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Research Article

Changes in Fatty Acid and Mineral Compositions of Rose-Shrimp Croquettes During Production Process

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Abstract

Background and Objective: Croquette production technology is one of the most using food processing method in the world. When the croquette technology implemented to aquatic products, it is nutritious and delicious as well as economically valuable products are obtained at the same time. The goal of this study is to produce croquettes from rose-shrimp meat and to specify changes occurred in the content of fatty acids and mineral during the production. **Materials and Methods:** First of all, croquettes were produced from shrimp meat. In the latter, croquettes were fired at 180°C and samples were stored for analysis. Thus, fatty acid, mineral and proximate composition of shrimp meat, raw and fried croquettes were determined. Finally, obtained data were analyzed with one-way ANOVA in SPSS statistical package programme. **Results:** Findings of this study demonstrate that, moisture and protein rate decreased, while fat and ash rate increased during production of croquettes. Unsaturated fatty acids such as docosahexaenoic, eicosapentaenoic, oleic and palmitoleic acids decreased whereas saturated fats were increased after the croquette production ($p \leq 0.05$). After the deep-frying process, saturated fatty acids decreased. However, unsaturated fatty acids especially oleic and linoleic acids increased due to high monounsaturated fatty acid contents of sunflower oil used in frying process ($p \leq 0.05$). On the other hand, most of the minerals of shrimp meat decreased except sodium, potassium, manganese and zinc throughout the production process ($p \leq 0.05$). While the bromine, boron, copper, manganese and zinc decreased, calcium, magnesium, iron and potassium remained statistically the same after the frying process ($p \leq 0.05$). **Conclusion:** Despite the decrease of some fatty acids and trace metals due to cooking, it should be noted that shrimp croquettes as well as fried ones are still valuable in terms of nutritional quality. In the view of the results, with minimal production loss, croquette technology can be implemented to shrimp meat for achieve healthy and delicious final product.

Key words: Croquette, rose-shrimp, fatty acid, trace mineral, seafood, proximate composition, food quality, deep-fry

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Three billion people consume seafood as a major source of animal protein in the world¹. Likewise, shrimp species have high content of proteins, essential amino acids, poly unsaturated fatty acids which mostly consist of docosahexaenoic and eicosapentaenoic acids and vital minerals such as potassium, phosphorus, magnesium, calcium and iron²⁻⁵. Thus, the culturing, processing and marketing of several shrimp species has become more prevalent nowadays^{6,7}. Especially in Europe, three species which are northern prawn (*Pandalus borealis*), brown shrimp (*Crangon crangon*) and deep-water rose shrimp (*Parapenaeus longirostris*) mostly dominated continental shrimp production⁷. Deep-water rose shrimp distributed from Mediterranean water, East to West Atlantic and entire^{8,9}. Thus, this species was caught all over the world as well as Turkish waters except Black Sea coast due to their economic value^{6,10,8}. Some marine fish and invertebrate species such as deep-water rose shrimp are expensive with their exquisite sensorial quality^{11,12}. Thus, it's usually used by seafood processing plants as a valuable food source^{10,11}. Shrimp species can be consumed as raw, marinated, smoked and dried^{10,13}. Besides, a new and desired sensorial property can be achieved with different processing techniques just as croquette production¹⁴. Several seafood sources such as fish, shellfish and crustacean meats, minces and by-products of them could be preferred in croquette production^{15,16}. Frozen processed foods which mostly consist of coated products such as croquettes have a leading role in European food industry and international trade of the frozen ones especially made from fishery products is increasing steadily^{17,18}. Fried foods are also appreciated for the consumers all over the world due to their unique flavour¹⁹.

The aim of this study is to produce croquettes from rose-shrimp meat and to specify changes occurred in the contents of fatty acids and mineral during the production. For these reasons, this precious and flavoured species were used in croquette production in order to achieve nutritious and delicious seafood products having high market value. This study reveals changes in the nutrient content during the production of shrimp croquettes. Our study can contribute to future studies which are intended to minimize production losses.

