The frozen samples were defrosted at +4°C, 1 day before the marinating process and then were put as a whole into boiling water and kept there for 5 min. The boiled fish meat were placed at a rate of 1:1.5 (fish: solution ratio) in three plastic cans of 10 L which contained brine with 3% of acetic acid and 8% of sodium chloride and the plastic cans were sealed and stored in refrigerator conditions (4±1°C).

In order to determine the shelf life of the samples, the following monthly analyses were done on the fish samples stored in a cold place for 3 months and the samples after the marinating. For chemical composition analyses; (James, 1995) for protein, Bligh and Dyer (1959) for lipid, Ludorff and Meyer (1973) for moisture, Mattissek *at al*. (1988) were used for ash analyses. For monitoring chemical quality changes (Tarladgis *at al*., 1960) for Thiobarbituric Acid number (TBA) analysis, Antonacopoulos and Vyncke (1989) for Total Volatile Basic-Nitrogen (TVB-N) analysis and for peroxide (AOAS, 1994) and Hanna HI 991001 brand pH metre for pH analyses were used (Ludorff and Meyer, 1973).

The evaluation of sensory analyses was done according to the calculating table developed by Amerine *et al*. (1965). In this table, 10-7,0 points are regarded as very good, 6,9-4,0 points as good and 3,9- 1,0 points as decayed.

RESULTS AND DISCUSSION

The changes in nutritional and chemical quality parameters in African Catfish (*Clarias gariepinus*) fillet, in the material kept frozen for 3 months and in the marinated products during storage period were examined and the results are shown in Table 1 and 2.

Ersoy and Yilmaz (2003) determined in their study that moisture rate in raw African Catfish was 73.20%, raw protein 21.22%, raw lipid 4.6% and raw ash 1.10%. In their study on the effects of cooking methods on the mineral and vitamin contents of the products, Ersoy and Ozeren (2009) determined that raw protein in the raw African Catfish material was 16.2%, moisture 76.8%, raw lipid 5.02% and raw ash 0.83%

Chomnawang *et al*. (2007) determined the raw protein, raw lipid, moisture and raw ash rates of hybrid cat fish (*Clarias macrocephalus* x *Clarias gariepinus*) at the beginning of storage period as 18.68, 3.03, 75.68 and 1.17%, respectively. It was determined that the nutritional values of African Catfish raw material obtained in the study are compatible with literature data.

It was observed that while the TVB-N value of fresh African Catfish used for marinating was determined to be 17.15 mg/100 g, it dropped to 11.62 mg/100 g at the end of 3 months of storage period. The TVB-N value recorded to be 11.07 mg/100 g on the day 0, when the marinades matured, increased continuously during the storage

Table 1: The changes in the nutritional composition of raw material, frozen fillet and marinated products during storage period

Storage of time	Protein	Lipid	Moisture	Ash
Raw material	16.42±1.45	4.93±0.12	73.37±0.46	1.15±0.02
Frozen fillet	16.02±0.08	4.52±0.04	75.27±2.55	4.15±0.02
Day 0 (After marinating)	19.01±0.88	3.30±0.06	75.63±0.23	5.72±0.03
Day 30	19.37±0.53	3.67±0.06	71.40±0.10	5.66±0.01
Day 60	18.04±1.69	3.72±0.10	71.30±0.30	5.82±0.06
Day 90	19.03±0.02	3.86±0.04	72.83±0.45	6.17±0.31
Day 120	20.35±0.05	3.48±0.08	74.57±0.81	5.82±0.12
Day 150	20.19±0.85	4.15±0.05	71.70±0.82	5.74±0.27

Values are as $\bar{X} \pm S_{\bar{x}}$

Table 2: The changes in the chemical quality parameters of raw material, frozen fillet and marinated products during storage period

Storage of time	TVB-N (mg/100 g)	TBA (mgMA kg^{-1})	POS (meq kg^{-1})	pH	Sensory
Ham materyal	17.15±0.81	1.23±0.48	1.78±0.08	6.11±0.03	*
Raw material	11.62±0.91	1.64±0.11	2.10±0.05	4.35±0.04	*
Frozen fillet	11.07±0.11	2.54±0.08	2.22±0.11	3.80±0.00	4.47±0.50
Day 0 (After marinating)	12.53±0.05	3.34±0.06	2.47±1.04	3.95±0.01	4.37±0.32
Day 30	12.83±0.46	2.42±0.23	2.61±0.15	4.09±0.02	2.50±0.10
Day 60	12.11±0.82	3.38±0.08	2.88±0.04	4.14±0.03	2.20±0.00
Day 90	14.90±0.80	3.68±0.42	3.26±0.03	4.17±0.01	1.00±0.00
Day 120	17.23±0.79	4.18±0.19	3.57±0.06	4.24±0.02	1.00±0.00

No evaluation was made, Values are as $\bar{X} \pm S_{\bar{x}}$

period and reached 17.23 mg/100 g. It was determined, as a result of our analyses that the TVB-N value in marinades was lower than the 32-36 mg/100 g limit value Varlik *et al*., (2000) cited Ludorff and Meyer (1973) defined for fresh water fish and that the TVB-N value of the defrosted samples after freezing was lower than the 25 mg/100 g limit value defined by the same researchers for trout stored in a cold place.

