

STUDY OF MAIN QUALITY AND SAFETY PARAMETERS OF STRUCTURED OLIVES AND THEIR CHANGE UNDER THE INFLUENCE OF TECHNOLOGICAL FACTORS

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Abstract

Today scientific-practical bases of technologies of structured food products allow to create a principally new segment of products at the food market. Introduction of new principles of processing raw materials and ingredients, practical production methods allows to get food products with a new commodity and consumption form.

There were studied technological aspects of producing structured food products of a round form on the example of the structured olive technology. Experimental studies and practical achievements in structuring (capsulation) allowed to create a product-analogue with quality and safety parameters, maximally approximated to the natural product. Principles of extruding formation with the synchronous combination of principles of external gel-creation allow to get a three-phase structure of a product (skin, internal content, filler), high organoleptic indices and target food value. At the same time the developed technology allows to involve in the technological process low-value parts of an olive-fruit and raw materials with decreased commodity-technological properties. In its turn, it allows to increase profitability indices and economic capacity of the new technology.

Keywords: structured olive, extruding formation, thermotropic-ionotropic gel-creation, modified gels.

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1. Introduction

Under conditions of market relations the assortment and quality of food products on the consumption market depends on world tendencies of the food industry development. The aim of such technologies is creation of competitive food products with high organoleptic and consumption characteristics, decreased cost price, comfort use and so on. Such technologies include ways of food products processing by methods of structuring and restructuring. The analysis of literary sources [1–3] allows to state that the production technology of structured food products is based on realization of functional-technological properties of raw materials and/or food ingredients of

protein or carbohydrate nature. As a result of the influence of such factors as temperature, medium pH, chemical potential, extrusion at the technological flow, a new structure with given firm properties appears. Solutions of high-molecular substance and ashes of several hydrophobic colloids are able under certain conditions to undergo changes that cause the loss of fluidity – gel-creation of solutions. At that gels form. Many scientific works [3–5] are devoted to studying the mechanism of structure formation. Gels can be obtained at structuring solutions of polymers and ashes or at swelling of xerogels. At the same time they can form as a result of reactions of polymerization, condensation or fermentation. Gel-creation is connected with the viscosity increase of the system and braking of the Brownian motion [6, 7]. As a result of decreasing ζ -potential of the experimental system, particles in the form of a spatial network or nuclei, filled with a big amount of liquid, combine. At that, the distribution in phases doesn't take place, because a dissolvent together with a disperse phase forms a single whole – gel. The gel structure is constructed of long chains of micelles, in which hydrophilic areas ($-\text{OH}$, $-\text{COOH}$; $-\text{CO}-\text{NH}$, $-\text{SH}$) are changed by hydrophobic ones ($-\text{CH}-$, $-\text{CH}_2-$). Hydrophilic areas of micelles protect them from aggregation, and hydrophobic ones, under correspondent conditions, interact, creating at that the cell construction of the colloid system.

Among existing structuring methods of polysaccharides the most effective is ionotropic gel-creation. As a result of realization of chemical potentials, thermostable gels with necessary structural-mechanical parameters are obtained. But the list of food ingredients, able to ionotropic gel-creation, is rather narrow. It is presented by pectin substances, salts of alginate acid, carrageenans [8, 9].

Mechanisms of gel-creation of low-etherified pectins and alginates are familiar and need ions of polyvalent metals in the system. Macromolecules of alginates have a configuration of corrugated strips that form cavities. The radius of these cavities corresponds to the size of the full radius of Ca^{2+} . Such geometry of placing hydrocolloid molecules provides homogenous gels of calcium alginate under certain conditions [10].

The fact that the chemical composition of animal and vegetable raw materials may be very diverse essentially complicates formation of united principles of structuring such systems.

