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TRENDS IN THE MANUFACTURE OF PROCESSED SQUID PRODUCTS

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Abstract. Nowadays, special attention is paid to technologies that allow preserving in the finished product as many native properties of raw materials as possible due to the soft modes of technological processes. An important precondition for obtaining healthy food products is the availability of sources of raw materials and technical means of exploiting aquatic biological resources. The article shows that in China, a healthy lifestyle and consumption of healthy food products are gaining popularity. China is the absolute leader both in the production of molluscs as an aquaculture object and in squid fishing. Still, in China's domestic food market, there is a shortage of healthy food products due to the uneven distribution of aquatic bioresources. The main type of processed molluscs is squid traditionally very popular in China. Besides frozen processed squid and other products of primary processing, the main products from squid are minced squid, sliced squid, and chopped squid, as well as various tinned squid products. The article shows the high nutritional and biological value of squid due to their content of complete proteins and essential polyunsaturated fatty acids. But when processing squid, a number of problems arise, namely the deterioration of the sensory properties and a decrease in the biological value of the finished product. This survey article considers a number of issues related to the fractional composition of muscular tissue proteins of various raw materials. It has also been analysed how the physical and chemical parameters of proteins change being acted upon by a wide range of temperatures. The article describes a promising type of technological processing, which allows eliminating certain disadvantages of traditional technologies such as coarse and dry texture, weight loss in the finished product, and the loss of valuable extractive substances that determine the organoleptic properties of food. Such technologies least affecting the technological properties of finished products include the Sous-vide technology. Sous-vide is a technology of low-temperature preparation of food in a vacuum. It ensures reliable monitoring of the sensory criteria and microbiological safety of products, with strict observance of technological regulations.

Keywords: squid, squid fishing, consumer, healthy food, protein, Sous-vide technology.

Introduction. Formulation of the problem

The Chinese food industry has been export-oriented for many years. Fish and seafood trading companies have always attached a lot of importance to the international trading market. Products are mainly exported to the EU, Japan, South Korea, and the United States. The excessive concentration of trade relations has aggravated trade frictions, and the market of export aquatic products is vulnerable to shocks. In China, there are quite a lot of consumers that form the domestic consumer market, and they can provide enough consumption of squid products [1]. Currently, due to the increase in the living standards of the Chinese people and the growing popularity of the healthy lifestyle, the domestic food market in China is experiencing a shortage of wholesome natural food which is not varied enough, though China has a powerful fishing fleet and a significant raw material base.

Squid are traditionally very popular in China. An active and healthy lifestyle requires the creation and production of healthy food. Over the past decade, the global organic food market has developed significantly. China's organic food industry is also export-oriented, with production growing rapidly, although the domestic market remains relatively small [2]. Moreover, quality is the most important factor influencing the Chinese consumers' choice. The outward appearance of a product does matter, too. The price is one of the least important factors affecting the choice of the Chinese, and therefore should not be the focus of marketing activities [3]. The Sous-vide technology allows you to produce the right kind of squid food products, as it helps retain high nutritional value and prevents their weight loss.

However, there are a lot of issues of the Sous-vide squid processing technology that have not been studied so far. So, it is relevant to study the raw material base and the trends in squid processing.

The **purpose** was to analyse the raw material base and study the trends in squid food production in China.

The **objective** of the research was to show the prospects of using the Sous-vide technology in the manufacture of squid products with improved consumer characteristics.

Analysis of recent research and publications

For five years since 2010, the catch of cephalopods was increasing. In 2015, the volume of catch stabilised, and in 2016 it decreased [4]. The catch of the three main species – Humboldt squid (*Dosidicus gigas*), Argentine shortfin squid (*Illex argentinus*), and Pacific flying squid (*Todarodes pacificus*) – decreased, respectively, by 26, 86, and 34%, and in general, a decrease in the volume of catch in 2016, compared to 2015, amounted to 1.2 million tons. The decrease was partially offset by the catch of the Humboldt squid, which cost a lot, and the volumes of which have increased significantly since 2000. In the past two years, China and Morocco remained the largest producers of shellfish, while China, Peru and India were the top three suppliers of squid and cuttlefish. The main markets for cephalopods were Japan, the United States of America, and the largest countries in Southern Europe, in particular Spain and Italy. The world-wide demand, primarily for octopuses and squid, was fuelled by the growing popularity of Japanese cuisine, Hawaiian poké (fish salad), and Spanish tapas. However, the catch in 2016-2017 was small, which led to a significant increase in prices. The main areas for catching these squid are in the Pacific Ocean, Peruvian waters, and the Atlantic Ocean. Aquaculture is a promising activity, too. Fig. 1 shows the encouraging growth rates of world aquaculture in 1980-2020 [4].