It was determined that the TVB-N value found to be 17.15 mg/100 g in our study for raw material was higher than the value Ersoy and Yilmaz (2003) defined as 14 mg/100 g for African Catfish raw material. Olgunoglu (2007) reported, in his study on anchovy marinades, that the TVB-N value which was 11.90 mg/100 g at the beginning of storage period, reached a value of 16.91 mg/100 g at the end of a 7 month storage period.

Aksu *et al*. (1997) reported that the TVB-N value 8.3 mg/100 g in marinated anchovy (*Engraulis encrasicolus*) reached 15.2 mg/100 g at the end of a 150 day storage period and Dokuzlu (2000) reported that the TVB-N value 9.8 mg/100 g in marinated anchovy reached 14 mg/100 g at the end of a 8 month storage period at +4°C.

Ozden and Baygar (2003) reported, in their study in which they investigated the effects of different packaging methods on the quality criteria of marinated fish that the TVB-N values of anchovy (*Engraulis encrasicolus*), scad (*Trachurus trachurus*) chub mackerel (*Scomberjaponicas*) and sardine (*Sardina pilchardus*) recorded up to the day 120 were considerably below the edible limit values although increases in TVB-N during storage periods varied. In another study by Varlik *et al*. (2004) it was reported that the TVB-N value of fish balls on the 150th day was 10.45 mg/100 g.

In the study, the TBA values were found to be 1.23 mg MA kg^{-1} for raw material used to make products and 2.54 mg MA kg^{-1} at the beginning of storage and 4.18 mg MA kg^{-1} at the end of storage for the marinated African Catfish.

In his study, he investigated some quality changes in anchovy (*Engraulis encrasicolus*) marinades prepared by using two different maturing solutions (Group 1:10% salt +2% vinegar, Group 2:15% salt +2% vinegar), Yapar (1998) reported that while the TBA value was 1.65 mg MA kg^{-1} in the 1st week in Group 1, it increased to 2.35 mg MA kg^{-1} in the 10th week and it varied between 1.13 and 2.34 mg MA kg^{-1} in group 2.

Sallam *et al*. (2007) found the raw TBA value of pacific saury (*Cololabis saira*) which they marinated in different acid solutions to be 0.37 mg MA/kg and emphasized that marinades were of good quality although no steady increase had happened during the 90 days of storage period. Olgunoglu (2007) found out that the TBA value of anchovy (*Engraulis encrasicolus*) marinades at the beginning of storage period was 1.16 mg MA kg^{-1} and it steadily increased and reached 4.20 mg MA kg^{-1} at the end of 7 months of storage period. Varlik *et al*. (2007) maintained that the TBA number should not be <3 in a very good material and it should not be >5 in a good material (Varlik *et al*., 2007).

When all the TBA values obtained throughout the study are taken into consideration, it was determined that TBA values increased as the storage period came to an end but still, marinades were within the limits of a good quality marinade at the end of a 150 days storage period.

Varlik *et al*. (2007) reported that the peroxide number of an aquaculture product that could be defined as of good quality should be between 2 and 5 $mmolO_2$/kg in fat (Varlik *et al*., 2007). The peroxide number of the prepared marinades calculated until the end of the 150 days of storage period showed that African Catfish marinades were of good quality.

While Ersoy and Yilmaz (2003) calculated the pH value in raw African Catfish material as 6.67 and Chomnawang *et al*. (2007) as 6.41, Suvanich and Marshall (1998) stated that the pH value in fish after rigor mortis was between 6.2 and 6.5. It was observed that the pH values of the raw material recorded in our study are in accordance with those obtained by the researchers. It was determined that the pH values of the marinated products calculated throughout the storage period show similarity with the values 4.0-4.5 Varlik *et al*. (2004) defined for good quality marinated products (Suvanich and Marshall, 1998).

According to the sensory analyses of marinated African Catfish fillets it was determined that they were marketable up to the 30th day and decayed after the 60th day.

CONCLUSION

As a result of the analyses it was determined that no nutritional loss happened in the marinated products. In the light of data obtained from the analyses of the chemical quality parameters it was concluded that although African Catfish marinades were of good quality, it was not acceptable sensorily. It is thought that it will be beneficial to carry out studies on sensorily different methods of marinating in the future.

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