For creating structured products of the round form as a capsule it is possible to use the mixed type of gel-creation. This way includes external and internal diffusion types. Diffusing gel-creation appears, when a drop penetrates in a solution that contains Ca^{2+} . At the same time there appears a surface layer of a pseudo-capsule at the expanse of sorption of Ca^{2+} by AlgNa surface. External gel-creation is possible at the expanse of successive binding of AlgNa Ca^{2+} , released from low-soluble salt, suspended in AlgNa solution. An important factor in forming a product of the correct round form is a viscosity of a mixture for capsulation, set by AlgNa viscosity. So, it is expedient to choose alginates with the least viscosity and it is necessary to correct the extrusion process by increasing a temperature of a mixture. The mixed type of gel-creation allows to get capsulated products with a controlled content of calcium and necessary rheological properties from firm and brittle to soft and plastic ones.

Based on researches of many years, there was developed and introduced the wide assortment of imitated products of the round form [11, 12]. A promising direction is creation of capsules, based on olive raw materials, olive puree, brines. As a result of system studies, there was developed a production technology of structured olive. This technology is based on principles of extrusion formation of encapsulant, based on olive puree with thermotropic-ionotropic polysaccharides in the water solution CaCl_2 . Provision of laminarity of the recipe mixture flow allows to form a structure, maximally approximated to natural olive. Correction of an orifice diameter of a capsulation head of an extruder allows to regulate size characteristics of ready products [13]. Formation of given structural-mechanical parameters of structured olive is achieved by regulating a concentration of gelling recipe components. Provision of thermo- and acid-stability of a ready product is achieved at the expanse of introducing thermotropic polysaccharides and modifying supplements in the recipe mixture.

An important aspect of the technology is a study of main quality and safety parameters of developed products. So, the aim of the article is to study regularities, forming organoleptic, physical-chemical, toxicological parameters of structured olive and their change at storage. It is necessary for analyzing the level of innovation and estimating the export potential of ready products.

2. Materials and Methods

Within the experimental studies the research objects were semi-products of structured systems, based on mixed gels and ready products – structures olives with the internal content of capsulated olive oil (**Fig. 1**).



Fig. 1. Photo-image of the research objects: *a* – outlook of structured olive;
b – cut of structured olive with the internal content of capsulated olive oil

The organoleptic quality estimation of structured olive was realized by profile analysis methods [14]. This method is in using a set of descriptive terms for estimating separate organoleptic parameters of a product (smell, consistence, taste and so on) by the scheme: determination of typical signs of parameters, their intensity degree, revelation order.

For estimating the quality composition and quantity ratio of separate classes of lipids in experimental samples, the method of thin-layer chromatography was used. This method allows to make the objective estimation of changes that take place in the system at storage and under the influence of disturbing factors [15].

Determination of the mass share of chloride was realized by the argenometric method. The mineral composition of the ash residue was realized by method [16], ash mass share – by burning of the experimental sample in the muffle stove at the temperature $t=400...450\text{ }^{\circ}\text{C}$ [17].

Determination of toxic elements and salts of heavy metals in the composition of new products was realized by [18]. Preparation of the samples for determining the content of radiologic substances (^{137}Cs and ^{90}Sr) and direct study of their content in the composition of new products were realized by method [19].

3. Results

As a result of technology realization, it is provided to get structured olives with the internal content of capsulated olive oil. Structured olive is a three-phase structure: thermotropic-ionotropic film-like coat (skin), internal content, based on olive puree and brine for storing olive crops, by which volume capsules of olive oil are evenly distributed. **Fig. 2** presents the model of the technological process of new products creation.

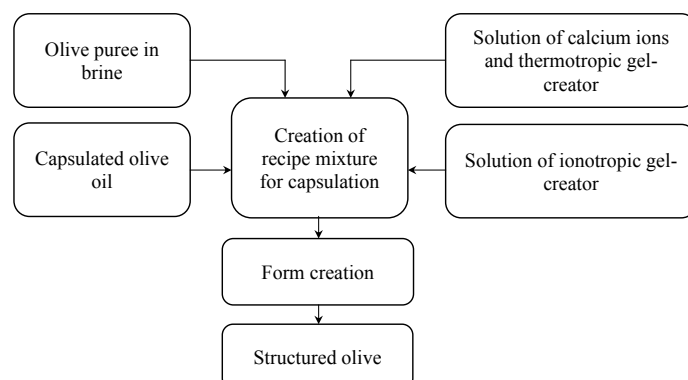


Fig. 2. Model of the technological process of creation of structures olives with the internal content of capsulated olive oil

The main feature of the technological process of this product creation is in providing the necessary viscosity of mixtures for providing the process of co-axial extrusion in the air medium and synchronous structuring of food systems (Fig. 3) [20].