The average annual growth rate of aquaculture is slowing down: in 2003–2016, the production grew, on average, by 5.7%, but in 2017–2020, this figure has not exceeded 2.1%. Despite the slowdown, aquaculture in this regard remains the leader among all sectors producing food of animal origin [4].

Cephalopods as an object of aquaculture are only characteristic of Asia (Table 1).

In 2016, aquaculture production in inland waters amounted to 51.367 thousand tons in live weight [4]. No other region of the world is engaged in this type of production, while the share of molluscs amounted to 286 thousand tons. In total, the volume of aquaculture amounted to 80.031 thousand tons, the share of molluscs is 17.139 thousand tons.

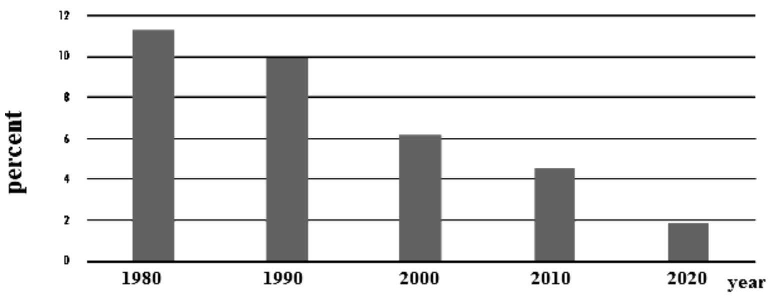

Fig. 1. Growth rates of world aquaculture, 1980–2020 [4]

Table 1 – Manufacture of aquaculture products by continent, 2016 (thousand tons in live weight) [4]

Category	Africa	Americas	Asia	Europe	Oceania	Worldwide
Inland aquaculture						
Molluscs	–	–	286	–	–	286
Total	1954	1140	47765	502	5	51367
Marine and coastal aquaculture						
Molluscs	6	574	15550	613	112	16853
Total	28	2207	23781	2443	205	28664

The geographical distribution of aquaculture and the largest producers are shown in Fig. 2. According to the FAO, aquaculture is currently present in the economies of 202 countries and territories, with production being actively developed in recent years in 194 countries. The imbalance in the geographical distribution of aquaculture by region and by country within individual regions, as before, is quite pronounced. Despite the increase in production in absolute terms, this situation has remained for ten years. For two decades, 89% of global aquaculture production has been in China. Over the years, Africa, North and South America have slightly increased their shares in global production, while Europe and Oceania have slightly reduced [4].

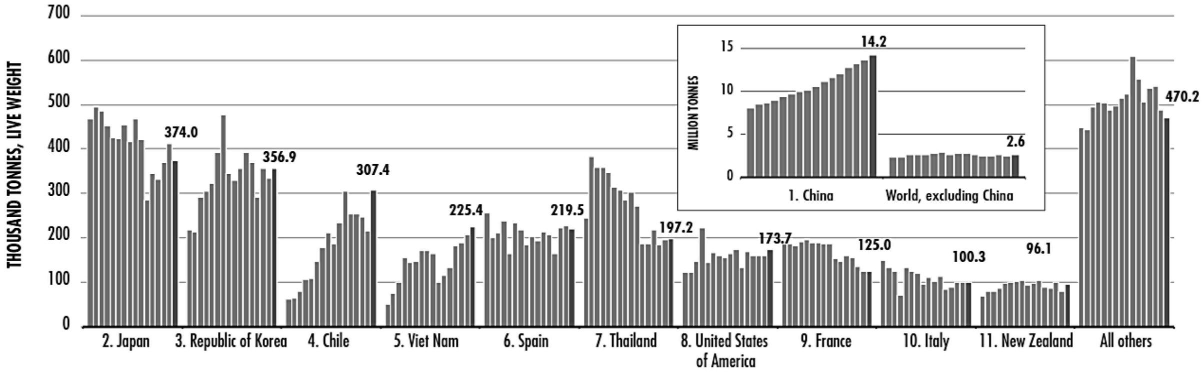

Fig. 2. Largest producers of cultured marine molluscs [4]

Fig. 2 clearly shows that the level of aquaculture differs greatly with geographical region, and that there are several major producing countries that dominate in raising the main groups of species both in inland waters and in the sea and coastal areas. China is showing an absolute dominance in mollusc production – 14.2 million tons compared to 2.6 million tons produced by the rest of the world.