MATERIALS AND METHODS

Raw materials: The deep-water rose shrimp (*Parapenaeus longirostris*) was chosen for croquette production due to its high nutritional and sensorial value. Shrimps were caught by

beam trawl in Sea of Marmara and brought to laboratories. First, shrimps were sub-sampled according to Avsar²⁰ as 10 kg. Later, shrimps were combed out of their shells and 4.8 kg shrimp meat was obtained and used for croquette production.

Ingredients and coating materials: Croquette paste contains 75.50% shrimp meat. The remaining ratio consists of some ingredients such as wheat flour (9.70%), bread crumbs (9.70%), corn flour (1.31%), coconut powder (1.78%), salt (1.00%), wheat starch (0.68%), onion (0.43%), garlic (0.20%), cilantro (0.13%), black pepper (0.28%) and white pepper (0.23%). Besides; wheat flour, corn flour, bread crumbs, baking-soda, drinking water were used as covering materials. Sunflower oil which is most used oil kind in frying process in Turkey preferred in the frying process. All materials were bought from local market.

Technical infrastructure: Grinder 3 mm long as Tefal 1800 w, deep electric fryer with temperature controls, analytical balance as Kern/ABJ (± 0.001 g), moisture analyzer as Xm50 Precisa Kjeldahl digestion and distillation system as Behro test, drying oven as Shin Saeng/SDON-302, muffle furnace as Elektro-Mag/M-181, rotary evaporator as IKA/RV 10 Basic, soxhlet evaporator as Elektro-mag, microwave as Speedwave Berghof, Perkin ICP-OES as Elmer Optima 8000, GC-MS as Thermo Finnigan Trace GC-MS couple with multiplier quadruple mass selective detector and Thermo auto sampler AI 3000 injector were used in this study.

Data tools and software: Xcalibur Home Page version 1.4 SR1 Software for fatty acid analysis, libraries of NIST and Wiley for chromatograms, Varian Liberty AX Sequential ICP-AES for element analysis and IBM SPSS Statistics package programme version 21.0 for statistical analysis were used in this study, purpose of evaluation and comparisons of all results.

Chemicals, reagents and other expandable supplies:

Sulphuric acid, Kjeldahl catalyst (containing selenium), hydrochloric acid, boric acid, chloroform, methanol, sodium hydroxide, boron trifluoride (Bf₃), heptane, sodium chloride, hexane, nitric acid and helium were used in analysis and all chemicals and reagents were supplied from Merck Millipore. Moreover, vial as 2 mL amber with polytetrafluoroethylene cover, injector filter 1.2 μ m, Whatman filter 1.2 μ m and 0.47 mm and capillary column for GC-MS as ZB-5MS (5% phenyl methylsiloxane) with a dimension of 30 m \times 0.25 mm I.D \times 0.25 mm film thickness (Phenomenex, Zebron, USA) were also used.

Croquette production: Croquettes were produced based on researcher's previous studies²¹⁻²³. First, shrimps were cleaned and washed after their combs were eviscerated. In the latter, shrimp meat was minced by grinder for 60 sec and the ingredients were added. This mixture was kneaded for approximately 5 min and shaped by hand and sliced. The obtained croquettes were coated by liquid and dry coating materials, in that order. In the liquid coating step, croquettes were dipped into baking soda-water based coating material. In the dry coating step, croquettes were coated with mixtures of wheat flour, corn flour and bread crumbs. Finally, obtained croquettes were fried at 180°C and frying oil renewed before the all frying for healthy nutrition.