Subsystem C_1 «Creation of the semi-product “Olive puree” (main raw material) uses olives, including ones with decreased commodity-technological properties, which are comminuted to the homogenous mass with the diameter $d=(0,5...1,0)\times 10^{-3}$ m. Subsystem C_2 «Creation of the semi-product “Water solution of gel-creators” (coat of capsule) provides preparation of agar and AlgNa. AlgNa is dissolved in drinking water at the temperature $t=80...85$ °C and kept during $\tau=(1...1,5)\times 60^2$ s. Agar is dispersed in drinking water at the temperature $t=80...85$ °C with further heating to the temperature $t=98...100$ °C and keeping during $\tau=(2,0...2,5)\times 60^2$ s for complete dissolution of dry substances and getting stationary properties. Both solutions are heated to the temperature $t=65...65$ °C and mixed to getting the homogenous consistence during $\tau=(3...7)\times 60$ s.

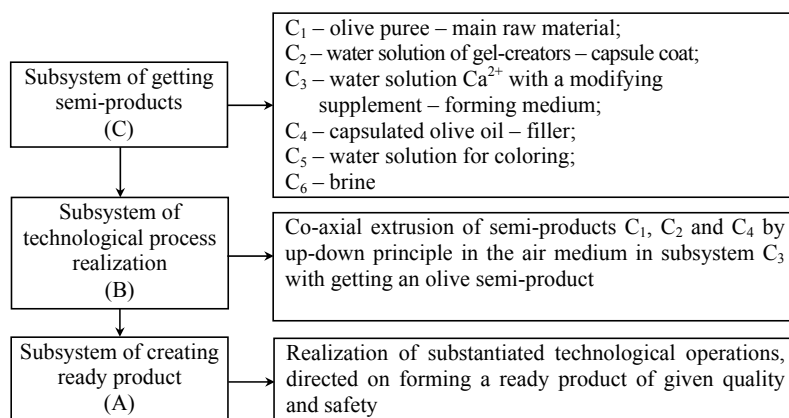


Fig. 3. Structural model of the technological process of structures olive production

Subsystem C_3 «Creation of the semi-product «Water solution Ca^{2+} with a modifying supplement” is directed on creating a forming medium. For that CaCl_2 and modifying supplement are dissolved in drinking water by dispersing at the temperature $t=18...20$ °C and keeping during $\tau=(1...1,5)\times 60^2$ s for complete dissolution. The obtained solution is filtered.

Subsystem C_4 «Creation of semi-product «“Capsulated olive oil” is presented in [11, 20].

Subsystem C_5 «Creation of the semi-product “Water solution for coloring” is directed on creation of black or blue color in structured olives. For that the semi-product is at first kept in the tea solution ($C=10,0$ %) at the temperature $t=4...8$ °C, during $\tau=(10...15)\times 60$ s, then – in iron chloride (III) during $\tau=(1,0...1,5)\times 60$ s. Depending on keeping time, the correspondent color intensity is obtained.

Subsystem C_6 «Creation of the semi-product “Brine” provides creation of the kitchen salt water solution ($C_{\text{kitchen salt}} - 12,0$ %), mixed with food vinegar $9,0$ % ($C_{\text{vinegar}} - 24,0$ %). The obtained solution is filtered.