Thus, cephalopods are among the main raw materials to provide the Chinese domestic market with healthy food.

Squid used as food (in which case they are known as calamari) belong to the phylum of molluscs (*Mollusca*), class *Cephalopoda*, family *Loliginidae* [4]. Currently, about 200 species of squid have been discovered. In China, the main types of squid that are commercially collected and processed are: Argentine shortfin squid, North Pacific squid, Peruvian squid, Pacific flying squid, and Japanese sea squid [5,6].

The squid has three main characteristics: short growth cycle, strong reproductive ability, and rapid resource recovery [8]. Therefore, stocks of squid can be exploited at the highest level without affecting their biological stability [4]. It is because of their abundant resources and delicious taste that squid have become the main marine fishing and aquatic product to process and consume. Squid are mainly fished for in coastal areas.

The squid is rich in nutrients, high in protein, and low in fat. It as rich in essential amino acids, and its essential amino acid composition is close to whole egg protein. It is a nutritional and health-improving product with a good flavour. Every 100 g of fresh squid contains 16–18% of protein, 1–2% of fat, 35 μg of vitamin A, 20 μg of thiamine, 60 μg of riboflavin, 1600 μg of niacin, 600 μg of vitamin E1, 290 mg of potassium, 110 mg of sodium, 44 mg of calcium, 42 mg of magnesium, 0.9 mg of iron, 0.08 mg of manganese, 2.38 mg of zinc, 0.45 mg of copper, 19 mg of phosphorus, 38.18 mg of selenium [9].

The fractional composition of proteins of the squid mantle is represented by sarcoplasmic proteins (54.71%) and myofibrillar proteins (35.20%) [10, 11]. The content of essential amino acids (EAA) in squid meat is presented in Table 2.

Table 2 – Biological value of squid proteins, g/100 g protein [10, 11]

Amino acids	EAA content in squid meat	"Ideal" protein according to the FAO/WHO scale
Essential, incl.	55.91	36.5
Valine	5.21	5.0
Isoleucine	6.33	4.0
Leucine	9.11	7.5
Lysine	8.56	5.5
Methionine + cystine	6.23	3.5
Threonine	5.21	4.0
Tryptophan	1.05	1.0
Phenylalanine + tyrosine	14.21	6.0

The data in Table 2 indicate that squid meat proteins are complete, they do not contain limiting amino acids.

Squid lipids are characterised by high biological effectiveness (Table 3) [12]. Table 3 shows that the largest fraction is that of phospholipids (33.7%). Triglycerides of marine organisms are more fully assimilated by the human body (95–97%) than triglycerides of oil (89–94%) and fats of terrestrial animals (75–88%), due to the low melting point of lipids of hydrobionts (22–35°C).

Table 3 – Fractional composition of squid mantle lipids Loligo [12]

Fraction of lipids	Mass fraction, % of the sum of fractions
Phospholipids	33.7
Waxes, hydrocarbons	22.1
Monoglycerides	17.5
Sterids	9.7
Diglycerides	7.8
Free fatty acids	3.9
Triglycerides	5.2

The fatty acid content in the lipids of the squid mantle is given in Table 4 [12, 13].

Table 4 – Fatty acid content in squid mantle lipids [12, 13]

Fatty acid	Mass fraction, % of total fatty acids
Polyunsaturated, including	31.7
Arachidonic ($C_{20:4}$) ω 6	1.91
Eicosapentaenoic ($C_{20:5}$) ω 3	9.23
Docosahexaenoic ($C_{22:6}$) ω 3	20.57
The ratio of long-chain poly-unsaturated fatty acids ω3 and ω6	1:0.06

The data in Table 4 indicate that squid mantle lipids are the highest in ω3 fatty acids, namely docosahexaenoic (DHA) and eicosapentaenoic (EPA) fatty acids. Omega-6 fatty acids account for only 1.9% due to the content of arachidonic fatty acid, which caused the ratio of long-chain polyunsaturated fatty acids ω3 and ω6 to be 1:0.06.