Calculating of meat and product yields: The meat and product yields were carried out by Oztan²⁴. The meat yield was calculated as weight of shrimp meat after the shrimps were combed out their shells and cleaned out of all organs. The product yield was calculated as ratio of obtained croquettes weight to uncleaned shrimp weight with shells. Thus, amount of shrimp croquettes can be made per one kilogram of shrimps with this formulation is revealed. The equations were used to estimation of meat yield (1) and product yield (2) were given below:

$$\text{Meat yield} = \frac{\text{Meat weight (g)}}{\text{Total shrimp weight (g)}} \times 100 \quad (1)$$

$$\text{Product yield} = \frac{\text{Croquette weight (g)}}{\text{Total shrimp weight (g)}} \times 100 \quad (2)$$

Determination of proximate composition: Total moisture, crude protein, fat and ash contents were determined to identify proximate composition. Moisture content was analyzed via moisture analyzer. Crude protein was determined by AOAC²⁵ method. In this method, the samples were digested with AOAC catalyst and sulphuric acid in 120°C. Later, these mixtures were titrated 0.1 N hydrochloric acid and obtained data was evaluated by using nitrogen conversion factor as 6.25. The crude fat content of shrimp meat was extracted with methanol: chloroform mixture firstly. After that, these extracts were evaporated with rotary evaporator at 55°C and under reduced pressure²⁶. The crude ash content was specified by Horwitz²⁷ method. According to this method, samples were burned in 600°C for 6 h. Ultimately; the obtained data of analysis were estimated as percentages.

Acquiring fatty acid methyl esters: Fatty acid analysis was carried out according to IUPAC²⁸. The samples were

evaporated with soxhlet evaporator with 0.5 N NaOH for 15 min, 5 mL BF₃ reagent for 2 min and 2 mL Heptane for 1 min in 55°C, respectively. Afterwards, the concentrated mixtures were blended with saturated NaCl solution and a liquid phase was obtained contain fatty acid methyl esters. These liquid phases were filtrated into 2 mL amber vials with hexane.

GC-MS conditions and peak identification: The fatty acid analysis was carried out with GC-MS according to Paul and Southgate²⁹. A capillary column was used in the analysis. The split ratio was 1:20 and helium was used as a carrier gas (flow rate of 1.0 mL min⁻¹). The injector was 220°C and ion source was 230°C. The mass spectrometer was operated in the Electron Impact (EI) mode at 70 eV in the scan range of 50-650 m/z.

The peaks of fatty acids were calculated according to mass spectra of known standards (Supelco 37 Component FAMES Mix) as well as comparing the retention times. Libraries were used to identification of chromatograms and obtained data was evaluated as percentages with Xcalibur Software. Percentage values were converted to g/100 g wet weight as described by Paul and Southgate²⁹.

Element analysis: The element analysis was carried out by Environmental Protection Agency³⁰. According to this method, the samples were burned in microwave with concentrated nitric acid. Afterwards, the burned mixtures were filtered with 2 µm filter paper and they were analyzed via ICP-AES. The analyzed elements were boron (B), bromine (Br), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb) and zinc (Zn). Ultimately, obtained data were compared with the standards obtained with metal salts and calculated as milligram per kilogram of wet matter.

Statistical analysis: Statistical analysis were carried out according to Zar³¹. Differences between groups were determined by one-way analysis of variance ANOVA using Tukey's multiple comparison tests. Values are expressed as Mean ± SD (n = 3). The level of significance was set as 0.05 and mean values in row with different superscripts were significantly different (p<0.05).

RESULTS

The mean weight of shrimp individuals was calculated as 4.73 g as well as maximum as 19.32 and minimum as 2.32. In the calculating of yields, 10 kg of shrimp were

evaluated. After the cleaning process, 4.8 kg shrimp meat was obtained. Afterwards, 6.9 kg croquettes were produced from shrimp meat. Thus, meat yield of deep-water rose shrimp was calculated as 48.46% and product yield as 69.34%.

According to analyzed results, deep-water rose shrimp meat has $72.89 \pm 0.29\%$ moisture, $18.68 \pm 0.26\%$ crude protein, $5.05 \pm 0.43\%$ crude fat and $2.08 \pm 0.15\%$ crude ash. While the ratios of water and protein decreased, the ratios of fat and ash increased statistically in obtained croquettes ($p \leq 0.05$). Same changes were observed in the sequel of frying process. Proximate composition of shrimp croquettes were shown in Table 1.