Subsystem B “Creation of the semi-product of structures olives” provides the following succession of technological operations: semi-product “Olive puree” is heated to the temperature $t=60...65$ °C and mixed with the semi-products “Water solution of gel-creators” and “Olive capsulated oil”. The mixture is extruded by the drop way in the forming medium (semi-product “Water solution Ca^{2+} and modifying supplement”) with synchronous creation of round forms. Formed capsules are kept in the forming medium during $\tau=(1,5...2,0)\times 60$ s. The semi-product “Structured olive” is placed in the water solution Ca^{2+} and kept during $\tau=(4,5...5,0)\times 60^2$ s to the end of the external gel-creation process. After that, coloring is realized at first in the tea solution, then in $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ to attaining the set color and tint. Immersion of structured olives in the semi-product “Brine” is necessary for forming the set taste and smell. For this aim they are washed after coloring and placed in the brine at the temperature $t=2...6$ °C, during $\tau=(11...12)\times 60^2$ c.

Subsystem A “Creation of the ready product” provides packing in a consumption package (glass or metal) with further pasteurization at the temperature $t=80...85$ °C during $\tau=(30...35)\times 60$ s.

After that the product is cooled to the temperature $t=2...6$ °C, marked, according to the legislation of a country-producer and put in a secondary package for further transportation and realization.

It must be noted, that the assortment is formed by using different main raw materials, capsulated fillers, mixing of brines, forms of package and realization.

Structured olive with the internal content of capsulated olive oil is a principally new food product with no analogues at the world level. Realization of the innovative technology is directed on getting export oriented products. That is why it was necessary to study main quality and safety parameters of structured olives. **Table 1** presents the requirements to the organoleptic parameters of new products, and **Fig. 4** – photo image of them.

Table 1

Main organoleptic parameters of structured olive

| Parameter name | Main requirements |
|-------------------------|---|
| Outlook and consistence | Product is evenly distributed by the package volume. The upper layer is not pressed or deformed. The olive form is round, oblong. The consistence is firm, homogenous, elastic, easily chewed. Its surface is glossy. The depth of the product contains easily destructed capsules with olive oil |
| Taste and smell | Pure, expressed, correspondent to the used raw material. The smack is typical for olive oil. Side smells and smacks are not permitted |
| Color | Pure, even, from light-pink to black, depending on destination of a product |

Fig. 4. Photo image of structured olive in the primary consumption package

The food value is determined, the general chemical composition (**Table 2**), fatty-acid composition of lipids (**Table 3**), mineral and vitamin composition (**Table 4**) structured olives and their changes at storage are calculated.

Table 2

General chemical composition of structured olive

| Parameter name | Storage term, days | | | |
|---------------------------------|--------------------|-----------|-----------|-----------|
| | 0 | 30 | 90 | 180 |
| Mass share of dry substances, % | 26,6±0,2 | 26,6±0,2 | 26,8±0,2 | 26,9±0,3 |
| Mass share of protein, % | 0,9±0,01 | 0,9±0,01 | 0,9±0,01 | 0,9±0,01 |
| Mass share of fat, % | 19,3±0,3 | 19,3±0,3 | 19,3±0,3 | 19,3±0,3 |
| Mass share of carbohydrates, % | 4,7±0,03 | 4,7±0,03 | 4,8±0,04 | 4,9±0,03 |
| Food fibers, % | 0,81±0,01 | 0,82±0,01 | 0,84±0,01 | 0,87±0,01 |
| Mass share of ash, % | 0,92±0,01 | 0,94±0,01 | 0,96±0,01 | 0,98±0,01 |
| Caloric value (kcal) | 196,1 | 196,1 | 196,5 | 196,9 |

The fatty-acid composition of lipids of structured olive, presented by saturated and unsaturated fatty acids, is studied (**Table 3**).

The total content of saturated fatty acids is 7,13 %, among them the dominating are palmitic acid, which mass share is 47,68 % of the total content of saturated fatty acids. The content of monounsaturated fatty acids is 87,60 %, one of polyunsaturated fatty acids is 5,27 %, among them linoleic acid dominates (3,16 %) respectively.

Capsulated olive oil is a source of fatty acids, related to the classes omega-3 ($\omega-3$ – 1,93 %) and omega-6 of acids ($\omega-6$ – 0,24 %). From the physiological point of view, the developed products gain a “prophylactic” status, because they favor regulation of protective functions of the organ-

ism, prevent the development of cardiac diseases, ones of the musculoskeletal apparatus, central nervous system and so on. New products didn't contain trans-isomers of fatty acids and may be recommended to all population layers.