The muscles of the squid do not accumulate fat, so the corpus callosum is low in fat, and the main component of the lipid is the phospholipid (40% to 45%). The fat of the squid mainly accumulates in the internal organs. The viscera of the squid are extremely high in fat. Mainly, this fat is highly unsaturated fatty acids, from which eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) can be extracted. EPA and DHA have the effect of enhancing the brain function, improving memory, and preventing brain aging. Besides, the squid is also rich in taurine, lysine, betaine, guanidine, nucleotides, sugars, trimethylamine oxide, and other flavouring substances [9].

Although the tradition of eating squid in China has a long history, fresh squid are not easy to store, so they are often made into semi-finished products such as dried squid to extend their shelf life. In Western countries, squid is mostly distributed in the form of tinned products. Since the 1920s, the Japanese have been studying the processing of visceral squid products and the use of squid viscera to obtain fish oil and soya sauce. As to the richness of squid products and the progress of processing technology, Japan is much more advanced than China [14].

Squid products are divided into three categories: ready-to-eat products, semi-processed products, and tinned products. Ready-to-eat squid products include squid silk, shredded squid fillets, smoked squid rings, and other aquatic products that can be eaten directly without cooking. It is because squid products, rich and diverse, meet consumers' needs for food of different forms and different flavours, thus being a factor of the rapid development of the squid production and processing industry.

With the gradual improvement of the level of consumption, consumers' different demands for the price, consumption habits and preferences, and the forms of consumer goods, squid products are also undergoing subtle changes. As an important link between the upstream and downstream of the industrial chain, the processing stage not only plays a vital role in the diversification of the production and form of the product itself, but also determines the form of the entire circulation system [15].

In recent years, people's living standards have been gradually improving, and their understanding of food has changed. People have proceeded from a simple taste experience to the requirements of food quality, safety, texture, and health. When it comes to processed products, people prefer them to be green and natural. When eating healthy foods from water raw materials, people want to enjoy the product's original taste and texture and its nutritional value higher than that of conventional foods. Long-term observations have shown that the traditional technology of manufacturing food products from water raw materials involves the use of high temperatures, high pressure, high salt concentration, low moisture content. This processing helps to destroy microorganisms or inhibit their growth. As a result of this processing, a coarse texture is formed, a product loses much of its taste and aroma and a lot of its nutrients, which leads to a decrease in its consumer properties. Recently, much attention has been paid to technologies that allow regulating the consumer properties of ready-to-eat foods from water raw materials: mild heat treatment and other gentle processing methods are needed. Technological development and research of this kind are very important [16].

Many scientists have conducted studies of the effect of high temperature on changes in the physical, chemical, and organoleptic properties of food. It has been shown that heating the muscular tissue of various raw materials leads to loss of mass and nutrients, to changes in the colour, aroma, and texture [17-31]. The authors conducted research in a wide temperature range. The temperature was measured in the central part of the muscle. In accordance with the temperature change in the central part of the muscle, the studies were divided into three stages. At each stage, changes in the quality parameters were identified.

At the first stage, the muscle temperature is 40~60°C. At this temperature, myosin is first denatured, and its thermal stability is the worst [20]. Myofibrillar proteins and sarcoplasmic proteins begin to lose their high-grade structure and undergo degeneration [20]. At this time, changes in myofibrillar proteins are the main factors leading to changes in the muscle texture, myofibrillar proteins are denatured and condensed, and contraction takes place [22]. The cellular fluid slowly drains out of the cell, causing an increase in the hardness. Degeneration of myofibrillar proteins can also cause sarcomere shortening [23,24]. Besides, collagen partially denatures and shrinks. This causes the originally crimped fibres to become straight, can compress the muscular fibres and reduce their diameter, and also makes the muscles less tender and harder [25,26]. This temperature is also the temperature at which the Maillard reaction is most likely to occur, and the carbonyl group reacts with the amino group to form black pigment [27].