Table 1: Proximate compositions of shrimp meat, raw and fried croquettes (%)

Parameters	Shrimp meat	Croquettes	Fried croquettes
Moisture (water)	72.89 ± 0.29^a	56.88 ± 0.82^b	45.90 ± 0.72^c
Crude protein	18.68 ± 0.26^a	15.65 ± 0.22^b	14.48 ± 0.20^c
Crude fat	5.05 ± 0.43^c	7.36 ± 0.12^b	12.09 ± 0.34^a
Crude ash	2.08 ± 0.15^c	2.89 ± 0.05^b	3.25 ± 0.08^a

Values are expressed as Mean \pm SD (n = 3), mean values in row with different superscripts were significantly different ($p \leq 0.05$)

In the shrimp meat, docosahexaenoic acid ($24.79 \pm 0.36\%$), oleic acid ($19.20 \pm 0.13\%$) and eicosapentaenoic acid ($15.35 \pm 0.59\%$), palmitoleic acid ($9.069 \pm 0.08\%$) were detected as the most abundant unsaturated fatty acids as well as palmitic acid ($14.81 \pm 0.08\%$) among saturated ones. Remarkable amounts of arachidonic, linoleic, dihomo-gamma-linolenic, eicosadienoic acids in PUFA, heptadecanoic and eicosenoic acids in MUFA, stearic, heptadecanoic, myristic and pentadecanoic acids in saturated fatty acids were detected. Those unsaturated fatty acids decreased except linoleic and nervonic acids during production process. However, nervonic acid completely lost after the frying process. Also, eicosenoic, dihomo-gamma-linolenic and eicosadienoic acids completely lost with deep-frying. On the contrary, oleic acid which is decreased in croquettes and linoleic acid increased after frying. Nevertheless, DHA decreased in fried croquettes ($p \geq 0.05$). Palmitoleic, heptadecanoic, arachidonic acid and EPA remained the same statistically after frying ($p \leq 0.05$). Fatty acid compositions of shrimp croquettes were shown in Table 2.

Table 2: Fatty acid compositions of shrimp meat, raw and fried croquettes (%)