Table 3

Fatty-acid composition of lipids of structured olive

| Fatty acid name | Acid index | COO during storage, days | | | |
|--------------------------------------|-------------------|--------------------------|-----------|-----------|-----------|
| | | 0 | 30 | 90 | 180 |
| Palmitic | C _{16:0} | 3,40±0,1 | 3,48±0,1 | 3,56±0,1 | 3,70±0,1 |
| Stearic | C _{18:0} | 1,47±0,1 | 1,47±0,1 | 1,48±0,1 | 1,49±0,1 |
| Arachidic | C _{20:0} | 1,14±0,1 | 1,17±0,1 | 1,20±0,1 | 1,24±0,1 |
| Lignoceric | C _{24:0} | 1,12±0,1 | 1,13±0,1 | 1,15±0,1 | 1,16±0,1 |
| Saturated fatty acids totally: | | 7,13±0,3 | 7,25±0,3 | 7,39±0,3 | 7,59±0,3 |
| Palmitoleic | C _{16:1} | 1,26±0,1 | 1,23±0,1 | 1,20±0,1 | 1,17±0,1 |
| Oleic | C _{18:1} | 85,44±3,0 | 85,25±3,0 | 85,01±3,0 | 84,72±2,0 |
| Gadoleic | C _{20:5} | 0,90±0,02 | 0,88±0,1 | 0,84±0,1 | 0,80±0,02 |
| Monounsaturated fatty acids totally: | | 87,60±3,0 | 87,36±3,0 | 87,05±3,0 | 86,69±3,0 |
| Linoleic | C _{18:2} | 3,16±0,4 | 3,28±0,5 | 3,45±0,5 | 3,59±0,5 |
| Linolenic | C _{18:3} | 1,02±0,01 | 1,02±0,01 | 1,02±0,01 | 1,03±0,01 |
| Eicosatrienoic acid | C _{20:3} | 1,09±0,01 | 1,09±0,01 | 1,09±0,01 | 1,1±0,01 |
| Polyunsaturated fatty acids totally: | | 5,27±0,1 | 5,39±0,1 | 5,56±0,1 | 5,72±0,1 |
| Fatty acids totally: | | 100,0 | 100,0 | 100,0 | 100,0 |

Table 4

Mineral and vitamin content of structured olive

| Parameter name | Storage term, days | | | |
|-------------------------------------|--------------------|-----------|-----------|-----------|
| | 0 | 30 | 90 | 180 |
| Mineral composition, mg % | | | | |
| Potassium (K) | 8,4±0,2 | 8,38±0,2 | 8,34±0,2 | 8,30±0,2 |
| Calcium (Ca) | 10,4±1,0 | 10,3±1,0 | 10,2±1,0 | 10,0±1,0 |
| Magnesium (Mn) | 2,2±0,2 | 2,2±0,2 | 2,2±0,2 | 2,2±0,2 |
| Sodium (Na) | 406,2±2,5 | 406,4±2,5 | 406,7±2,5 | 407,0±2,5 |
| Phosphorus (P) | 1,12±0,2 | 1,12±0,2 | 1,12±0,2 | 1,12±0,2 |
| Iron (Fe) | 0,86±0,06 | 0,86±0,06 | 0,86±0,06 | 0,86±0,06 |
| Vitamin content, mg | | | | |
| Vitamin B ₄ (choline) | 2,84±0,2 | 2,84±0,2 | 2,85±0,2 | 2,86±0,2 |
| Vitamin B ₉ (folic acid) | 0,60±0,02 | 0,61±0,02 | 0,63±0,02 | 0,65±0,02 |
| Vitamin E (tocopherol) | 2,69±0,2 | 2,69±0,2 | 2,70±0,2 | 2,71±0,2 |
| Vitamin K (fyllochinone) | 0,29±0,01 | 0,28±0,01 | 0,28±0,01 | 0,27±0,01 |

Structured olive is a source of potassium (8,4 mg %), calcium (10,4 mg %) and sodium (406,2 mg %), water-soluble vitamins of B (to 4,0 mg), E – 2,69 mg and K – 0,29 mg respectively.