At the second stage, the muscular temperature is 60–80°C. In this temperature range, actin begins to denature, its denaturation temperature being 71–83°C. Collagen is also denatured, and its denaturation temperature is 60–70°C [28]. The denaturation temperature of muscular protein differs with species: the collagen denaturation temperature of the chicken is 65°C, and the beef collagen denaturation temperature is 69°C [26,29]. Li's studies have shown that changes in the connective tissue are the main cause of texture changes in this temperature range [22]. With further denaturation of collagen, the spiral structure is digested: the binding of muscular fibres is lost, and their diameter begins increasing [26]. At this temperature, with the further contraction of the myofibrils, the muscular fibres are separated from the endomysium and the fascia, and the shear force is maximised [23,24]. Then myofibrillar protein begins to degrade. The fibre structure becomes blurred, and the hardness changes. A decrease has occurred. Besides, at this temperature, the endomysium, muscular fascia, and extramuscular membrane contract, actomyosin contracts and becomes dehydrated, the muscle fibre diameter becomes smaller, and more cooking properties are lost [20].

At the third stage, the muscle temperature is above 80°C. In this temperature range, collagen gelatinises, the muscular shear force decreases, and meat becomes soft [20,30]. The epithelium, endomysium, and fascia are almost completely destroyed and even flaky [20,23,24]. In the meat processing industry, muscular protein has a greater influence on the water retention, tissue structure, cohesiveness, and emulsifying properties of meat products [31]. The main muscular proteins are sarcoplasmic proteins, myofibrillar proteins, and muscle matrix proteins. Sarcoplasmic protein is water-soluble, myofibrillar protein is salt-soluble, and muscle matrix protein is insoluble in a neutral buffer of high ionic strength. Therefore, these two proteins do not have the ability to form a gel, so they have a weaker effect on the quality of meat products.

Analysis of the physical and chemical parameters, the composition and structure of protein, and the Sous-vide thermal processing characteristics of myofibrillar protein made it possible to discuss in depth the mechanism of the quality change of squid meat. This provided a theoretical basis for further establishing the correct thermal processing technology.

Myofibrillar protein is a unit of muscular contraction. It consists of filamentous protein gel, mainly including actin, myosin, actomyosin, and tropomyosin. Myofibrillar protein accounts for more than 50% of the muscular protein content, and it was the main object for research and utilisation in aquatic food processing. Molecular expansion of the solution of myofibrillar protein starts at 30–32°C, then the protein begins to crosslink at 36–40°C, gel formation begins at 45–50°C, the gel begins to denature at 53–63°C, and then the gel begins to shrink [31,32]. At 18.5–75.0°C, the surface hydrophobicity of myosin increased with increasing temperature, while the denaturation temperatures of back muscle myosin and actin were 48.09°C and 64.70°C, respectively [33,34]. For the protein denaturation temperature of the carp, the denaturation temperatures of myosin and actin were 41.50°C and 72.40°C, respectively [35]. The denaturation temperatures of squid myosin and actin were 43.5°C and 73.6°C, respectively. It can be seen that the denaturation temperature of myosin is about 40–45°C, while that of actin is about 70–75°C, and the protein denaturation temperature is different in different types [36].

Invertebrates such as squid have different proteins. Besides sarcoplasmic proteins, myofibrillar proteins, and muscular matrix proteins, they also contain partial paramyosin, a protein which is unique to invertebrates. Proteins of invertebrates exhibit some special properties that are different from ordinary fish protein. The molecular weight of paramyosin in different animals is slightly different. Studies have shown that it is about 130 nm long and about 2 nm wide, almost all composed of α-helix [37]. Paramyosin is a motor protein associated with long-term stress contraction of muscular cells. It can be dissolved at high ionic strength, which has a great influence on various properties such as stability of myofibrillar protein and gel strength. The presence of paramyosin reduces the levels of actin and myosin in myofibrillar proteins, which in turn reduces the gelatinousness of myofibrillar proteins [38-41]. The protein does not form a gel, but it has a synergistic or antagonistic effect on myosin [42,43]. Therefore, in-depth study of variations of squid myofibrillar protein provides scientific basis and technical guidance for the processing of squid products.