Fatty acids	Shrimp meat	Croquettes	Fried croquettes
Saturated fatty acids			
C _{10:0} capric acid	-	1.457 ± 0.03^a	0.286 ± 0.04^b
C _{12:0} lauric acid	0.043 ± 0.01^c	10.703 ± 0.30^a	4.288 ± 0.07^b
C _{13:0} tridecylic acid	-	0.033 ± 0.02^a	0.012 ± 0.01^a
C _{14:0} myristic acid	0.724 ± 0.01^c	2.709 ± 0.05^a	1.065 ± 0.11^b
C _{15:0} pentadecylic acid	0.645 ± 0.02^a	0.371 ± 0.01^b	0.343 ± 0.01^b
C _{16:0} palmitic acid	14.808 ± 0.08^a	14.285 ± 0.18^{ab}	13.849 ± 0.19^b
C _{17:0} heptadecanoic acid	1.145 ± 0.02^a	0.687 ± 0.03^b	0.646 ± 0.02^b
C _{18:0} stearic acid	4.530 ± 0.23^a	4.015 ± 0.03^{ab}	3.835 ± 0.11^b
C _{20:0} arachidic acid	0.151 ± 0.01^a	0.130 ± 0.01^a	0.094 ± 0.01^b
C _{21:0} heneicosanoic acid	0.014 ± 0.01^a	0.046 ± 0.04^a	-
C _{22:0} docosanoic acid	0.112 ± 0.01^a	0.376 ± 0.27^a	0.139 ± 0.01^a
C _{23:0} tricosylic acid	0.027 ± 0.01^a	-	-
C _{24:0} lignoceric acid	0.037 ± 0.01^a	0.038 ± 0.01^a	0.025 ± 0.01^a
Total	22.242 ± 0.46^c	33.397 ± 0.59^a	24.302 ± 0.66^b
Monounsaturated fatty acids			
C _{15:1} pentadecanoic acid	0.047 ± 0.01	-	-
C _{16:1} palmitoleic acid	9.069 ± 0.08^a	3.516 ± 0.09^b	3.556 ± 0.11^b
C _{17:1} heptadecanoic acid	1.009 ± 0.05^a	0.413 ± 0.01^b	0.460 ± 0.01^b
C _{18:1(n-9)} cis-oleic acid	19.204 ± 0.13^b	17.369 ± 0.30^b	23.325 ± 0.17^a
C _{20:1(n-9)} eicosenoic acid	0.982 ± 0.06^a	0.591 ± 0.03^b	-
C _{24:1} nervonic acid	0.006 ± 0.01^b	0.173 ± 0.13^a	-
Total	30.320 ± 0.81^a	22.065 ± 0.74^c	27.343 ± 0.69^b
Polyunsaturated fatty acids			
C _{18:2(n-6)} linoleic acid	1.832 ± 0.19^c	14.428 ± 0.22^b	21.747 ± 0.31^a
C _{20:2} eicosadienoic acid	0.650 ± 0.02^a	0.438 ± 0.01^b	-
C _{20:3} dihomo-gamma- linolenic acid	0.982 ± 0.06^a	0.527 ± 0.01^b	-
C _{20:4(n-6)} arachidonic acid	3.671 ± 0.18^a	2.255 ± 0.08^b	2.307 ± 0.13^b
C _{20:5(n-3)} eicosapentaenoic acid	15.360 ± 0.59^a	7.291 ± 0.09^b	8.667 ± 0.45^b
C _{22:6(n-3)} docosahexaenoic acid	24.797 ± 0.36^a	17.478 ± 0.36^c	12.932 ± 0.33^c
Total	47.296 ± 0.52^a	42.420 ± 0.52^c	45.655 ± 0.34^b

Values are expressed as Mean \pm SD (n = 3), mean values in row with different superscripts were significantly different ($p \leq 0.05$)

Table 3: Mineral compositions of shrimp meat, raw and fried croquettes (mg kg⁻¹)

Minerals	Shrimp meat	Croquette	Fried croquette
Macro minerals			
Calcium	1105.70±7.09 ^a	703.03±4.57 ^b	704.41±6.55 ^b
Magnesium	485.27±6.24 ^a	419.07±1.83 ^b	411.40±5.17 ^b
Potassium	2213.23±8.12 ^b	2634.58±7.24 ^a	2641.54±8.57 ^a
Sodium	3662.46±1.69 ^c	4509.80±1.16 ^b	5394.21±1.10 ^a
Micro minerals			
Bromine	2.57±0.01 ^a	2.20±0.06 ^b	1.78±0.01 ^c
Boron	16.31±0.23 ^a	11.23±0.05 ^b	10.29±0.18 ^c
Chromium	<0.010	<0.010	<0.010
Cobalt	<0.035	<0.035	<0.035
Copper	8.45±0.01 ^a	6.06±0.33 ^b	4.59±0.22 ^c
Iron	66.20±1.06 ^a	31.02±0.36 ^b	31.25±0.90 ^b
Manganese	2.95±0.01 ^c	4.99±0.01 ^a	4.60±0.06 ^b
Nickel	<0.035	<0.035	<0.035
Zinc	36.74±2.13 ^a	33.33±0.18 ^a	11.39±1.29 ^b
Toxic minerals			
Cadmium	<0.035	<0.035	<0.035
Lead	<0.035	<0.035	<0.035

Values are expressed as Mean±SD (n = 3), mean values in row with different superscripts were significantly different (p≤0.05)

According to results, while the levels of Ca, Mg, Br, B, Cu, Fe and Zn decreased, K, Na and Mn increased in obtained croquettes (p≤0.05). Just Zn level remained the same in croquettes (p≥0.05). In the following, the levels of Br, B, Cu, Mn and Zn decreased, whereas only Na level increased after the frying (p≤0.05). The levels of Ca, Mg, K and Fe remained the same (p≥0.05). Besides that, Cr, Co, Ni and some toxic metals such as Cd and Pb were not detected in all stages because they were none completely or very small amounts below the detection limits. Ultimately, levels of each mineral were found below the legal limits stated by food codex in all samples³²⁻³⁶. Mineral compositions of shrimp croquettes were shown in Table 3.