There was studied the dynamics of physical-chemical parameters of structured olive during its storage. At the expense of syneresis of the structured system, there is observed the unessential change of the content of dry substances, titrated acidity, increased in 1,2 times. Probably at storage

the part of organic compounds is destructed at the expense of the influence of acids and salts, contained in the food products storing medium (**Table 5**).

Table 5

Physical-chemical parameters of structured oil

| Parameter name | Storage term, days | | | |
|---|--------------------|-----------|-----------|-----------|
| | 0 | 30 | 90 | 180 |
| Mass share of dry substances, % | 26,6±0,2 | 26,6±0,2 | 26,8±0,2 | 26,9±0,3 |
| Mass share of sodium chloride, % | 1,30±0,01 | 1,32±0,01 | 1,34±0,01 | 1,36±0,01 |
| Titrated acidity (I recalculation for acetic acid), % | 0,27 | 0,28 | 0,30 | 0,31 |
| Mineral admixtures, % | Not revealed | | | |
| Side admixtures, % | Not revealed | | | |

Toxicological parameters and content of radionuclides of the new products were studied and presented in tables 6 and 7.

Table 6

Results of the toxicological studies of structured olive

| Parameter name | Permitted levels, mg/kg no more | Actual content in olive, mg/kg |
|--------------------------------------|---------------------------------|--------------------------------|
| Toxic elements: | | |
| – lead | 0,5 | 0,25 |
| – arsenic | 0,5 | 0,15 |
| – cadmium | 0,05 | 0,02 |
| – mercury | 0,05 | 0,01 |
| – copper | 1,0 | 0,5 |
| – iron | 5,00 | 2,00 |
| – zinc | 5,00 | 1,00 |
| Mycotoxins: aflatoxin B ₁ | 0,005 | 0,002 |

Table 7

Results of the study of the radionuclide content of structured olive

| Parameter name | Permitted levels, Bq/kg | Actual content in olive, Bq/kg |
|-------------------|-------------------------|--------------------------------|
| ¹³⁷ Cs | 40 | 10 |
| ⁹⁰ Sr | 20 | 4 |

Thus, the conducted complex of studies on determining the main quality and safety parameters allowed to establish that innovative products are characterized by the high organoleptic and consumption indices and correspond to standards and norms of normative of the European Union. The storage term of structured olive in a brine is 6 months at the temperature $t=4...6\text{ }^{\circ}\text{C}$.

4. Conclusions

There were studied technological principles of forming the main safety and quality parameters of structured olive with the internal content of capsulated olive oil. The realized approach is characterized by the effective resource-saving effect: vegetable raw material is comminuted in puree, including pulp, on which base the recipe mixture with gel-creators is prepared. It consists of capsulated olive oil with the given organoleptic properties. After that the mixture

is subjected to extruding formation of the given diameter and structured. In the technological and consumption sense the production technology of structured olive has several advantages. Especially, there are dosage, masking of the taste and smell of a fatty component that widens the spectrum of oil-fatty raw materials, used as a filler and improver. Storage terms of the internal content (filler) increase in near 2 times, comparing with the ordinary filler in a package. The intactness of the internal component of the filler relative to other recipe components gives a possibility to use fillers of different nature, namely, hydrophilic, hydrophobic and their emulsions. That is why realization of new taste parameters of structured olive with the internal content of capsulated olive oil forms through using capsulated fillers. There have been determined the main organoleptic, physical-chemical and toxicological parameters of new products. It has been established, that structured olive has the stable quality and safety parameters during 6 months of storage at temperature 2...6 °C.

Generalization of the research results allow to transform other types of vegetable raw materials by this scheme.

Directions of using the capsulated forms of fillers gained further development. The innovative developing strategy of the new technology favors the development of the segment of industrial food products at institutions of restaurant economy and food industry.

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