Sous-vide is a cooking method, in which food is placed in a vacuum bag and cooked under strictly controlled temperature and time conditions [44]. Sous-vide cooking was first used in the production of foie gras, and it successfully reduced the water loss while cooking [45]. Generally, according to the Sous-vide cooking technology, food is processed as follows: pretreatment of the raw materials → packing in a vacuum bag with accessories → heating for a certain time in a water bath → cooling in an ice bath below 4°C → storage. The Sous-vide technology is low-temperature long-time (LTLT) cooking, usually at 55–90°C, that lasts from a few minutes to several hours. Sous-vide differs from traditional cooking in a number of aspects. The Sous-vide cooking technology has the advantage of vacuum packing that makes it possible to avoid pollution in food processing, reduce the growth of aerobic microorganisms in food, eliminate the specific smell and loss of weight in finished products [46]. This technology prevents the oxidation of volatile flavour components and loss of moisture and nutrients. Precise control of the temperature and time of cooking helps preserve the native properties of raw materials and increase the shelf life of products [47]. At present, lots of scholars are doing Sous-vide-related research that focus on increasing storage time, improving the overall texture, colour of foods, nutritional bioavailability, etc. [44,48-54].

Conclusion

Higher standards of living, the increased popularity of a healthy lifestyle, and a shortage of healthy food products make it necessary to redistribute them and orientate them towards the domestic consumer market. The modern fishing fleet, the volumes of water resources exploited, the level of development of the food industry and technology in China make it possible to achieve these goals. To create food products that satisfy the above requirements, it is necessary to develop technologies with soft modes of technological processes. Sous-vide cooking has the advantages of precise heating temperature and heating time control, which can help the shortcomings of traditionally processed aquatic products such as hard texture and poor taste. Food prepared by Sous-vide cooking can fully retain the original characteristics of fresh aquatic products (texture, flavour, and colour). This technology is especially suitable to process seafood such as shellfish, shrimps, and cephalopods. The development of the Sous-vide method of cooking seafood will meet consumers' requirements for the best quality and safety of aquatic products. This method opens rich market prospects, and is great advancement in the technology of processed aquatic products.

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ДОСЛІДЖЕННЯ ТЕНДЕНЦІЙ ВИРОБНИЦТВА ПРОДУКТІВ ІЗ КАЛЬМАРІВ

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Анотація. В даний час особливої уваги заслуговують технології, що дозволяють максимально зберегти нативні властивості сировини у готовому продукті завдяки м'яким режимам технологічних процесів. Для отримання здорових харчових продуктів важливою умовою є наявність сировинної бази та технічних засобів видобутку водних біоресурсів. У статті показано, що у Китаї великими темпами росту набуває популярності здоровий спосіб життя і споживання здорових харчових продуктів. Китай являється країною, яка демонструє абсолютне домінування у виробництві молюсків, як об'єкта аквакультури так і у видобуванні їх. Незважаючи на це на внутрішньому ринку харчових продуктів Китаю спостерігається дефіцит здорових харчових продуктів через нерівномірний перерозподіл водних біоресурсів. Основним видом перероблюваних молюсків є кальмари, які традиційно користуються великою популярністю у Китаї. Крім замороженого обробленого кальмара та інших продуктів первинної переробки, основними продуктами кальмара є подрібнений кальмар, нарізаний кальмар і рубаний кальмар, а також різноманітні види консервів. У статті висвітлено високу харчову та біологічну цінність кальмару, яку забезпечують повноцінні білки та ессенціальні поліненасичені жирні кислоти. Але при переробці кальмарів виникає ряд проблем, пов'язаних з погіршенням органолептичних властивостей та зниженням біологічної цінності готового продукту. Дана стаття є оглядовою та розкриває ряд питань пов'язаних з особливостями фракційного складу білків м'язової тканини різних сировинних джерел. Також проаналізовано зміни фізико-хімічних показників білків в широкому діапазоні температурного впливу. У статті представлено перспективний вид технологічної обробки, який дозволяє усунути певні недоліки традиційних технологій такі як жорстка, суха консистенція, втрата маси готового продукту, а також втрати цінних екстрактивних речовин, які забезпечують органолептичні властивості харчових продуктів. До таких технологій з мінімальним впливом на технологічні властивості готового продукту відноситься технологія Sous-vide. Sous-vide – технологія низькотемпературного приготування продуктів харчування у вакуумі, який дозволяє здійснювати надійний контроль за сенсорними показниками і мікробіологічною безпекою продуктів при суворому дотриманні технологічного регламенту.

Ключові слова: кальмар, добування кальмарів, споживач, здорові харчові продукти, білок, технологія Sous-vide.

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