DISCUSSION

After the shrimp species cleaned out their shells which is mostly consist of carapace, abdomen, head and extremities³⁷ they lose approximately 50% of their weight. According to Daenorvst *et al.*³⁸ meat yields of *Parapenaeus* species ranged from 47.2-55.1%. This weight loss can be recovered partly with adding ingredients with the aim of croquette production. Thereby, some ingredients like flour kinds and some spices were added to shrimp mince which is consisting of 75% croquettes in order to get croquette paste. Therefore, weight of croquette paste was increased to 69.34% due to this adding.

The changes on proximate composition of shrimp meat and croquettes mostly related to moisture loss and ingredients addition which they have different ratios of proximate

content. While the total unsaturated fatty acids decreased in croquette production, they increased especially linoleic acid and EPA after the frying process. Contrary to this, saturated ones increased in obtained croquettes, however decreased with frying (p≤0.05). Reasons for this alteration were adding ingredients having low fat content into croquettes paste and the high unsaturated fatty acid content of sunflower oil absorbed by the croquettes with frying in the following stage^{39,40}. Moreover, unsaturated fatty acids degrades increasingly to epoxy, keto and hydroxyl fatty acids during frying process parallel with long duration and high temperatures, actually^{19,41}. According to Zribi *et al.*⁴², the adequate frying temperature and method are very important as well as choosing of frying oil. Main degradation of unsaturated fatty acids is mostly observed in cooling process due to oxidation^{41,42}. Thus, in this study, croquettes were fried at 180°C for 2 min with sunflower oil which is renewed before every operation for preserve unsaturated fatty acids. Also, Khazaei *et al.*⁴³ stated that, the coating treatment is effective to reduce oxidation associated with deep-frying in coated shrimps more than the uncoated ones.

Marine species are rich in terms of mineral content¹². Some minerals such as Ca, Na, Mg and K are biologically important and essential for humans⁴⁴. Also, some micro minerals must be taken daily with small amounts for maintaining health³². The minerals identified in this study; B, Br, Cu, Fe, Mn and Zn are playing important role in immune, cardiac, skeletal and nervous systems⁴⁵⁻⁴⁷. When shrimp meat were turned to croquettes, most of minerals of shrimp meat especially trace ones decreased except Mn due to high Mn

content of wheat flour added into croquette paste^{48,49}. After then frying stage; all micro minerals decreased except iron which is most detected micro mineral in all stages ($p \leq 0.05$). However, macro mineral levels are not changed statistically ($p \geq 0.05$). In fact, level of Na increased. Similar findings stated in several researches^{50,51}. Considering these, the croquette production process mostly effects to amount of micro minerals than the macro ones.

CONCLUSION

The shrimp meat was used into croquette production which is one of the most preferred seafood processing techniques all over the world. According to results, while the levels of micro minerals decreased, macro minerals increased or remained the same in production stages. Besides, obtained croquettes were detected rich in unsaturated fatty acids even if they fried. Besides, when the shrimp combed out their shells, they lose 50% of their weight approximately. But, this loss was reduced to 30% with croquette application. Despite some production losses in the micro minerals, healthy and nutritional croquettes can be produced with shrimp meat.

SIGNIFICANT STATEMENTS

- This study states that rose-shrimp croquettes with nutritional value can be produced
- Unsaturated fatty acids and beneficial trace minerals were determined in products
- Effects of production process on meat quality were specified

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